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EVALUACIÓN DEL DESEMPEÑO OPERACIONAL Y AMBIENTAL DE LA DIGESTIÓN ANAEROBIA DE LODOS PROVENIENTES DEL TRATAMIENTO DE AGUAS SERVIDAS INCLUYENDO PRE-TRATAMIENTO MEDIANTE ULTRASONIDO E HIDRÓLISIS TÉRMICA

Tesis para optar al grado de Doctor en Ciencias Ambientales con mención en Sistemas Acuáticos Continentales

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"Todos los días me recuerdo a mí mismo que mi vida está basada en el trabajo de otros hombres, vivos y muertos, y que me debo dedicar yo mismo a dar en la misma medida que he recibido y sigo recibiendo"

Albert Einstein (1879 – 1955)

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“El error consistió en creer que la tierra era nuestra, cuando la verdad de las cosas es que nosotros somos de la tierra”

Nicanor Parra (1914)

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RESUMEN

El tratamiento de aguas servidas representa un pilar fundamental para la protección de la salud pública y la conservación de la integridad de los ecosistemas acuáticos. Sin embargo, las tecnologías de tratamiento utilizadas actualmente representan una fuente creciente de lodos sanitarios, que en caso de los lodos activados puede llegar a 7 – 8 kg/hab-año. Debido a su origen y características físicoquímicas y microbiológicas, la gestión de lodos implica un importante problema económico y ambiental, llegando a representar hasta el 50% de los costos operacionales en las plantas de tratamiento de aguas servidas (PTAS) y con potenciales impactos sobre suelos, cuerpos de agua y la salud de la población.

La digestión anaerobia es una tecnología de estabilización biológica que permite la recuperación de energía a partir del lodo a través de la transformación de la materia orgánica en CH_4 y CO_2 (biogás). Sin embargo, las tasas de hidrólisis durante la digestión limitan el proceso y su aplicabilidad en PTAS de menor tamaño (<50,000 personas equivalentes), debido a lo cual sólo 6 instalaciones existen actualmente en Chile. En este escenario, distintas estrategias de pre-tratamiento han sido propuestas para hidrolizar el lodo en un paso previo a la digestión anaerobia, lo que permite intensificar el proceso e incrementar la producción de biogás. En particular, el uso de procesos que integran diferentes mecanismos de hidrólisis ha sido reportado como una alternativa de interés, debido principalmente a los efectos sinérgicos observados sobre la solubilización del lodo y el rendimiento de metano durante la digestión.

En esta tesis, se evaluó el efecto de un pre-tratamiento secuencial mediante ultrasonido e hidrólisis térmica (55°C) sobre las características del lodo sanitario y el desempeño operacional y ambiental de su digestión anaerobia. El objetivo de dicho proceso es la solubilización del lodo mediante fenómenos físicos y biológicos, lo que se espera resulte en una mejora en la conversión de materia orgánica y la producción de biogás durante la digestión anaerobia. Además, para evaluar si la incorporación del pre-tratamiento resulta en compromisos entre los impactos ambientales asociados a las distintas etapas de la gestión del lodo, se realizó una evaluación del desempeño ambiental del proceso mediante un enfoque basado en Análisis de Ciclo de Vida (ACV).

Se realizaron ensayos batch de pre-tratamiento bajo distintas condiciones operacionales, incluyendo la aplicación de ultrasonido con energías específicas (EE) de 500 – 30500 kJ/kgST y 3 – 13 horas (T) de

tratamiento térmico a 55°C. La solubilización de materia orgánica causada por el pre-tratamiento fue evaluada en términos de proteínas, carbohidratos y la demanda química de oxígeno (DQO). Además, se determinó la influencia del proceso sobre la presencia de ácidos grasos volátiles (AGV) y la actividad endógena de proteasas y amilasas en el lodo. El desempeño de la digestión anaerobia después del pre-tratamiento fue evaluada mediante ensayos batch de cinética y biodegradabilidad anaerobia, así como durante la operación de digestores semi-continuos (6 L volumen de reacción) bajo 3 condiciones operacionales, correspondientes a tiempos de retención de sólidos (TRS) de 30, 15 y 7.5 días. El periodo experimental de los sistemas semi-continuos fue de un total de 303 días, incluyendo una fase de aclimatación de la biomasa de 96 días. Durante este periodo, se monitorearon parámetros de estabilidad del proceso (pH, alcalinidad, concentración de AGV, potencial de óxido-reduccion, concentración de NH_4^+-N), además del rendimiento de metano ($mLCH_4/gSV$), la eliminación de DQO total, sólidos totales (ST) y sólidos volátiles (SV) y la conversión de materia orgánica asociada a las fases de hidrólisis, acidogénesis y metanogénesis. Además, se establecieron balances de DQO para todas las condiciones experimentales. La influencia del pre-tratamiento sobre las características del digestado fue evaluada en términos de la deshidratabilidad (a través ensayos de centrifugabilidad), la concentración de N, P, As, Cu, Hg, Ni, Pb, Se y Zn en el sólido y sobrenadante del digestado, y la presencia y eliminación logarítmica (log_{rem}) de coliformes totales, coliformes fecales y colifagos somáticos. El ACV del proceso fue realizado en base a los resultados obtenidos durante la operación de los digestores y datos operacionales de la PTAS Biobío de Concepción (36° 48' S, 73° 08' O) durante el año 2015. La unidad funcional (UF) seleccionada para el estudio fue el tratamiento de 1 ton de lodo (base seca), y se incluyó la evaluación de 6 categorías de impactos ambientales potenciales: cambio climático ($kgCO_{2eq}$), agotamiento de recursos abióticos ($kgSb_{eq}$), acidificación ($mol_cH^+_{eq}$) y eutrofización en suelos ($molN_{eq}$), ecosistemas marinos (kgN_{eq}) y ecosistemas dulceacuícolas (kgP_{eq}). Se supuso que después de la estabilización anaerobia el digestado es utilizado como reemplazo de fertilizantes comerciales en cultivos de trigo, y los resultados fueron comparados con escenarios de referencia basados en alcalinización y disposición del lodo en rellenos sanitarios.

El pre-tratamiento secuencial resultó en una solubilización significativa de la materia orgánica, con incrementos en la concentración soluble de proteínas (252 – 674%), carbohidratos (458 – 1030%) y DQO (f = 3.5 – 17.1%), además de 1.6 – 3.8 mayor actividad de amilasa y 1.8 – 4.3 mayor actividad de proteasa en la fase soluble. La solubilización de DQO se vio influenciada tanto por la concentración del lodo como por las condiciones operacionales evaluadas (EE y T). El pre-tratamiento secuencial resultó en incrementos en la cinética de la digestión anaerobia y la biodegradabilidad del lodo, con incrementos de 30 – 80% en la tasa máxima de producción de metano (mLCH_4/gSV-d) y 16 – 50% en el rendimiento específico de metano (mLCH_4/gVS).

Durante la evaluación semi-continua, se observaron incrementos de 19 – 29% en el rendimiento específico de metano debido a la incorporación del pre-tratamiento, sin afectar la estabilidad del proceso y manteniendo concentraciones de NH_4^+-N y NH_3-N bajo los rangos de inhibición en todas las condiciones experimentales (≤1.8 gNH_4^+-N/L y ≤53 mgNH_3-N/L). El mayor incremento en la producción de metano fue observado a un TRS de 7.5 días (3.6 gSV/L-d), asociado con la mayor cinética de degradación. Los balances de materia orgánica mostraron que el incremento en la producción de metano resulta proporcional a la solubilización de DQO durante el pre-tratamiento, lo que sugiere que este es el principal mecanismo involucrado en los efectos observados sobre el desempeño operacional de la digestión anaerobia. Tanto el pre-tratamiento como el TRS influenciaron la recuperación de agua durante la centrifugación del digestado, con valores 4.2% y 13.3 – 20.5% menores debido a la incorporación del pre-tratamiento y la reducción del TRS desde 30 a 15 días, respectivamente. El sistema pre-tratamiento/digestión anaerobia permitió obtener $\log_{rem}$ de 2.8 para coliformes (totales y fecales) y 1.5 para colifagos somáticos, y se observaron incrementos de hasta un 58% en la concentración de As, Cu, Hg y Zn en la fracción sólida del digestado.

El desempeño ambiental de la digestión anaerobia incorporando el pre-tratamiento secuencial fue similar al de la digestión convencional. Las principales diferencias se asociaron con una disminución en el potencial de cambio climático y un aumento en el potencial de agotamiento de recursos abióticos, relacionados con la recuperación de energía a partir del lodo y los requerimientos de transporte del digestado. Ambos escenarios resultaron en menores impactos en todas las categorías estudiadas comparado con los escenarios de referencia. Los resultados obtenidos resultan dependientes de la presencia de carbono fósil en las emisiones de CO_2 y la valorización de la energía térmica generada durante la co-generación del biogás, y se observó que parámetros tales como el TRS y la tasa de aplicación del lodo al suelo pueden tener una mayor influencia sobre el desempeño ambiental de la gestión del lodo que la incorporación del pre-tratamiento.

ABSTRACT

Sewage treatment represents a cornerstone for public heath protection and conservation of aquatic ecosystems integrity. However, current treatment technologies represent a growing source of sewage sludge, which in the case of activated sludge facilities could be of 7 – 8 kg/inhab-year. Due to its source and related physic-chemical and microbiological characteristics, sludge management represents an important economical and environmental issue, representing up to 50% of the operational costs of sewage treatment plants (STP) and with potential impacts over soils, water bodies and population health.

Anaerobic digestion is a biological stabilization technology that allows energy recovery through the transformation of organic matter into CO_2 and CH_4 (biogas). However, hydrolysis rates during digestion limits the process and its applicability in smaller STP (<50,000 equivalent inhabitants), and therefore there are only 6 sewage sludge digestion plants currently in Chile. In this scenario, different pre-treatment strategies have been proposed to hydrolyze sludge previous to anaerobic digestion, which results in process intensification and increased biogas production. In particular, the use of processes that involves the action of different hydrolysis mechanisms has gained notoriety, mainly due to its synergistic effects over sludge solubilization and methane yield during digestion.

In this thesis, the influence of a sequential pre-treatment using ultrasound and thermal hydrolysis (55°C) over sewage sludge characteristics and the operational and environmental performance of anaerobic digestion was assessed. The objective of the process is sludge solubilization through physical and biological phenomena, which is expected to increase organic matter conversion and biogas production during anaerobic digestion. In order to asses if pre-treatment implementation results in trade-offs between the environmental impacts of the different steps of sludge management, an environmental performance evaluation of the process was done using a Life Cycle Assessment (LCA) perspective.

Batch assays of pre-treatment were performed under different operational conditions, including application of ultrasound with specific energies (SE) of 500 – 30500 kJ/kgTS and 3 – 13 h (T) of thermal treatment at 55°C. Organic matter solubilization was assessed in terms of proteins, carbohydrates and chemical oxygen demand (COD). Moreover, the process influence on Volatile Fatty Acids (VFA) presence and endogenous protease and amylase activity in sludge was evaluated. The performance of anaerobic digestion after pre-treatment was assessed through kinetic and biodegradability batch assays, as well as during the operation of semi-continuous digesters (6 L reaction volume) under 3 operational

conditions, corresponding to solids retention times (SRT) of 30, 15 and 7.5 days. The experimental period of the semi-continuous systems was of 303 days, including a biomass acclimation phase of 96 days. During this period, stability parameters of digestion (pH, alkalinity, VFA concentration, oxidation-reduction potential, NH_4^+-N concentration) were monitored, as well as the methane yield ($mLCH_4/gVS$), COD, total solids (TS) and volatile solids (VS) removals and the transformation of organic matter associated to the hydrolysis, acidogenesis and methanogenesis phases. Moreover, COD balances for all experimental conditions were calculated. The influence of pre-treatment over digestate was assessed in terms of dewaterability (through centrifugation assays), the concentration of N, P, As, Cu, Hg, Ni, Pb, Se and Zn in digestate solids and supernatant, and the presence and logarithmic removal (log_{rem}) of total coliforms, fecal coliforms and somatic coliphages. The LCA of the process was performed based on the results of digesters operation and operational data from the Biobío STP of Concepción (36° 48' S, 73° 08' W) for year 2015. The functional unit (FU) selected for the study was the treatment of 1 ton of sludge (dry basis), and the assessment of 6 potential impact categories was included: climate change ($kgCO_{2eq}$), abiotic depletion ($kgSb_{eq}$), acidification ($mol_cH^+_{eq}$) and eutrophication in terrestrial ($molN_{eq}$), marine (kgN_{eq}) and freshwater (kgP_{eq}) ecosystems. It was supposed that after anaerobic stabilization, digestate was used as replacement of commercial fertilizers in wheat crops, and the results were compared to reference scenarios based on sludge alkalinization and disposal in landfill.

Sequential pre-treatment to significant solubilization of organic matter, with increases in the soluble concentration of proteins (252 – 674%), carbohydrates (458 – 1030%) and COD (f = 3.5 – 17.1%), besides 1.6 – 3.8 higher amylase and 1.8 – 4.3 higher protease activities in the soluble phase. COD solubilization was influenced by sludge concentration and the studied operational conditions (SE and T). Sequential pre-treatment led to increases in anaerobic digestion kinetics and sludge biodegradability, with increases of 30 – 80% in the maximum methane production rate ($mLCH_4/gVS$-d) and 16 – 50% in the specific methane yield ($mLCH_4/gVS$).

During semi-continuous evaluation, increases of 19 – 29% in the specific methane yield were observed due to pre-treatment implementation, without affecting the process stability and with NH_4^+-N and NH_3-N concentrations under the inhibitory threshold for all experimental conditions (≤1.8 gNH_4^+-N/L y ≤53 $mgNH_3$-N/L). The highest increase in methane production was observed at 7.5 days SRT (3.6 gVS/L-d), associated with the higher kinetics of degradation during digestion. Organic matter balances showed that the increased methane production was proportional to solubilization during pre-treatment, which suggests that this is the main mechanism involved in the observed effects over anaerobic digestion operational performance. Both pre-treatment and SRT affected water recovery during digestate centrifugation, with 4.2% and 13.3 – 20.5% lower values associated to pre-treatment implementation and reduced SRT from 30 to 15 days, respectively. The pre-treatment/anaerobic digestion system showed 2.8 log_{rem} for coliforms (total and fecal) and 1.5 log_{rem} for somathic coliphages, besides increases of up to 58% in the concentration of As, Cu, Hg and Zn in the solids fraction of digestate.

The environmental performance of anaerobic digestion including the sequential pre-treatment was similar to conventional digestion. The main differences were associated with a decrease in climate change potential and an increase in abiotic depletion potential, related to energy recovery from sludge and transport requeriments fro digestate. Both scenarios showed lower impacts in all studied categories compared to the reference scenarios. The results are dependent on the presence of fossil carbon in CO_2 emissions and valorization of heat coming from the co-generation of biogas, and it was observed that parameters such as digestion SRT and sludge application rate in soil could have a bigger influence over the environmental performance of sludge management than the incorporation of pre-treatment.

CAPÍTULO I

INTRODUCCIÓN

1. TRATAMIENTO DE AGUAS SERVIDAS Y GENERACIÓN DE LODOS SANITARIOS

1.1. Situación nacional del tratamiento de aguas servidas

Debido a las actividades realizadas por las comunidades humanas, estas inevitablemente generan residuos líquidos, sólidos y gaseosos. Los residuos líquidos urbanos – o aguas servidas – corresponden al suministro de agua una vez utilizado por la población y descargado al alcantarillado (Tchobanoglous et al. 2003). Debido a esto, las aguas servidas constituyen una mezcla compleja de componentes orgánicos e inorgánicos naturales y sintéticos, incluyendo fecas, orina, restos de comida, aceites, grasas, jabones, sales, metales, detergentes, arenas y grava (Gray 2010), que de ser descargados directamente en ecosistemas acuáticos pueden generar una serie de impactos ambientales y sobre la salud humana. La Tabla 1 muestra la caracterización de algunos de los constituyentes más importantes de las aguas servidas.

Tabla 1. Caracterización de aguas servidas (Tchobanoglous et al. 2003)

Parámetros	Unidad	Tipo de agua servida		
		Concentrada	Media	Diluida
Sólidos totales	mg/L	390	720	1230
Sólidos Suspendidos Totales	mg/L	120	210	400
Volátiles	mg/L	95	160	315
Sólidos Disueltos Totales	mg/L	270	500	860
Volátiles	mg/L	110	200	340
Sólidos Sedimentables	mL/L	5	10	20
Demanda Bioquímica de Oxígeno	mgDBO$_5$/L	110	190	350
Carbono Orgánico Total	mg/L	80	140	260
Demanda Química de Oxígeno	mgDQO/L	250	430	800
Nitrógeno	mg/L	20	40	70
Orgánico	mg/L	8	15	25
Amonio	mg/L	12	25	45
Fósforo	mg/L	4	7	12
Orgánico	mg/L	1	2	4
Inorgánico	mg/L	3	5	10
Cloruro	mg/L	30	50	90
Sulfato	mg/L	20	30	50
Aceites y Grasas	mg/L	50	90	100
Compuestos Orgánicos Volátiles	mg/L	<100	100 – 400	>400
Coliformes Totales	No/100 mL	$10^6 – 10^8$	$10^7 – 10^9$	$10^7 – 10^{10}$
Coliformes Fecales	No/100 mL	$10^3 – 10^6$	$10^4 – 10^6$	$10^5 – 10^8$
Ooquistes de *Crystoporidium*	No/100 mL	$10^{-1} – 10^0$	$10^{-1} – 10^1$	$10^{-1} – 10^2$
Quistes de *Giardia lamblia*	No/100 mL	$10^{-1} – 10^1$	$10^{-1} – 10^2$	$10^{-1} – 10^3$

Los sistemas de tratamiento de aguas residuales constituyen por lo tanto un elemento clave para preservar la calidad del agua y la integridad ecológica de los ecosistemas acuáticos receptores, además de evitar la propagación de enfermedades infecciosas y facilitar la potabilización del agua en cuencas antropizadas. La implementación de los sistemas de tratamiento modernos dio comienzo a mediados del siglo XIX en Europa, como una reacción a la creciente industrialización y urbanización que llevó a la contaminación de las fuentes de agua y la propagación de enfermedades infecciosas, generando situaciones tales como los brotes de cólera ocurridos en Londres en 1832, 1849 y 1855 (Angelakis & Snyder 2015).

Hoy en día, el tratamiento de aguas residuales forma parte integral de las políticas ambientales de la mayor parte de los países desarrollados y en vías de desarrollo. En Chile, entre 1989 y 2015 la cobertura de tratamiento de las aguas servidas urbanas se incrementó desde un 8 hasta un 99.9% (SISS 2016), debido principalmente a consideraciones de salud pública y a la necesidad que tuvo nuestro país de alcanzar requisitos impuestos por acuerdos comerciales internacionales (Celedón & Alegría 2004). La cobertura de tratamiento de aguas servidas tuvo su mayor crecimiento durante la primera mitad de la década del 2000, impulsado en gran medida por la entrada en vigencia del DS 90/01 del Ministerio Secretaría General de la Presidencia, que regula la concentración máxima permisible para la emisión de residuos líquidos a cuerpos de agua superficiales (MINSEGPRES 2001).

El principal sistema adoptado en las Plantas de Tratamiento de Aguas Servidas (PTAS) de Chile es el de lodos activados convencionales, sistema aerobio de biomasa suspendida cuyo objetivo principal es la oxidación de la materia orgánica y bajo algunas configuraciones la remoción de nutrientes, principalmente N. Si bien al año 1998 no existía ningún sistema de estas características operando en Chile, de las 290 PTAS operando en el país al año 2015, 173 corresponden a tecnologías de lodos activados (Figura 1). En particular, la Región del Biobío es la región del país con el mayor número de PTAS y con el mayor número de instalaciones de lodos activos, cuya cantidad asciende a 49 y 36, respectivamente (SISS 2016).

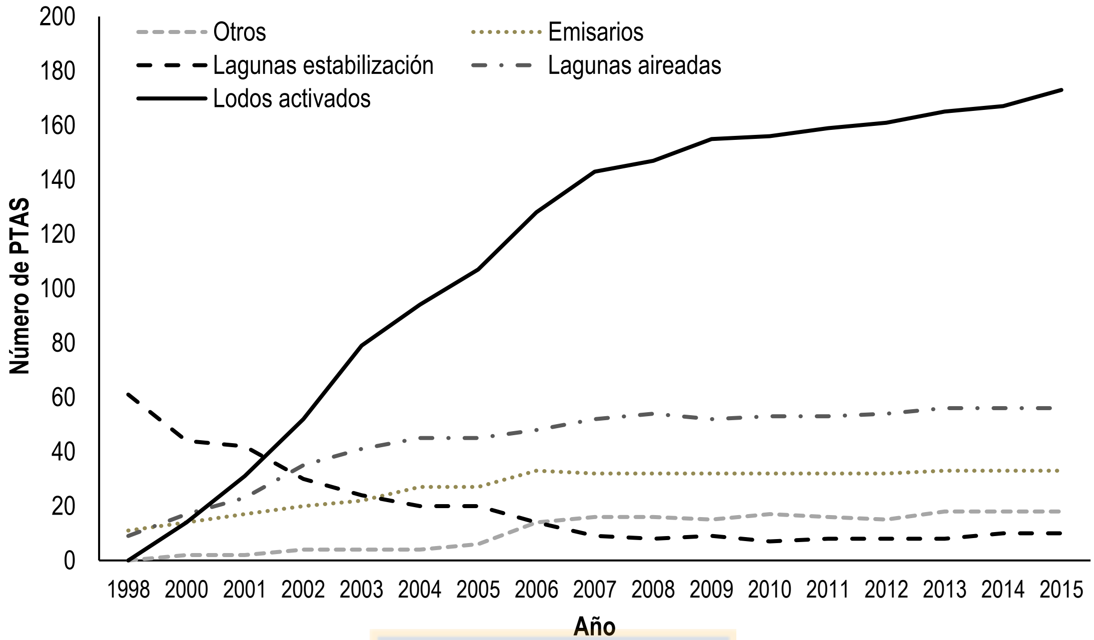

Figura 1. Evolución en el número de PTAS operando en Chile de acuerdo al tipo de tecnología (SISS 2016).

El proceso de tratamiento de aguas residuales involucra una serie de etapas físico-químicas y biológicas, orientadas principalmente a la eliminación de sólidos, materia orgánica y patógenos. Entre estas se encuentran el pre-tratamiento, tratamiento primario, tratamiento secundario, tratamiento terciario y desinfección, descritas brevemente a continuación (Ramalho 1996; Tchobanoglous et al. 2003; Gray 2010):

a. Pre-tratamiento: el principal objetivo del pre-tratamiento es la remoción de sólidos de gran tamaño, arenas, aceites y grasas. Dentro de los equipos utilizados para pre-tratar el agua residual se encuentran los desbastadores, desarenadores y sistemas de flotación para retención de compuestos de baja densidad (aceites y grasas).
b. Tratamiento primario: corresponde a un proceso llevado a cabo habitualmente mediante sistemas de sedimentación, cuyo objetivo es remover la mayor parte de las partículas sólidas en suspensión. El tratamiento primario puede reducir la Demanda Biológica de Oxígeno (DBO_5) en un 30 – 40% y la concentración de sólidos suspendidos en un 40 – 70%, mientras que hasta el 50% de los coliformes fecales del agua servida también son removidos (Gray 2010). Los sólidos separados durante esta etapa se acumulan en el fondo del estanque de sedimentación, desde donde son continuamente removidos y pasan a constituir los lodos primarios.

c. Tratamiento secundario: proceso de naturaleza biológica, realizado en la mayoría de los casos en reactores aeróbicos. Durante esta etapa, los microorganismos presentes en el reactor utilizan la materia orgánica del agua afluente para sustentar su metabolismo y crecimiento, generando CO_2 y transfiriendo alrededor de un tercio de la materia orgánica soluble hacia la generación de nuevos microorganismos (Ramalho 1996). En el proceso de tratamiento mediante lodos activados, el licor de mezcla conformado por el agua residual y los microorganismos pasa a una etapa de decantación secundaria, obteniéndose una corriente de agua tratada y una corriente de microorganismos concentrada, que constituye los lodos secundarios. Una fracción de estos es recirculada al biorreactor como una estrategia para independizar el tiempo de retención hidraúlico de las limitaciones cinéticas de los microorganismos, mientras que la fracción restante debe ser purgada del sistema y estabilizada de manera conjunta o separada de los lodos primarios.
d. Desinfección/Tratamiento terciario: el proceso de tratamiento concluye generalmente con la etapa de desinfección, orientada a la eliminación de organismos potencialmente patógenos. El proceso de desinfección puede ser realizado mediante métodos químicos o físicos, incluyendo cloración, ozonación o el uso de luz ultravioleta. En el caso de aguas residuales industriales, tratamientos terciarios orientados al abatimiento de parámetros específicos tales como el color también son utilizados. Además, dependiendo de la configuración del sistema de tratamiento la remoción de nutrientes también puede ser añadida como un tratamiento terciario, tanto para la remoción de P como N (Gray 2010).

Durante el tratamiento de aguas residuales, gran parte de la materia orgánica y otros contaminantes removidos pasa a formar parte de una matriz semi-sólida, constituida principalmente por los sólidos sedimentados durante el tratamiento primario y los microorganismos purgados desde el tratamiento secundario. A esta matriz se le denomina comúnmente lodos sanitarios, distinguiéndose en lodos primarios y secundarios (biológicos) dependiendo de la operación unitaria del tratamiento de la que provengan. Debido a las características de los lodos sanitarios, su gestión representa una etapa crítica desde el punto de vista ambiental y económico, llegando a representar hasta un 50% de los costos operacionales totales de las PTAS (Appels et al. 2008a).

1.2. Generación de lodos sanitarios durante el tratamiento de aguas servidas

Si bien el tratamiento de aguas servidas representa un avance fundamental en términos de protección de la salud pública y conservación de los ecosistemas acuáticos, las tecnologías utilizadas actualmente para su depuración representan una fuente creciente de lodos. El sistema de lodos activados presenta una de las generaciones de lodos específicas más altas en comparación con otras tecnologías de tratamiento, con valores de alrededor de 7 – 8 kg/hab-año versus 4 kg/hab-año para sistemas secuenciales por lote o 0.3 – 0.5 kg/hab-año para sistemas de lagunas aireadas (Von Sperling et al. 2007; Vera et al. 2013). Debido al crecimiento observado en la cobertura de tratamiento de aguas servidas urbanas, Chile ha sido testigo de un creciente incremento en la generación de lodos sanitarios (SISS 2016), tal como se aprecia en la Figura 2. En la Región del Biobío, la generación de lodos alcanza alrededor de 60 mil toneladas anuales, alrededor de un 10% del total nacional (SISS 2012).

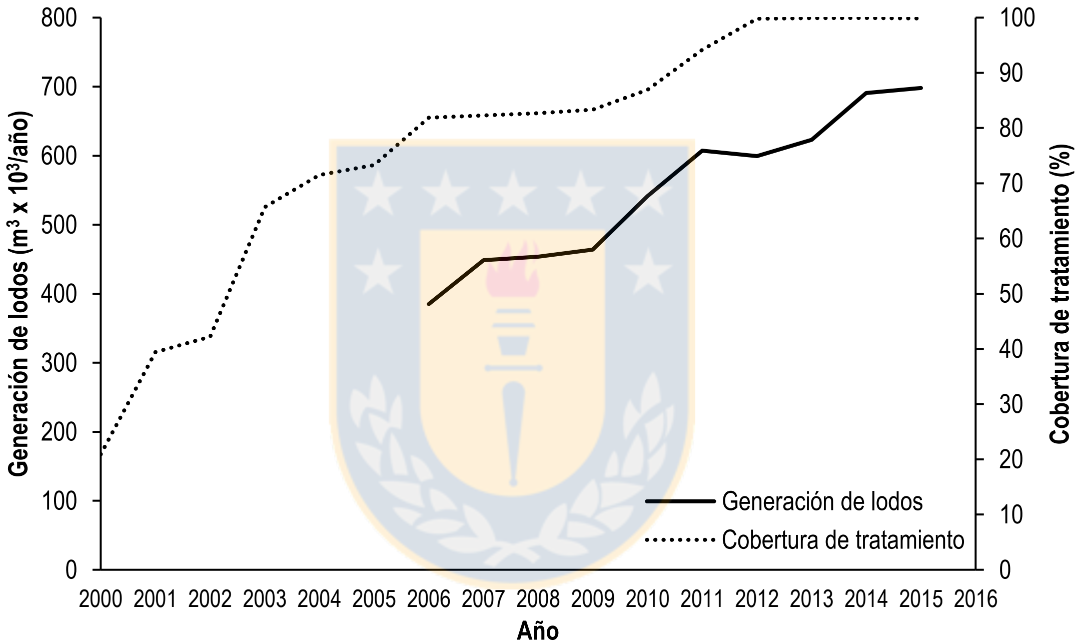

Figura 2. Cobertura de tratamiento de aguas servidas urbanas y generación de lodos sanitarios en Chile. Elaboración propia en base a SISS 2016.

Los lodos sanitarios se caracterizan por una alta presencia de sólidos (2 - 12% sólidos totales para lodos líquidos y 12 – 40% para lodos deshidratados), materia orgánica (75 – 85% en base seca constituidos por sólidos volátiles), patógenos (10^9 CF/100 mL, 2,500 – 70,000 Virus/100 mL, 200 – 1,000 Helmintos/100 mL), nutrientes (>10 mgP/kg, >30 mgN/kg, >3 mgK/kg) y microcontaminantes tales como metales (en concentraciones del orden de <25,000 mg/kg) y compuestos orgánicos (farmacéuticos, hidrocarburos aromáticos policíclicos, difeniles policlorados, ftalatos, surfactantes y otros en concentraciones del orden de <100 mg/kg) (Aguilera et al. 2007; de Souza Pereira & Kuch

2005; Johannesson 1999; Leiva et al. 2010; Maria et al. 2010; Paraíba et al. 2011; Retamal et al. 2010; Silva Oliveira et al. 2007; Villar & Garcia 2006).

Debido a sus características, la disposición de lodos en el ambiente sin las consideraciones adecuadas se asocia con distintos impactos ambientales, incluyendo contaminación por metales (Nogueirol et al. 2013), nutrientes y patógenos (Gottschall et al. 2007; Lapen et al. 2008) y micro-contaminantes orgánicos (Martín et al. 2012; Yang et al. 2012). Dichos elementos pueden alcanzar tanto los suelos como las aguas subterráneas y superficiales por medio de procesos de infiltración y escorrentía (Lapen et al. 2008; Gottschall et al. 2009; Martín et al. 2012; Yang et al. 2012) (Tabla 2), convirtiendo a los lodos en una potencial fuente de contaminación difusa y propagación de enfermedades infecciosas.

Sin embargo, debido a la presencia de nutrientes y materia orgánica, los lodos representan al mismo tiempo una oportunidad, cuya valorización dependerá de la implementación de tecnologías y estrategias de gestión adecuadas. Dentro de las alternativas de utilización destaca su aplicación como fertilizante y enmienda de suelos, ya que permite re-utilizar los nutrientes y la materia orgánica presentes en los lodos como reemplazo de fertilizantes comerciales y como mejoradores de las propiedades físico-químicas de suelos degradados, representando una alternativa ambientalmente sustentable frente a productos de origen fósil (Wong et al. 1998; Bozkur et al. 2010; Carballa et al. 2011). Más aún, la valorización del lodo permitiría eventualmente una disminución en los costos económicos de la gestión del lodo, que en la actualidad pueden alcanzar 20 – 60% de los costos operacionales de las PTAS (Uggetti et al. 2010). Sin embargo, debido a la presencia de contaminantes en el lodo, la aplicación de estos al suelo puede resultar en inquietud por parte de la población, principalmente debido a sus potenciales impactos en la salud pública (Milieu Ltd. 2008). En vista de esto, para que esta estrategia resulte viable resulta necesario la implementación de tecnologías de estabilización que disminuyan el potencial contaminante y de atracción de vectores de los lodos previo a su aplicación en el suelo, dentro de las que destaca la digestión anaerobia (Appels et al. 2008a).

Tabla 2. Impactos reportados en distintas matrices ambientales debido a la disposición de lodos sanitarios.

Contaminante	Matriz estudiada	Ubicación	Descripción del impacto observado	Referencia
Metales[1]	Suelo	Sao Paulo, Brasil	Incremento en la concentración de Cu, Fe y Mn en el suelo debido a la aplicación de lodos por un periodo de 13 años.	Nogueirol et al. (2013)
Nutrientes[2], **microorganismos**[3], **iones inorgánicos**	Aguas subterráneas y drenaje agrícola	Winchester, Canadá	Incremento en la concentración de nitratos y *Escherichia coli* en aguas subterráneas (1.2 – 2.0 m) debido a la aplicación de lodos deshidratados.	Gottschall et al. (2007)
			Incremento en la concentración y carga de nutrientes y microorganismos en el drenaje agrícola y aguas subterráneas debido a la aplicación de lodos líquidos.	Lapen et al. (2008)
	Aguas superficiales	Bahía de Cheseapeake, EEUU	Uso de lodos de acuerdo a las directrices del estado de Virginia representa una importante fuente de contaminación por nutrientes en la Bahía.	Land (2012)
	Aguas subterráneas, escorrentía, suelos y sedimentos	Colorado, EEUU	Disposición de lodos se asocia con contaminación de suelos y aguas subterráneas en parámetros como nitritos y nitratos, sodio, calcio, magnesio, sulfato, bicarbonato y cloruro.	Tindall et al. (1994)
Compuestos farmacéuticos[4]	Biota (evaluación ecotoxicológica)	Andalucía, España	15 de los 16 compuestos estudiados pueden ser sorbidos en lodos. En base a análisis de riesgo, la disposición de lodos en suelos muestra riesgo toxicológico para especies sensibles.	Martín et al. (2012)
Hormonas esteroidales[5]	Escorrentía superficial	Colorado, EEUU	Escorrentía moviliza las hormonas (andrógenos, estrógenos y progesterona) presentes en suelos donde se han aplicado lodos, principalmente en la fase disuelta.	Yang et al. (2012)

[1]Cu, Fe, Mn y Zn
[2] N y P
[3]*Escherichia coli, Clostridium perfringens* y otros
[4]Total de 16 compuestos, incluyendo diclofenaco, ibuprofeno, ketoprofeno, naproxeno, ácido salicílico, sulfametoxazol, trimetoprima, carbamazepina, propanolol, cafeína, 17α-etinilestradiol, 17β-estradiol, estriol, estrona, ácido clofíbrico y gemfibrozil
[5]Andrógenos, estrógenos, progestinas y esteroles, incluyendo cis-androsterona, androstenediona, testosterona, epitestosterona, dihidrotestosterona, 11-ketotestosterona, estrona, 17α-estradiol, 17β-estradiol, estriol, equilanina, progesterona, coprostanol y colesterol

2. DIGESTIÓN ANAEROBIA DE LODOS SANITARIOS

2.1. Descripción del proceso de digestión anaerobia

La digestión anaerobia es un proceso biológico de degradación de materia orgánica que ocurre en condiciones anaerobias estrictas, con potenciales de óxido-reducción menores a -200 mV (Appels et al. 2008a). Frente a la ausencia de aceptores inorgánicos de electrones como el oxígeno, la materia orgánica actúa tanto como dador como aceptor durante la cadena transportadora de electrones (Khanal 2008), lo que resulta en la generación de una mezcla de carbono totalmente oxidado y totalmente reducido (CO_2 y CH_4), conocida como biogás (Figura 3).

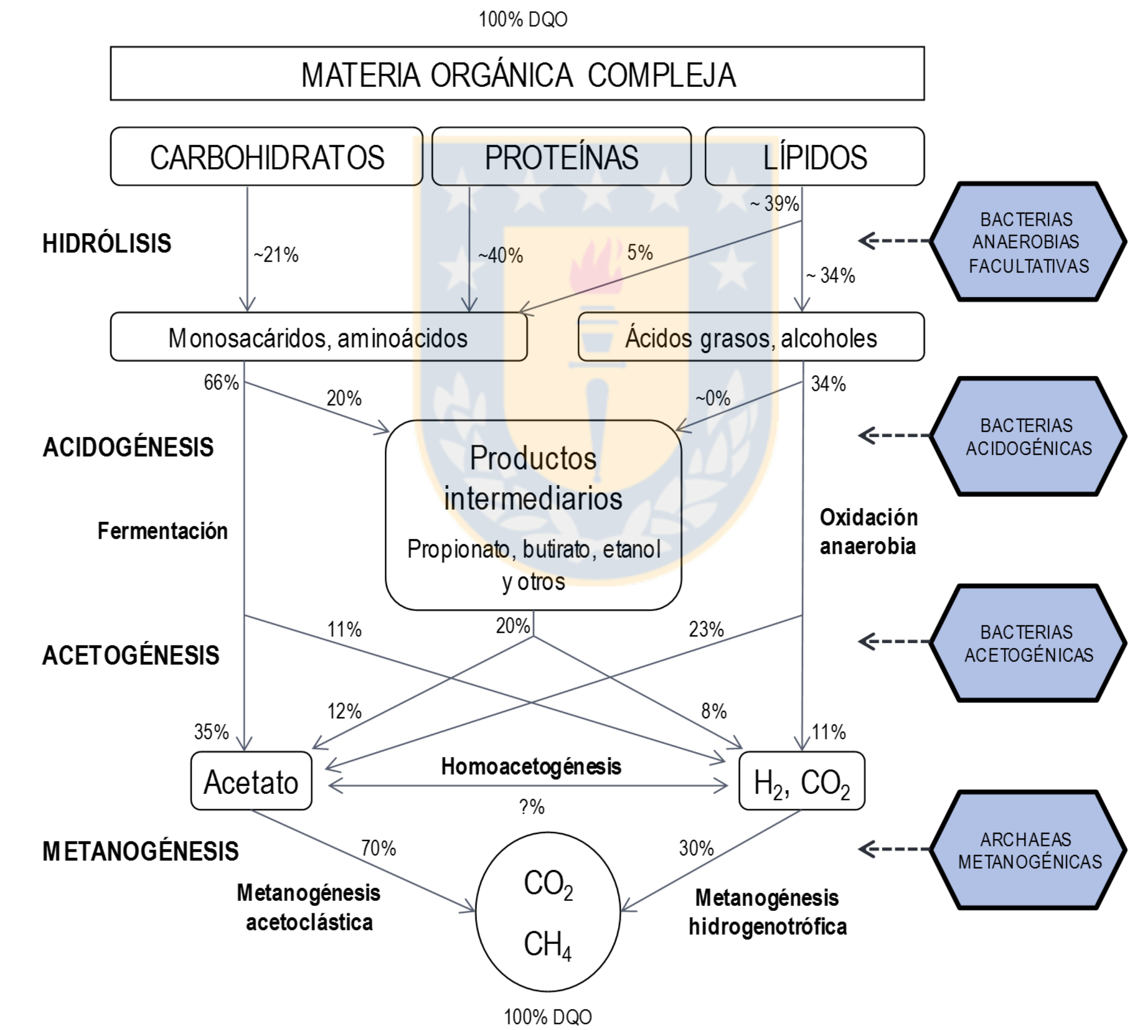

Figura 3. Representación esquemática del proceso de digestión anaerobia y los microorganismos involucrados. Los porcentajes representan los flujos netos de substrato, expresados en DQO (Gujer & Zehnder 1983; Van Lier et al. 2008).

La digestión anaerobia es un proceso complejo que involucra la acción de un consorcio microbiano sintrófico, durante el cual se distinguen cuatro etapas principales, descritas brevemente a continuación (Gujer & Zehnder 1983; Schink 1997; Christ et al. 2000; Gerardi 2003; Tchobanoglous et al. 2003; Khanal 2008; Van Lier et al. 2008; Stams & Plugge 2009; Angelidaki et al. 2011):

1. Hidrólisis: durante la hidrólisis, los sustratos de alto peso molecular son degradados a monómeros o dímeros por la acción de enzimas extracelulares, excretadas por una amplia gama de bacterias fermentativas. La hidrólisis ocurre como un fenómeno de superficie en el cual los compuestos poliméricos son degradados a moléculas de menor tamaño, capaces de atravesar la membrana celular y ser utilizadas por las bacterias para su metabolismo. En el caso de la degradación de lodos biológicos, la hidrólisis es precedida por la muerte y lisis de la biomasa, constituyendo generalmente el paso limitante durante la digestión anaerobia.

   Durante este proceso, las proteínas, carbohidratos y lípidos son degradados a aminoácidos, polisacáridos y ácidos grasos de cadena larga y glicerol, respectivamente. En general, la conversión de carbohidratos presenta constantes cinéticas entre 2.5 a 40 veces mayores que las constantes para la hidrólisis de lípidos (Figura 4) y hasta 13 veces mayores que las constantes para proteínas (Christ et al. 2000). La Tabla 3 muestra un resumen de las constantes de hidrólisis reportadas para algunos grupos de macromoléculas y compuestos orgánicos.

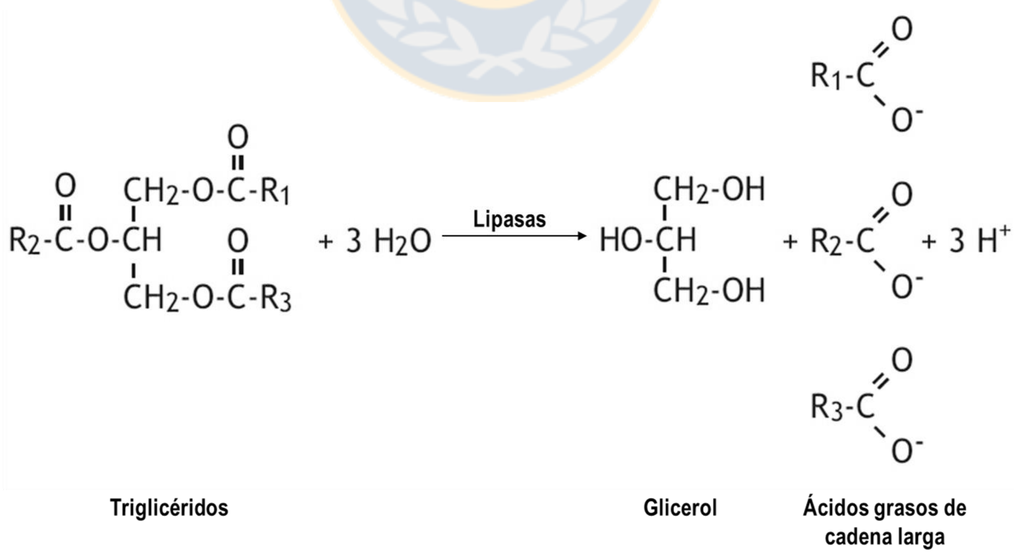

Figura 4. Hidrólisis enzimática de triglicéridos (Van Lier et al. 2008)

Tabla 3. Constantes de hidrólisis para distintos tipos de compuestos orgánicos

Compuesto hidrolizado	**Constante mínima (d^{-1})**	**Constante máxima (d^{-1})**	**Temperatura (°C)**	**Referencias**
Lípidos	0.005	0.010	55	Christ et al. (2000)
Proteínas	0.015	0.075	55	Christ et al. (2000)
Carbohidratos	0.025	0.200	55	Christ et al. (2000)
Celulosa	0.040	0.130	34 – 35	Gujer & Zehnder (1983)

2. Acidogénesis: durante la segunda etapa de la digestión, los compuestos orgánicos solubles y aquellos generados durante la hidrólisis ingresan al interior de las células bacterianas y son subsecuentemente convertidos en ácidos grasos volátiles y otros compuestos como alcoholes, ácido láctico, CO_2, H_2, NH_3 y H_2. La acidogénesis es un proceso microbiano muy común, realizado por una amplia gama de bacterias hidrolíticas y no-hidrolíticas (facultativas, anaerobias aerotolerantes y anaerobias estrictas), siendo muchas de ellas capaces de tolerar valores de pH de alrededor de 4. Alrededor de un 1% de todas las bacterias conocidas son fermentadores facultativos (Van Lier et al. 2008). La Tabla 4 muestra un resumen de los principales ácidos y alcoholes generados durante la etapa fermentativa de la digestión anaerobia.

Tabla 4. Principales ácidos y alcoholes generados durante la etapa fermentativa de la digestión anaerobia (Gerardi 2003).

Nombre del compuesto	**Fórmula química condensada**
Acetato	CH_3COOH
Butanol	$CH_3(CH_2)_2CH_2OH$
Butirato	$CH_3(CH_2)_2CH_2COOH$
Ácido hexanoico	$CH_3(CH_2)_4COOH$
Formato	$HCOOH$
Etanol	CH_3CH_2OH
Lactato	$CH_3CHOHCOOH$
Metanol	CH_3OH
Propanol	$CH_3CH_2CH_2OH$
Propionato	CH_3CH_2COOH
Succinato	$HOOCCH_2CH_2COOH$

De manera característica, los compuestos neutros como azúcares y proteínas son convertidos en ácidos grasos volátiles (AGV) y ácido carbónico. La Tabla 5 muestra algunas reacciones acidogénicas a partir de sacarosa, que producen diferentes cantidades de AGV, HCO_3^-, H_2, y H^+.

Tabla 5. Reacciones acidogénicas a partir de sacarosa (Van Lier et al. 2008)

Reacción	**ΔG°' (kJ/mol)**
$C_{12}H_{22}O_{11} + 9H_2O \rightarrow 4CH_3COO^- + 4HCO_3^- + 8H^+ + 8H_2$	- 457.5
$C_{12}H_{22}O_{11} + 5H_2O \rightarrow 2CH_3CH_2CH_2COO^- + 4HCO_3^- + 6H^+ + 4H_2$	- 554.1
$C_{12}H_{22}O_{11} + 3H_2O \rightarrow 2CH_3COO^- + 2CH_3CH_2COO^- + 2HCO_3^- + 6H^+ + 2H_2$	- 610.5

Las reacciones de acidogénesis son las reacciones de conversión más rápidas de la digestión anaerobia y presentan los cambios en la energía libre de Gibbs (ΔG°') más favorables del proceso. Debido a la diferencia en la velocidad de conversión con respecto a la metanogénesis (llegando a ser 5 veces mayor), los reactores anaerobios están sujetos a riesgo de acidificación por la acumulación de los productos de la acidogénesis. Una vez ocurrido esto, la alcalinidad dentro del reactor es consumida y el pH dentro del sistema baja bruscamente, lo que sumado a la existencia de actividad acidogénica a pH bajo conlleva una aún mayor acumulación de AGV y pérdida de la capacidad de producción de biogás del sistema.

3. Acetogénesis: esta etapa hace referencia a la síntesis de acetato ocurrida a partir de otros ácidos grasos de cadena corta y alcoholes, mediada por bacterias fermentativas y cuyos principales productos son ácido acético, hidrógeno y CO_2. Los substratos acidogénicos más importantes son el butirato y el propionato, pero otros como el lactato, etanol, metanol, H_2 y CO_2 también son transformados durante esta etapa.

   A diferencia de las reacciones acidogénicas, las reacciones de formación de acetato son termodinámicamente desfavorables y sólo son posibles a muy bajas concentraciones de H_2 (Khanal 2008). Debido a que las bacterias acetogénicas son productoras obligadas de H_2, estas solo son viables en relación sintrófica con organismos que consuman H_2, como las bacterias metanogénicas hidrogenotróficas. La oxidación de ácido propiónico a acetato resulta termodinámicamente favorable a presiones parciales de hidrógeno bajo 10^{-4} atm, mientras que la oxidación de butirato requiere presiones parciales bajo 10^{-3} atm (Khanal 2008). Esta relación sintrófica es de importancia fundamental para el proceso de digestión anaerobia, considerando que alrededor del 70% del metano se produce a partir del acetato generado durante las etapas fermentativas (Figura 3; Gujer & Zehnder 1983). La Tabla 6 muestra algunas reacciones de degradación de ácidos grasos que ocurren durante la digestión anaerobia y la relación que tiene la actividad hidrogenotófica sintrófica en la viabilidad termodinámica de la acetogénesis.

Tabla 6. Energía Libre de Gibbs estándar de las reacciones involucradas en el consumo sintrófico de butirato y propionato

Reacción	**ΔG°' (kJ/mol)**	**Referencias**
Oxidación de ácidos grasos		
Propionato$^-$ + 2 H_2O → acetato$^-$ + CO_2 + 3 H_2	+ 72	Stams & Plugge (2009)
Butirato$^-$ + 2 H_2O → 2 acetato$^-$ + H^+ + 2H_2	+ 48	Stams & Plugge (2009)
Metanogénesis		
4 H_2 + CO_2 → CH_4 + 2 H_2O	- 131	Stams & Plugge (2009)
Acetato$^-$ + H^+ → CH_4 + CO_2	- 36	Stams & Plugge (2009)
Oxidación de butirato sintrófica		
2 Propionato$^-$ + 2 H^+ + 2H_2O → 5 CH_4 + 3 CO_2	- 177*	Schink (1997)

*kJ/reacción

4. Metanogénesis: durante la etapa final de la digestión anaerobia, acetato, formato, metanol, H_2 y CO_2 son convertidos a metano (CH_4) y dióxido de carbono (CO_2) por la acción de arqueas metanogénicas, existiendo 6 órdenes filogenéticos actualmente identificados: *Methanosarcinales*, *Methanobacteriales*, *Methanomicrobiales*, *Methanococcales*, *Methanopyrales* y *Methanocellales* (Tabla 7).

Tabla 7. Características fisiológicas de los principales órdenes metanogénicos identificados (Angelidaki et al. 2011).

Orden	Fuentes de carbono	Rango de temperatura (°C)	Rango de pH
Methanosarcinales	Acetato, H_2/CO_2, CO, metanol, metilaminas, dimetilsulfuro, metilmercaptopropionato	1 – 70	4.0 – 10.0
Methanobacteriales	H_2/CO_2, formato, compuestos metilados C_1[c]	20 – 88	5.0 – 8.8
Methanomicrobiales	H_2/CO_2, formato, etanol[a], 2-propanol[b], 2-butanol[b], ciclopentanol[b]	15 – 60	6.1 – 8.0
Methanococcales	H_2/CO_2, formato	<20 – 88	4.5 – 9.8
Methanopyrales	H_2/CO_2	84 – 110	5.5 – 7.0
Methanocellales	H_2/CO_2, formato	25 – 40	6.5 – 7.8

[a]*Methanogenium* sp.; [b]*Methanoculleus* sp.; [c]*Methanosphaera* sp.

Los microorganismos metanogénicos son anaerobios estrictos, por lo que se encuentran principalmente en ambientes tales como sedimentos de cuerpos de agua, el tracto intestinal de rumiantes e insectos, aguas termales y suelos inundados (Angelidaki et al. 2011), donde no existe presencia de aceptores inorgánicos de electrones tales como O_2, NO_3^-, Fe^{3+}, y SO_4^{-2}. Como se aprecia en la Tabla 6, los microorganismos metanogénicos poseen un rango muy limitado de substratos utilizables: algunos solo pueden consumir para sus procesos metabólicos acetato, metilaminas, metanol, formato, H_2/CO_2 o CO (Van Lier et al. 2008). Desde el punto de vista de su aplicación en ingeniería, los metanógenos se clasifican principalmente en organismos acetoclásticos e hidrogenotróficos, aunque un tercer grupo constituido por los organismos metilotróficos que convierten compuestos metilados también resulta relevante (Gerardi 2003; Van Lier et al. 2008). La Tabla 8 resume algunas de las propiedades cinéticas y termodinámicas de las dos reacciones metanogénicas más importantes en sistemas de digestión anaerobia.

Tabla 8. Propiedades termodinámicas y cinéticas de las reacciones metanogénicas (Conklin et al. 2006; Van Lier et al. 2008)

Etapa	Reacción	$\Delta G°'$ (kJ/mol)	$\mu_{máx}$ (d^{-1})	T_d (días)	K_s (mgDQO/L)
Metanogénesis acetotrófica	$CH_3^-COO^- + H_2O \rightarrow CH_4 + HCO_3^-$	-31	0.12[a] 0.71[b]	5.8[a] 1.0[b]	30[a] 300[b]
Metanogénesis hidrogenotrófica	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	-131	2.85	0.2	0.06

[a]*Methanosaeta* sp.; [b]*Methanosarcina* sp; $\mu_{máx}$: tasa de crecimiento específico máximo; T_d: tiempo de duplicación; K_s: constante de afinidad por el sustrato

Debido a sus características cinéticas, los organismos filamentosos *Methanosaeta* sp. dominan en ambientes anaerobios con baja concentración de acetato, mientras que *Methanosarcina* sp., de forma cocoide, domina en ambientes con alta concentración de ácidos orgánicos (Van Lier et al. 2008; Angelidaki et al. 2011). *Methanosaeta sp*. es por lo tanto el microorganismo dominante en sistemas de tratamiento de aguas con altos tiempos de retención de sólidos, el cual sin embargo presenta una mayor sensibilidad a cambios en el pH y la concentración de amonio del sistema (Van Lier et al. 2008; Angelidaki et al. 2011).

La digestión anaerobia es utilizada tanto la estabilización de lodos como para el tratamiento de residuos sólidos y aguas residuales urbanas e industriales (Lettinga 1996; Lettinga et al. 1999; Van Lier 2008). La aplicación de la tecnología puede a su vez ser orientada hacia la recuperación de energía por medio del biogás (Van Lier 2008), debido principalmente a la diversidad de residuos que pueden ser digeridos y a la alta eficiencia de conversión energética desde el sustrato al biogás. En efecto, hasta un 85% de la energía química del sustrato puede ser canalizada a metano durante el proceso (Plugge et al. 2009).

2.2. Parámetros operacionales

La digestión anaerobia es un proceso sensible a las condiciones ambientales en las que se desarrolla. Algunos de los parámetros más importantes que afectan su desempeño son descritos a continuación, incluyendo temperatura, pH, alcalinidad, inhibidores y tiempo de retención:

a. Temperatura: la principal influencia de la temperatura sobre los sistemas de digestión anaerobia está relacionada con las tasas metabólicas de los microorganismos del sistema y las propiedades físico-químicas del substrato y otros componentes dentro del digestor (Appels et al. 2008a). En general, se distinguen tres rangos de temperatura en los que puede desarrollarse el proceso (Connaughton et al. 2006): psicrófilo (<20 °C), mesófilo (25 – 45°C) y termófilo (45 – 65°C). Debido a que las tasas de actividad metabólica de los microorganismos pueden duplicarse por cada 10°C (Khanal 2008), generalmente los rangos mesofílicos y termofílicos son los más utilizados en sistemas de carga orgánica elevada, tales como digestores de lodo o reactores para el tratamiento de aguas industriales. Convencionalmente, la mayor parte de los sistemas de digestión operan en rango mesófilo, con temperaturas que fluctúan alrededor de los 35 – 37°C. Esto se debe a que si bien el rango termófilo ofrece ventajas en términos de la carga orgánica tratada, velocidad de las reacciones bioquímicas y destrucción de microorganismos patógenos (Appels et al. 2008a), los sistemas termófilos requieren mayor energía, son más sensibles a efectos de toxicidad (destacando el efecto de la temperatura sobre la fracción de amonio libre), poseen un mayor potencial de malos olores y la deshidratabilidad del digestado tiende a ser menor debido a la mayor presencia de sólidos disueltos (Turovskiy 2006).

b. pH, AGV y alcalinidad: todos los microorganismos involucrados en la digestión anaerobia poseen un rango óptimo de pH, que en el caso de las arqueas metanogénicas corresponde a un estrecho margen entre aproximadamente 6.5 y 7.2 y en el caso de las bacterias fermentativas se extiende entre 4.0 y 8.5 (Appels et al. 2008a). Debido a la sensibilidad de los microorganismos metanogénicos a variaciones en el pH, este debe mantenerse cercano a la neutralidad para evitar posibles problemas de inhibición y pérdida de la actividad biológica. Además, debido a que los AGV producidos por la actividad fermentativa dentro del reactor tienden a disminuir el pH del medio, resulta necesario mantener un nivel de alcalinidad dentro de los digestores suficiente para contrarrestar dicho efecto. La principal fuente de alcalinidad endógena en sistemas de digestión anaerobia es la degradación de compuestos nitrogenados, cuya transformación genera amonio que reacciona con el CO_2 presente en el medio para obtener bicarbonato de amonio (Khanal 2008). Generalmente, los sistemas de digestión anaerobia operan con alcalinidades totales de 1,000 a 5,000 $mgCaCO_{3\text{-}eq}/L$, mientras que la relación entre la alcalinidad aportada por la presencia de AGV y la alcalinidad total es utilizada como un indicador de posible inhibición del sistema, debiendo mantenerse entre 0.1 a 0.3 (Tchobanoglous et al. 2003; Khanal 2008).

c. Tiempo de retención de sólidos: en el caso de reactores de mezcla completa sin recirculación, el tiempo de retención de sólidos (TRS) es el promedio del tiempo de residencia del sustrato y los microorganismos dentro del reactor (Appels et al. 2008a). El tiempo de retención necesario está directamente relacionado con la tasa a la que se desarrollan las reacciones del proceso de digestión, y en el caso de los sistemas de estabilización de lodos puede llegar a alcanzar 20 – 40 días debido a las bajas tasas de hidrólisis (Tchobanoglous et al. 2003).

d. Amonio y otros inhibidores: la actividad biológica durante la digestión anaerobia puede verse inhibida por una serie de compuestos que ingresan o son generados durante el proceso. Estos incluyen la presencia de iones metálicos (Na, K, Mg, Ca, and Al), metales pesados, compuestos orgánicos (incluyendo bencenos, fenoles, alcanos, compuestos halogenados, alcoholes, aldehídos, cetonas, éteres, acrilatos, ácidos grasos de cadena larga y otros) y amonio (Chen et al. 2008). En particular, la inhibición por amonio es un problema recurrente durante la digestión anaerobia de residuos que contienen proteínas y otros compuestos nitrogenados, incluyendo los lodos sanitarios (Yenigün & Demirel 2013). Durante la digestión, dichos compuestos son convertidos en amonio por la acción de los microorganismos anaerobios, el que permanece en el medio principalmente en las formas NH_4^+ y NH_3 y cuyo equilibrio depende principalmente del pH y de la temperatura. La fracción de nitrógeno presente como amonio libre o amoniaco (NH_3) puede estimarse a partir de la concentración de amonio total, temperatura (*T*; K) y pH de acuerdo a la Ecuación 1 (El-Mashad et al. 2004).

$$NH_3\text{-}N = (NH_4^+\text{-}N) \times \left[\frac{1+10^{-pH}}{10^{-\left(0,1075+\frac{2725}{T}\right)}}\right]^{-1} \qquad \text{Ecuación 1}$$

Distintos mecanismos han sido propuestos para explicar la inhibición debido a la presencia de amonio, incluyendo cambios en el pH intracelular, incrementos en el requerimiento de energía de mantenimiento e inhibición de reacciones enzimáticas específicas (Chen et al. 2008). En general, se reconoce que la fracción de amonio libre es la que juega un papel de mayor relevancia en el fenómeno de inhibición, debido a que esta forma permea a través de las membranas celulares y puede afectar la homeostasis de los microorganismos, siendo los metanógenos los de mayor sensibilidad a su presencia (Chen et al. 2008). Debido a que el pKa del equilibrio amonio – amoniaco es de alrededor de 8.9 a 37°C (Emerson et al. 1975), incrementos en el pH por sobre el rango óptimo de operación en digestores alimentados con substratos nitrogenados pueden conllevar episodios de inhibición de la actividad metanogénica. Si bien las concentraciones reportadas como inhibitorias en la literatura varían ampliamente dependiendo de las condiciones ambientales y el nivel de aclimatación de la biomasa, se estima que valores sobre 200 – 400 mg $N\text{-}NH_3/L$ pueden resultar en inhibición del proceso de digestión (Chen et al. 2008; Yenigün & Demirel 2013).

2.3. Rol de la digestión anaerobia en la gestión sustentable de lodos sanitarios

La digestión anaerobia es una de las alternativas de estabilización de lodos más extendida en grandes PTAS (>50.000 personas equivalentes), permitiendo reducir la presencia de patógenos, materia orgánica biodegradable, putrescibilidad y generación de olores, al tiempo que permite la obtención de biogás (Appels et al. 2008a). Esta tecnología ha sido utilizada desde fines del siglo XIX para la estabilización de lodos sanitarios (McCarty 2001), permitiendo obtener reducciones de sólidos volátiles de alrededor de un 50% y eliminaciones de patógenos del orden de 0.5 a 4.0 log dependiendo del tipo de organismo y las condiciones operacionales del proceso (EPA 1995; EPA 2003).

La digestión anaerobia cumple un rol fundamental para la gestión sustentable de los lodos sanitarios en el marco del ciclo antrópico del agua (Figura 5). La continua urbanización de la población en núcleos geográficos reducidos implica una intensificación de las actividades humanas y la subsecuente concentración de los flujos de agua, materiales y energía. Si bien el uso de los recursos naturales tiende a ser más eficiente en los núcleos urbanos que en zonas rurales (Fiala 2008; Meyer 2013), debido a la tendencias crecientes en consumo de la población (de Sherbinin et al. 2007) la mayor parte de los residuos son generados en ciudades, lo que trae como consecuencia la necesidad de intensificar de manera acorde las tecnologías para su tratamiento.

En el caso de las aguas servidas, los sistemas de tratamiento pueden ser entendidos como una intensificación de los procesos naturales de depuración que ocurren en los cuerpos de aguas, en dónde la sedimentación y degradación biológica juegan roles fundamentales para la eliminación de contaminantes y patógenos junto con la acción de la luz del sol, la filtración en sedimentos y otros procesos físicos, químicos y biológicos (Gray 2010). Análogamente, la digestión anaerobia de lodos puede entenderse como una tecnología que favorece las condiciones en que ocurren los procesos naturales de degradación de materia orgánica en ambientes anaerobios, con la ventaja que permite recuperar los productos de la degradación (biogás) para ser utilizados con fines prácticos.

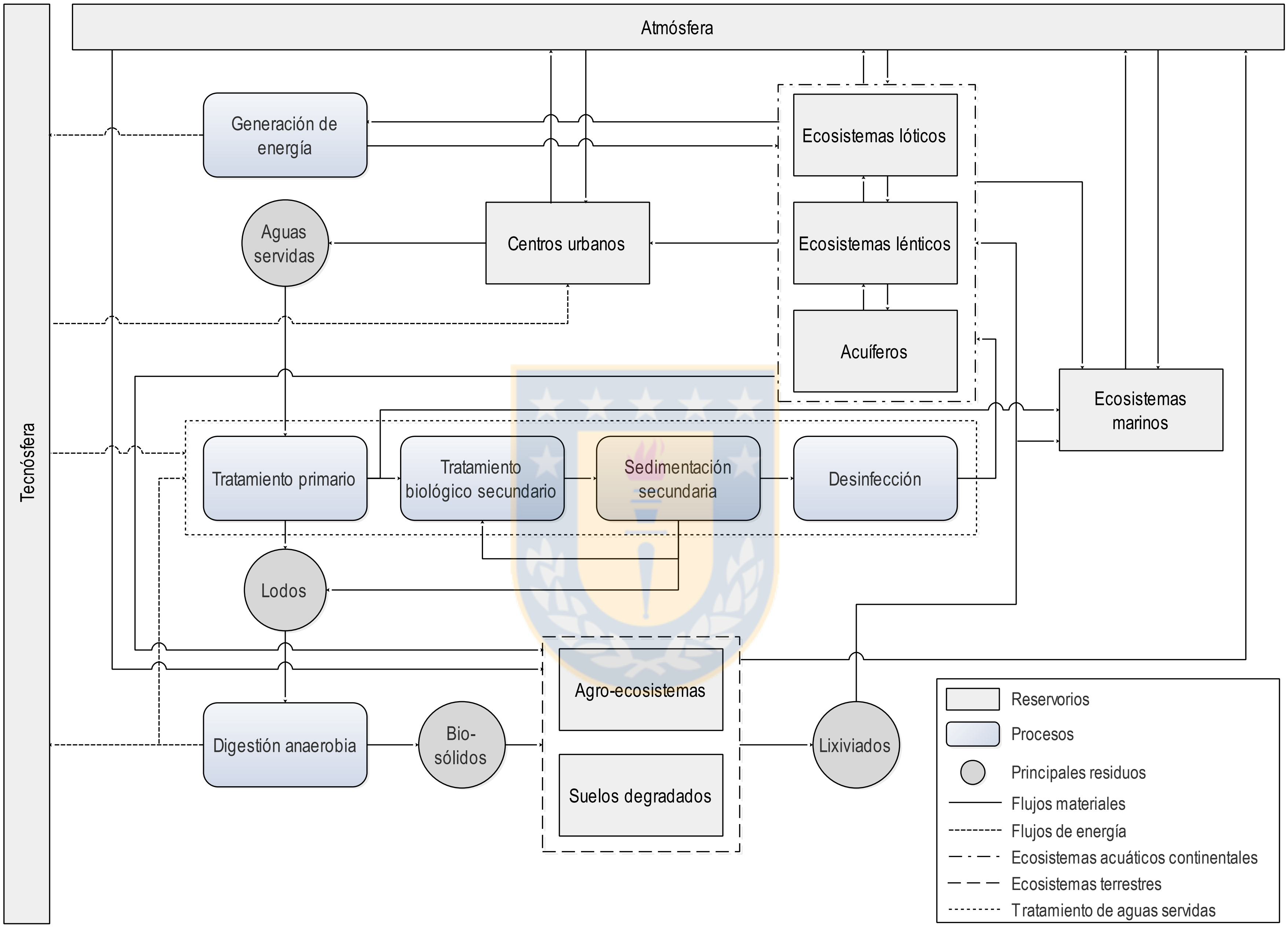

Figura 5. Gestión y valorización de lodos sanitarios y su relación con el ciclo antrópico del agua

Por una parte, el proceso de digestión anaerobia permite disminuir el potencial contaminante y de atracción de vectores de los lodos (Appels et al. 2008a), permitiendo su valorización como fuente de nutrientes (N, P, K) y materia orgánica estabilizada, caracterizada por la presencia de ácidos húmicos y fúlvicos (Yang et al. 2014). Por otra parte, el biogás generado durante el proceso constituye una fuente de energía carbono-neutral (Muradov & Veziroğlu 2008), que puede ser utilizada como reemplazo de fuentes convencionales de energía eléctrica y térmica y así disminuir las presiones ejercidas sobre recursos hídricos y recursos no-renovables.

En Chile, actualmente existen 6 PTAS que utilizan esta tecnología para la estabilización de lodos. En total, dichas plantas generan alrededor de 59.4 millones de m^3 de biogás por año, de acuerdo al detalle presentado en la Tabla 9.

Tabla 9. Generación de biogás en las PTAS de Chile que cuentan con sistemas de digestión anaerobia (SISS 2016)

PTAS	Región	Generación de biogás ($m^3 \times 10^6$/año)	% del total
La Farfana	Metropolitana	33,6	56,6
Mapocho-El Trebal	Metropolitana	21,2	35,7
Concepción	Biobío	2,5	4,2
Talagante	Metropolitana	1,0	1,7
Temuco	Araucanía	0,6	1,1
Osorno	Los Lagos	0,5	0,8

Sin embargo y pesar de su potencial, la valorización de lodos sanitarios mediante digestión anaerobia se enfrenta a algunas limitaciones, relacionadas principalmente con el desempeño del proceso en términos de degradación de la materia orgánica (Appels et al. 2008a). Debido a esto, distintas configuraciones de digestión avanzada empleando procesos de pre-tratamiento han sido propuestas, principalmente orientadas a mejorar la hidrólisis y la conversión de la materia orgánica a biogás (Carrère et al. 2010; Neumann et al. 2016).

3. LIMITACIONES DE LA DIGESTIÓN ANAEROBIA DE LODOS Y USO DE PRE-TRATAMIENTOS

A pesar de las ventajas de la digestión anaerobia como tecnología de estabilización de lodos, la presencia de materia orgánica particulada y compuestos de alto peso molecular causa que la hidrólisis sea la etapa limitante del proceso (Dohányos et al. 2004). Más aún, la presencia de sustancias poliméricas extracelulares (SPE) en los lodos secundarios, excretadas por los microorganismos durante el tratamiento de las aguas servidas, disminuye la biodegradabilidad de los lodos y por ende la cantidad de biogás potencialmente recuperable (Carrère et al. 2010). Dichas sustancias extracelulares están constituidas principalmente por proteínas (~185 – 210 mg/gSSV) y carbohidratos (~18 – 26 mg/gSSV), con rangos de proteína a polisacáridos de alrededor de 6.4 a 10.9 (McSwain et al. 2005). La presencia de las SPE es uno los principales parámetros que controlan la hidrólisis del lodo y determinan la estructura, integridad y resistencia de este a la acción de agentes externos, incluyendo la acción microbiana y enzimática de los microorganismos durante la digestión (Gianico et al. 2013).

Las limitaciones observadas en la hidrólisis tienen importantes implicaciones en el diseño y operación de los sistemas de estabilización anaerobios, siendo la principal consecuencia la necesidad de largos tiempos de retención para obtener una estabilización adecuada del lodo, que habitualmente oscila entre los 20 y 40 días (Tchobanoglous et al. 2003).

En vista de esto, distintos procesos de hidrólisis o pre-tratamientos han sido propuestos como estrategias para mejorar la biodegradabilidad y tasas de hidrólisis del lodo, con consecuentes mejoras en la reducción de materia orgánica y producción de biogás (Neyens & Baeyens, 2003). Los pre-tratamientos pueden tener efectos sobre la degradabilidad intrínseca o sobre la tasa de degradación de los lodos, intensificando el proceso y permitiendo obtener un rendimiento equivalente en digestores de menor tamaño o con un menor tiempo de retención (Carrère et al. 2010).

3.1. Pre-tratamiento de lodos sanitarios

Debido a las mejoras que pueden introducirse en la digestión anaerobia de lodos mediante los distintos procesos de pre-tratamiento, estos han recibido considerable atención durante los últimos años (Carrère et al. 2010; Carlsson et al. 2012; Ariunbaatar et al. 2014). En la actualidad, existen una serie de procesos de naturaleza física, química y biológica en distintas etapas de desarrollo y aplicación. A continuación, se presenta una breve descripción de los procesos más importantes y sus mecanismos de acción, mientras que en el Capítulo III de la presente tesis se entrega una revisión detallada de dichas tecnologías y su efecto sobre las propiedades de los lodos y el desempeño operacional de la digestión anaerobia.

3.1.1. Pre-tratamientos físicos

El primer grupo de pre-tratamientos corresponde a aquellos de naturaleza física. Dentro de este grupo es posible distinguir un amplio número de tecnologías, destacándose los procesos térmicos y aquellos basados en fenómenos hidrodinámicos.

Los pre-tratamientos térmicos corresponden a aquellos en los cuales los lodos son sometidos a altas temperaturas con el objetivo de hidrolizar y solubilizar la materia orgánica, lo que genera mejoras tanto en la capacidad de deshidratabilidad del lodo como en el rendimiento de la digestión anaerobia (Carrère et al. 2010). Además, debido a las condiciones del proceso, es posible mejorar el nivel de higienización del lodo y obtener lodos Clase A (sin restricciones sanitarias para aplicación al suelo) de acuerdo a las directrices de la USEPA (Gianico et al. 2013).

En general, se identifican dos tipos de pre-tratamientos térmicos: a) Pre-tratamientos a baja temperatura (<100 °C) (Gavala et al. 2003; Bougrier et al. 2008; Appels et al. 2010; Val del Río et al. 2011), y b) pre-tratamientos a alta temperatura (100 – 200°C) (Bougrier et al. 2006b, 2007, 2008; Pickworth et al. 2006; Fdz-Polanco et al. 2008; Val del Río et al. 2011; Gianico et al. 2013). Debido al hecho de que la solubilización de materia orgánica se relaciona de manera directa con la temperatura aplicada (Bougrier et al. 2008; Carrère et al. 2008; Val del Río et al. 2011), el grupo de pre-tratamientos realizados a altas temperaturas ha generado mayor interés y ha sido más estudiado. Sin embargo, a temperaturas por sobre los 170 – 190°C la generación de compuestos no biodegradables tales como las melanoidinas pueden disminuir la biodegradabilidad del lodo (Bougrier et al. 2008; Carrère et al. 2010), y la mayor liberación de compuestos inhibitorios (NH_3, AGV) puede afectar negativamente la estabilización anaerobia (Bougrier et al. 2008; Appels et al. 2010).

Además de la aplicación de temperatura, otros procesos físicos que han sido estudiados como pre-tratamiento de lodos son aquellos basados en principios hidromecánicos y electromagnéticos, tales como el uso de ultrasonido, microondas, cambios de presión, molienda y pulsos eléctricos (Engelhart et al. 2000; Lee & Rittmann 2011; Zhang et al. 2012; Appels et al. 2013; Şahinkaya & Sevimli 2013).

Los mecanismos de hidrólisis y pre-tratamiento involucrados en estos procesos dependen del tipo de tecnología. Por ejemplo, la aplicación de ondas ultrasónicas impacta la estructura celular y de los flóculos mediante dos fenómenos principales: la cavitación (favorecida a bajas frecuencias) y la generación de radicales libres oxidantes tales como $OH^{\bullet}$, $HO_2^{\bullet}$ y $H^{\bullet}$ (Carrère et al. 2010). El fenómeno de cavitación puede llevar a aumentos en la temperatura local del lodo hasta valores cercanos a 1000°C y aumentos en la presión hasta 500 bar (Chu et al. 2002). El uso de microondas, vale decir aquellas ondas electromagnéticas con longitud de onda entre 1 mm y 1 m y con una frecuencia de 300 – 0,3 GHz (Appels et al. 2013), tiene efectos tanto térmicos como no térmicos sobre el lodo. El efecto térmico ocurre debido a la interacción entre el campo eléctrico oscilante de la radiación con las moléculas dipolares como el agua y las proteínas, que genera un aumento en la temperatura debido a la continua rotación y fricción de estas (Appels et al. 2013). El efecto no térmico se asocia al rápido cambio en la orientación del dipolo de las macromoléculas que conforman la membrana celular, lo que conlleva el rompimiento de los puentes de hidrógeno entre las moléculas y finalmente la disrupción de la membrana celular (Appels et al. 2013). En los homogenizadores de alta presión, el lodo es sometido a presiones de hasta 900 bar, para luego pasar por una válvula que genera una despresurización drástica hasta la presión atmosférica (Carrère et al. 2010). Los mecanismos involucrados en el pre-tratamiento incluyen la desintegración del lodo debido a gradientes de presión, turbulencia, cavitación y esfuerzos de corte (Zhang et al. 2012). Finalmente, la aplicación de campos eléctricos de alta energía genera la disrupción de la estructura de las membranas bacterianas y la liberación de los componentes intracelulares al medio, debido a la naturaleza polar de los fosfolípidos y el peptidoglucano (Lee & Rittmann, 2011; Salerno et al., 2009).

3.1.2. Pre-tratamientos químicos

Los pre-tratamientos químicos corresponden a todos aquellos procesos basados en la incorporación de compuestos y aditivos que favorezcan la hidrólisis del lodo. Principalmente, se utilizan tres tipos de agentes para los tratamientos químicos: compuestos ácidos (Appels et al. 2011), alcalinos y oxidantes (Carrère et al. 2010), siendo el ozono uno de los más extendidos.

La aplicación de ozono en lodos genera solubilización de las células, lo que se manifiesta en desintegración de los flóculos, oxidación del material particulado y aumento en la fracción de sólidos orgánicos (Cheng & Hong, 2013). Debido a la naturaleza compleja del lodo, el ozono se descompone en radicales libres y reacciona con las distintas fracciones de este: particulada, soluble, mineral y orgánica, con un rango para las dosis óptimas que fluctúa entre 0.05 – 0.5 g O_3/gST (Bougrier et al. 2006a). Dosis más elevadas de ozono pueden generar disminución en el potencial metanogénico del lodo debido a la oxidación y mineralización de la materia orgánica.

Otra tecnología de pre-tratamiento química que ha sido ampliamente estudiada es la hidrólisis alcalina. En este proceso se añaden compuestos que incrementan el pH del lodo y solubilizan la materia orgánica, siendo el NaOH el compuesto que presenta mejores resultados (Kim et al. 2003). La aplicación de pre-tratamientos alcalinos va acompañada habitualmente de temperaturas elevadas, asociadas a la adición de los mismos compuestos (Carrère et al. 2010). Comparado con la adición de compuestos ácidos, la aplicación de compuestos alcalinos permite solubilizar de mejor manera el lodo, motivo por el cual esta estrategia tiende a ser favorecida (Chen et al. 2007).

Otros compuestos que han sido estudiados como manera de pre-tratar lodos incluyen agentes oxidantes tales como el reactivo de Fenton y el peróxido de hidrógeno, además del uso de ácidos orgánicos como el ácido periacético (Appels et al., 2011; Dhar et al., 2011; Erden & Filibeli, 2010).

3.1.3. Pre-tratamientos biológicos

El último grupo de pre-tratamientos de lodos corresponde a los sistemas de tipo biológico. Este tipo de tecnologías pueden estar basadas tanto en procesos aerobios como anaerobios, y su objetivo principal es realizar la etapa de hidrólisis de la materia orgánica compleja en un reactor previo a la etapa de digestión principal.

Existen una serie de configuraciones utilizadas para este tipo de pre-tratamientos, entre las que se encuentran los reactores de dos fases (Athanasoulia et al. 2012; Ferrer et al. 2008; Nges & Liu 2009), sistemas de digestión aerobia (Dumas et al. 2010; Jang et al. 2014), reactores anaerobios por fases térmicas y sus modificaciones (Ge et al. 2010, 2011a,b; Bolzonella et al. 2012; Yu et al. 2013) y sistemas que aprovechan la actividad enzimática endógena de los lodos activados (Carvajal et al. 2013). La adición de enzimas comerciales también ha sido propuesta como estrategia de pre-tratamiento (Barjenbruch & Kopplow 2003; Gavala et al. 2004), aunque el elevado costo de estas puede ir en detrimento de su aplicación a escala industrial.

Tanto los sistemas de pre-tratamiento aerobios como anaerobios operan habitualmente en temperaturas entre 50 a 70°C, debido a las mayores tasas de hidrólisis a esas temperaturas (Ge et al.

2010), lo que además permite incrementar la remoción de organismos patógenos (De Leén & Jenkins 2002). Los pre-tratamientos biológicos permiten solubilizar la materia orgánica particulada (Carvajal et al. 2013), aumentar la remoción de DQO y sólidos (Bolzonella et al. 2012; Yu et al. 2013) y mejorar la producción de biogás (Ge et al. 2011a). Debido a su baja intensidad energética y resultados comparables a otros procesos, los pre-tratamientos biológicos representan una alternativa de hidrólisis viable. Dentro de las estrategias utilizadas destaca la posibilidad de utilizar el potencial enzimático inherente del lodo, lo que permitiría la aplicación de un proceso simple desde el punto de vista técnico, con bajo tiempo de retención y menores consumos energéticos que otras alternativas (Carvajal et al. 2013).

3.2. Pre-tratamientos combinados y aplicación secuencial de ultrasonido y temperatura

Si bien los procesos de pre-tratamiento permiten obtener mejoras significativas en el desempeño del proceso de digestión de lodos, su principal desventaja consiste en su elevado consumo energético, que muchas veces limita su aplicabilidad a escala industrial (Cano et al. 2015). Una de las estrategias que ha sido propuesta para superar esta barrera involucra la aplicación de pre-tratamientos que combinen distintos mecanismos de hidrólisis, incluyendo procesos termo-químicos (Valo et al. 2004; Dhar et al. 2011a; Kim et al. 2013b), físico-químicos (Doğan & Sanin 2009; Tian et al. 2014; Fang et al. 2014) y físico-biológicos (Coelho et al. 2011; Gianico et al. 2014). Debido a la integración de distintos fenómenos, la aplicación de procesos combinados tiene el potencial de generar efectos sinérgicos sobre la solubilización del lodo y la generación de biogás (Doğan & Sanin 2009; Tian et al. 2014, 2015), lo que puede resultar en un mejor desempeño energético del proceso.

En particular, tanto el ultrasonido como los tratamientos térmicos a baja temperatura (<100°C) ejercen efectos similares sobre el lodo. Durante el tratamiento secundario del agua servida, los componentes orgánicos que ingresan al reactor tales como proteínas, lípidos y carbohidratos son degradados a través de reacciones bioquímicas, mediadas por enzimas (Frolund et al. 1995). Debido a esto, los flóculos que conforman los lodos secundarios presentan actividad de diversas enzimas, entre las que se encuentran proteasas, amilasas, lipasas, fosfatasas, aminopeptidasas, dehidrogenasas y glucosidasas (Frolund et al. 1995; Yan et al. 2010). Si bien estas tienen el potencial de actuar sobre la materia orgánica de los lodos y favorecer su hidrólisis y transformación, la mayor parte se encuentran asociadas a las SPE (Frolund et al. 1995; Burgess & Pletschke 2008), por lo que previamente resulta necesaria la disrupción la matriz de los flóculos y su liberación al medio mediante procesos tales como la aplicación de temperatura (Yan et al. 2008; Guo & Xu 2011; Carvajal et al. 2013), radiación (Chu et al. 2011) o ultrasonido (Yu et al. 2009; Yan et al. 2010; Guo & Xu 2011). Tales procesos pueden además favorecer la actividad de las enzimas liberadas, ya sea mediante incrementos en las tasas cinéticas o a través de mejoras en las condiciones de transferencia de masa y una mayor interacción enzima-substrato (Peterson et al. 2007; Leaes et al. 2013; Souza et al. 2013). La Tabla 10 sumariza los resultados de estudios asociados a la presencia y actividad de enzimas endógenas en lodos provenientes del tratamiento de aguas servidas, bajo diferentes condiciones experimentales.

Utilizar pre-tratamientos que favorezcan la actividad enzimática endógena del lodo permite utilizar una capacidad intrínseca de este, evitando la adición de compuestos químicos y grandes consumos de energía. Carvajal et al. (2013) reportaron que el uso de un pre-tratamiento térmico (55°C) orientado a favorecer la actividad hidrolítica y biológica en lodo secundario permitió una solubilización de hasta 39% en términos de DQO, mayores tasas de productividad de metano (hasta 30%) y mejoras de más de un 20% en la producción de biogás.

En particular, la integración de ultrasonido y tratamiento térmico permitiría tanto la disrupción física de los flóculos del lodo como el generar condiciones favorables para la actividad enzimática endógena (Carvajal et al. 2013; Leaes et al. 2013; Souza et al. 2013). Estudios previos reportan que dicho proceso resulta en efectos sinérgicos e incrementos de hasta un 30% sobre el rendimiento de metano (Şahinkaya & Sevimli, 2013), además de mejoras de hasta 38% en la reducción de sólidos volátiles (Dhar et al. 2012). Además, las condiciones utilizadas durante el proceso permitirían la eliminación potencial de microorganismos patógenos (Ruiz-Espinoza et al. 2012; Gao et al. 2014), repercutiendo positivamente en la calidad del digestado.

Tabla 10. Actividad enzimática reportada en lodos sanitarios bajo distintas condiciones.

Lodo	Tratamiento	Enzimas estudiadas	Principales resultados	Referencias
Secundario (PTAS Shanghái)	Ultrasonido	Proteasa, α-glucosidasa, α-amilasa, fosfatasa alcalina y fosfatasa ácida.	Actividad enzimática total del lodo es de alrededor de 50 U/gST e incrementa hasta ~400% debido a la aplicación de ultrasonido (30,000 kJ $kgST^{-1}$).	Yan et al. (2010)
			Actividad de 1.9 – 16.3 µmol min^{-1} $gSSV^{-1}$ en el lodo, dependiendo del tipo de enzima y condiciones de tratamiento. La mayor parte se encuentra ligada fuertemente a las SPE. Ultrasonido incrementa actividad enzimática y favorece degradación aerobia del lodo.	Yu et al. (2008)
Secundario (PTAS Tokio)	Tratamiento térmico a 60°C	Proteasa	Tratamiento induce lisis celular en organismos mesófilos y proliferación de bacterias termodúricas y termofílicas a partir de las 7 h. Actividad de hasta ~1.0 U/mL en el sobrenadante del lodo debido a lisis celular y secreción por parte de organismos activos.	Yan et al. (2008)
Secundario (PTAS Beijing)	Irradiación gamma ^{60}Co	Superóxido dismutasa, proteasa, catalasa	Irradiación produce desintegración de flóculos y liberación de proteínas, carbohidratos y enzimas. El tratamiento disminuye las actividades de superóxido dismutasa y catalasa, mientras que proteasa incrementa de ~120 a ~140 U $gSST^{-1}$ con dosis bajo 15 kGy.	Chu et al. (2011)
Secundario (PTAS Aalborg)	Extracción por intercambio catiónico	Glucosa-6-fosfato deshidrogenasa, esterasa, glucosidasas, leucina aminopeptidasa, β-glucuronidasa, quitinasa, proteasa y lipasa	Actividad de esterasa y leucina aminopeptidasa fue de 55 x 10^{-12} y 61 x 10^{-12} µmol $célula^{-1}$ h^{-1}. Otras enzimas presentan menor actividad. La mayor parte de las enzimas están asociadas a las SPE de los flóculos.	Frolund et al. (1995)
			Actividad de proteasa y lipasa en extractos del lodo secundario fue de >300 U $gSSV^{-1}$. Ultrasonicación favorece eficiencia de extracción del tratamiento y actividad de las enzimas.	Gessesse et al. (2003)

U: Unidades de actividad enzimática; ST: Sólidos Totales; SSV: Sólidos Suspendidos Volátiles; SPE: Sustancias Poliméricas Extracelulares; kGy: Kilogray; SST: Sólidos Suspendidos Totales

4. INFLUENCIA DEL PRE-TRATAMIENTO SOBRE EL DESEMPEÑO AMBIENTAL DE LA DIGESTIÓN ANAEROBIA DE LODOS SANITARIOS

Como se describió previamente, los pre-tratamientos constituyen una alternativa cuya eficiencia ha sido ampliamente reportada para mejorar el desempeño operacional de la digestión anaerobia de lodos y otros residuos sólidos y semisólidos (Carrère et al. 2010; Carlsson et al. 2012; Ariunbaatar et al. 2014). Si bien el balance energético de muchos de los procesos aparece como una sus principales limitaciones (Cano et al. 2015), un aspecto que ha recibido considerablemente menos atención en la literatura tiene relación con los impactos ambientales asociados a su implementación. Entre otros aspectos, los pre-tratamientos involucran el consumo de recursos e infraestructura, alteran el desempeño operacional de la digestión anaerobia y etapas subsequentes y alteran la calidad del digestado obtenido después de la estabilización (Stuckey & McCarty 1984; Neyens & Baeyens 2003; Gavala et al. 2004; Carballa et al. 2008; McNamara et al. 2012), lo cual puede resultar en modificaciones en las emisiones e impactos ambientales durante las distintas etapas de la gestión del lodo (Carballa et al. 2011).

El Análisis de Ciclo de Vida (ACV) es una metodología de carácter interdisciplinario, estandarizada internacionalmente en directrices ISO (ISO 14040:2006; ISO 14044:2006) y utilizada para cuantificar los impactos ambientales de productos, procesos o servicios desde una perspectiva integral, incluyendo potencialmente las etapas desde la extracción de los recursos naturales hasta la disposición de los residuos en el ambiente (Finnveden et al. 2009). Esta herramienta se desarrolló a partir de las décadas de 1960 y 1970 como una aproximación para extender los análisis de energía e incluir criterios tales como el requerimiento de recursos, cargas de emisiones y generación de residuos (Guinée et al. 2011). El principal interés era comparar ambientalmente distintos productos, comprendiendo que en muchos casos los impactos ambientales no ocurren durante la etapa de uso, sino durante la producción, transporte o disposición de residuos (Guinée et al. 2011). De manera gradual, el ACV pasó de ser una técnica orientada a la estimación de algunos indicadores generales de desempeño ambiental a cuantificar el potencial de impactos ambientales específicos tales como cambio climático, eutrofización, acidificación, ecotoxicidad, agotamiento de recursos y otros, lo que ha elevado significativamente la complejidad de la herramienta y de los modelos involucrados en su evaluación (Pennington et al. 2004; Guinée et al. 2011). Aún más, la herramienta se ha extendido a áreas tales como los costos económicos y los impactos sociales en el ciclo de vida, lo que ha llevado al desarrollo de técnicas y enfoques tales como el Coste del Ciclo de Vida y Análisis de Ciclo de Vida Social, además de la integración de estos con el ACV ambiental en el marco del Análisis de Ciclo de Vida de la Sustentabilidad (Guinée et al. 2011; Zamagni 2012).

El ACV permite abordar de manera comprehensiva las distintas etapas involucradas en la generación, uso y disposición de bienes y servicios, cuantificando su impacto potencial sobre tres esferas principales: recursos naturales, integridad de los ecosistemas y salud humana (Pennington et al. 2004; JRC European Commission 2011). La realización de estudios de ACV asociados a sistemas de tratamiento de aguas servidas lleva en la actualidad más de 15 años (Corominas et al. 2013), existiendo una importante literatura relacionada con el estudio de las estrategias asociadas a la gestión de los lodos sanitarios (Yoshida et al. 2013). Si bien los resultados de dichos estudios tienden a ser particulares a las condiciones y suposiciones técnicas bajo los cuales fueron desarrollados, un número substancial de estos identifica las etapas asociadas a la estabilización y disposición del lodo como puntos críticos en el desempeño ambiental de las estrategias de gestión, debido principalmente a las emisiones y el consumo y valorización de energía y materiales (Hospido et al. 2005, 2010; Murray et al. 2008; Peters & Rowley 2009; Sablayrolles et al. 2010; Lederer & Rechberger 2010). La Tabla 11 muestra algunos de los aspectos e impactos ambientales asociados con el ciclo de vida de la gestión de lodos sanitarios, enfocándose en los impactos más reportados en literatura y las alternativas de estabilización y disposición utilizadas convencionalmente en Chile (SISS 2011; Yoshida et al. 2013).

Sin embargo, la literatura relacionada con las implicaciones que conlleva la implementación de sistemas de pre-tratamiento desde el punto de vista ambiental es más bien limitada. Uno de los estudios más comprehensivos fue el realizado por Carballa et al. (2011), el cual determinó la influencia de 7 tipos distintos de pre-tratamientos sobre los impactos ambientales de la digestión anaerobia de lodos y residuos de alimentos. Dentro de las principales conclusiones de dicho estudio, se cuenta el hecho de que los pre-tratamientos mecánicos (específicamente presurización – despresurización) y químicos presentaron un mejor desempeño ambiental, en gran medida debido al perfil asociado al consumo de energía y reactivos en el contexto estudiado (España). Las categorías de impacto estudiadas incluyeron potencial de cambio climático, agotamiento de recursos, eutrofización, acidificación, ecotoxicidad y toxicidad humana. Mills et al. (2014), por otra parte, determinaron que la implementación de hidrólisis térmica (165°C, 7 bar, 30 min) permite mejorar el desempeño económico y ambiental de la digestión anaerobia de lodos sanitarios, en términos del impacto potencial ponderado para las categorías cambio climático, eutrofización, acidificación, agotamiento de recursos y generación de ozono fotoquímico.

Gianico et al. (2015), por otra parte, reportó que el costo energético asociado con la implementación de oxidación de los lodos primarios y pre-tratamiento térmico de los lodos secundarios (134°C) superaba el beneficio asociado a la implementación de un sistema de co-generación a partir del biogás. Sin embargo, el sistema mejorado resultó en un incremento significativo en la remoción de sólidos y su desempeño ambiental fue similar al del sistema convencional, considerando impactos potenciales de cambio climático, acidificación, eutrofización y generación fotoquímica de oxidantes. Enfocándose en residuos de alimentos, Franchetti (2013) reportó que un escenario incluyendo pre-tratamiento mediante ultrasonido y digestión anaerobia en dos fases presenta el mejor desempeño económico y en términos de emisión de gases de efecto invernadero que otras 4 alternativas de gestión, incluyendo disposición en relleno sanitario, digestión convencional, generación termofílica de hidrógeno y estabilización anaerobia en un sistema de alto tiempo de retención.

De esta manera, una evaluación integral de las tecnologías de pre-tratamiento debiera considerar tanto sus dimensiones técnicas como ambientales. Si bien el objetivo principal de su incorporación está asociado generalmente con incrementar la producción de biogás, resulta relevante comprender su influencia en el marco de la relación que tienen las distintas etapas de la gestión del lodo con el medioambiente. Adoptar una perspectiva de ciclo de vida permite por lo tanto evaluar los impactos ambientales en todas las etapas afectadas por la implementación de pre-tratamientos, evaluando los posibles compromisos y desplazamientos de las cargas ambientales y permitiendo proponer medidas de gestión orientadas al mejoramiento del desempeño ambiental global.

Tabla 11. Sumario de aspectos e impactos ambientales relevantes asociados con la gestión de lodos sanitarios.

Impactos ambientales	Escala	Aspectos ambientales	Etapas o procesos asociados
Cambio climático	Global	Consumo de combustibles fósiles y electricidad	Bombeo, espesamiento, estabilización, deshidratado, transporte
		Emisión de CH_4	Estabilización anaerobia, almacenamiento y secado
		Emisión de N_2O	Disposición (suelos, rellenos sanitarios)
		Reemplazo de combustibles fósiles y electricidad*	Estabilización anaerobia (co-generación)
		Reemplazo de fertilizantes comerciales*	Disposición (suelos agrícolas)
Agotamiento de recursos	Global	Consumo de combustibles fósiles y electricidad	Bombeo, espesamiento, estabilización, deshidratado, transporte
		Consumo de reactivos	Espesamiento, deshidratado, estabilización química
		Consumo de materiales	Disposición (rellenos sanitarios)
		Reemplazo de combustibles fósiles y electricidad*	Estabilización anaerobia (co-generación)
		Reemplazo de fertilizantes comerciales*	Disposición (suelos agrícolas)
Eutrofización (terrestre, aguas continentales y marinas)	Regional	Emisión de NH_3	Estabilización alcalina, disposición (suelos, rellenos sanitarios)
		Lixiviación de nutrientes	Disposición (suelos, rellenos sanitarios)
Acidificación	Regional	Emisión de NH_3	Estabilización alcalina, disposición (suelos, rellenos sanitarios)
Ecotoxicidad	Local	Acumulación de metales y microcontaminantes	Disposición (suelos)
		Lixiviación de metales y microcontaminantes	Disposición (suelos, rellenos sanitarios)
Toxicidad humana	Local	Traslocación de metales a cultivos	Disposición (suelos agrícolas)
Enfermedades infecciosas y disminución en la calidad de vida	Local	Contagio de enfermedades por parte de operarios	Operaciones en planta, transporte y disposición
		Generación de olores y atracción de vectores	Operaciones en planta, transporte y disposición
		Propagación de organismos patógenos	Disposición (suelos, rellenos sanitarios)

*Impactos positivos; Elaborado en base a Carballa et al. (2011), Yoshida et al. (2013) y Harder et al. (2014).

5. SUMARIO Y ESTRUCTURA DE LA TESIS

En base a lo anteriormente expuesto, la presente tesis tiene como objetivo principal evaluar la influencia de un proceso de pre-tratamiento de lodos sanitarios sobre el desempeño operacional y ambiental de la digestión anaerobia. En particular, el proceso consiste en la aplicación secuencial de ultrasonido y tratamiento térmico a 55°C (Figura 6).

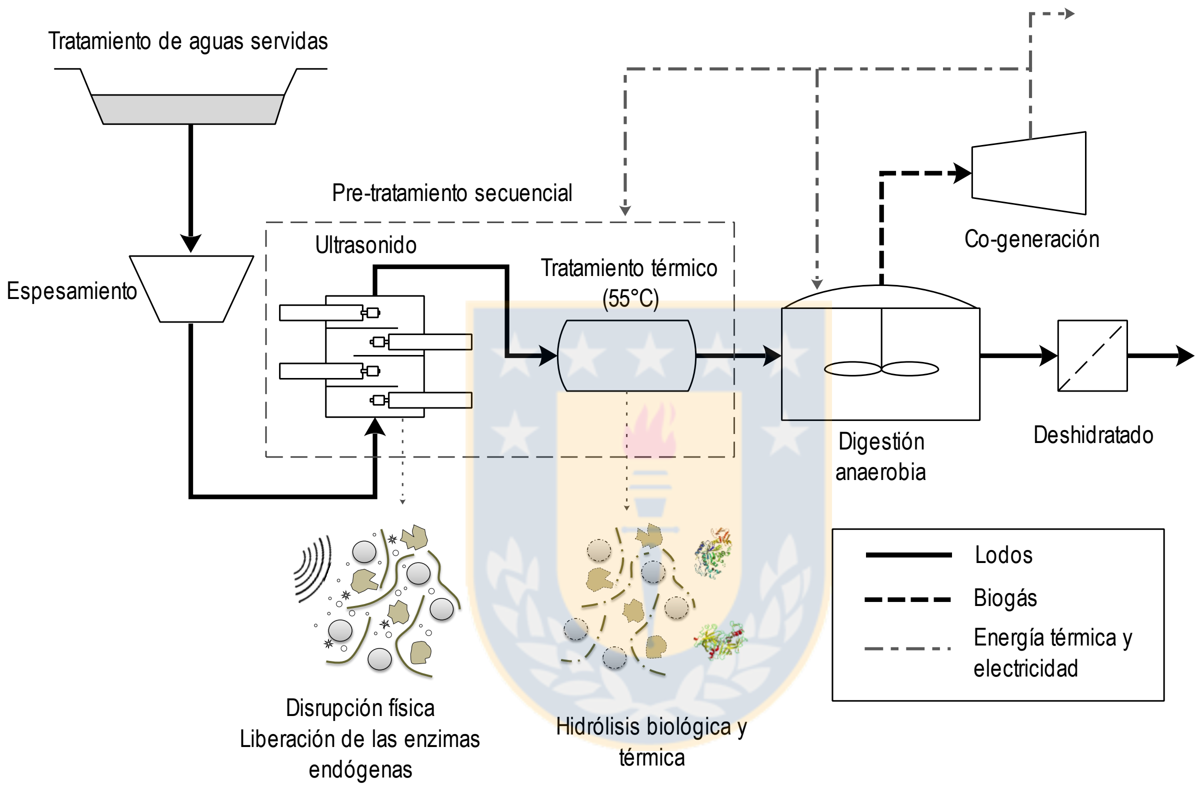

Figura 6. Diagrama del proceso de pre-tratamiento secuencial propuesto.

Considerando las condiciones operacionales en las que se desarrollará, se espera que dicho proceso resulte en la solubilización e hidrólisis de la materia orgánica de los lodos debido a la integración de procesos físicos y biológicos, lo que se espera influencie la digestión anaerobia en términos de conversión de materia orgánica y producción de biogás. Para evaluar si la incorporación del pre-tratamiento resulta en el desplazamiento de cargas ambientales a otras etapas de la gestión del lodo, se adoptará un enfoque basado en ACV, para lo cual resulta necesario evaluar los efectos operacionales del pre-tratamiento tanto en términos de producción de biogás como sobre las características del digestado.

En el Capítulo II del presente documento se establecen las hipótesis de trabajo del estudio, así como su objetivo general y objetivos específicos. El Capítulo III, por otra parte, presenta una revisión bibliográfica de la literatura referente al pre-tratamiento de lodos sanitarios, incluyendo la mayor parte de las tecnologías que han sido propuestas y sus efectos sobre las caraterísticas de los lodos y el desempeño de la digestión anaerobia. La revisión concluye con una discusión de los principales desafíos identificados para el desarrollo e implementación de los pre-tratamientos en PTAS.

En el Capítulo IV se presentan los resultados de la evaluación de la influencia del pre-tratamiento propuesto sobre la caracterización del lodo, específicamente sobre la solubilización de macromoléculas (proteínas y carbohidratos) y las actividades de proteasa y amilasa en fase soluble. Además, se realizó una optimización de las condiciones operacionales del pre-tratamiento sobre la solubilización de DQO. El capítulo finaliza con una evaluación del efecto del pre-tratamiento sobre la biodegradabilidad y cinética de la digestión anaerobia del lodo y un balance energético preliminar.

El Capítulo V presenta los principales resultados de la evaluación del efecto del pre-tratamiento sobre la digestión anaerobia del lodo en operación semi-continua, bajo distintas condiciones experimentales. Los resultados de dicho estudio se relacionan principalmente con la conversión de materia orgánica durante el proceso, la producción de biogás y la calidad del lodo estabilizado (digestado), específicamente en parámetros relacionados con la capacidad de deshidratabilidad, concentración de nutrientes y metales y presencia de indicadores de contaminación microbiológica.

El Capítulo VI presenta los resultados del ACV realizado al proceso de digestión anaerobia incluyendo pre-tratamiento, además de su comparación con estrategias de gestión de lodos utilizadas en Chile. En este estudio se evaluaron 6 categorías de impacto ambiental, incluyendo los potenciales de cambio climático, agotamiento de recursos abióticos, acidificación y eutrofización en ecosistemas terrestres, marinos y dulceacuícolas.

Finalmente, el Capítulo VII presenta una discusión general de los principales resultados de la tesis, mientras que en el Capítulo VIII se presentan las principales conclusiones y recomendaciones surgidas del trabajo.

CAPÍTULO II

HIPÓTESIS Y OBJETIVOS

1. HIPÓTESIS

- El pre-tratamiento de lodos sanitarios consistente en la aplicación secuencial de ultrasonido e hidrólisis térmica (55°C) permitirá favorecer la conversión de materia orgánica y desempeño operacional de la digestión anaerobia, incrementando en al menos un 20% la producción de biogás.

- Debido a la mayor recuperación de energía, los impactos asociados a la gestión de los lodos sanitarios se verán disminuidos por la incorporación del pre-tratamiento secuencial mediante ultrasonido e hidrólisis térmica (55°C), mejorando su desempeño ambiental.

2. OBJETIVOS

2.1. Objetivo general

Evaluar el desempeño operacional y ambiental de la digestión anaerobia de lodos provenientes del tratamiento de aguas servidas incluyendo pre-tratamiento mediante ultrasonido e hidrólisis térmica (55°C).

2.2. Objetivos específicos

1. Evaluar y optimizar la influencia del pre-tratamiento secuencial sobre las características del lodo sanitario y la solubilización de materia orgánica.
2. Determinar la influencia del pre-tratamiento secuencial sobre la digestión de lodos sanitarios, en términos de conversión de materia orgánica, producción de biogás y calidad del lodo estabilizado.
3. Evaluar comparativamente la influencia del pre-tratamiento secuencial sobre el desempeño ambiental asociado a la gestión del lodo sanitario.

CAPÍTULO III

DEVELOPMENTS IN PRE-TREATMENT METHODS TO IMPROVE ANAEROBIC DIGESTION OF SEWAGE SLUDGE

Neumann P., Pesante S., Venegas M., Vidal G. 2016. Developments in pre-treatment methods to improve anaerobic digestion of sewage sludge. *Reviews in Environmental Science and Bio/Technology*, 15 (2):173–211.

Developments in pre-treatment methods to improve anaerobic digestion of sewage sludge

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Abstract

During wastewater treatment, most organic matter is transferred to a solid phase commonly known as sludge or biosolids. The high cost of sludge management and the growing interest in alternative energy sources have prompted proposals for different strategies to optimize biogas production during anaerobic sludge treatment. Because of the high solid content and complex structure of sludge-derived organic matter, methane production during digestion is limited at the hydrolysis step. Therefore, large digester volume and long retention times of over 20 days are necessary to achieve adequate stabilization. Pre-treatments can be used to hydrolyze sludge and consequently improve biogas production, solids removal and sludge quality after digestion.

This paper reviews the main pre-treatment processes, with emphasis on the most recent developments. An overview of the different technologies is presented, discussing their effects on sludge properties and anaerobic digestion. Future challenges and concerns related to pre-treatment assessment and implementation are also addressed.

Nomenclature

AD	anaerobic digestion
ATH	advanced thermal hydrolysis
BOD	biochemical oxygen demand
COD	chemical oxygen demand
CST	capillary suction time
DD	disintegration degree
DMDO	dimethyldioxirane
DOC	dissolved organic carbon
DS	dry solids
EDC	endocrine disrupting compounds
EPS	extracellular polymeric substances
F/I	feed/inoculum ratio
FC	fecal coliforms
GRS	growth rate of solubilization
HE	helminth eggs
HPH	high pressure homogenization
MW	microwave
ODS	organic dry solids
OLR	organic loading rate
OM	organic matter
OUR	oxygen uptake rate
PAA	peracetic acid
POMS	peroxymonosulfate
PT	pre-treatment
SBOD	soluble biochemical oxygen demand
SCOD	soluble chemical oxygen demand
SN	salmonella
SS	suspended solids
SRF	specific resistance to filtration

SRT	solids retention time
SVI	sludge volumetric index
TCOD	total chemical oxygen demand
TN	total nitrogen
TPAD	thermally-phased anaerobic digestion
TSBP-AD	temperature-staged biologically-phased anaerobic digestion
TS	total solids
TSS	total suspended solids
US	ultrasound
VFAs	volatile fatty acids
VS	volatile solids
VSS	volatile suspended solids
WAS	waste activated sludge

1. INTRODUCTION

Although sewage treatment is a cornerstone of public health and environmental protection, there is concern about the large quantity of sludge generated by treatment facilities. Current sewage and wastewater treatment technologies are mainly based on physical and biological processes. During treatment most organic matter is transferred to a semisolid phase known as sludge or biosolids. Sludge disposal is a potential source of soil and water pollution, and its management can account for up to 50% of the cost of wastewater treatment (Appels et al. 2008a).

Sewage sludge is characterized by high concentrations of solid and organic matter, with a significant presence of pathogens, nutrients, and organic and inorganic pollutants. Table 1 characterizes important constituents of untreated sewage sludge. Due to its characteristics, sludge represents both a problem and an opportunity. While sludge can be used as fertilizer, in most cases it must first be stabilized to decrease its potential as a pollutant.

Table 1. Characterization of sewage sludge (Adapted from EPA 1995)

Parameter	Value	Unit
Solids	2 – 12 (liquid sludge)	%
	12 – 40 (dehydrated sludge)	%
Organic matter	75 – 85	% d.w.
Fecal coliforms	10^9	No./100mL
Virus	2500-70000	No./100mL
Helminth	200-1000	No./100mL
P	<0.1 – 17.6	% d.w.
N	<0.1 – 14.3	% d.w.
K	0.02 – 2.64	% d.w.
Cr	119	mg/kg d.w.
Cu	741	mg/kg d.w.
Hg	5.2	mg/kg d.w.
Pb	134.4	mg/kg d.w.

Anaerobic digestion (AD) is one of the most widely used stabilization technologies. During AD, a combustible gaseous mixture composed principally of CO_2 and CH_4 is produced by biological activity (Appels et al. 2008a), investing sludge with commercial value as a bioenergy source. However, the presence of high molecular weight compounds and complex organic matter in sludge limits the hydrolysis step of AD, requiring large reactor volumes and long retention times to achieve adequate stabilization prior to disposal or re-use.

One strategy to overcome this limitation is to pre-treat sludge before AD. Pre-treatment involves single or combined physical, chemical and biological means to disrupt the floc structure of sludge and hydrolyze organic matter. This provides significant enhancements in terms of solids reduction, biogas production and digested sludge properties (Carrère et al. 2010). This work reviews the most recent developments in sewage sludge pre-treatment for AD, with a focus on historical developments, their principal results and future research challenges. The objective is to provide broad insights on recently published information about sludge pre-treatment technologies, complementary to previously published reviews on the subject (Carrère et al. 2010; Carlsson et al. 2012; Ariunbaatar et al. 2014).

2. DEVELOPMENT OF SLUDGE PRE-TREATMENT TECHNOLOGIES

AD is a complex biochemical process that involves the action of microorganisms forming syntrophic consortia. It follows four fundamental steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis. The first step, hydrolysis, consists of the degradation of high molecular weight compounds to monomers and other smaller molecules. Hydrolysis is widely regarded as the limiting step because of the presence of particulate organic matter and complex macromolecules such as extracellular polymeric substances (EPS) excreted by microorganisms during biological treatment of wastewater (Dohányos et al. 2004; Gianico et al. 2013). This results in limited biodegradation and biogas production, with pre-treatment as one of the most studied alternatives to overcome this drawback.

Pre-treatment technologies have been studied since the late 1970s. The first applications of sludge pre-treatment were based on thermal processes. While those proved to be interesting alternatives to improve sludge dewaterability and anaerobic biodegradability (Haug et al. 1978), other processes have since been studied and proposed as alternatives.

As shown in Fig. 1, there have been a growing number of publications on sludge pre-treatment methods since the mid-90s, which could be related to the need for sustainable sludge management methods in the wake of more restrictive legislation and bans on practices like ocean dumping. Sludge pre-treatment has become an important area of research, as can be noted by the growing number of publications in recent years.

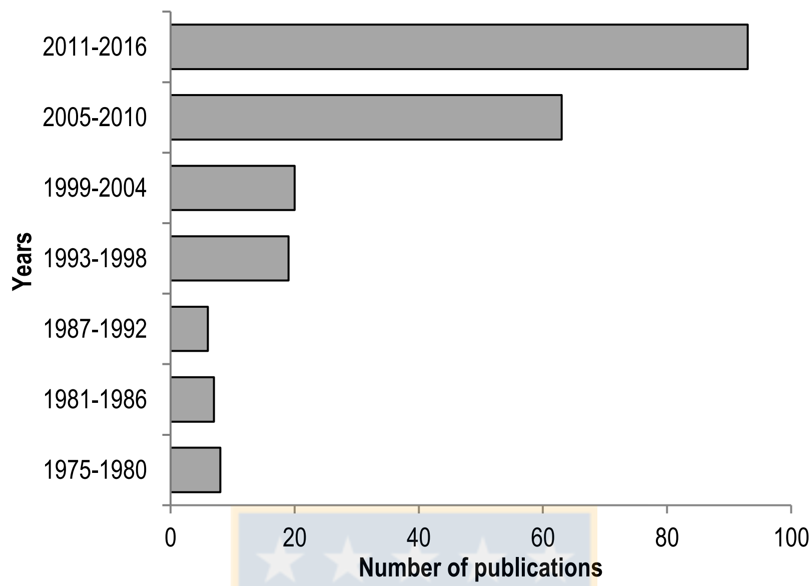

Figure 1. Number of papers on sludge pre-treatment for AD published between 1975 and 2016

Pre-treatment can be applied to primary, secondary or mixed sludge. Most of the reports we found are oriented to waste activated sludge (secondary sludge; WAS) pre-treatment, followed by mixed and primary sludge. The predominance of reports on WAS pre-treatment may be related to the lower biodegradability of secondary compared to primary sludge, especially with older sludge (Gossett 1982; Bolzonella et al. 2005). However, thermal and other pre-treatment techniques can significantly improve pathogen deactivation and sludge quality, and therefore their application to mixed and primary sludge can be attractive depending on the main objective (Wilson and Novak 2009; Carrère et al. 2010).

According to the nature of the technology, pre-treatment can be classified as thermal, physical (non-thermal), chemical and biological. Combinations of these have also been studied. Fig. 2 shows that physical and thermal pre-treatments are the most studied, each representing more than a third of the total references found. Electric pulse, microwave, irradiation, grinding, high pressure homogenization, centrifugation and ultrasound are among the technologies that fall under the physical pre-treatment category, with ultrasound representing around half of the reports of this group. The least studied pre-treatments are chemical, accounting for 14% of total references and with alkaline treatment and ozonation as the prevalent methods. The addition of acids and other oxidant agents such as hydrogen peroxide have also been reported. Finally, biological processes represent around 16% of the references. Within this group, anaerobic pre-treatments (dual-digestion and thermal phased AD), enzyme addition, aerobic digestion and auto-hydrolysis have been studied, with anaerobic processes being predominant. Although temperature phased anaerobic digestion (TPAD) and dual-digestion can be considered both AD operational strategies and pre-treatment processes (Pérez-Elvira et al. 2006; Carrère et al. 2010), they are included in this work because of their relevance and for having a common aim as other pre-treatment technologies. An important trend in sludge pre-treatment is evaluation of combined processes, with significant growth in the last 6 years (Fig. 2). The most common pre-treatment combinations are physical/chemical and thermo/chemical. Processes based on the integration of mechanical or chemical disruption and dual-digestion or TPAD have also received attention. The growing number on reports of combined processes reflects the need to overcome the limitations of single processes and achieve more significant improvements in AD through synergistic effects. The lower number of references related to single physical and chemical pre-treatments in the last six years could also be related to a shift in focus towards combined processes, while the increase in single biological pre-treatment reports could be related to their good results and low energy consumption compared to other processes.

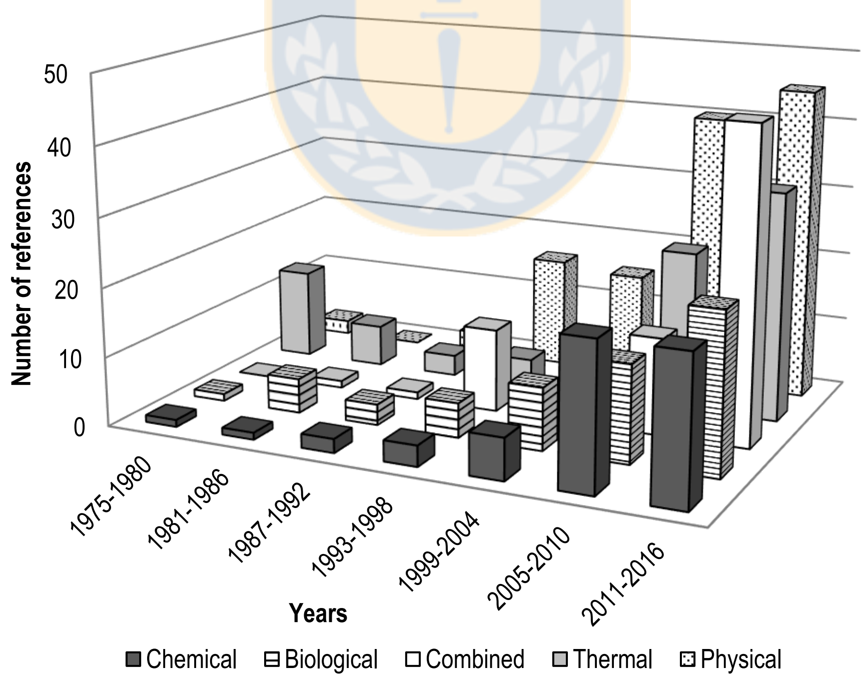

Figure 2. Evolution of references between 1975 and 2016 on sludge pre-treatments according to the type of process

As pre-treatments can have different effects on sludge properties, the main objective for their application can vary from one study to another. Most published reports have dealt with the general performance of digestion (Fig. 3), including at least improvements in biogas production and solids reduction. A significant 22% fall in the *others* category, representing studies on either hydrogen production (Wang and Wan 2008; Massanet-Nicolau et al. 2008; Xiao and Liu 2009), toxicity (Stuckey and McCarty 1984), removal of micro-pollutants (Gavala et al. 2004; Carballa et al. 2007; Bernal-Martinez et al. 2007), sulfur control (Dhar et al. 2011b; Dhar et al. 2011a), foaming (Barjenbruch and Kopplow 2003), kinetics and modeling (Riau et al. 2012; Saha et al. 2014), or techno-economic and environmental assessments (Salsabil et al. 2010; Carballa et al. 2011; Dhar et al. 2012). In addition to assessing AD performance in biogas production and solids reduction, most authors have considered organic matter solubilization, pathogen elimination (Skiadas et al. 2005; Lu et al. 2008), dewaterability (Braguglia et al. 2010; Pérez-Elvira et al. 2011) or the effects of pre-treatment on microbial digester communities (Zhang et al. 2009; Braguglia et al. 2012; Jang et al. 2014).

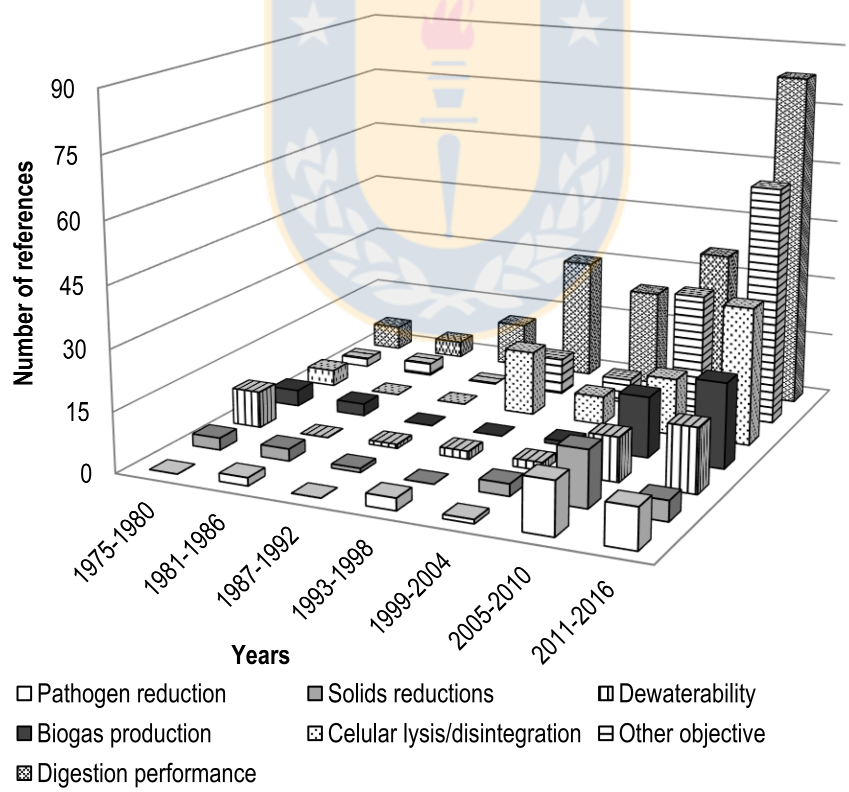

Figure 3. Evolution of references between 1977 and 2014 on sludge pre-treatment according to the main objective

Most of the published works are oriented to improving mesophilic AD. The mesophilic temperature range (35 – 37°C) is the conventional and therefore the most often used range for AD, so it can be expected that most research is oriented to its study. Moreover, pre-treatment tends to show better results before mesophilic digestion than before thermophilic digestion (55°C), probably due to a masking effect of the higher hydrolysis rates in thermophilic reactors (Benabdallah El-Hadj et al. 2007).

3. ASSESSMENT OF THE MAIN PRE-TREATMENT TECHNOLOGIES

3.1. Physical pre-treatments

The first and most studied group of sewage sludge pre-treatment technologies is physical processes, including high temperature, ultrasound, high pressure, electric pulse and others, with a prevalence of thermal and ultrasound technologies. The following section describes the most relevant physical processes and their impacts on sludge properties and digestion. Table 2 presents a summary of some of the most important effects of thermal pre-treatment on sludge properties and AD, while Table 3 presents a summary of reports on ultrasonic and other physical pre-treatments. The results of the reviewed publications are further developed in the following paragraphs.

3.1.1. Thermal processes

There are two main thermal treatment/hydrolysis processes according to the applied temperature: a) High temperature treatment (100 – 210°C) (Pickworth et al. 2006; Bougrier et al. 2006b, 2007, 2008; Fdz-Polanco et al. 2008; Val del Río et al. 2011; Gianico et al. 2013), and b) Low temperature treatment (<100°C) (Gavala et al. 2003; Bougrier et al. 2008; Appels et al. 2010; Val del Río et al. 2011). A third group of thermal pre-treatments is freezing/thawing (Wang et al. 2001; Montusiewicz et al. 2010).

3.1.1.1. High temperature treatment

Organic matter solubilization has been reported to be directly related to the temperature used in the process (Bougrier et al. 2008; Carrère et al. 2008; Val del Río et al. 2011). Chemical oxygen demand (COD) solubilization by high temperature pre-treatments have been reported to achieve values of 12 to 80% (Table 2). However, temperatures over ~170 – 190°C can result in the formation of recalcitrant compounds such as melanoidins (Bougrier et al. 2008; Carrère et al. 2010). Moreover, a higher release of inhibitory compounds such as ammonia and metals can be expected, resulting in detrimental effects on digestion (Bougrier et al. 2008; Appels et al. 2010). Thermal treatment at high temperatures can also result in agglomeration and larger particle size, probably related to the formation of chemical bonds (Bougrier et al. 2006a). Carrère et al. (2008) reported that solubilization correlates linearly to temperature, with little or no effect of pre-treatment time and sample origin. Most solubilization occurs while heating the sample, as it takes a significant amount of time to raise sludge temperature to the desired level. Nevertheless, treatment time has been reported to affect maximum biogas production after high temperature processes (Donoso-Bravo et al. 2011).

Pyrolysis of organic matter and formation of non-biodegradable compounds can occur at temperatures over 180°C due to the reaction of carbohydrates with protein amino termini (Bougrier et al. 2008; Wilson and Novak 2009). The degradation of proteins to free ammonia during pre-treatment can be a precursor of what is termed Maillard reactions, which result in the formation of melanoidins responsible for the dark brown color of thermal hydrolysis effluents. Besides the decrease in biodegradability associated with generating melanoidins, the color of the effluent can disrupt disinfection by ultraviolet light (UV) (Dwyer et al. 2008; Wilson and Novak 2009). Lower temperatures during pre-treatment can decrease effluent color without preventing improvements in biodegradability (Dwyer et al. 2008).

Ammonia solubilization during thermal pre-treatment is mostly related to temperature and the type of sludge. It is prevalent in high-temperature WAS pre-treatments. While ammonia concentration effectively increases during thermal pre-treatment, most proteins are solubilized but not degraded to ammonia. Graja et al. (2005) reported a 32% increase in protein solubilization during pre-treatment at 175°C, but just a fifth of this was converted to ammonia.

The generation of volatile fatty acids (VFAs) during pre-treatment is mainly related to lipid degradation, but is also influenced by temperature (Wilson and Novak 2009; Donoso-Bravo et al. 2011). Since primary sludge generally contains high concentrations of lipids, pre-treatment of primary or mixed sludge raises concerns about generating VFAs and acidification. Regarding carbohydrates, the main effect of thermal pre-treatment is the solubilization of complex polysaccharides present in the floc matrix and bacterial membrane, without significant degradation of complex compounds such as cellulose (Bougrier et al. 2008; Wilson and Novak 2009). Carbohydrate solubilization is more important at lower temperatures (<150°C), as it is related to exopolymers, while protein solubilization is related to intracellular compounds (Bougrier et al. 2008).

Other effects of thermal pre-treatment on sludge properties include reduced viscosity, increased specific electric charge and the generation of colloids. Gianico et al. (2013) reported that at 134°C thermal pre-treatment did not change sludge structure, but that properties such as specific charge increased due to the release of colloids and polymeric substances to the media. Dwyer et al. (2008) reported that high temperature hydrolysis (over 140°C) can significantly reduce sludge viscosity, allowing easier handling and lowering pumping costs (Graja et al. 2005).

Divergent results have been reported regarding the influence of high temperature lysis on digestion performance, with some authors reporting no increase in biogas production due to thermal pre-treatment (Climent et al. 2007) and others describing increases of up to 150% (Carrère et al. 2008). Similarly, improvements in solids reduction ranging from 7 to 105% have been reported (Table 2). These differences could be related to process conditions and sludge characteristics. Since thermal pre-treatment increases digestion kinetics, the most significant improvements in methane production are normally achieved with short solid retention times (SRT) (Carrère et al. 2008).

The effectiveness of thermal pre-treatment on sludge dewaterability is influenced by the temperature applied. It has been reported that treatments at temperatures >150°C result in better sludge dewaterability, with reductions in capillary suction time (CST) of up to 99% for 190°C pre-treatment (Bougrier et al. 2008). There have been contradictory results at temperatures of 130 – 135°C, with reports indicating decreases of 45% at 135°C and increases of 56% at 130°C (Bougrier et al. 2007, 2008). There have also been contradictory results regarding dewaterability after AD of pre-treated sludge (Bougrier et al. 2007; Gianico et al. 2013). Nevertheless, Wett et al. (2010) showed that the combined effect of solids reduction and better centrifugability caused by hydrolysis at 160 – 180°C can represent a 25% reduction in sludge volume, highlighting the positive influence that high temperature hydrolysis can have on disposal costs.

Table 2. Summary of reviewed effects of thermal pre-treatment (PT) technologies

Technology	Pre-treatment conditions	Principal impacts on sludge properties	Digestion conditions	Principal reported effects on digestion	References
High temperature treatment (100 – 210°C)	Temperature: 100 – 210 °C Time: 20 – 60 min Pressure: 3 – 21 bar Sludge type: mixed – secondary	12 – 80% COD solubilization Increased concentration of ammonia, soluble inert and color 70% of reduction of SVI at 170°C Reduction of CST at temperatures of 130°C – 150°C (up to 99% at 190°C)	Digestion assay: batch – (semi)continuous Scale: laboratory – full scale Temperature: mesophilic and thermophilic	Biogas production improvements: 25 – 150% VS reduction improvements: 7 – 105% Divergent effects of PT on CST of digested sludge Increased color and ammonia in the effluent	(Graja et al. 2005; Pickworth et al. 2006; Bougrier et al. 2006b, 2007, 2008; Climent et al. 2007; Fdz-Polanco et al. 2008; Carrère et al. 2008; Dwyer et al. 2008; Wett et al. 2010; Val del Río et al. 2011; Gianico et al. 2013)
Low temperature treatment (<100°C)	Temperature: 70 – 95°C Time: 15 min – 7 d Sludge type: primary – mixed – secondary	1– 20% COD solubilization Increased CST and VFAs – heavy metal concentrations in the soluble phase 40% reduction of SVI at 95 °C Increased fecal *Streptococcus* removal Consumption of OM with 72h of treatment (70°C) Reduced pre-treated sludge viscosity to levels equal to untreated samples with half % TS	Digestion assay: batch – (semi)continuous Scale: laboratory Temperature: mesophilic and thermophilic	Biogas production improvements: 10 – 984% VSS reduction improvements: 28 – 617% VS reduction improvements: 10 – 40% Increased methane production rate Increased methane concentration in biogas (2 – 10%)	(Gavala et al. 2003, 2004; Skiadas et al. 2005; Bougrier et al. 2008; Ferrer et al. 2008; Appels et al. 2010; Val del Río et al. 2011; Ruffino et al. 2015)
Freezing/ thawing	Temperature: -80°C to -10°C Time: 24 h (freezing); 12 – 15h (thawing) Sludge type: mixed – secondary	9% COD solubilization Consumption of organic matter during thawing (12% COD, 17% solids) Increase in sludge settling speed (0 cm/min to ~0.3 cm/min) Reduction of viable cell counts	Digestion assay: (semi)continuous Scale: laboratory Temperature: mesophilic	Biogas production improvements: 52% VS reduction improvements: 4% Final moisture content reduced from 75 to 62%	(Wang et al. 2001; Montusiewicz et al. 2010)

Finally, energy balances for thermal hydrolysis/AD systems have been evaluated with positive results when high sludge concentrations and proper energy integration are achieved (Pickworth et al. 2006; Bougrier et al. 2007; Fdz-Polanco et al. 2008). Pickworth et al. (2006) and Fdz-Polanco et al. (2008) have shown that it is possible to establish a self-sufficient process with increased electricity generation of around 40% due to the introduction of thermal pre-treatment.

3.1.1.2. Low temperature treatment

Low temperature pre-treatment consists of applying moderately high temperatures to sludge, normally under 100°C. While the main mechanism of high temperature lysis is physical disruption and solubilization of organic matter, low temperature hydrolysis can include thermal solubilization, stimulation of thermophilic bacteria and solubilization by hydrolytic enzymes released from the sludge (Climent et al. 2007; Ferrer et al. 2008a; Carvajal et al. 2013).

Low temperature pre-treatment has resulted in solubilization levels ranging from negligible values to 20% in terms of COD (Table 1). Unlike high temperature hydrolysis, both pre-treatment temperature and time are important variables for low temperature processes. Climent et al.(2007) found that the main effect of the first 9 hours of pre-treatment at 70°C was the solubilization of organic matter, followed by significant VFA production. This effect is also related to the temperature of the process (Climent et al. 2007; Appels et al. 2010). Xue et al. (2015) recently reported that thermal pre-treatments improved solubilization of organic matter, proteins and carbohydrates, influenced by higher temperatures and longer treatment times. Solubilization values are also positively related to higher total solids (TS) content in the sludge (Ruffino et al. 2015).

The application of low temperature pre-treatment influences macromolecule solubilization and can also result in ammonification, VFA production and the release of heavy metals to the soluble phase. Applying a 90°C thermal pre-treatment, Appels et al. (2010) achieved up to 10% protein and carbohydrate solubilization related to pre-treatment time (15-90 min). Moreover, a positive correlation was found between VFA formation and treatment temperature and time. Higher diffusivity of ions at higher temperatures coupled with EPS disruption also led to increased heavy metals concentration in the soluble phase.

Biogas production during AD after low temperature pre-treatment can be significantly enhanced, as reports show improvements that vary from 10 to 984% (Table 1). While the range is very wide, it is important to note that most of the reports are in the range between 10 – 40%. Higher values could be related to low biodegradability of raw sludge, as Appels et al. (2010) reported an improvement of 984% for a sample with a biogas yield of only 34.83 mL/g ODS. Similarly, Skiadas et al. (2005) reported that thermal pre-treatment at 70°C greatly increases the destruction of volatile suspended solids, up to levels of 28 and 617% for primary and secondary sludge, respectively. This important improvement for secondary sludge reflects the very low biodegradability of raw sludge (~6% of VSS destruction), and reaffirms the suitability of this process to improve the digestion of recalcitrant sludge. Improvements in VS and TS reduction are not necessarily proportional to improvements in biogas production. Moreover, low temperature pre-treatment has also been reported to improve sludge rheology and increase methane concentration in biogas (Ruffino et al. 2015).

The origin and type of sludge can play a significant role in pre-treatment results. Val del Río et al.(2011) studied the effect of pre-treating two different aerobic granular sludges at 60 – 210°C. At temperatures <170°C no effects on AD were observed for sludge used to treat synthetic sewage, while pre-treatment at 60 – 90°C was enough to improve the biodegradability of sludge used to treat swine manure by 20 – 40%. Gavala et al. (2003) reported that the effects of pre-treatment at 70°C depend on sludge type and temperature of digestion (mesophilic or thermophilic). Pre-treatment at 70°C degrees improved mesophilic methane production by 7.7 – 16.2% for primary sludge and 19.8 – 144.6% for secondary sludge. In contrast, pre-treatment at 70°C improved methane production during thermophilic digestion by 38 – 86% for primary sludge, while no effect was observed for secondary sludge. Therefore, the ratio of primary to secondary sludge can significantly influence the effects of pre-treatment on digestion.

Low temperature pre-treatment has also been studied for removing organic pollutants from sludge. Gavala et al. (2004) reported that pre-treatment of primary sludge at 70°C did not significantly reduce the concentration of polycyclic aromatic hydrocarbons (PAHs). Moreover, pre-treatment decreased the biodegradability of two of the three studied compounds during mesophilic digestion. Therefore, higher temperatures may be necessary to degrade complex organic pollutants.

3.1.1.3. Freezing/thawing

The last group of thermal pre-treatments is freezing/thawing. While this method is very energy-intensive, in regions where freezing occurs naturally it could be a sustainable alternative to other technologies (Montusiewicz et al. 2010). Freezing/thawing has been studied principally as a method to improve sludge dewaterability, as freezing allows the separation of solid and liquid fractions during the formation of ice crystals. The process compacts the floc structure and reduces the sludge-bound water content, thus improving dewateration (Jean et al. 2001).

Wang et al. (2001) reported that the WAS filtration rate can be significantly improved by freezing/thawing. The best results were obtained for slow-frozen sludge (-10°C, -20°C), compared to fast-frozen (-80 °C) and unfrozen sludge. Moisture content can be reduced from 75 to 62% with this process. Slower freezing rates are associated with higher damage to cell membranes, which allows better solubilization and higher viable cell removal counts (1.42 log removal at -10°C).

Montusiewicz et al. (2010) studied the influence of freezing/thawing on mixed sludge properties and subsequent AD. The overall process consisted of a 24-h freezing phase at -25°C, followed by thawing at 20°C for 12 h. They observed a 12% reduction in TCOD and doubling of CODs during pre-treatment. The media was acidified owing to a 114% increase in VFAs, which in turn was attributed to anaerobic biological reactions during the thawing phase. Similarly, solubilization of COD during storage of sludge at low temperature (4°C) has been previously reported, more likely associated with biological activity (Bougrier et al. 2007). Solubilization of total nitrogen (TN), ammonia and orthophosphates was also observed, with increases of 79%, 39% and 114% in their respective soluble concentrations. Biogas production increased ~52%, with no significant effects on methane concentration.

3.1.2. Ultrasound

Ultrasound is one of the most extensively studied technologies for sludge disintegration and pre-treatment. When perturbations like ultrasound waves propagate in sludge, they generate low-pressure zones known as rarefactions. The liquid in rarefaction zones becomes gaseous due to pressure, forming microbubbles. The bubbles migrate to high-pressure zones and grow to a critical size before violently collapsing. The process of bubble formation and collapse is known as cavitation (Khanal et al. 2007), and can generate strong hydromechanical shear forces that disrupt sludge structure and increase local temperature and pressure to values up to 1000°C and 500 bar respectively (Chu et al. 2002).

The application of energy in the form of ultrasonic waves promotes different phenomena associated with hydrolysis/solubilization of sludge: (1) Hydromechanical shear forces, (2) Radical formation ($^{\bullet}OH$, $^{\bullet}O$, $^{\bullet}H$), (3) Thermal decomposition of volatile hydrophobic substances, and (4) Temperature increase.

Studies indicate that mechanical shear forces induced by cavitation are the principal cause of sludge solubilization (Pilli et al. 2011), while radical formation can be significant at high ultrasonic densities and intensities (Wang et al. 2005). Parameters such as frequency, ultrasound density and temperature have been reported to influence cavitation during sludge pre-treatment (Erden and Filibeli 2010b; Pilli et al. 2011). Ultrasound can exert physical, chemical and biological effects on sludge, including particle size reduction, organic matter solubilization, enzyme release and stimulation of biological activity (Yu et al. 2009; Yan et al. 2010; Pilli et al. 2011; Guo et al. 2013).

Most ultrasound pre-treatment processes have been evaluated at low frequency and with specific energy values between 1250 and 40000 kJ/kgTS. Specific energy is a parameter that exerts a significant effect on sludge during ultrasound pre-treatment. Pérez-Elvira et al. (2009) studied the effect of sonication in batch and continuous assays at 1.4 – 10.8 kWh/kgTS (5040 – 38880 kJ/kgTS) specific energy. They reported that COD solubilization and biogas yield improvements were proportional to the specific energy applied, achieving values up to 22% and 42%, respectively. For a given specific energy, power increases gave better solubilization results than did increased treatment time. Working with 1250 – 5000 kJ/kgTS specific energy, Braguglia et al. (2011) also found that biogas production increases were directly related to the disintegration degree and the specific energy applied. However, Erden and Filibeli (2010a) found that energy inputs over ~9700 kJ/kgTS can decrease sludge disintegration, probably related to the oxidation of soluble organic matter due to the radicals generated by ultrasound. Therefore, it is necessary to determine optimal energy levels to avoid degradation that reduces the benefits of ultrasound disintegration.

Particle size reduction is also related to the specific energy applied to sludge, with consequent increases in turbidity due to disintegration (Benabdallah El-Hadj et al. 2007; Erden and Filibeli 2010b). However, particle re-flocculation can occur as bacterial polymers released with extended ultrasonication generate favorable conditions for flocculation (Bougrier et al. 2005; Pilli et al. 2011). Because methane production in digesters is proportional to particle size reduction (Pilli et al. 2011), the re-flocculation effect should be avoided. Bougrier et al. (2005) observed that while diameter (d_{50}) decreased progressively with higher specific energy, the volume occupied by particles of 100 µm also increased significantly, mostly related to re-flocculation.

Chu et al. (2002) studied the influence of ultrasonic pre-treatment on flocculated and non-flocculated secondary sludge and subsequent AD (batch). Flocculation of particles decreased methane production from untreated samples due to mass transfer resistance. However, ultrasonication improved it for both samples, achieving better results for flocculated sludge. Sonication improved methane production by 104 and 260% for the original and flocculated samples, respectively. Confocal laser scanning microscope images showed that the flocculated/sonicated biosolids exhibit a looser structure than non-flocculated/sonicated biosolids, which could be related to the higher methane production observed for that sample.

It has been reported that digestion of sonicated sludge decreases CST to values even lower than those of digested raw sludge. Shao et al. (2010) observed that while ultrasonication increased CST of activated sludge from 2.3 to 44.4 s-L/gTSS, subsequent AD decreased CST to 11.1 s-L/gTSS. On the other hand, AD of untreated sludge increased CST from 2.3 to 51.4 s-L/gTSS, reaching a value far higher than that obtained in the ultrasonicated-fed reactor. Braguglia et al. (2010) reported similar results, but while AD decreased the CST of sonicated sludge from 15 to 11 s-L/gTS, this value was higher than that obtained after raw sludge digestion (CST increased from 1 to 7 s-L/gTS). Pérez-Elvira et al. (2010) reported that CST increased with ultrasonic pre-treatment before and after AD, whether all or only part of the sludge was sonicated. It has also been reported that adding flocculants before sonication can positively impact on sludge dewaterability (Pilli et al. 2011). Therefore, while most reports of sludge dewaterability show that sludge CST increases significantly after ultrasonic pre-treatment (Shao et al. 2010; Erden and Filibeli 2010b; Braguglia et al. 2010), this effect does not always reflect the impact of the pre-treatment over digested sludge dewaterability and therefore its quality and management.

Reports show sludge solubilization results between 1 – 40% for COD and 2 – 47% for disintegration degree (DD) after sonication (Table 3). Solubilization during ultrasonic pre-treatment is mainly related to the effects on EPS, and even at high specific energy levels it does not promote cell disruption (Salsabil et al. 2009). Biogas production has been reported to increase up to 83% after ultrasound (most reports in the range of 20 – 40%), with increases of 6 to 47% in volatile solids reduction (Table 3). Solids reduction during the sonication step has been reported, accounting for up to 29.7% of total suspended volatile solids removed from the system (Salsabil et al. 2009). Significant nitrogen and VFA solubilization have also been reported after sonication (Martín et al. 2015).

Operational parameters of digestion, such as F/I (Feed/Inoculum ratio), SRT and the organic loading rate (OLR), have also been shown to influence the impact of ultrasound on digestion. Braguglia et al.

(2011) evaluated different OLRs during meshophilic digestion of sonicated sludge, achieving increases in solids removal of 8 – 21%, with the optimum at a medium loading rate. Biogas production increased 12 – 37%, related to the disintegration degree and lower OLR. Neis et al. (2008) reported the influence of sonication over pilot and full-scale AD of secondary sludge. Pilot scale pre-treatment improved both the solid destruction rate and the degree of degradation by more than 30% in digesters operating at 8 – 16 d SRT. Improvements of 10 – 16% in biogas production (m^3/m^3 day) due to sonication were also reported, with biogas production improvement favored by short SRT and solids reduction improvement favored by long SRT.

Most ultrasound pre-treatments use low frequency waves (20 – 35 kHz) because they favor cavitation (Chu et al. 2002; Neis et al. 2008; Braguglia et al. 2011). However, high frequency ultrasonication has also been studied as it promotes the formation of oxidant radicals that can be useful to degrade micropollutants (Braguglia et al. 2012; Gallipoli et al. 2014). Gallipoli et al. (2014) studied high frequency ultrasound (200 kHz) to improve AD performance and surfactant removal (linear alkylbenzene sulphonates, LAS). Improvements in both reducing solids and producing biogas depend on the F/I ratio, with solids reduction favored by a high F/I ratio (0.9), and biogas production favored by a low F/I ratio (0.3). This is attributed to metabolic decoupling between hydrolysis and methanogenesis at higher F/I, causing soluble organic substance accumulation. LAS removal was improved only with low F/I, as those conditions promote higher kinetics. Under similar conditions, Braguglia et al. (2012) also reported that high frequency ultrasound had better effects on biogas production at low F/I (40% improvement at 0.5 VS basis), while better results were found for solids destruction at a F/I equal to 1 (35% against 13% at F/I 0.5). At high F/I, no biogas improvements were observed, probably also related to the accumulation of soluble organic matter. On the other hand, low frequency ultrasound has been shown to remove about 64% and 53% of naphthalene and pyrene with thermophilic digestion and 54% and 32% with mesophilic digestion, respectively (Benabdallah El-Hadj et al. 2007).

Sonication can be improved by applying it at high temperatures. Şahinkaya and Sevimli (2013) studied the effect of ultrasound pre-treatment at 80°C on mesophilic batch digestion and achieved higher rates of disintegration than with conventional sonication or heating. Pre-treatment increased final production of methane from sludge by 13.6%, with synergistic effects on COD solubilization and methane production. Sedimentability of sludge increased significantly after pre-treatment due to re-flocculation, disintegration of filamentous microorganisms and thermal conditioning. Moreover, VS removal increased by 47% due to pre-treatment.

One of the principal drawbacks of ultrasound pre-treatment is its high energy cost, which is not always compensated by increased biogas production. Thickening is considered fundamental to achieve a positive energy balance during ultrasound pre-treatment (Braguglia et al. 2011). Based on a laboratory assessment, Pérez-Elvira et al. (2009) argued that it is necessary to achieve concentrations of 6% TS in order to obtain sustainable results from ultrasound. However, studies at the pilot and full scale levels have shown different results, as Xie et al. (2007) reported a net energy gain/energy consumption ratio of 2.5 at low solids concentration (1 – 2% TS). The difference between laboratory and full-scale applications could be related to the low energy efficiency of laboratory devices, which reach only 15 – 30% (Pérez-Elvira et al. 2009; Gallipoli et al. 2014). Zielewicz and Sorys (2008) observed that using the same energy density, a technical ultrasonic module achieved disintegration effects three times higher than those of a laboratory device, which is associated with the configuration of the tested equipment. This fact is acknowledged by Pérez-Elvira et al. (2009), who reported that with a level of energy consumption corresponding to that of industrial equipment (6 kWh/m^3), the ultrasound energy balance is positive at any sludge concentration.

3.1.3. High pressure homogenization

High-pressure homogenization pre-treatment (HPH) subjects sludge to pressures of up to 600 bar and subsequent depressurization as it passes through a valve. Depressurized sludge impacts on a solid surface as it comes out of the valve, releasing cell contents due to the action of the pressure gradient, shear stress, turbulence and cavitation. The high pressure and consequent pressure drop along the valve are the main disruptive factors of the process (Zhang et al. 2012). HPH is widely used in the food industry because of its low cost and easy operation and because it allows high lysis efficiency without the use of chemicals.

Zhang et al. (2012) studied HPH to improve mesophilic AD of secondary sludge (20 – 50 MPa, 1 – 2 cycles). Solubilization after pre-treatment was low (3 – 8%), with a proportional increase in methane yield when solubilization was >4%. Removal of solids improved up to 138% during AD, while accumulated biogas production improved up to 64 – 115%. Methane content of biogas increased from 47% to 64% due to pre-treatment. AD performance after homogenization was related to the intensity of the pre-treatment in terms of pressure and number of pressurization cycles. Specific energy needed for the process was 3380 kJ/kgTS, lower than the energy needed for sonication or microwave pre-treatment. Assessment of the energy performance of HPH has shown increased net energy production from mesophilic AD at short SRT (Wahidunnabi and Eskicioglu 2014). However, these results cannot be extrapolated to thermophilic AD, as the HPH energy balance is lower under those conditions.

Engelhart et al. (2000) studied the combined effect of HPH and fixed bed reactors on sludge digestion. The disintegration degree reached 4 – 43% depending on the pressure (50 – 600 bar), while specific biogas production was related to the disintegration degree and the retention time in the reactor. While it was possible at 2 – 5 d SRT to achieve gas production levels comparable to those of conventional systems at 10 – 15 days SRT, a shorter SRT appears to promote loss of methane in the liquid stream and therefore is not recommended. The integration of HPH and fixed bed reactors results in significant removal of solids with very short SRT in the reactor. Under similar conditions, Kopplow et al. (2004) achieved around 17% improvement in biogas production (600 bar; 60 kJ/L). Besides the effect on sludge solubilization and AD performance, HPH at 600 bar has been found to exert a moderate effect on foaming control during digestion (Barjenbruch and Kopplow 2003). However, sludge dewaterability could decrease, as CST measured after digestion in the last study showed a 10% increase.

3.1.4. Microwave

Microwave application has also been studied as an AD pre-treatment. Microwave irradiation occurs in wavelengths from 1mm to 1m and at frequencies of 300 GHz to 300 MHz, respectively (Eskicioglu et al. 2007). Application of microwaves has both thermal and non-thermal effects on sludge properties. Thermal effects occur due to the interaction of the electric field of the radiation with dipolar molecules, increasing temperature due to molecular rotation and friction. Non-thermal effects are associated with a rapid change in the dipole orientation of the macromolecules making up the cell membrane, breaking the hydrogen bonds between molecules and therefore disrupting the membrane (Appels et al. 2013). While the thermal effects of microwave irradiation are well studied, the non-thermal effects are harder to measure and therefore their influence on the overall pre-treatment process is not fully understood. Eskicioglu et al. (2007) studied the non-thermal effects of microwave on waste activated sludge batch digestion, comparing it to conventional heating systems (50 – 96°C). Microwave achieved an estimated 19% SCOD/TCOD ratio, similar to conventional heating. However, cumulative biogas production was higher with microwaved sludge than with conventionally heated sludge, suggesting the influence of non-thermal effects.

At lower temperatures, microwave has shown better pre-treatment results than conventional heating, probably related to the aforementioned non-thermal effect. Kuglarz et al. (2013) studied the effect of both microwave and thermal lysis in the range of 30 – 100°C. They found that the application of microwave until 70°C was the most effective method to improve biogas production and energy gain. Microwave also showed higher COD, protein and inorganic matter (NH_4^+, PO_4^{-3}) solubilization, and a significant improvement in pathogens removal. Pre-treatment alone has been shown to achieve around 2.1 log elimination of total coliforms (Coelho et al. 2011). While microwave has shown better performance than conventional heating, under current conditions the energy balance presents a negative yield, and even if sludge disposal is included, the process results in increased costs (Appels et al. 2013; Kuglarz et al. 2013).

MW pre-treatments of both mixed and secondary sludge have improved AD performance, but the pre-treatment of primary sludge has not shown any effect on sludge solubilization or biodegradation efficiency (Zheng et al. 2009). Coelho et al. (2011) studied the effects of microwave pre-treatment on mesophilic and thermophilic digestion of secondary sludge, achieving biogas yield improvements of up to 32% and 35% for mesophilic and thermophilic digesters, respectively. Additionally, solids reduction improved 48% for thermophilic and 38% for mesophilic systems. Eskicioglu et al. (2009) studied the effect of microwave pre-treatment over batch mesophilic AD of secondary sludge, achieving a maximum solubilization of 31% and biogas production improvements on the same order. At 336 kJ/kg sludge specific energy (800 W, 80°C), Appels et al. (2013) achieved 6.6% COD solubilization and a more than 3-fold increase in VFA concentration. Methane production increased around 50% and organic solids reduction increased 37.5%.

3.1.5. Electric pulse and electrolysis

Electric pulse technology uses high voltage pulsing electric fields (20 – 30 kV) to disrupt bacterial cell membranes. Since phospholipids and peptidoglycan are polar molecules, the applied electric field directly attacks the basic components of bacterial membrane and cell walls, releasing intracellular organic matter, disrupting floc structure and possibly reducing complex organic molecules to simpler chemical forms (Lee and Rittmann 2011). This technology is commonly used in medicine, biotechnology and the food processing industry, where it serves as an non-thermal disinfection method (Kopplow et al. 2004; Lee and Rittmann 2011).

Lee and Rittmann (2011) studied the effect of electric pulse technology at 34 kWh/m^3 on the digestion of secondary sludge. They found that while solubilization was low (2.3%), methane production improved by 10 – 33% and TCOD removal increased 18%. Similarly, Kopplow et al. (2004) achieved a disintegration degree of 2 – 15% (2000 – 8000 kJ/kgST), with improved biogas production and volatile solids reduction of about 20% and 9%, respectively. Improvements of up to 100% in methane production have been observed at the laboratory scale (Salerno et al. 2009). At full scale, focused pulse pre-treatment has increased biogas production by 15 – 40% and sludge reduction by 2 – 30%, depending on the fraction of the sludge stream that is subjected to pre-treatment (Rittmann et al. 2008; Zhang et al. 2009). Other effects of this process include transformation of VSS and TSS to colloids during pre-treatment, which can account for 42% of loss (Salerno et al. 2009).

Pulse pre-treatment causes significant changes in microbial communities during AD. Zhang et al. (2009) studied the effect of focused pulse at 16 kWh/m^3 on the bacterial and archaea communities of a full-scale digester treating mixed sludge. Pre-treatment changed an archaea community to a more acethoclastic-dominant ambient (*Methanosaeta* instead of hydrogenothophic *Methaculleus*), and higher abundance of *Ruminococcus* (cellulolytic bacteria producing acetate in the presence of methanogens) was observed (Rittmann et al. 2008; Zhang et al. 2009). Higher diversity of microorganisms is associated with the pre-treatment, which generates a wide array of different organic compounds.

Overall, focused pulse is an effective cell-disruption and sludge pre-treatment technique. It improves methane production, VS and TCOD removal and exerts a moderate effect on foaming during digestion, with lower reported energy consumption than other physical pre-treatments. However, there are operational side-effects like electrode corrosion that need to be avoided. Kopplow et al. (2004) observed that when the energy dose increases from 150 kJ/L to 280 kJ/L, biogas production improvement decreased from 20% to 5%, related to the corrosion of the electrodes used during pre-treatment.

Table 3. Summary of reviewed effects of physical pre-treatment (PT) technologies

Technology	Pre-treatment conditions	Principal impacts on sludge properties	Digestion conditions	Principal reported effects on digestion	References
Ultrasound	Specific energy: 112 – 108000 kJ/kgTS Power: 60 – 480 W Frequency: 20 – 200 kHz Time: 0.5 – 60 min Sludge type: mixed –secondary	1 – 40% COD solubilization 2 – 47% Disintegration Degree CST increases by 15-20 times Particle size reduction, increased specific charge and turbidity Increased concentrations of soluble nitrogen and VFAs	Digestion assay: batch – (semi)continuous Scale: laboratory – full scale Temperature: mesophilic – thermophilic	Biogas production improvement: 4 – 83% (~14 – 260% CH_4) VS reduction improvements: 6 – 47 % (22 – 83% VSS) Possible net energy gain at full scale Increased removal of some organic pollutants Reduction of fecal coliform and *E.coli* before and after AD	(Chu et al. 2002; Davidsson and Jansen 2006; Benabdallah El-Hadj et al. 2007; Xie et al. 2007; Neis et al. 2008; Pérez-Elvira et al. 2009, 2010; Salsabil et al. 2009; Erden and Filibeli 2010a; Shao et al. 2010; Braguglia et al. 2010, 2011, 2012; Şahinkaya and Sevimli 2013; Gallipoli et al. 2014; Martín et al. 2015)
High pressure homogenization	Pressure: 50 – 600 bar Cycles: 1 – 2 Specific energy: 300 – 3380 kJ/kgTS Sludge type: secondary	3 – 8% COD solubilization 4 – 43% disintegration degree	Digestion assay: (semi)continuous Scale: laboratory Temperature: mesophilic	Biogas production improvements: 17 – 115% VS reduction improvements: 7 – 138% Increased digested sludge CST Increased methane concentration in biogas (47 to 64%) Moderate control of foaming	(Engelhart et al. 2000; Barjenbruch and Kopplow 2003; Kopplow et al. 2004; Zhang et al. 2012; Wahidunnabi and Eskicioglu 2014)
Microwave	Specific energy: 336000 kJ/m^3 Temperature: 30 – 175°C Power: 800 – 1250 MW Frequency: 2450 MHz Sludge type: mixed – secondary	7 – 31% COD solubilization VFA concentrations increase by up to 3 times Possible Maillard reactions at high temperatures (>80°C)	Digestion assay: batch – (semi)continuous Scale: laboratory Temperature: mesophilic and thermophilic	Biogas production improvements: 16 – 50% VS reduction improvements: 23 – 48% Removal of *Salmonella spp*. and *E. coli*, 50% decrease of *C. perfringens.* Reduction of 2.1 log in total coliforms	(Eskicioglu et al. 2007, 2008 2009; Coelho et al. 2011; Appels et al. 2013; Kuglarz et al. 2013)

Table 3. continued

Technology	Pre-treatment conditions	Reported impacts on sludge properties	Digestion conditions	Principal reported effects on digestion	References
Electric pulse and electrolysis	Specific energy: 1.1 – 34 kWh/m^3 Field strength: 8 to 30 kV/cm Configuration: single and dual chamber Sludge type: mixed – secondary	2 – 10% COD solubilization Settled sludge volume reduced 25% at 280 kJ/L treatment Possible loss of solids due to generation of colloids (42% at 19.8 kWh/m^3)	Digestion assay: batch – (semi)continuous Scale: laboratory – full scale Temperature: mesophilic	Methane production improvements: 10 – 100% VS reduction improvements: 9% Partial elimination of foaming during digestion Increased diversity of microbial communities	(Kopplow et al. 2004; Rittmann et al. 2008; Salerno et al. 2009; Zhang et al. 2009; Lee and Rittmann 2011; Charles et al. 2013)
Dual irradiation	Temperature: 55 °C Light intensity: 100 ± 10 $\mu mol/m^2$ s Time: 8 – 48 h Power: 60 W Sludge type: secondary	9 % DOC increase after PT VS removal during PT (up to 14.4%) Generation of crystal-like structures at PT times >24 h	Digestion assay: batch – (semi)continuous Scale: laboratory Temperature: thermophilic	Methane production improvements: 12 and 42% (batch and irradiated semicontinuous DA, respectively) VS reduction improvements: 53% (73% with irradiated semicontinuous DA) Irradiation during digestion increased methane in biogas from 70.5% to 84.1% Increased removal rate of DOC and VS	(Yang et al. 2011)
Cavitation nozzle	Pressure: 12 bar Time: 15 – 90 min (3-min cycle) Sludge type: secondary	Disintegration degree up to 55% (42% during first 30 min) PT of foam generated more SCOD than PT of WAS	Digestion assay: batch Scale: laboratory Temperature: mesophilic	Biogas production improvements: 94% (L biogas/L-d) Co-digestion of pre-treated foam and WAS further improved biogas production	(Grübel and Machnicka 2009)

Another electrical-based method consists in the use of electrolysis. Charles et al. (2013) used a 12V two-chamber electrolysis process with an anion exchange membrane to alter WAS pH as an alternative to chemical addition. The pH level in the anode decreased from 6.9 to 2.5, while in the cathode pH increased to 10.1, achieving COD solubilization of 9.5% and 6.4% respectively. Mixing the two pre-treated currents neutralized pH to 6.5, and therefore chemical neutralization was not necessary. Biogas yield during the following mesophilic batch AD increased 31%, which was attributed to the effects of the pH level and not to cell disruption by electrolysis.

3.1.6. Other physical pre-treatments

While the majority of recent reports on physical pre-treatments fall into one of the aforementioned categories, other innovative processes have been proposed. Yang et al. (2011) reported that pre-treatment using light irradiation at 100±10 μmol/m^2 s improved thermophilic (55°C) digestion due to cell disruption and increased organic carbon dissolution (9% after pre-treatment). In this study, methane yield improved up to 12% and VS removal up to 53% with 24 h treatment time, with partial VS removal occurring during pre-treatment. Application of light for more than 24 h causes formation of crystal-like structures that affect anaerobic degradation. However, irradiation during semicontinuous digestion further increased methane yield, solids reduction and methane content in biogas. Moreover, VS and DOC reduction occurred faster when anaerobic reactors were irradiated.

Although ultrasound is the most widely studied cavitation sludge pre-treatment, other cavitation-based methods have been tested. Grübel and Machnicka (2009) studied the effects of a hydrodynamic pre-treatment based on the cavitation induced by passing WAS through a depressurizing nozzle. The conditions include 12-bar pressure and a 15 – 90 min treatment time (using 3-min cycles). Digestion was performed under mesophilic conditions, feeding only a fraction of pre-treated WAS to avoid detrimental effects on dewaterability. Solubilization was up to 55% with 90 min treatment time, achieving around 42% within the first 30 min. Higher SCOD and biogas production rates (L/d-L) were generated by pre-treating the foam generated by filamentous microorganisms during wastewater treatment. This could be related to the more fragile structure of these microorganisms.

3.2. Chemical pre-treatments

Chemical pre-treatments involve the use of chemical reagents to hydrolyze sludge. Different chemical processes have been studied, including alkaline and acid hydrolysis, ozonation and other oxidation methods like the Fenton reaction. The following section focuses on the effects of chemical pre-treatments, while thermo-chemical and physical-chemical technologies are discussed in the section on combined pre-treatments. Table 4 summarizes the results of alkaline and other chemical pre-treatments.

3.2.1. Alkaline pre-treatment

Alkaline pre-treatment disrupts sludge cells and EPS, leading to leakage of intracellular material and solubilization of organic matter (Kim et al. 2003; Neyens et al. 2003; Li et al. 2008). Alkaline pre-treatment has been reported to be very effective in damaging cellular substances and solubilizing EPS (Fang et al. 2014) and can greatly accelerate the solubilization/hydrolysis of residual sludge, especially waste activated sludge (WAS) (Lin et al. 1997; Penaud et al. 1999; Vlyssides and Karlis 2004; Li et al. 2008; Xu et al. 2014). COD solubilization during alkaline pre-treatment occurs through various mechanisms, namely saponification of uronic acids and acetyl esters, reactions occurring with free carboxylic groups and neutralization of various acids formed from the degradation of particulate matter (Kim et al. 2003).

Alkaline pre-treatment is relatively simple and with low energy requirements (Neyens and Baeyens 2003). It is very effective for solubilizing COD. A “maximum hydrolysable” COD protocol has been proposed based on 24-hour alkaline disintegration (Müller 2003). Solubilization efficiency depends on the reactant used for pre-treatment, in descending order: NaOH >KOH > $Mg(OH)_2$ and $Ca(OH)_2$ (Kim et al. 2003; Li et al. 2008). As can be seen, monobasic agents result in higher solubilization rates than do dibasic ones, probably because dibasic alkali agents only partially dissolve in sludge (Penaud et al. 1999).

The chemical dosage is one of the key operational parameters of alkaline pre-treatment. While high doses are normally associated with higher levels of solubilization, excessively high doses can reduce the activity of anaerobic consortia due to the pH of pre-treated sludge or the presence of inhibitors (Li et al. 2012; Fang et al. 2014). Kim et al. (2003) studied the application of different concentrations of

NaOH to 300 ml of WAS at ambient temperature. They found that COD solubilization of WAS sludge was around 43.5% after pre-treatment with 7 g/L NaOH. Further increases in dosage (up to 21 g/L NaOH) showed a lower rate of COD solubilization. Moreover, an increase of 13% in biogas and methane production was observed, with no effect on methane concentration.

COD and solid removal rates also improve with increases in alkali dosage (Lin et al. 1997; Fang et al. 2014). Lin et al. (1997) found that COD removal improved 123% compared to a control reactor after applying a dosage of 20 meqNaOH/L sludge. Under the same conditions, maximum VS removal was 133% higher than the control reactor. These results were obtained with the maximum concentration of sludge solids, and the authors concluded that increasing sludge concentration is more effective for organic removal than increasing NaOH doses. Regarding methane production, improvements of up to 120% were observed, related to higher NaOH doses and sludge concentration and shorter SRT during AD. Contrary to the report of Kim et al. (2003), methane concentration in biogas improved from 72 to 85% due to pre-treatment, even while doses were significantly lower.

Shao et al. (2012) indicated that biogas production increased as the alkali dose augmented during pre-treatment. They adjusted sludge pH to 8, 9, 10, 11 and 12 using 4 mol NaOH/L before neutralization and digestion, achieving a biogas yield improvement between 7.2% – 15.4% with pH 8 to 11. However, when alkalinity increased to pH 12, biogas yield decreased by 18.1% compared to the control, probably related to the extreme pH conditions or a high concentration of Na^+, a widely reported inhibitor of AD (Chen et al. 2008). Excessive alkali dosages have also been reported to promote the formation of refractory compounds through the Maillard reaction (Penaud et al. 1999), similar to the effect observed when thermal lysis is conducted at temperatures exceeding 180°C.

In addition to COD solubilization, alkaline pre-treatment has been reported to increase the concentration of soluble macromolecules like proteins. Xu et al. (2014) achieved an increase in soluble protein concentration from 30.2 to 1665.4 mg/L after application of 7 g/L of NaOH. The authors found that the improvements in AD were related to the concentration of soluble protein after pre-treatment, achieving a 41% increase in biogas production compared to the control. Similar to the study by Kim et al. (2003), no effects on methane concentration in biogas were reported.

Alkaline pre-treatment can improve sludge suitability for final disposal, as it is an efficient method to remove pathogens that are not normally killed during conventional AD. Carballa et al. (2008) found that while *Salmonella spp.* and other pathogens were effectively inactivated by conventional digestion, removal of *C. perfringens* was improved by the inclusion of the pre-treatment (from ~28% to >70%). Moreover, dewaterability can also be improved after AD (Lin et al. 1997; Carballa et al. 2008; Shao et al. 2012), despite an initial negative impact following pre-treatment (Carballa et al. 2008).

The main disadvantages of alkaline pre-treatment are associated with the presence of residual chemicals in the pre-treated sludge that can destroy the bicarbonate buffer system in anaerobic digesters and inhibit anaerobic microorganisms (Li et al. 2012; Kim et al. 2013b), as well as the high consumption of reagents.

3.2.2. Acid pre-treatment

Acid pre-treatment, on the other hand, has received considerably less attention than alkaline pre-treatment, with few studies reporting its influence on sludge properties and subsequent AD. The principle of acid pre-treatment is similar to alkaline, as the acid breaks down polymers into monomers or oligomers, which increases the digestion rate as partial hydrolysis has been carried out (Devlin et al. 2011). However, current results show that alkaline pre-treatment is more effective than acid in terms of hydrolysis and solubilization of organic matter (Chen et al. 2007).

During acid pre-treatment, solubilization of COD and macromolecules is mostly related to applied pH, and therefore strong acidic environments result in more solubilization than milder ones. The increase in solubilization accounts for the observed increase in the rate of biogas production, and therefore pre-treatment pH is also related to digestion performance (Devlin et al. 2011). Devlin et al. (2011) reported an increase of 12 – 32% in biogas production after acidic pre-treatment with HCl compared to untreated WAS, while VS removal increased by 5%. No effects were observed over methane concentration in biogas. Others effects on digestion include a 40% lower polymer requirement prior to dewatering, effective destruction of *Salmonella* and close to a 3-log reduction in *E. coli*.

The use of peracetic acid (PAA) is an innovative alternative for sludge acid pre-treatment. PAA is an aqueous quaternary equilibrium mixture of acetic acid, peracetic acid and hydrogen peroxide, with an oxidation potential of 1.81 eV (Appels et al. 2011). The mechanism consists of forming hydroxyl radicals that further react and degrade organic matter. Appels et al. (2011) evaluated the application of a 15% PAA solution with a dose ranging between 15 and 100 gPAA/kgDS. A linear increase of soluble COD with a dosage of PAA was observed, and a maximum increase in cumulative biogas production of 21%

after batch AD (using a dose of 25 gPAA/kgDS). However, the application of higher dosages (60 - 100 gPAA/kgDS) resulted in lower biogas production. Inhibition due to high VFAs concentrations may explain this observation.

3.2.3. Ozonation

Ozone (O_3) is a powerful oxidant often used to disinfect drinking water and deactivate pathogens (Appels et al. 2008a). The oxidant properties of ozone can be used to pre-treat sludge, partially hydrolyzing organic matter and increasing the biodegradability of waste activated sludge. Moreover, recalcitrant and toxic compounds can be removed by the action of ozone (Yeom et al. 2002; Pérez-Elvira et al. 2006). The mechanism of ozone action involves rapid decomposition into radicals that oxidize both particulate and soluble organic matter through indirect and direct reactions. Indirect reactions are based on the high reactivity of hydroxyl radicals, which do not react specifically, whereas the direct reaction rate depends more on the structure of the reactants (Carballa et al. 2007). Ozone decomposes organic matter in two steps: solubilization due to disintegration of suspended solids and mineralization due to oxidation of soluble organic matter (Ahn et al. 2002). The objective of pre-treatment is partial oxidation and hydrolysis of sludge, and therefore complete oxidation should be avoided (Carballa et al. 2007). The final quantity of residual sludge and the digestion time can be reduced with ozone pre-treatment, while biogas production can be increased (Weemaes et al. 2000; Yeom et al. 2002; Bougrier et al. 2006a; Carballa et al. 2007).

As with alkaline and acid pre-treatments, dosage is an important parameter of the process. While reported ozone doses vary widely and are based on different units (Table 4), the optimal dose to enhance AD is around 0.05 - 0.5 gO_3/gTS (Weemaes et al. 2000; Yeom et al. 2002; Goel et al. 2003; Bougrier et al. 2006a; Pérez-Elvira et al. 2006; Carballa et al. 2007). It is important to note that an excess of ozone can cause formation of refractory compounds and organic matter consumption (Weemaes et al. 2000; Kim et al. 2013b).

Ak et al. (2013) reported that sludge ozonation increased COD release and TSS disintegration up to a 2 mgO_3/gVSS dose. Biogas production increased by almost 200% with a dose of 1.33 mgO_3/gVSS. As with other pre-treatments, digestion improvements are more significant with mesophilic systems. Carballa et al. (2007) obtained around 5 and 26% increases in specific methane production in thermophilic and mesophilic reactors, respectively, compared to control reactors after ozone treatment (0.02 gO_3/gTSS). While they administered a dose 15 times as high as that used by Ak et al. (2013), the improvement in biogas production observed in their reactors was significantly lower, highlighting that dose is not the only parameter controlling the effect on AD performance. In both studies, methane concentrations in the biogas increase with pre-treatment (Carballa et al. 2007; Ak et al. 2013).

In addition to improving biogas production, the positive effects of ozone pre-treatment include significant mass reduction of sludge, elimination of chemical residues and better sludge settleability (Weemaes et al. 2000; Ahn et al. 2002; Carballa et al. 2007). The large amount of unsettleable micro-particles produced after disintegration pre-treatment may adversely affect dewaterability (Weemaes et al. 2000; Park et al. 2005; Bougrier et al. 2006a; Carballa et al. 2007). However, digested pretreated sludge has shown better dewaterability compared to untreated digested sludge (Weemaes et al. 2000; Carballa et al. 2007). Other advantages of ozone include removal of recalcitrant compounds like carbamazepine (Carballa et al. 2007) and enhanced removal of endocrine disrupting compounds (EDCs) absorbed into the sludge (Ak et al. 2013). However, EDC removal is not improved with increasing doses of ozone, most likely due to the presence of reducing agents in the sludge that deplete free ozone (Ak et al. 2013). It is important to note that while ozonation does not affect total heavy metal content, after pre-treatment metals can be transferred to the soluble phase and therefore removal may be necessary (Pérez-Elvira et al. 2006).

Weemaes et al. (2000) applied ozone in a range between 0.05 – 0.2 $gO_3/gCOD$ and found that the soluble COD concentration of the sludge increased gradually, reaching 29% solubilization with a dose of 0.2 $gO_3/gCOD$. Sludge sedimentation tests revealed that SVI decreased from 100 – 120 mL/g to 25 – 30 mL/g due to the stabilization of the surface charges of macroscopic particles. However, the turbidity of the supernatant increased due to fine particles and CST values increased sharply. Results of microscopic observation indicated that sludge flocs were dispersed, which could cause filter clogging. During digestion, methane production per unit of COD was enhanced 80% at an ozone dose of 0.1 $gO_3/gCOD$, while the negative effect on dewaterability was attenuated after AD to levels close to untreated digested sludge. Bougrier et al. (2006a) applied ozone in the range of 0.1 – 1.16 gO3/gTS, resulting in a similar solubilization rate of 20 – 25% of COD. Batch AD tests showed 11 – 23% and 8 – 25% higher methane and biogas production than untreated sludge, respectively. Ozone pre-treatment also reduced pH to a value of 5.8 due to the formation of acidic compounds. Likewise, Weemaes et al. (2000) found that pH dropped significantly to 4.9 after ozonation.

Pathogen removal can also be achieved through ozonation. Carballa et al. (2007) achieved significant removal of all pathogens included in their study (>85%) during pre-treatment, with the exception of *F. streptococcus* (around 63%) and *Salmonella* spp., which were still present after ozonation. Inactivation of *C. perfringens* increased with digestion temperature and the inclusion of ozonation.

While ozone has important effects on sludge properties and AD, one of its main drawbacks is the high-energy consumption necessary for ozone generation. As ozone quickly decays into diatomic oxygen, it is necessary to produce it in situ before use. While there are different methods to produce ozone, all are energy consuming, representing the main obstacle to widespread ozone use in AD plants. Strategies like microbubble generation can reduce ozonation energy demand due to the better mass transfer associated with a lower surface area to volume ratio (Cheng et al. 2012).

3.2.4. Other chemical pre-treatments

Other chemical methods have been proposed to pre-treat sludge. One is the Fenton process (mixture of H_2O_2 and ferrous ions), which is commonly used for advanced oxidation. Ferrous ions (Fe^{+2}) initiate and catalyze the decomposition of H_2O_2, resulting in the generation of highly reactive hydroxyl radicals that oxidize organic matter (Neyens and Baeyens 2003; Appels et al. 2008a). WAS dewaterability improves with the disintegration of EPS, the breakdown of cell walls and release of intracellular water due to Fenton process (Neyens and Baeyens 2003). One of the major drawbacks of this method is the corrosive effects due to operational conditions (pH 3) (Appels et al. 2008a). Erden and Filibeli (2010b) found that by applying 0.067 gFe(II)/gH_2O_2 and 60 gH_2O_2/kgDS, total methane production increased 1.3 times compared to the control reactor at 30 day of operation.

Another innovative alternative is the use of other peroxidants, such as peroxymonosulfate (POMS) and dimethyldioxirane (DMDO), which do not require stringent reaction conditions. It has been reported that specific biogas production increased around 11% after pre-treatment with POMS (60 gPOMS/kgDS) and 33% with DMDO (660 mL DMDO/kg DS) (Dewil et al. 2007).

Table 4. Summary of reviewed effects of chemical pre-treatments (PT) technologies

Technology	Pre-treatment conditions	Reported impacts on sludge properties	Digestion conditions	Principal reported effects on digestion	References
Alkaline pre-treatment	Reagents: NaOH, KOH, $Mg(OH)_2$, $Ca(OH)_2$, lime Reported doses: 20 – 40 meqNaOH/L; 0 – 26.1 gNaOH/L; 0.05 – 1.0 molNaOH/L; 0.02 – 0.5 mol$Ca(OH)_2$/L pH: 8 – 12 Time: 30 min – 8 d Sludge type: secondary	Values of up to 80% on SCOD/TCOD ratio after PT. Up to 50% COD solubilization 33% solids removal during PT Elimination of *Salmonella spp.*, reduction of total coliforms, *E. Coli*, *F. Streptococcus* and *C. perfringens* Increased SRF and decreased particle size. High doses can led to re-flocculation	Digestion assay: batch – (semi)continuous Scale: laboratory Temperature: mesophilic and thermophilic	Methane production improvements: 13 – 120% VS reduction improvements: up to 133% Divergent effects on biogas methane concentration High doses/pH could led to decreased biodegradability due to possible Maillard reactions Increased dewaterability of digested sludge	(Lin et al. 1997; Penaud et al. 1999; Kim et al. 2003; Li et al. 2008; Carballa et al. 2008; Shao et al. 2012; Xu et al. 2014)
Acid pre-treatment	Reported doses: 1.25 – 17.5 mL HCl/kg wet sludge, 15 – 100 gPAA/kgDS pH: 1 – 6 Time: 1 – 24 h Sludge type: secondary – mixed	Up to 4 fold increase in SCOD and soluble carbohydrates concentration. Up to 8 fold increase in soluble proteins concentration 3 log reduction of *E. coli* after 24 h acidification with HCl (pH 1)	Digestion assay: batch – (semi)continuous Scale: laboratory Temperature: mesophilic	Biogas production improvements: 12 – 32% VS reduction improvements: 5% Possible inhibition at high PAA doses Elimination of *Salmonella* and reduction of *E. coli* with HCl. Reduced consumption of dewatering polymers	(Devlin et al. 2011; Appels et al. 2011)
Ozonation	Doses: 0.05 – 0.2 gO_3/gCOD, 0.02 – 2 gO_3/gSS, 0.1 – 0.16 gO_3/gTS, 20 mgO_3/gTSS, 0.66 – 2.65 mgO_3/g biomass Time: 1 – 3 h Sludge type: mixed – secondary	10 – 29% COD solubilization. 9% protein solubilization and 7.1% carbohydrates solubilization Oxidation of 38% of TCOD and 73% VSS during PT at 0.2 gO_3/gCOD Acidification of sludge and decreased apparent viscosity. Increased CST and SRF	Digestion assay: batch – (semi)continuous Scale: laboratory Temperature: mesophilic and thermophilic	Biogas production improvements: 8 – 200% (5 – 80% CH_4) TSS reduction improvements: 9% Increased removal of carbamazepine, EDC, total coliforms, *E. coli* and *C. perfringens.* Reduced CST. CST reduced to values close to digested raw sludge.	(Weemaes et al. 2000; Yeom et al. 2002; Bougrier et al. 2006a; Carballa et al. 2007, 2008; Salsabil et al. 2010; Ak et al. 2013)

Table 4. continued

Technology	Pre-treatment conditions	Reported impacts on sludge properties	Digestion conditions	Principal reported effects on digestion	References
Fenton process	Doses: 5 – 100 gH_2O_2/kgDS and 0.4 – 5.0 gFe(II)/kgDS; 10 – 100 mgH_2O_2/L and 1 – 5 mgFe(II)/L Time: 60 min at pH 3 (H_2SO_4) Sludge type: secondary	7 – 24% Disintegration Degree Significant increase in BOD/COD ratio Up to 6 times increase in SCOD and SBOD Reduced particle size	Digestion assay: batch – (semi)continuous Scale: laboratory Temperature: mesophilic and thermophilic	Methane production improvements: 19 – 30% VS reduction improvements : 31 – 72% Lower CST of digested sludge. No improvements in filterability	(Dewil et al. 2007; Kaynak and Filibeli 2008; Erden and Filibeli 2010a; Erden and Filibeli 2011)
POMS/DMDO peroxidation	Doses: POMS (30 – 60 g/kgDS) and DMDO (330 – 660 ml/kgDS) Time: 1 h Sludge type: secondary	Significant increase in BOD/COD ratio Up to 5 and 7 times increase in SCOD and SBOD with POMS and DMDO, respectively	Digestion assay: batch Scale: laboratory Temperature: mesophilic	Biogas production improvements: 11% (POMS) and 33% (DMDO) ODS reduction improvement: 79% (POMS) and 185% (DMDO)	(Dewil et al. 2007)

3.3. Biological pre-treatments

Biological pre-treatment processes aim to intensify hydrolysis during aerobic or anaerobic pre-steps or through the use of enzymes. Table 5 summarizes some of the most important results of biological pre-treatment methods, including aerobic pre-digestion, dual digestion, enzyme addition and auto-hydrolytic processes.

3.3.1. Aerobic digestion

Aerobic digestion has been proposed as an alternative to physical and chemical pre-treatments due to its self-heating capacity and rapid degradation rate (Jang et al. 2014). The presence of proteolytic bacteria like *Geobacillus stearothermophilus* in the activated sludge makes aerobic thermophilic pre-treatment possible without bio-augmentation, providing important benefits to the overall stabilization process (Dumas et al. 2010). Moreover, aerobic processes can degrade materials that do not degrade under anaerobic conditions, further improving stabilization (Carrère et al. 2010).

Different configurations have been proposed to improve AD using aerobic microorganisms. Pre-treatment before conventional mesophilic digestion (Pagilla et al. 1996; Borowski and Szopa 2007; Jang et al. 2014), co-treatment in sludge recirculation (Dumas et al. 2010), aerobic post-treatment after digestion (Novak et al. 2011; Tomei et al. 2011a, 2011b) and the addition of aerobic bacteria to anaerobic digesters (Miah et al. 2005) have all been reported. Jang et al. (2014) studied the effect of thermophilic aerobic digestion at 55°C to improve meshophilic AD of mixed sludge. The methane production rate improved 42%, while methane yield improved 12% due to the pre-treatment. Also, volatile solids reduction improved 27 to 64% at 10 – 40 days SRT, respectively, during AD. Around 27% of VSS and 25% of TCOD removal of the combined process occurred in the aerobic reactor. Molecular analyses using PCR-DGGE showed that *Clostridia spp.* and *Bacillus spp.* were the predominant microorganisms in the aerobic reactor, while *Methanosaeta concilli* was the main methanogen in anaerobic reactors. Pre-treatment promoted the appearance of a higher diversity of methanogens, similar to the results reported by Zhang et al. (2009) for an electric pulse technology. Aerobic pre-treatment has also been reported to positively affect the centrifugability of digested sludge (Pagilla et al. 1996).

Dumas et al. (2010) studied the effect of incorporating a thermophilic digester at 65°C in the recirculation of a meshophilic AD system. Their results indicate that the aerobic-anaerobic system improved the reduction of volatile suspended solids by 39 – 83%. However, there was no improvement in methane production, and improvement in solids reduction was related to aerobic oxidation of organic matter during pre-treatment. Miah et al. (2005) studied the effect of adding aerobic thermophilic bacteria to an anaerobic digester. Methane yield improved by 21 – 112% and VS reduction by 4 – 44%. Similarly, aerobic post-treatment has been reported to improve VS removal by 12 – 26% (Novak et al. 2011; Tomei et al. 2011a, 2011b). As with other processes, the most significant improvements are achieved when applied to low-biodegradability sludge (Miah et al. 2005).

Methane content in biogas increases with the incorporation of an aerobic process in most of the studied configurations (Pagilla et al. 1996; Miah et al. 2005; Dumas et al. 2010; Jang et al. 2014). Jang et al. (2014) suggested that this is related to higher concentrations of HCO_3^- and CO_3^{2-} in the sludge after aerobic pre-treatment, which could be used by hydrogenotrophic methanogens as a substrate during AD. Moreover, lower H_2S concentrations in biogas have also been reported, most likely due to air stripping removal during the thermophilic aerobic step (Pagilla et al. 1996).

3.3.2. Enzyme addition

Hydrolytic enzymes have an important role during sludge stabilization, transforming polymeric substances into more biodegradable compounds (Yang et al. 2010). The addition of external enzymes to AD can therefore generate important benefits during AD, such as improved dewaterability and methane production (Davidsson and Jansen 2006; Dursun et al. 2006).

Studies using enzymes in pre-treatment have mainly focused on the use of enzymatic mixtures, as those show synergistic effects during sludge hydrolysis (Yang et al. 2010). Dursun et al. (2006) studied the application of a commercial mixture of enzymes (Envirozyme 216, Winston Company, USA) to improve anaerobically digested sludge dewaterability at laboratory and pilot scales. They found that it was possible to increase the presence of cake solids in laboratory assays, but not under pilot conditions. Further studies showed that these results are associated with the difference in the dewatering, mixing and conditioning methods. Barjenbruch and Kopplow (2003) also reported improvements in sludge dewaterability by applying enzymes, with a reduction of 25% in CST using a carbohydrase pre-treatment. Moreover, a 12% increase in biogas yield was achieved during the subsequent AD. Davidsson and Jansen (2006) also reported a small increase in methane potential during mesophilic batch digestion of secondary sludge (~3%) using a mixture of polysaccharide-degrading enzymes, lipase and protease. The integration of enzymatic pre-treatment with ultrasound and thermal processes further increased methane yield by 18% and 14%, respectively.

Yang et al. (2010) assessed the synergistic effect of different enzymes during pre-treatment. They supplemented variable doses (3 – 18% in TS basis) of different mixtures of commercial protease and α-amylase to waste activated sludge. Higher volatile solids reduction and COD solubilization were obtained with mixtures of the two enzymes than with a single enzyme pre-treatment. The highest VSS reduction (68%) was observed with the mixture ratio of 1:3 for protease and amylase at 50 °C. Under those conditions, concentration of reducing sugar and ammonia increased by around 150% and 78%, respectively.

Different enzymes and enzyme mixtures can have different effects on sludge hydrolysis. Selecting the appropriate enzymes is an important step to maximize the influence of pre-treatment on AD. Yang et al. (2010) reported that amylase achieved higher COD solubilization and VSS destruction than protease. Rashed et al. (2010) studied the effect of six commercial enzyme mixtures on different sludge combinations (with primary, secondary and digested sludge). They found that VS reduction during batch assays depends on both enzyme and sludge combinations. Optimal enzyme doses were around 0.1% (TS basis), and VS reductions improved by 16.3%. The synergistic effect of using enzyme mixes was observed, with consistently good results.

3.3.3. Dual digestion

The purpose of dual digestion is to improve AD by adding an anaerobic pre-digestion step oriented to hydrolysis. Anaerobic pre-treatment can be conducted under mesophilic or thermophilic conditions, but higher hydrolysis kinetics has been reported at high temperatures, prompting more interest in thermophilic pre-treatment. The most common method of anaerobic pre-treatment is temperature phased AD (TPAD), which uses thermophilic (~55°C) or hyperthermophilic (60 – 70°C) conditions for hydrolysis (Carrère et al. 2010). Ge et al. (2011a) found that the optimal conditions for TPAD pre-treatment are a retention time of 1 – 2 days, neutral pH (6 – 7) and a temperature of 65°C. However, pre-treatment at a "mild" thermophilic temperature (50°C) can also result in improvements such as COD solubilization of 13 – 21% and volatile solids reduction increases of 10% (Nges and Liu 2009). In the latter study, improvements in methane production did not always correlate to COD solubilization, and the authors hypothesized that improvements in volatile solids removal were related to both biogas and intermediary product formation.

The principal aim of TPAD systems is to separate hydrolysis and methanogenesis into two steps. Yu et al. (2013a) recently proposed separating hydrolytic/acidogenic and methanogenic microorganisms based on both SRT and temperature criteria, in a process they called temperature-staged biologically-phased AD (TSBP-AD). The optimum conditions for the pre-treatment were a 4-day SRT at 45°C, allowing a significant improvement of 85% in daily methane production compared to a single-phase system. The system was energy self-sufficient under the studied conditions.

Thermophilic-thermophilic systems have also been studied, with interesting results. Bolzonella et al. (2012) evaluated the performance of a hyper-thermophilic (65°C) hydrolytic step followed by thermophilic digestion (55°C). Working with 2 days of SRT, the hydrolytic step improved SV removal by 53% and biogas yield by 48% compared to conventional digestion. Unlike aerobic pre-treatment, thermophilic anaerobic pre-treatment does not increase methane concentration. Under hyperthermophilic conditions (70°C), Bolzonella et al. (2007) achieved COD solubilization of 23% during pre-treatment, with improvements of 20 – 50% in specific biogas production with mesophilic and thermophilic systems without pre-treatment. The thermophilic step removed around 25% of volatile solids.

Thermophilic and hyperthermophilic conditions constitute an interesting alternative to improve pathogen inactivation and sludge sanitization (Ge et al. 2010). Rubio-Loza and Noyola (2010) studied two-phased processes (thermophlic-mesophilic and thermophilic-thermophilic) to improve digestion and obtain class-A biosolids. They found that the thermophilic-mesophilic system produced around 24 – 28% more methane per kg of removed VS than the thermophilic-thermophilic system. Volatile solids reduction of the systems was 30%, with 14 – 17% during pre-treatment. The inclusion of pre-treatment allowed reaching 5-log destruction of fecal coliforms, 97% inactivation of helminth eggs and no detectable *Salmonella* in the sludge after digestion. Two serial mesophilic digester configurations have also shown improvements. Athanasoulia et al. (2012) studied the performance of a pilot scale (40 – 60 L) anaerobic digestion system consisting of two reactors at 37°C. They found that biogas yield of waste activated sludge from an extended aeration system improved by 20 – 33% and solids reduction by 15%.

Ge et al. (2010, 2011b) reported that thermophilic anaerobic pre-treatment of primary and secondary sludge is more efficient than mesophilic pre-treatment in terms of biogas improvement and solids reduction. The difference in performance is attributed to better hydrolysis kinetics rather than an improvement in intrinsic biodegradability. Given this, it is possible to achieve the same results with a larger conventional digester. However, thermophilic pre-treatment may be desirable as it can enhance sludge sanitation (Ge et al. 2010).

3.3.4. Auto-hydrolytic processes

Auto-hydrolytic processes are based on stimulating hydrolytic enzymes and/or active microorganisms present in secondary sludge. While soluble enzymatic activity in sludge is normally low due to the association of enzymes with the extracellular sludge matrix (Burgess and Pletschke 2008; Song and Feng 2011), disruption via thermal or physical means can be used to release enzymes and increase hydrolytic activity to levels suitable for sludge pre-treatment (Song and Feng 2011). Low temperature pre-treatment, ultrasound, gamma irradiation or other methods can physically disrupt EPS and are suitable for hydrolytic enzyme stimulation in the soluble phase (Yan et al. 2010; Song and Feng 2011). The use of the inherent hydrolytic potential of the sludge can reduce the energy costs of sludge pre-treatment, while avoiding the addition of chemical compounds or external enzymes.

While there are reports indicating the high enzymatic potential of secondary sludge (Yan et al. 2010; Song and Feng 2011; Yu et al. 2013b), few studies have focused on the pre-treatment of sludge using auto-hydrolytic phenomena or assessing its role during conventional pre-treatment processes (e.g. low temperature). However, there are commercial applications of auto-hydrolytic processes, with the *Enzymic Hydrolizer* marketed by Monsal being one of the most extended processes (Mayhew et al. 2002).

Carvajal et al. (2013) studied an auto-hydrolytic process at 55°C to promote enzymatic activity in secondary sludge and enhance AD. Concentration of SCOD increased significantly with pre-treatment, achieving 39% solubilization after 24 h, comparable to more energy-intensive processes. Organic matter solubilization is attributed to both the thermal disruption of the sludge and the hydrolytic action of enzymes released from the sludge flocs. Total COD and protein content of the sludge did not change during pre-treatment, but a slight decrease in carbohydrates was observed, possibly related to thermophilic bacterial activity. Pre-treatment reduced resistance to sludge flow, and methane production during AD improved by 23% after 12 h of pre-treatment. The energy balance of the process was positive with 8% TS concentrated sludge and 12-h treatment time.

Table 5. Summary of reviewed effects of biological pre-treatments (PT) technologies

Technology	Pre-treatment conditions	Principal impacts on sludge properties	Digestion conditions	Principal reported effects on digestion	References
Aerobic digestion	Temperature: 55 – 65°C Time: 0.5 – 2 d O_2 supply: 5 L_{air}/min; 10 – 20 mg/L OUR Sludge type: secondary – mixed	8% COD solubilization Possible consumption of TCOD (25%) and VS (26%) during PT Removal of *Nocardia* filaments (related to foaming) Significant generation of ammonia	Digestion assay: batch – (semi)continuous Scale: laboratory – pilot Temperature: mesophilic	Methane production improvements: 10 – 79% VS improvement: 11 – 67% Increased concentration of CH_4 and reduced concentration of H_2S in biogas Increased diversity of microbial communities Increased centrifugability and virus/HE removal on digested sludge	(Pagilla et al. 1996; Miah et al. 2005; Borowski and Szopa 2007; Dumas et al. 2010; Jang et al. 2014)
Enzyme addition	Enzymes and doses: Protease, Amilase, Carbohydrase, Cellullase; 0,06 – 18% (w/w TS) Temperature: 37 – 50°C Time: 4h – 11d Sludge type: primary – secondary – mixed	15.1 – 25.0% increase in SCOD/TCOD ratio 25% reduction on CST; 9% increase in sludge cake solids (enzymes applied as post-treatment after digestion) Up to 58% VSS reduction during treatment	Digestion assay: batch – (semi)continuous Scale: laboratory – pilot Temperature: mesophilic	Biogas production improvement: 12% (3% CH_4) Solids reduction improvement: 1 – 16.3%	(Barjenbruch and Kopplow 2003; Davidsson and Jansen 2006; Dursun et al. 2006; Yang et al. 2010; Rashed et al. 2010)
Dual-digestion	Temperature (pre-digestion): 37 – 70 °C Retention time (pre-digestion): 0.5 d – 6 d Sludge type: primary – secondary – mixed	13 – 23% COD solubilization Production of biogas during PT at SRT >3 – 5 days Up to 25% VS removal during PT Reduction of FC, SN and HE at 55°C and 2 – 3 days SRT	Digestion assay: batch – (semi)continuous Scale: laboratory – pilot Temperature: mesophilic and thermophilic	Biogas production improvement: 11 – 50% (6–85% CH_4) VS improvement: 10 – 53% 5 log destruction of FC, 97% HE inactivation and no detection of SN	(Bolzonella et al. 2007, 2012; Nges and Liu 2009; Ge et al. 2010, 2011a, 2011b; Rubio-Loza and Noyola 2010; Athanasoulia et al. 2012; Yu et al. 2013a)
Auto-hydrolytic processes	Temperature: 42 – 55°C Time: 12 – 48 h Sludge type: secondary	32 – 39% COD solubilization Significant consumption of carbohydrates during treatment Increased removal of *E. coli* from 1.3 to 3.5 log	Digestion assay: batch – (semi)continuous Scale: laboratory - full scale Temperature: mesophilic	Methane production improvement: 16 – 23%	(Mayhew et al. 2002; Carvajal et al. 2013)

3.4. Combined pre-treatments

The integration of different pre-treatment methods has been proposed as an alternative to overcome single-process limitations. Different configurations have been proposed, including thermo-chemical, physical-chemical and combined biological processes. Reviewed results of thermochemical processes are summarized in Table 6, while Table 7 presents the results of physical-chemical pre-treatments and Table 8 summarizes the reviewed combined biological pre-treatments reports

3.4.1. Thermo-chemical pre-treatments

Thermo-chemical pre-treatment consists of thermal disruption with the simultaneous addition of acid, alkaline or oxidative compounds. There are two main pre-treatment groups: a) High temperature thermo-chemical processes (115 – 170°C), and b) Low temperature thermo-chemical processes (50 – 90°C). In both cases, chemical agents such as NaOH, KOH, O_3, Na_2CO_3, HCl or H_2O_2 are added to the pre-treatment separately or in combination.

3.4.1.1. High temperature thermo-chemical processes

High temperature thermo-chemical pre-treatment has been reported to significantly increase sludge solubilization and AD performance. COD solubilization values after pre-treatment range between 28 and 87%, with increases in methane production between 40 and 154% during AD (Tanaka et al. 1997; Penaud et al. 1999; Kim et al. 2003; Valo et al. 2004; Takashima and Tanaka 2008). An important advantage of thermo-chemical processes is the reduced reagent consumption, four to six times lower than single-stage chemical pre-treatments (Park et al. 2014).

Kim et al. (2003) reported that adding NaOH at 121°C resulted in 87% COD solubilization, which is higher than most results reported for either thermal or chemical pre-treatments. Under these conditions, VS reduction was twice as high as that of the control. Similarly, Valo et al. (2004) found that compared to single thermal and chemical pre-treatments, the most efficient process in terms of COD solubilization was a combined oxidant and thermal process, with a value of 8%3 at 170°C and pH 12 Biogas production and volatile solids removal improved by around 72% using the thermo-chemical process.

Tanaka et al. (1997) also compared chemical, thermal and thermo-chemical pre-treatment methods. Alkaline pre-treatment with NaOH caused 15% VSS solubilization. In contrast, thermal pre-treatment at 180°C and thermo-chemical pre-treatment at 130°C achieved 30 and 45% VSS solubilization, respectively. Park et al. (2014) concluded that thermo-chemical pre-treatment with NaOH (pH 12, 121°C, 1 h) achieved higher COD solubilization and removal during a subsequent anaerobic/aerobic stabilization process. Moreover, methane yield increased by 154%. While adding chemicals increased salinity and exerted significant effects on microbiological communities, operational performance during digestion was not reduced.

While alkaline reagents have received more attention, the use of acid media during thermo-oxidative pre-treatment has been reported to improve sludge dewaterability, color generation, and methane yield compared to thermo-oxidative alkaline processes (Takashima and Tanaka 2008). However, maximum VSS reduction was achieved under alkaline conditions. Depending on oxidant strength, either methane production or solids reduction were favored. Therefore, the choice of pre-treatment should be based on the particular objectives of its incorporation to the AD process.

A recent study by Abelleira-Pereira et al. (2015) reported that the application of advanced thermal hydrolysis (ATH) using H_2O_2 under lower temperature conditions (115°C) can significantly improve methane yield and VS removal during batch mesophilic AD. Moreover, ATH outperforms conventional thermal hydrolysis at higher temperatures. Improvements in the dewaterability of digested sludge have also been observed (Abelleira et al. 2012). Solubilization of COD can be considerably improved compared to conventional thermal hydrolysis, but the results do not always correlate to improvements in biogas production.

Table 6. Summary of reviewed effects of thermochemical pre-treatments (PT) technologies

Technology	Pre-treatment conditions	Principal impacts on sludge properties	Digestion conditions	Principal reported effects on digestion	References
High temperature thermo-chemical processes	Doses: 1.2 – 26 gNaOH/L, 30 – 65 meqKOH/L, O_2 (+0.1 – 0.35 gNa_2CO_3/gVS or 0.005 mol HCl/gVS), 0.5 – 2 gH_2O_2/gVS, O_2, 0.01 – 0.05 gO_3/gVS pH: 2 – 12 Temperature: 115 – 170 °C Time: 5 – 35 min Sludge type: mixed – secondary – digested	28 – 87% COD solubilization 22% TCOD degradation at 170°C and pH 12 Possible degradation of TSS and VSS due to thermo-oxidative PTs Increased VFAs concentration Possible formation of refractory compounds with high doses of hydroxide	Digestion assay: batch – (semi)continuous Scale: laboratory – pilot Temperature: mesophilic	Methane production improvements: 40 – 154 % VS reduction improvements: 72% (450% VSS) Increased CST and color using thermo-oxidative PT at alkaline conditions. Decreased CST at acid conditions	(Penaud et al. 1999; Kim et al. 2003; Valo et al. 2004; Takashima and Tanaka 2008; Park et al. 2014; Abelleira-Pereira et al. 2015)
Low temperature thermo-chemical processes	Doses: 2 gH_2O_2/gVSS, 0.6 mg H_2O_2 + 1.5 mg $FeCl_2$/mg S^{2-}, 0.05 – 0.25 g NaOH/gTS, 0.1 – 0.2 M NaOH pH: 8 – 11 Temperature: 50 – 90 °C Time: 0.5 – 33h Sludge type: secondary – mixed	11 – 76% COD solubilization Up to 45% reduction of VSS during PT Increased soluble carbohydrate (250%) and protein (167%) concentration Increased VFAs concentration	Digestion assay: batch – (semi)continuous Scale: laboratory Temperature: mesophilic – thermophilic	Methane production improvements: 20 – 70.6% VSS reduction improvements: 11 – 58% Improved removal of fecal coliforms Decreased concentration of sulfur compounds in biogas (using H_2O_2 +$FeCl_2$)	(Vlyssides and Karlis 2004; Cacho Rivero et al. 2006; Dhar et al. 2011a; Yi et al. 2013; Kim et al. 2013b; Xu et al. 2014)

3.4.1.2. Low temperature thermo-chemical processes

While promising results have been reported for high temperature thermo-chemical processes, high temperatures and high consumption of chemical reagents limits their implementation. Therefore, studies have more on the application of lower temperatures (50 - 90°C) as this represents an alternative to decrease energy consumption (Vlyssides and Karlis 2004; Cacho Rivero et al. 2006; Kim et al. 2013b; Xu et al. 2014).

Low temperature thermo-chemical processes have been reported to achieve very significant sludge solubilization. Yi et al. (2013) increased SCOD/TCOD from 1.4 to around 68.2% using a sequential alkaline-thermal treatment at 70°C (24 + 9 h). Xu et al. (2014) achieved up to 44% COD solubilization using a thermo-alkaline pre-treatment at 90°C and pH 11, similar to values achieved during 8 d alkaline pre-treatment. Moreover, soluble protein concentrations increased by a factor of 8.2 and soluble carbohydrates by 7.4. Total VFAs increased 8.5 fold, with predominance of acetic and propionic acids. At short pre-treatment times, NaOH concentrations is more significant in improving COD solubilization than temperature. An optimum of 0.16 M NaOH was reported, and further increases in NaOH concentration result in decreased solubilization (Kim et al. 2013b).

Regarding AD performance, Kim et al. (2013b) found that the application of 0 – 0.2 M NaOH at a temperature range of 60 – 90°C was sufficient to increase methane production by 23.4 – 70.6%. An optimum for methane production was found at 0.1 M NaOH and 73.7 °C. Further increases in NaOH concentration and temperature led to diminished methane production due to Na^+ toxicity and decreased hydrolytic activity of the sludge. Cacho Rivero et al. (2006) studied a thermo-oxidative process using H_2O_2 at 90°C during 24 h, achieving a 38% increase on methane yield per gram of removed COD. However, overall production of methane decreased, probably related to organic matter oxidation during pre-treatment. Overall improvement in VSS removal was 58% and a significant improvement in fecal coliform removal was observed due to pre-treatment.

Thermo-oxidative processes have also been studied to improve biogas quality. Dhar et al. (2011a) studied a pre-treatment in the presence of H_2O_2+$FeCl_2$ at 60°C with the aim of controlling sulfur compounds and improve AD performance. Sulphur compounds are removed principally through different chemical pathways that generate mainly FeS, S and H_2SO_4. Solubilization of COD after pre-treatment achieved 11%, while H_2S and dimethyl sulfide concentrations decreased by an average of

75 and 40%, respectively. Moreover, removal of VSS improved 11% and daily methane production by around 20%.

3.4.2. Physical-chemical pre-treatments

Physical – chemical processes include the use of high pressure, ultrasound, microwave or mechanical crushing/grinding devices under acid/alkaline conditions or as aids to ozone oxidation. Chemically aided electrolysis also has been proposed as an alternative to more conventional pre-treatments. Membrane disruption and cell lysis caused by physical pre-treatments can be improved by mechanisms like saponification of lipidic membranes (Kim et al. 2003; Neyens et al. 2004), improving solubilization and pre-treatment performance.

3.4.2.1. Microwave-chemical processes

Alkaline pre-treatment in combination with MW represents an effective sludge pre-treatment technology (Doğan and Sanin 2009; Chi et al. 2011; Jang and Ahn 2013). Doğan and Sanin (2009) evaluated the effect of MW irradiation combined with NaOH addition. After pre-treatment, the sludge SCOD/TCOD ratio increased by a significant 600% compared to the control. VS and TCOD removal during semicontinuous AD were 35% and 30% higher than the control, respectively. The authors also found that the maximum increase in methane yield during semicontinuous AD was 53%. Chi et al. (2011) studied the effect of MW–NaOH treatment at 170°C on thermophilic digestion. Performance improvements were lower than the results of Doğan and Sanin (2009), as 28% and 18% increases in VS and TCOD removal were achieved and methane yield was only 17% higher. This could be related to the use of thermophilic digesters during this study and the fact that pH was not adjusted prior to digestion. Jang and Ahn (2013) investigated the effects of MW–NaOH pre-treatment, achieving a SCOD/TCOD ratio increase of 18 times after pre-treatment. VS and COD removal from pretreated sludge was enhanced as SRT was reduced, and at day 5 of SRT, VS and COD removal were 262% and 132% higher than the control, respectively. Biogas yield also increased by about 228% at 5 days SRT. However, there is an important drawback to MW–alkaline pre-treatment related to effluent quality, as increased concentrations of SCOD, NH_3-N and turbidity have been reported (Doğan and Sanin 2009).

Different results have been observed in terms of sludge dewaterability. While some authors report that digested sludge after MW–alkaline pre-treatment has better dewaterability properties than raw sludge (Doğan and Sanin, 2009), other authors have observed the opposite effect (Jang and Ahn, 2013). Alkaline conditions and microwave irradiation disrupt WAS floc structure, releasing biopolymers and colloids into the soluble phase (Eskicioglu et al. 2008). This is most probably related to the observed effects on sludge dewaterability, and can result in increased soluble concentrations of proteins and other macromolecules (Doğan and Sanin 2009; Chi et al. 2011). It has been reported that protein release after combined MW–alkaline pre-treatment is higher than the sum of proteins released during alkaline and microwave pre-treatments, indicating the existence of synergistic effects (Doğan and Sanin, 2009). The OUR of biological sludge has been reported to decrease after pre-treatment, which is probably also related to sludge disruption and disintegration (Doğan and Sanin 2009).

3.4.2.2. High pressure-chemical processes

High pressure has also been studied in combined physical–chemical processes. Fang et al. (2014) investigated the combination of NaOH with HPH at 60 MPa. The dosage was directly related to the disintegration degree and VS removal, reaching a plateau at 0.04 mol/L. Biogas and methane yield both increased, achieving improvements of 47% and 107% respectively over the HPH pre-treatment alone. The combined HPH–Alkaline treatment is more effective to disintegrate sewage sludge than the single alkaline treatment and the single HPH treatment in terms of COD solubilization and anaerobic biodegradability (Zhang et al. 2012; Fang et al. 2014).

Combined high pressure cycles with O_3 pre-treatment has yields solubilization levels of 21% for COD and 25% for TSS, with a possible 22% loss of VSS during the process (Cheng et al. 2012; Cheng and Hong 2013). Biogas production improvements seem dependent on application of batch or semicontinuos digestion, with F/I and the origin of inoculum as relevant operational factors (Cheng and Hong 2013).

3.4.2.3. Ultrasound-chemical processes

Ultrasound has been studied in combination with ozone, alkali and acid addition. US plus alkaline addition has been reported to achieve 50 – 70% COD solubilization and biogas yield increases of 38 – 55% (Kim et al. 2010; Tian et al. 2015b). Synergistic solubilization effects have been observed and attributed to greater release of soluble microbial products, mechanical disruption and solubilization of humic acids due to basic conditions (Kim et al. 2010; Tian et al. 2015b). Synergistic effects on methane yield have also been observed (Tian et al. 2015b). Optimal operational conditions for the process have been reported as pH 9 and 7500 kJ/kgTS US specific energy. Contrary to what has been observed under alkaline conditions, the integration of US with acid has synergistic solubilization effects only at extreme pH values (pH 2), increasing the rate and degree of solubilization (Sahinkaya 2015). High levels of TS in the sludge during this process negatively affecs solubilization, which is related to low specific energy application, and possibly to wave attenuation.

US–O_3 has been studied in different configurations. Sequential combinations of both processes have allowed improvements of 26 – 36% in biogas yield and 18 - 21.4% in volatile solids reduction during mesophilic digestion of mixed sludge (Tian et al. 2015a). The highest improvements in biogas production were observed at low SRT due to the influence of pre-treatment in digestion kinetics. CST after digestion worsened due to US–O_3, and a higher concentration of humic acid-like molecules was observed in digested sludge. Simultaneous application of US–O_3 has been reported to generate synergistic effects on COD solubilization and methane yield of WAS and mixed sludge (Xu et al. 2010; Tian et al. 2014). Under those conditions, a significant reduction in particle size was also observed (Xu et al. 2010). Proposed mechanisms for synergistic effects include increased contact between sludge and O_3 due to US-induced disaggregation, increased mass transfer conditions, higher generation of radicals and O_3 bubbles acting as cavitation nuclei. Methane yield has been reported to increase from 15 to near 100% due to the simultaneous application of US and O_3 (Xu et al. 2010; Tian et al. 2014).

Table 7. Summary of reviewed effects of physical-chemical pre-treatment (PT) technologies

Technology	Pre-treatment conditions	Principal impacts on sludge properties	Digestion conditions	Principal reported effects on digestion	References
MW–alkaline	Doses: 20 meq NaOH/L, 0.05 – 2.5 gNaOH/gSSV (SST) pH: 10 – 12.5 Time: 1 – 51 min Temperature (MW): 100 –210°C Sludge type: secondary	35% COD Solubilization SCOD/TCOD increases 6 – 18 times Decreased OUR activity after MW and combined PT Increased CST after PT (higher pH reduces this effect)	Digestion assay: batch – (semi)continuous Scale: laboratory – pilot Temperature: mesophilic – thermophilic	Biogas production improvements: 44 – 228% (17 – 228% CH_4) VS reduction improvements: 28– 262% Divergent effects on sludge dewaterability Increased effluent SCOD, turbidity and NH_3–N concentrations	(Doğan and Sanin 2009; Chi et al. 2011; Jang and Ahn 2013)
HPH–Alkaline	Doses: 0.02 – 0.05 mol NaOH/L pH: 7 – 12 Time: 0.5 h Pressure 60 MPa Sludge type: secondary	Linear increase in COD solubilization with NaOH dose up to 54.1%	Digestion assay: batch Scale: laboratory Temperature: mesophilic	Biogas production improvement: 47% (107% CH_4) VS reduction improvements: 16 – 41% TCOD removal increase: 10 – 41%	(Fang et al. 2014)
High pressure–O_3	Doses: 6 – 11 mgO_3/gTSS Cycles: 5 – 20 pressure cycles Pressure: 690 – 1040 kPa Time: 16 min Sludge type: secondary	Up to 21% COD solubilization Up to 25% TSS solubilization Possible 22% reduction of VSS during PT Pressure improves COD and solids solubilization compared to single O_3 PT	Digestion assay: batch – (semi)continuous Scale: laboratory Temperature: mesophilic	Biogas production improvements: 6 and 800% (semicontinuous and batch DA, respectively) VSS reduction improvements: 60% (batch) Increased methane concentration (51 to 56%) Biogas production improvements are dependent of F/I ratio(higher improvements at low F/I)	(Cheng et al. 2012; Cheng and Hong 2013)
US–Alkaline	Doses: 0.025 – 0.25 gNaOH/gTS; 2 – 46.8 mL NaOH/L sludge pH: 8 – 13 Specific energy: 6000 – 30000 kJ/kgTS Frequency: 20 kHz Sludge type: mixed	50 – 70% COD solubilization 10 – 90% Disintegration Degree Release of soluble microbial products and humic acids at basic conditions Synergistic effects on solubilization and organics size reduction	Digestion assay: batch – (semi)continuous Scale: laboratory Temperature: mesophilic	Biogas production improvements: 38 – 55% Synergistic effects on methane yield Increased effluent nitrogen and ammonia concentration	(Kim et al. 2010; Tian et al. 2015b)

Table 7. continued

Technology	Pre-treatment conditions	Principal impacts on sludge properties	Digestion conditions	Principal reported effects on digestion	References
US–O_3	Specific energy (US): 1000 – 12000 kJ/kgTS O_3 Doses: 0.4 – 1 gO_3/h; 0.012 – 0.12 gO_3/gTS Frequency: 20 kHz Specific Energy: 9 kJ/kgTS Sludge type: secondary– mixed	6 – 37 % COD solubilization Synergistic effects on COD solubilization. Decreased average particle size (53.9 μm to 18.12 – 38.99 μm) and 10 times increased turbidity	Digestion assay: batch – (semi)continuous Scale: laboratory Temperature: mesophilic	Biogas production improvements: 26 – 36% (15 - 100% CH_4) VS improvements: 18 – 21% Synergistic effects on methane yield Increased digested sludge CST (140 and 215%) and concentrations of humic-like compounds	(Xu et al. 2010; Tian et al. 2014; Tian et al. 2015a)
Mechanical–Alkaline	Rotation frequency: 2500 rpm Tangential velocity: 5430 m/s pH: 11 – 13 (NaOH) Time: 30 – 90 min Sludge type: secondary	64% VSS solubilization Possible generation of inhibitory/recalcitrant compounds	Digestion assay: batch Scale: laboratory Temperature: mesophilic	Methane production improvement: 84 – 832% Synergistic effects on methane yield (possible co-metabolism)	(Cho et al. 2014)
Electro-chemical	Doses: 0.6%v/v NaClO pH: 7 – 12.2 (NaOH) Tension: 5 – 20 V Time: 40 min Sludge type: secondary	22% COD solubilization 1.6 – 54.7% Disintegration Degree 19%, 24% and 38% carbohydrates, protein and COD GRS, respectively	Digestion assay: batch Scale: laboratory Temperature: mesophilic	Biogas production improvement: 63% (20% CH_4) VS reduction improvements: 17% Increased hydrolysis rates (0.13 d^{-1} to 0.36 d^{-1}) Increased methane concentration in biogas (56 to 65%)	(Xu et al. 2014; Yu et al. 2014; Zhen et al. 2014)

3.4.2.4. Mechanical-alkaline pre-treatment

Alkaline-aided mechanical disruption has been also studied. Cho et al. (2014) proposed the use of a crushing device with NaOH addition to pH up to 13. Under optimal conditions, the studied process can achieve 64% solubilization in terms of VSS, with 84 – 832% increases in methane yield. The significant improvement in methane yield could be related to the low degradability of raw sludge, as the control showed only a 25 $mLCH_4/gST$ yield. Solubilization and methane yield improvement did not totally correlate, attributed to the possible generation of recalcitrant/inhibitory compounds such as melanoidins, furfural and hydroxymethylfurfural. Moreover, the authors found that the digestion of different fractions of raw and pre-treated sludge showed improvements in methane yield higher than predicted based on single digestion of pretreated and un-pretreated sludge. This could be explained by a possible co-metabolism phenomenon, with the best results obtained at a 50% v/v mixture.

3.4.2.5. Electrochemical pre-treatment

Chemically-aided electrolysis has also shown significant effects on sludge properties and AD. Zhen et al. (2014) assessed the effects of electrolysis with the addition of NaOH on secondary sludge mesophilic batch digestion. The addition of NaOH increased the disintegration degree (COD) of electrolysis from 0.1 – 8% to up to 54.7%, and a 20.3% higher methane yield was observed at pH 9.2 and 5 V. Moreover, the hydrolysis constant improved from 0.13 to 0.36 d^{-1} due to pre-treatment.

Yu et al. (2014) studied the effect of electrolysis with hypochlorite addition on secondary sludge mesophilic digestion. Compared to thermal, thermochemical, and alkaline processes, electrochemical pre-treatment achieved the highest values for COD and macromolecule solubilization (reported as growth rate of solubilization, GRS). Biogas improvement for the electrochemical pre-treatment was also the highest, with a 63% increase. Sludge solubilization was not related to methane yield increases, possible due to mineralization, solubilization of recalcitrant compounds or inhibition. Moreover, methane concentration in the biogas increased, and the authors hypothesized that electrochemical pre-treatment could lead to conditions that promote the growth of homoacetogens or inhibit syntrophic acetogen activity.

Comparing thermal, alkaline, thermo-alkaline and electro-chemical pre-treatments, Xu et al. (2014) found that electro-chemical pre-treatment (using NaClO) produced the highest improvement in biogas yield: 64% compared to 32, 53 and 41% for thermal, thermo-alkaline and alkaline, respectively. However, solubilization was in the order alkaline>thermo-alkaline>thermal>electro-chemical, showing there was no direct relation between solubilization and biogas yield improvement. All pre-treatments generated improvements in VS removal, with relative increases of 12.3, 18.8, 12 and 17% for thermal, thermo-alkaline, alkaline and electro-chemical pre-treatment, respectively.

3.4.3. Combined biological pre-treatments

Combined biological pre-treatments mainly consist of the application of physical and chemical pre-treatments prior to phased sludge digestion. As such, it involves sequential rather than simultaneous application of pre-treatments.

Coelho et al. (2011) evaluated the integration of microwave pre-treatment with two-phased thermophilic-thermophilic (T-T) and thermophilic-mesophilic (T-M) AD, achieving improvements of up to 106% and 94% in biogas yield for the T-T and T-M systems, respectively. The integration of MW and two-phased systems also allowed improvements of the same order in solids reduction and the total hygienization of sludge in terms of total coliforms. Dewaterability (measured as CST) improved due to microwave pre-treatment and phased digestion.

Wahidunnabi and Eskicioglu (2014) studied the influence of HPH in the presence of NaOH and digestion phasing in the treatment of mixed sludge (including both thermophilic-mesophilic and thermophilic-thermophilic combinations). The integration of HPH with phase digestion (HPH-TPAD) showed better performance than one-phase mesophilic/thermophilic and two-phase digestion systems (TPAD), with improvements in VS reduction of 14 – 21% and 5 – 9% for the HPH-TPAD system compared to mesophilic and thermophilic controls, respectively. Methane yield was improved by 75 – 81% compared to the mesophilic reactor and 45 – 54% compared to the thermophilic reactor. Compared to the mesophilic control, improvements in methane yield due to the HPH-TPAD system are higher than the sum of improvements produced by TPAD and HPH alone, suggesting the existence of synergistic effects. However, for most scenarios, the TPAD system showed better energy performance than HPH-TPAD due to lower energy consumption associated with pre-treatment.

Sequential US and TPAD processes have also been studied. Gianico et al. (2014) reported that a US plus mesophilic/thermophilic AD process showed different performances depending on the organic loading rate (OLR). At a low OLR, sonication caused a biogas production increase of 19% during the mesophilic step. When the OLR was higher, an increase of 17% in biogas production was associated with the thermophilic reactor. This could be related to the accumulation of VCA during mesophilic digestion at a higher OLR. At a higher OLR, methane concentration in biogas increased 8% due to higher conversion rates of VFAs during the thermophilic step. Compared to a conventional mesophilic digester, pre-treatment increased methane production up to an estimated 33%. Pathogen reduction was similar to that with single-stage thermophilic systems (*E. coli*, somatic coliphags and *Salmonella*), with little reduction due to mesophilic digestion or US. Thermal balances are positive only in direct combustion schemes (no co-generation) at high OLR, while electricity gains can be achieved if a pre-thickening step is included.

Grübel and Suschka (2015) studied integrated hydrodynamic-alkaline pre-treatment based on cavitation effects before two-stage AD of WAS. Dual digestion was performed in serial mesophilic and thermophilic steps. They observed a synergistic effect in COD solubilization after hydrodynamic-alkaline pre-treatment. Digestion was performed with a mixture of pre-treated and raw sludge, achieving the highest VS removal at 7 days of mesophilic SRT and 17 days of thermophilic SRT (55.5%). Biogas yield was maximal at the highest mesophilic SRT of 9 days (842 mL/gVS removed). Biogas production improvement for TPAD was around 13 – 28% compared to results with a mesophilic digester. After dual digestion, somatic coliphages, *E. coli* and *Salmonella* were totally eliminated.

Table 8. Summary of reviewed effects of combined biological pre-treatments (PT) technologies

Technology	Pre-treatment conditions	Principal impacts on sludge properties	Digestion conditions	Principal reported effects on digestion	References
MW + TPAD	Frequency: 2450 MHz Temperature (MW): 96°C Temperature (pre-digestion): 55°C Retention Time (pre-digestion): 2 d Sludge type: secondary	COD solubilization (MW): ~18% Increased VFAs concentration (1.6 to 3.6 fold) after MW	Digestion assay: (semi)continuous Scale: laboratory Temperature: thermophilic – mesophilic and thermophilic – thermophilic AD	Biogas production improvement: 94 – 106% VS improvements: 99 – 106% Reduction of fecal coliforms to levels under detection limit Reduced CST compared to mesophilic control	(Coelho et al. 2011)
HPH/NaOH + TPAD	Dose: 9 – 36 mgNaOH/gTS (pH: 10 – 11) Pressure: 6000 – 12000 PSI Time: 30 min Temperature (pre-digestion): 55°C Retention time (pre-digestion): 2 d Sludge type: secondary (PT), mixed (during digestion)	Reduction of 35 – 58% in particle size after HPH CST increased about 4 times after HPH CODs/CODt relation increase from 5% to 27% after HPH Percentages of soluble sugars, proteins and humic substances were 18.5%, 18.5% and 31%, respectively after HPH	Digestion assay: (semi)continuous Scale: laboratory Temperature: thermophilic - mesophilic TPAD	Methane production improvements: 75 – 81% and 45 – 54% compared to mesophilic and thermophilic controls, respectively VS reduction improvements: 14 – 21% and 5 – 9% compared to mesophilic and thermophilic controls, respectively Digestion at 20 days SRT decrease CST to levels close to control	(Wahidunnabi and Eskicioglu 2014)
US + TPAD	Frequency: 24 kHz Specific energy: 0.4 – 0.5 kWh/kgTS Temperature (pre-digestion): 37°C Retention time (pre-digestion): 3 – 5 d Sludge type: secondary	Increase of 8 – 16 times in SCOD after US (2 – 3% Disintegration Degree)	Digestion assay: (semi)continuous Scale: laboratory Temperature: mesophilic – thermophilic TPAD	Methane production improvements: 33% VS reduction improvements: 40 – 70% Increased methane in biogas (8%) Log removal of >3.5, >2.3, and >0.8 for *E. coli*, somatic coliphages, and *Salmonella*, respectively	(Gianico et al. 2014)

Table 8. continued

Technology	Pre-treatment conditions	Principal impacts on sludge properties	Digestion conditions	Principal reported effects on digestion	References
Hydrodynamic /NaOH + TPAD	Doses: 14.4 – 15.2 mmol NaOH/L sludge (pH: 9 – 11) Pressure: 12 bar Time: 30 min (10 3-min cycles) Temperature (pre-digestion): 35 °C Retention time (pre-digestion): 5 – 9 d Sludge type: secondary	Increase in SCOD from <500 to ~4500 mg/L after hybrid hydrodynamic/NaOH PT 35% synergistic increase of SCOD after hydrodynamic/NaOH PT Up to 31% SV reduction during pre-digestion	Digestion assay: batch (combined digestion of raw and pre-treated sludge) Scale: laboratory Temperature: mesophilic – thermophilic TPAD	Biogas production improvements: 13 – 28% VS removal: up to 56% for combined process Total elimination of microbiological contamination was achieved (except for sulphite-reducing *Clostridia*)	(Grübel and Suschka 2015)

4. FUTURE CHALLENGES FOR SLUDGE PRE-TREATMENT

One of the most critical aspects for the development of sustainable pre-treatment methods is achieving positive energy and economic balances. While most pre-treatment methods show good AD performance improvements, their high-energy costs prevent broader application in sewage treatment facilities. In this regard, thickening sludge is viewed as a critical step to decrease pre-treatment energy costs (Pérez-Elvira et al. 2009; Braguglia et al. 2011; Gianico et al. 2013). However, sludge with high solid concentrations could be difficult to treat given the rheology of sludge changes with increasing solid content. Sludge yield stress increases exponentially with increased concentrations of solids (Mori et al. 2006), which could affect energy requirements in pumping and mixing and favor the existence of dead regions in digesters and other equipment (Cheng 1986). Furthermore, increased substrate concentration during AD has been reported to decrease methane yields and rates, mostly related to a decrease in the hydrolysis rate, mass transfer limitations and VFA accumulation (Abbassi-Guendouz et al. 2012). As well, the effectiveness of pre-treatments with ultrasound can be affected by high solid concentrations that attenuate sound waves (Pilli et al. 2011).

Other approaches can be used to reduce pre-treatment costs. Using local environmental conditions like low temperatures for freezing/thawing, where it is possible, can greatly reduce energy costs (Montusiewicz et al. 2010). The synergistic effects of combined pre-treatment methods is another interesting alternative to overcome energy limitations (Kim et al. 2003; Valo et al. 2004). The integration of different phenomena during pre-treatment can result in major biogas production improvements, with lower energy consumption and possible positive energy and economic balances. A recent report by Cano et al. (2015) concluded that thermal pre-treatments have better energy feasibility than electrical pre-treatments under current conditions, with self-sufficiency achieved when proper energy integration is involved (including the implementation of a combined heat and power system and sludge pre-thickening).

Notably, laboratory and industrial devices used for pre-treatment can yield different results regarding energy consumption (Zielewicz and Sorys 2008; Pérez-Elvira et al. 2009). Laboratory devices are often not as energy efficient as industrial level devices, and consequently energy balances based on laboratory tests do not necessarily indicate costs at a larger scale. Therefore, rigorous assessment of the implications of scaling is necessary to realistically estimate the energy and economic costs of laboratory-tested pre-treatment processes.

Another important issue regarding upscaling sludge pre-treatment is environmental performance. The costs of consumption of energy and chemicals includes the environmental impacts of their production, and while the incorporation of pre-treatment in wastewater treatment facilities can improve AD performance, it is important to assess whether environmental burdens are being transferred to stages like energy generation or sludge disposal. Carballa et al. (2011) assessed the life cycle of seven different pre-treatments applied to sewage sludge and kitchen waste in the context of Europe. They found that HPH and chemical pre-treatments have the lowest environmental burdens in the studied scenario. Energy consumption had higher associated impacts than chemical consumption, and the application of sludge to soils had significant eutrophic and toxicological potential (terrestrial eco-toxicity and human toxicity). It is important to note that results of this study are heavily influenced by the high fossil fuel profile of the Spanish energy matrix. Local conditions like the availability and cost of chemical additives and the local energy matrix and policies can affect the environmental and economic performance of pre-treatment, and therefore alternatives should be selected considering local factors

While COD solubilization has been widely used to evaluate pre-treatment efficiency, it does not always correlate to AD performance improvements (Kim et al. 2013a). Therefore, other factors that could influence methane yield and solids reduction after pre-treatment should be studied, including, but not limited to particle size reduction, hydrolytic enzyme stimulation, improved rheology and increased mass transfer conditions. Moreover, studies of the solubilization products after pre-treatment could shed light on the mechanisms related to AD improvements (Tian et al. 2015b).

Several pre-treatment processes have shown reduced particle size after pre-treatment (Kim et al. 2003). Particle size reduction has been reported to decrease digestion time and improve AD performance by increasing contact area and the release of cell compounds (Palmowski and Müller 2000). Moreover, processes such as low temperature and ultrasonic pre-treatment have been reported to increase biological sludge hydrolytic activity through enzyme solubilization and stimulation (Yan et al. 2010; Song and Feng 2011; Chu et al. 2011), leading to the proposal of pre-treatment methods that integrate physical effects with the inherent hydrolytic capacity of secondary sludge (Carvajal et al. 2013). Likewise, as sludge viscosity decreases during different pre-treatment processes (Bougrier et al. 2006a), mixing and mass transfer could be improved due to increased diffusivity coefficients and decreased resistance to flow during digestion (Terashima et al. 2009; Abbassi-Guendouz et al. 2012).

Therefore, it is clear that in order to predict the impact of pre-treatment on AD, a more detailed understanding of the fundamental phenomena during pre-treatment and its influence on sludge properties is necessary. Moreover, understanding the changes in the dynamics of microbial communities promoted by pre-treatment-induced substrate modification is also important. Knowledge of the influence of substrate changes on microbial ecology is necessary to fully understand pre-treatment mechanisms and the observed effects during AD.

While the influence of pre-treatment on biogas production and solids reduction has been widely studied, apart from a couple of reports (Carballa et al. 2008; Braguglia et al. 2015), few studies have focused on evaluating the influence of pre-treatment on sludge quality. During conventional mesophilic digestion, moderate pathogen inactivation and organic matter reduction occurs. Thus, there is limited application of digested sludge for agriculture to avoid potential disease propagation and soil and water contamination. Increased sludge quality with pre-treatment could allow broader application of sludge in soil, reducing the pressure on sludge disposal and generating a more acceptable product. As well, as pre-treatment improves biodegradable organic matter removal, the relative presence of humic substances could increase, therefore improving the agricultural value of sludge. Humic substances are ubiquitous compounds that derive from physical, chemical and microbiological transformations of biomolecules. Humic substances play an important role in agriculture, as they influence soil quality and productivity. In sewage sludge, fulvic and humic acids can account for around 20% of sludge organic matter, with predominance of humic acids (Yang et al. 2014). Zhen et al. (2014) evaluated the humification of sludge after the inclusion of an electrical-alkali pre-treatment. At the end of the assays, pre-treated samples showed relatively higher humification levels and were associated with a possible increase in maturation rates during AD. Other studies show that thermal treatment (180°C; 30 min) of digested sludge allows solubilization of humic substances and decomposition of humic acids to fulvic acids, without changes in the total amount of humic substances (Yang et al. 2014). Treatment also reduced the average molecular size of humic substances and increased maturity of humic and fulvic acids due to the increase in aromatic structures. While there have been studies oriented to sludge quality, none of the reviewed reports included a full assessment of the agricultural quality of digested sludge.

Another issue regarding digested sludge quality is the presence of organic micro-contaminants and heavy metals. Conventional digestion does not fully degrade pollutants in sludge like pharmaceuticals and cosmetics, while heavy metals are only removed with additional physical-chemical treatments. Pre-treatment of sludge can promote the removal of organic pollutants (Benabdallah El-Hadj et al. 2007), but the mechanisms involved are not fully understood and operational parameters during digestion can greatly impact the observed effects. Moreover, no reports were found regarding the impact of pre-treatment on the recovery or removal of heavy metals from digested sludge. Because pre-treatment can have considerable effects on sludge properties, such as higher rates of organic matter removal, the proportion of heavy metals in sludge can increase after pre-treatment and digestion. Additionally, some conditions used during pre-treatment can promote the recovery of heavy metal, as metals tend to solubilize at low pH conditions. In this scenario, it would be interesting to determine whether pre-treatments before AD affects the presence of heavy metals in digested sludge, as well as the question of whether current technologies for heavy metal removal can be integrated to improve sludge digestion and quality.

5. CONCLUSIONS

Depending on local conditions, sludge pre-treatment can be a very promising strategy for improving sewage sludge AD. In recent years pre-treatment has become an important research topic, mainly because of the significant enhancements that it can provide. While early research was focused primarily on single processes, there is now growing interest in the evaluation of novel technologies (e.g. electric pulse) and the combination of processes (e.g. thermo and physical-chemical combinations). Moreover, other effects in addition to organic solubilization have been evaluated, including particle size reduction, macromolecule behavior, changes in rheology, enzymatic/biological stimulation, organic pollutant removal and changes in the microbial dynamics during digestion. While these studies have shed light on the mechanisms involved in sludge pre-treatment, they are still not fully understood.

The most important obstacle for sludge pre-treatment is probably the high energy costs of the processes, involving at the same time economic and environmental burdens that in most cases make them unsustainable. Energy integration and a more detailed understanding of the phenomena involved during pre-treatment and subsequent digestion would be helpful to overcome this limitation. This is important in order to optimize current technologies and develop new ones that take advantage of our better understanding of how these mechanisms work. The synergistic effects triggered by the combination of pre-treatments appear to be a good alternative to overcome the limitations of current pre-treatments. As well, low temperature pre-treatments and other “mild” processes may offer advantages over more energy-intensive technologies, allowing comparative improvements during AD with lower energy and chemical requirements.

Finally, we can expect more focus on improving sludge quality by pre-treatment in the future. Sludge management is one of the main concerns of wastewater treatment facilities, and while biogas production improvement is desirable, reducing the amount of sludge and its pollution potential is the first priority from both the economic and environmental points of view. Moreover, improving the agricultural value of stabilized sludge can result in producing an attractive product with economic value, which could improve the economic balance of the process and positively impact on the environmental performance of agricultural activities by replacing products from non-renewable sources.

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CAPÍTULO IV

SEQUENTIAL ULTRASOUND AND LOW-TEMPERATURE THERMAL PRETREATMENT: PROCESS OPTIMIZATION AND INFLUENCE ON SEWAGE SLUDGE SOLUBILIZATION, ENZYME ACTIVITY AND ANAEROBIC DIGESTION

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Sequential ultrasound and low-temperature thermal pretreatment: process optimization and influence on sewage sludge solubilization, enzyme activity and anaerobic digestion

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Abstract

The influence of sequential ultrasound and low-temperature (55°C) thermal pretreatment on sewage sludge solubilization, enzyme activity and anaerobic digestion was assessed. The pretreatment led to significant increases of 427 – 1,030% and 230 – 674% in the soluble concentrations of carbohydrates and proteins, respectively, and 1.6 – 4.3 times higher enzymatic activities in the soluble phase of the sludge. Optimal conditions for chemical oxygen demand solubilization were determined at 59.3 kg/L total solids (TS) concentration, 30,500 kJ/kg TS specific energy and 13 h thermal treatment time using response surface methodology. The methane yield after pretreatment increased up to 50% compared with the raw sewage sludge, whereas the maximum methane production rate was 1.3 – 1.8 times higher. An energy assessment showed that the increased methane yield compensated for energy consumption only under conditions where 500 kJ/kg TS specific energy was used for ultrasound, with up to 24% higher electricity recovery.

1. INTRODUCTION

Concerns regarding growing sludge generation in wastewater treatment plants (WWTPs) have increased. During 2012, the annual generation of sludge from sewage treatment facilities in Europe was approximately 10.0 x 10^6 tons (dry matter basis), whereas in China, sludge generation was over 6.0 x 10^6 tons (Eurostat 2016; Zhang et al. 2016). The situation in Chile has not been different, with an estimated sludge generation of 300 ton/day during 2010 (Celis et al. 2008). In this scenario, sludge valorization through the recovery of energy and nutrients represents a fundamental step toward developing sustainable WWTPs.

Anaerobic digestion (AD) is an environmentally friendly alternative for sludge stabilization. AD processes significantly reduce odor, pathogens and organic matter (Appels et al. 2008a). Moreover, biogases with significant percentages of methane (60 – 70% CH_4) and nutrient-rich digestates are obtained during digestion, which can be utilized as energy sources and commercial fertilizers, respectively (Carballa et al. 2011).

Modern WWTPs have integrated the benefits of AD; however, a few noteworthy AD performance drawbacks exist. Low performance rates are typically observed during the hydrolysis of organic matter in sewage sludge, which includes solids, flocs, extracellular polymeric compounds, cell walls and recalcitrant proteins and lipids (Abelleira-Pereira et al. 2015). This inefficiency requires sludge retention times of over 20 d, making the implementation of the technology unfeasible for most small-sized WWTPs.

Therefore, efforts have been made toward improving hydrolysis efficiency and the overall AD process. One preferred strategy is the use of physical, chemical and/or biological pretreatments that hydrolyze sludge in a step prior to AD (Carrère et al. 2010; Neumann et al. 2016). While a wide array of pretreatment technologies has been proposed, only a few have been successfully implemented at full scale, mostly due to limitations caused by energy consumption (Cano et al. 2015).

To overcome this issue, the use of low-temperature thermal hydrolysis (55 – 90°C) has been proposed as an alternative to other more intensive technologies (Ferrer et al. 2008a; Dhar et al. 2012; Carvajal et al. 2013). These process conditions promote the physical disruption and release of endogenous enzymes present in biological sludge flocs, resulting in organic matter solubilization and biogas production improvements during AD (Carvajal et al. 2013). Pretreatments at 55°C have been reported to increase waste-activated sludge methane yields up to 23% after 12 h of pretreatment, with 1.3- to 1.7-fold higher maximum methane productivity rates than non-pretreated sludge (Carvajal et al. 2013).

Ultrasound has also proposed as an economically feasible pretreatment alternative (Xie et al. 2007; Dhar et al. 2012). The effects of ultrasound on sludge includes particle size reduction, organic matter solubilization, enzyme release and stimulation of biological activity (Zhang et al. 2008; Yan et al. 2010; Song and Feng 2011; Pilli et al. 2011). Ultrasound has been reported to increase biogas production by 4 – 83% and volatile solids removal by 6 – 47% during AD (Neumann et al. 2016). The implementation of ultrasound for full-scale AD could lead to increased energy recovery from sludge. Xie et al. (2007) reported an increase of 45% in methane production in a full-scale facility, with a 2.5 to 1 ratio between net energy gain and energy consumption.

Another strategy that has gained relevance for improving the energetic performance of pretreatments is the use of combined processes. Combined pretreatment processes have been reported to promote hydrolysis mechanisms that result in improved effects over organic matter solubilization and biogas production (Tyagi et al. 2014). Because ultrasound and low-temperature thermal hydrolysis cause physical disruption and increased endogenous enzyme activity in sludge (Yan et al. 2010; Carvajal et al. 2013), their sequential combination is expected to improve organic matter hydrolysis through the integration of physical and biological phenomena. Therefore, the objective of this study was to assess the influence of this sequential process on sludge solubilization, enzyme activity and anaerobic digestion. Additionally, the operating conditions of the pretreatment were optimized. Finally, the energy balance of the process was estimated to preliminarily assess its feasibility at full-scale facilities.

2. MATERIALS AND METHODS

2.1 Sludge samples

Thickened mixed-sewage sludge (MSS) samples were obtained from the Biobío WWTP, Concepción, Chile (36° 48' S, 73° 08' W). The plant treats wastewaters generated in the metropolitan area of Concepción, serving approximately 500,000 inhabitants. The primary to secondary sludge ratio of the MSS was approximately 40/60% in volume and 65/35% in total solids (TS). Anaerobic inoculum for the AD assays was obtained from one of the two 8,000 m^3 digesters used to stabilize the MSS in the WWTP.

2.2 Pretreatment assays

Configurations for single ultrasound, single low-temperature thermal hydrolysis and the sequential application of both processes were studied. Ultrasound was applied using a UP200ST ultrasonic homogenizer (Hielscher Ultrasonics GmbH, Germany) operating at 26 kHz. Samples of 500 mL were placed inside a beaker and continually agitated with a magnetic stirrer during sonication. Low-temperature thermal hydrolysis was performed in a Gerdhardt Thermoshake incubator at 55°C temperature and under 70 rpm continuous agitation. Sludge samples were placed inside 500-mL beakers and covered with perforated tops to prevent water evaporation and promote microaerobic conditions (Carvajal et al. 2013). Plastic hoses were placed inside the sample to enhance O_2 diffusion into the sludge. Ultrasound was tested at specific energies (SE) of 500, 15,500 and 30,500 kJ/kg TS. Low-temperature thermal hydrolysis was performed with retention times (T) of 3, 8 and 13 h. All assays were performed in triplicate.

Solubilization was studied in terms of increases in soluble proteins, carbohydrates and chemical oxygen demand (COD). In addition to solubilization, the influence of the pretreatment over volatile fatty acids (VFA) concentration and the activity of protease and amylase enzymes in the soluble phase of the sludge were assessed. Acetic, propionic, butyric and valeric VFA concentrations were determined through gas chromatography and expressed as COD according to their stoichiometric oxygen demand.

Optimizations of three operational conditions (i.e., sludge concentration (SC), SE and T) over the solubilization of COD during ultrasound and sequential ultrasound/low-temperature thermal hydrolysis pretreatment were performed using response surface methodology (RSM). RSM is a statistical technique that can be used to simultaneously explore the relationship between several independent variables and selected responses and determine optimal conditions. The solubilization factor f (%) of the COD was defined as the response for this assay and corresponds to the ratio between the increase in soluble COD due to pretreatment and the initial particulate COD. The soluble COD increase corresponds to differences between the COD determined in the soluble phase of the MSS after pretreatment (CODs) and the COD determined in the soluble phase of the raw MSS ($CODs_R$). The particulate COD is estimated as the difference between the total COD of the raw MSS ($CODt_R$) and the $CODs_R$, as shown in Equation (1) (Bougrier et al. 2006a).

$$f\ (\%) = (CODs - CODs_R)/(CODt_R - CODs_R) * 100 \quad (1)$$

A 3^2 full-factorial design with three levels (-1, 0, 1) was utilized to assess the relationship between the variables SC and SE and the response f during ultrasound application. SC was fixed at 18.3, 40.7 and 63.1 kg TS/L, whereas the SE levels were fixed at 500, 15,500 and 30,500 kJ/kg TS. The total number of observations required was 9, and the central point was replicated three times. On the other hand, a Box-Behnken design with three levels (-1, 0, 1) was utilized to study the relationship between SC, SE and T with f after sequential ultrasound and low-temperature thermal hydrolysis pretreatment. Values for the three levels of SC and SE were the same as in the ultrasound experimental design. T was fixed at 3, 8 and 13 h. The total number of observations required was 13, and the central point was replicated three times. All experimental points were tested in duplicate. Table 1 summarizes the experimental conditions tested during the pretreatment assays.

Table 1. Summary of experimental conditions used during the pretreatment assays

Ultrasound			**Low temperature hydrolysis**			**Ultrasound - Low temperature hydrolysis**				
Coded factors	**SC (kgTS/L)**	**SE (kJ/kgTS)**	**SC (kgTS/L)**	**T (h)**	**Temp (°C)**	**Coded factors**	**SC (kgTS/L)**	**SE (kJ/kgTS)**	**T (h)**	**Temp (°C)**
NA	32.4	500	32.4	3	55	NA	32.4	500	3	55
NA	32.4	15500	32.4	13	55	NA	32.4	500	13	55
NA	32.4	30500				NA	32.4	15500	3	55
						NA	32.4	15500	13	55
						NA	32.4	30500	3	55
						NA	32.4	30500	13	55
(-1,-1)	18.3	500				(-1,-1, 0)	18.3	500	8	55
(-1, 0)	18.3	15500				(-1, 0,-1)	18.3	15500	3	55
(-1, 1)	18.3	30500				(-1, 0, 1)	18.3	15500	13	55
(0,-1)	40.7	500				(-1, 1, 0)	18.3	30500	8	55
(0, 0)	40.7	15500				(0,-1,-1)	40.7	500	3	55
(0, 1)	40.7	30500				(0,-1, 1)	40.7	500	13	55
(1,-1)	63.1	500				(0, 0, 0)	40.7	15500	8	55
(1, 0)	63.1	15500				(0, 1,-1)	40.7	30500	3	55
(1, 1)	63.1	30500				(0, 1, 1)	40.7	30500	13	55
						(1,-1, 0)	63.1	500	8	55
						(1, 0,-1)	63.1	15500	3	55
						(1, 0, 1)	63.1	15500	13	55
						(1, 1, 0)	63.1	30500	8	55

SC: Sludge concentration; SE: Ultrasound specific energy; T: Low-temperature hydrolysis time; NA: Not applicable.

2.3 Anaerobic digestion tests

The AD tests were performed in batch conditions (biomethane productivity potential tests; BMP) using sealed vials of 120 mL total volume. The reaction volume was 50 mL, and the substrate concentration was 0.5% in terms of volatile solids (VS), with a feed/inoculum ratio of 1.5:1.0 g VS/g VS. Macronutrients were added to the vials in the following concentrations to ensure optimal digestion conditions: 0.28 g NH_4Cl/L, 0.25 g KH_2PO_4/L, 0.01 g $CaCl_2$/L and 0.01 g $MgSO_4*7H_2O$/L. $NaHCO_3$ was added at the same concentrations of substrate (5 g/L) to prevent acidification. N_2 was flushed through the vial headspaces for 30 – 40 s to displace air and create anaerobic conditions. The vials were then sealed and placed inside a Gerdhardt Thermoshake incubator at 35°C temperature under 100 rpm agitation. Biogas production was determined through headspace pressure increases (Neumann et al. 2015) using a Sper Scientific 840065 pressure meter with a 0 – 29 psi range transducer. The methane concentration in the biogas was determined using gas chromatography, and the results were expressed as mL CH_4/g VS_{added}. A blank without substrate was tested, and the baseline results were subtracted from the results of the assays. The samples that were subjected to AD tests corresponded with the following pretreatment conditions: raw sewage sludge; 500 kJ/kg TS SE and 3 h T; 500 kJ/kg TS SE and 13 h T; 15,500 kJ/kg TS SE and 8 h T; 30,500 kJ/kg TS SE and 3 h T; and 30,500 kJ/kg TS SE and 13 h T. All BMP assays were performed in duplicate.

The methane production results were adjusted according to a modified Gompertz equation using non-linear regression (Carvajal et al. 2013). Theoretical methane productivity potential (P; mL CH_4/g VS), maximum methane production rate (R_m; mL CH_4/g VS-d) and lag-phase time (λ; d) were determined after adjusting the experimental data of BMP to Equation (2).

$$BMP\ (t)=P\ *\exp[-\exp\{(R_m/P)*(\lambda-t)+1\}] \qquad (2)$$

An energy assessment of the different AD scenarios was performed based on the experimental results. An activated sludge treatment facility serving a population of 500,000 was assumed. Sludge-specific generation was based on data from Vera et al. (2013). Pretreatment electricity consumption (EE_{PT}) was estimated based on ultrasound specific energy and stirring needs during low-temperature thermal hydrolysis (Tchobanoglous et al. 2003). Heat requirements during thermal hydrolysis (TE_{PT}) included heating from ambient temperature (13°C) to process temperature (55°C) and heat losses. Losses were calculated assuming a cylindrical hydrolysis reactor with similar characteristics to an anaerobic digester (Malina and Pohland 1992). Heating and losses during AD (TE_{AD}) were estimated using the same criteria for pretreatment. When the pretreatment scenarios were evaluated, the heating needs during AD were assumed equal to zero. Stirring electricity consumption during AD (EE_{AD}) was estimated based on Tchobanoglous et al. (2003). Electricity and heat generation from biogas (EE_{BG} and TE_{BG}, respectively) were estimated based on the methane yields of the BMP assays and assuming co-generation heat and electricity efficiencies of 49% and 46%, respectively (Pertl et al. 2010).

2.4 Analytical methods

Total and soluble COD and TS and VS concentrations were determined according to Standard Methods for the Examination of Water and Wastewater (APHA, AWWA, WEF, 1998). The soluble fraction of sludge was defined as the liquid obtained after centrifugation and successive filtration through 1.5-µm and 0.7-µm pore diameter filters. Protein concentration was determined according to Lowry et al. (1951), whereas carbohydrate concentration was determined using the methodology proposed by Dubois et al. (1956). VFA and biogas composition (CO_2 and CH_4) were measured using a Shimadzu GC 2014 gas chromatograph equipped with an AOC 20i auto-injector. Flame ionization and thermal conductivity detectors were used for VFA and biogas analysis, respectively. VFA chromatographic separation was performed using a Stabilwax – DA column (0.25 µm x 30 m x 0.32 mm ID) at an initial temperature of 90ºC and increased to 120ºC at a rate of 10ºC/min, while a 60/80 carboxen 1000 column (4.6 m x 1/8 in x 2.10 mm ID) at 170ºC was used for biogas composition analysis (Omil et al. 1999).

Amylase activity was determined in the soluble phase of the sludge using a modified Miller method (Miller 1959), whereas protease activity was determined using a modified Lowry method (Lowry et al. 1951). The results are expressed as units of enzyme per volume of sample (U/mL). One unit of amylase activity corresponded with the amount of enzyme releasing 1 µmol of glucose equivalent per minute using starch as a substrate, whereas one unit of protease activity is defined as the amount of enzyme that releases 1 µmol of l-tyrosine equivalent per minute using casein as a substrate.

2.5 Data analysis

The significances of the differences observed in the results were determined through Student's t-test (α = 0.05) using SigmaPlot 11.0 software. RSM assays were designed and analyzed using Modde 7 software. Determination of significance of the polynomial models and its factors was conducted using the F-test (ANOVA) at a significance level of 0.05. Determination of the kinetic parameters of BMP was performed through non-linear regression using SigmaPlot 11.0 software.

3. RESULTS AND DISCUSSION

3.1 Sludge sample characterization

Table 2 shows the characterization of the MSS samples used during the assays. Averages of 53.8 g COD/L and 28.4 g VS/L were observed, corresponding to a COD/VS ratio of approximately 1.9 g COD/g VS. This value was comparatively higher than previously reported values for mixed sludge of 1.3 – 1.7 g COD/g VS (Davidsson and Jansen 2006; Borowski and Szopa 2007; Xie et al. 2007; Montusiewicz et al. 2010) and could be attributed to the high primary/secondary sludge solids ratio of the samples. The total solids concentration ranged between 32.4 and 40.7 g TS/L, with a VS/TS ratio of 0.78 g/g, in agreement with previously reported values of 0.69 – 0.81 g VS/g TS (Davidsson and Jansen 2006; Borowski and Szopa 2007; Xie et al. 2007; Montusiewicz et al. 2010). The soluble COD represented approximately 3.2 – 3.5% of the total COD, with approximately 39 – 45% corresponding to VFA. The sample pH and soluble concentrations of carbohydrates and proteins were of the same order as those of previous reports (Borowski and Szopa 2007; Wilson and Novak 2009).

Table 2. Characterization of mixed sludge samples used during assays (n = 2).

Parameter	Unit	Minimum	Maximum	Average	Standard deviation
Total COD	g/L	48.5	59.1	53.8	3.8
Soluble COD	g/L	1.7	1.9	1.8	0.1
Total solids	g/L	32.4	40.7	36.6	5.9
Volatile solids	g/L	25.3	31.5	28.4	4.4
pH	--	5.5	6.0	5.8	0.4
Soluble proteins	mg/L	330	489	409	113
Soluble carbohydrates	mg/L	54	145	100	65
VFA	mgCOD/L	671	851	761	127

COD: Chemical Oxygen Demand; VFA: Volatile Fatty Acids

3.2 Influence of pretreatment over sludge solubilization and enzyme activity

Figure 1 shows the concentration of soluble carbohydrates and proteins after pretreatment.

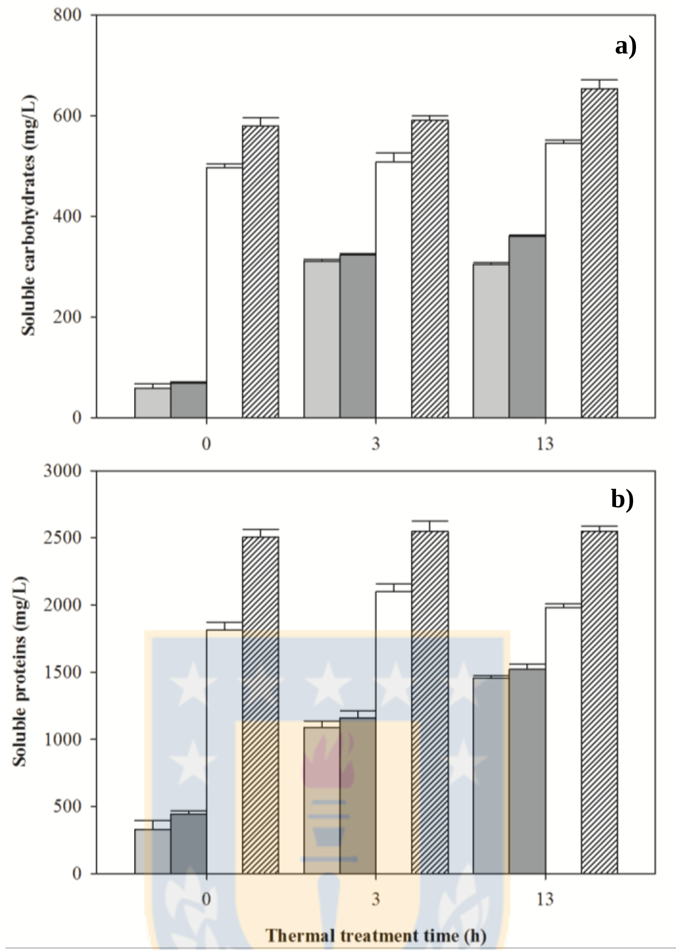

Figure 1. Carbohydrates (a) and proteins (b) concentration in the soluble phase of sludge after pretreatment at different conditions. Ultrasound specific energy: 0 kJ/kgTS, 500 kJ/kgTS, 15,500 kJ/kgTS, 30,500 kJ/kgTS. Average and standard deviation of triplicates.

The soluble carbohydrates concentration after pretreatment ranged between 69 mg/L and 653 mg/L, whereas the soluble proteins concentration ranged between 442 mg/L and 2,551 mg/L. All pretreatment conditions led to significant increases in soluble macromolecule concentrations when compared with raw sludge, except ultrasonication at 500 kJ/kg TS SE ($\alpha = 0.05$). Previous reports have indicated that the threshold for sludge disruption using ultrasound in laboratory conditions is approximately 1,000 – 3,000 kJ/kg TS (Bougrier et al. 2005), and it is thus possible that treatments at 500 kJ/kg TS were not able to generate significant sludge disruption or solubilization of macromolecules.

Single ultrasound treatments resulted in higher macromolecule solubilization than single thermal treatments. When considering only the significant effects, ultrasound application resulted in increases of 759 – 902% in soluble carbohydrate concentrations compared with 427 – 436% achieved through thermal treatment. Similarly, the soluble proteins concentration increased 450 – 659% after ultrasound application, whereas thermal treatments led to increases of 230 – 342%. These results were in agreement with Dhar et al. (2012), who reported that ultrasound treatments resulted in better carbohydrate and protein solubilization than thermal treatments at 50 – 90°C using comparable energy inputs. When the thermal treatment time was increased from 3 h to 13 h, increases of less than 12% in carbohydrate solubilization and less than 25% in protein solubilization were obtained. Therefore, most of the observed solubilization during thermal hydrolysis was associated with sample heating and the first hours of pretreatment.

Overall, the increases in the concentrations of soluble carbohydrates were higher than the observed increases in soluble protein concentrations, with values ranging from 458 – 1,030% and 252 – 674% after sequential pretreatment, respectively. Comparatively, Dhar et al. (2012) reported increases of 162 to 1,400% in soluble carbohydrate concentrations and 200 to 900% in soluble protein concentrations after sequential ultrasound-thermal pretreatments of sludge. Similar effects have been reported previously for the thermal pretreatment of waste-activated sludge at 130 – 150°C, concluding that the susceptibility of carbohydrates to solubilization was correlated to its weaker association with sludge flocs compared with proteins (Bougrier et al. 2008; Wilson and Novak 2009).

Figure 2 shows the relative VFA concentrations and compositions after pretreatment at different conditions. The total VFA concentration after pretreatment was up to 2.1-fold higher when compared with the raw sludge VFA concentration. Single low-temperature thermal hydrolysis did not lead to changes in the VFA concentration or composition (Figure 2), in agreement with observations made by Carvajal et al. (2013). Ultrasound application led to increases of 23%, 60% and 86% in the total VFA concentration at 500, 15,500 and 30,500 kJ/kg TS, respectively. Appels et al. (2008b) reported that the sonication of waste-activated sludge at 168 – 8,180 kJ/kg TS resulted in increases of 150 – 500% in total VFA concentration and suggested that the formation of oxidizing radicals, such as H• and OH•, through cavitation could be related to the observed VFA release.

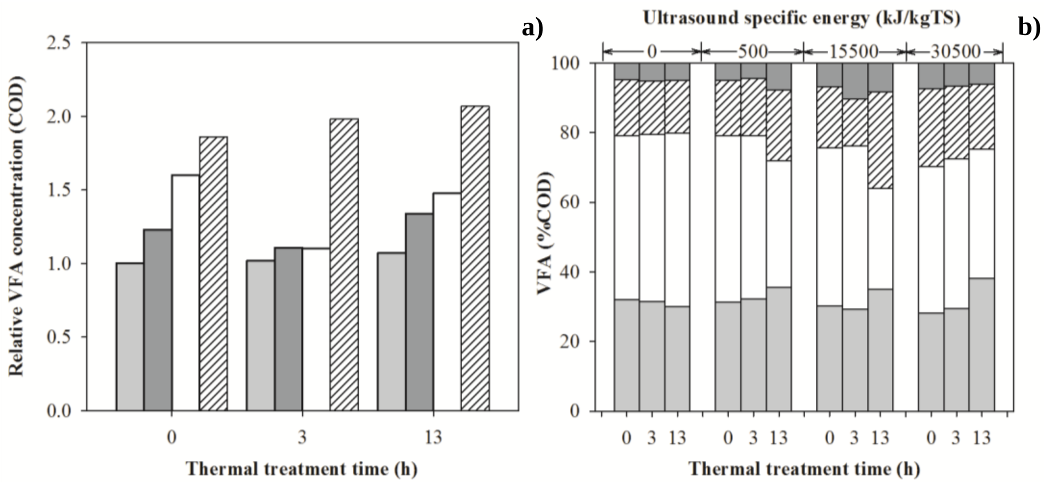

Figure 2. a) Total VFA concentration relative to raw sewage sludge after pretreatment at different conditions (Ultrasound specific energy: 0 kJ/kgTS, 500 kJ/kgTS, 15,500 kJ/kgTS, 30,500 kJ/kgTS) and, b) VFA relative composition (Acetic, Propionic, Butyric, Valeric acids) in sludge after pretreatment at different conditions**.**

The sequential pretreatment led to increases of 10 – 107% in total VFA concentration, which was comparatively lower than the 65 – 233% increases reported by Dhar et al. (2012) for waste-activated sludge. The total VFA concentration during thermal hydrolysis after ultrasound application at 500 and 15,500 kJ/kg TS decreased during the first 3 h and incremented after 13 h (Figure 2a). At these conditions, increases in the relative concentrations of acetic (9 – 11%), butyric (27 – 72%) and valeric (62 – 76%) acids were measured as well as decreases in propionic acid (23 – 39%; Figure 2b). This could be indicative of biological activity during thermal treatment. Previous reports had suggested the possibility of biological activity in sludge during treatment at 55°C (Carvajal et al. 2013), which could be attributed to the presence of thermophilic bacteria in the sludge samples, even without previous thermal adaptation (Dumas et al. 2010). Moreover, it is possible that the ultrasound application resulted in increased biological activity during pretreatment. Zhang et al. (2008) reported this effect on biological sludge at similar power densities.

The results for the enzymatic activity are presented in Figure 3. Amylase activity showed values of 0.09 – 0.51 U/mL after pretreatment, whereas protease activity ranged between 0.01 and 0.03 U/mL. Single ultrasound treatment at 500 kJ/kg TS did not result in significant changes in amylase or protease activity ($\alpha = 0.05$). Amylase and protease activities were 1.6 to 3.8 and 1.8 to 4.3 times higher for pre-treated samples than for raw MSS, respectively, with the highest values observed after sequential pretreatment at 30,500 kJ/kg TS SE – 3 h T for amylase and at 15,500 kJ/kg TS SE – 13 h for protease. Both studied enzymes showed similar trends in their activity in function of SE and T, and no inactivation was observed. Yan et al. (2010) reported that the optimum SE for enzyme activity stimulation in sludge using ultrasound was approximately 30,000 kJ/kg TS, in agreement with our results.

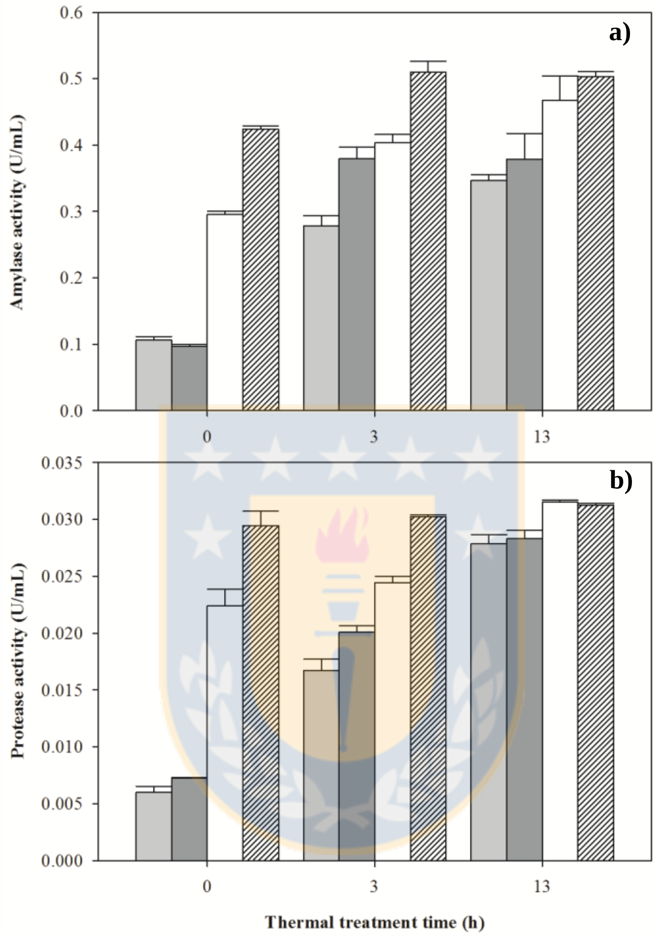

Figure 3. Amylase (a) and protease (b) activities in the soluble phase of sludge after pretreatment at different process conditions. Ultrasound specific energy: ▒0 kJ/kgTS, ■500 kJ/kgTS, □15,500 kJ/kgTS, ▨ 30,500 kJ/kgTS. Average and standard deviation of triplicates.

3.3 Optimization of chemical oxygen demand solubilization by response surface methodology

Figure 4 shows the surface and contour plots of f after ultrasound application. Experimental f values ranged between 0.8 and 7.4%, depending on the process conditions. A quadratic model was fitted to the results. Table 3 shows that while the model was significant, with a R^2 of 0.98, the lack-of-fit was not significant relative to pure error, and the predictive capacity of the polynomial equation in the studied range was thus a good fit with low noise. Moreover, all model parameters were significant, including the linear and quadratic factors of SC and SE and their interaction (Table 3).

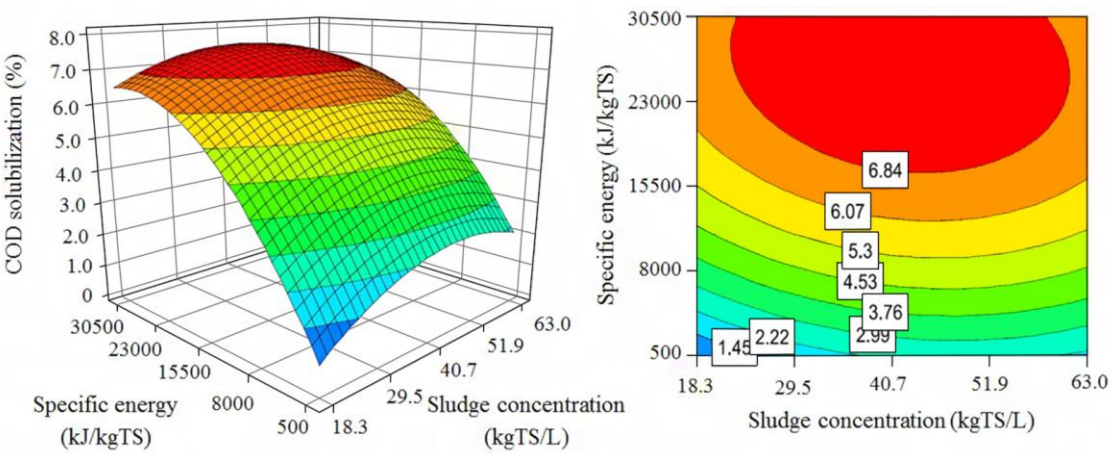

Figure 4. Surface and contour plots for the chemical oxygen demand solubilization factor after ultrasound application.

Table 3. ANOVA of the fitted model for the solubilization factor after the ultrasound assay.

Source	Sum of squares	Degrees of freedom	Mean square	F value	*p* (95%)
Model	106.77	5	21.35	326.51	<0.0001*
SC	1.40	1	1.40	21.42	0.0003*
SE	78.03	1	78.03	1193.12	<0.0001*
SC^2	4.97	1	4.97	76.05	<0.0001*
SE^2	14.92	1	14.92	228.07	<0.0001*
SC*SE	0.98	1	0.98	14.96	0.0014*
Residual	1.05	16	0.07		
Lack of Fit	0.26	3	0.09	1.44	0.2756**
Pure Error	0.78	13	0.06		
Total	107.81	21			

SC: Sludge Concentration; SE: Ultrasound Specific Energy; *: Significant at 95% level; **: Not Significant at 95% level

Equation (3) shows the regression model for ultrasound application in terms of the coded factors.

$$f\ (\%)=6.63+0.34*SC+2.55*SE-0.99*SC^2-1.72*SE^2-0.35*SC*SE \quad (3)$$

The larger the magnitude of the F-values and the smaller the magnitude of the p-values, the more significant the corresponding coefficient. Thus, the most significant regression coefficients were the linear and quadratic factors for SE, followed by the quadratic factor for SC (see Table 3).

The results showed a positive correlation between SE and f, but the effect reached a plateau between 15,500 and 23,000 kJ/kg TS. Therefore, the energy levels over this range did not seem to further promote COD solubilization. This agreed with previous reports that indicated that sludge disintegration degree did not significantly increase over 15,000 kJ/kg TS (Pérez-Elvira et al. 2010). Moreover, other authors have reported that energy levels over 9,690 kJ/kg TS could lead to decreased disintegration degrees of COD due to the formation of radicals that oxidize soluble organic matter (Erden and Filibeli 2010b).

Solubilization effects were higher at SC values near the central point (40.7 kg TS/L). While increasing sludge concentration has been suggested to optimize ultrasound energetic performance (Pérez-Elvira et al. 2009), concentrations over 3 – 4% TS have been reported to decrease solubilization due to wave attenuation, absorption and increased viscosity in the sludge (Show et al. 2007; Pilli et al. 2011). The optimum SE and SC conditions in the studied range were determined through numerical optimization and found to be at 0.05 SC and 0.73 SE coded values, which corresponded with 41.8 kg TS/L SC and 26,450 kJ/kg TS SE and resulted in a predicted f of 7.6%. Comparatively, Show et al. (2007) reported an optimum between 2.3% and 3.2% TS for COD solubilization during ultrasound treatment.

Figure 5 shows the surface and contour plots of f as functions of SC, SE and T after the sequential application of ultrasound and low-temperature thermal hydrolysis. The experimental f values ranged between 3.5 and 17.1%. The three studied independent variables showed significant effects over the response. All linear and quadratic factors and the interaction between SE and T were found to be significant at 95% levels (Table 4).

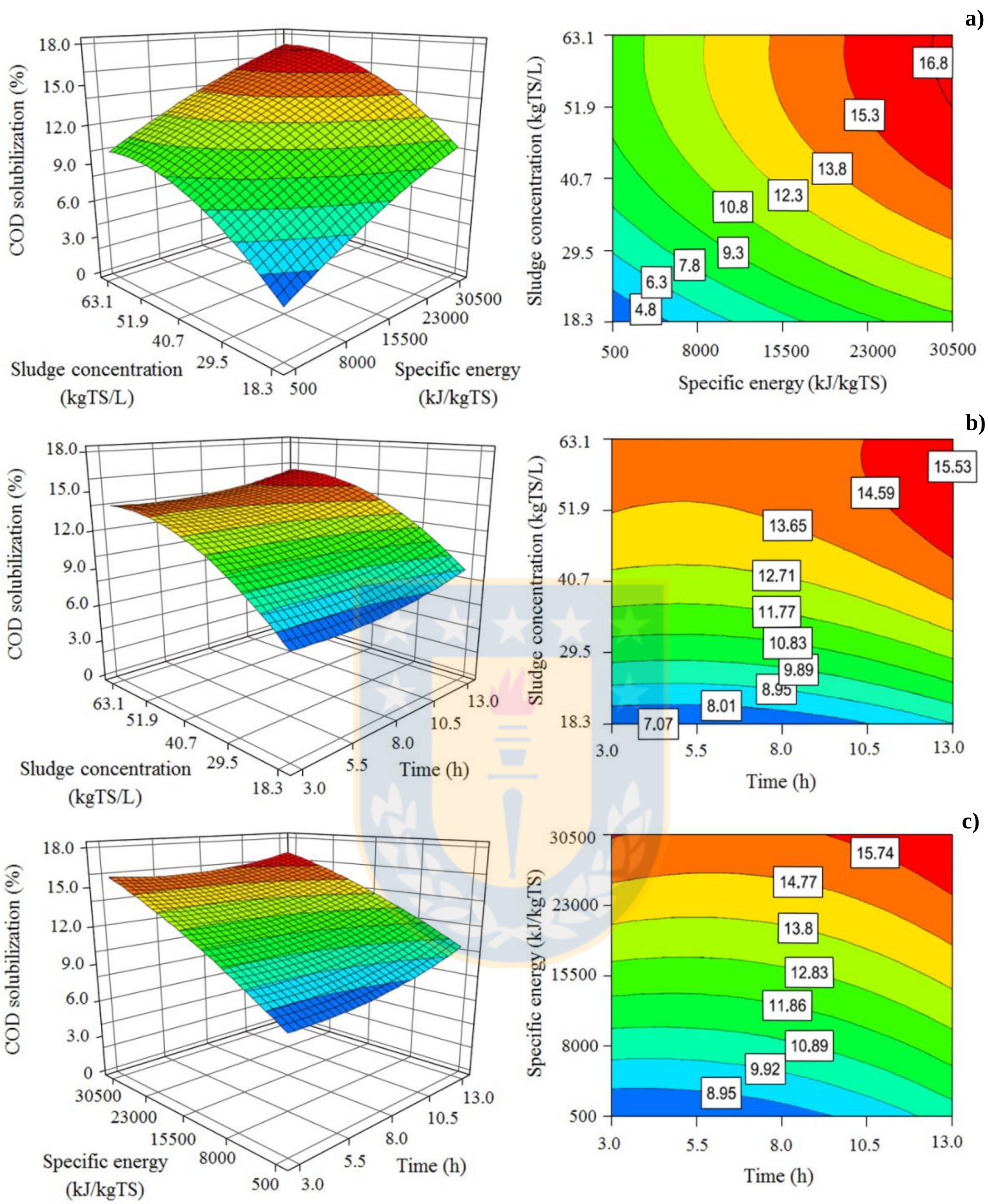

Figure 5. Surface and contour plots for the chemical oxygen demand solubilization factor after sequential ultrasound and low temperature thermal pretreatment at constant a) Time (8 h), b) Specific energy (15,500 kJ/kgTS), and c) Sludge concentration (40.7 kgTS/L).

Table 4. ANOVA of the fitted model for the solubilization factor after the sequential ultrasound and low temperature thermal pretreatment assay.

Source	Sum of squares	Degrees of freedom	Mean square	F value	*p* (95%)
Model	424.21	9	47.13	247.83	<0.0001*
SC	179.56	1	179.56	944.12	<0.0001*
SE	199.52	1	199.52	1049.05	<0.0001*
T	11.06	1	11.06	58.13	<0.0001*
SC^2	26.31	1	26.31	138.33	<0.0001*
SE^2	2.23	1	2.23	11.75	0.0027*
T^2	3.36	1	3.36	17.69	0.0004*
SC*SE	0.01	1	0.01	0.06	0.8103**
SC*T	0.03	1	0.03	0.16	0.6895**
SE*T	1.13	1	1.13	5.92	0.0245*
Residual	3.80	20	0.19		
Lack of Fit	1.29	3	0.43	2.92	0.0640**
Pure Error	2.51	17	0.15		
Total	428.01	29			

SC: Sludge Concentration; SE: Ultrasound Specific Energy; T: Low temperature thermal hydrolysis Time; *: Significant at 95% level; **: Not Significant at 95% level

The quadratic model had an R^2 equal to 0.98, while the lack-of-fit value was not significant with respect to the pure error. The regression model obtained for the response is shown in Equation (4) in terms of the coded factors.

$$f\ (\%)=12.6+3.35*SC+3.53*SE+0.83*T-1.89*SC^2-0.55*SE^2+0.67*T^2-0.38*SE*T \qquad (4)$$

The linear effects of SE and SC were the most significant factors of the model, followed by the quadratic factor for SC and the linear and quadratic factors for T. While the quadratic nature of the SC influence over f was observable after ultrasound and sequential pretreatment, SE showed a more linear influence compared with the effect after the ultrasound step, as can be observed in Figure 5. The small effect of T over f suggested that most of the solubilization occurred during heating, as has been reported in other studies (Carrère et al., 2008) and in agreement with observed results for carbohydrate and protein solubilization. Therefore, short retention times during low-temperature thermal hydrolysis should be sufficient to favor sludge solubilization after ultrasound application.

While the influence of T over solubilization was less significant than that of SC and SE, it exerted a positively correlated and significant effect over f. Therefore, higher solubilization effects were observed after 13 h of thermal treatments. The optimum operational conditions for the sequential pretreatment in the studied range were determined through numerical optimization and found to be at 0.83 SC, 1.00 SE and 1.00 T coded values, which corresponded with 59.3 kg TS/L SC, 30,500 kJ/kg TS SE and 13 h T and resulted in a predicted f of 18.2%.

3.4 Methane production and energetic balance during anaerobic digestion

Figure 6 shows the experimental results of the batch anaerobic digestion tests. Raw sewage sludge showed a methane production potential of 407 mL CH_4/g VS. Specific methane yields ranged between 472 and 611 mL CH_4/g VS after pretreatment. Most of the studied pretreatment conditions were observed to have significant increases in methane yield when compared with the content in raw sewage sludge. The only exception was under pretreatment conditions of 500 kJ/kg TS SE and 3 h T ($\alpha = 0.05$). When considering only the significant effects, the pretreatment led to increases of 32 – 50% in the methane yield of the MSS. Pretreatment SE and T were positively associated with f and methane yields (Table 5).

Comparing similar conditions, the sequential process led to higher increases in methane yield than previous reports of single ultrasound and low-temperature thermal pre-treatment. Carvajal et al. (2013) observed an increase of about 23% in the methane yield of waste-activated sludge after pretreatment at 55°C for 12 h, while in our study pretreatment at 500 kJ/kg TS and 13 h led to an increase of 32% in methane yield. Similarly, Pérez-Elvira et al. (2009) reported increases of 17% and 42% in the methane yield of waste-activated sludge with ultrasound pretreatment at 14,440 and 38,880 kJ/kg TS, compared to the 41% and 50% increases observed in our study for sequential pre-treatment at 15,500 and 30,500 kJ/kg TS followed by thermal treatment during 8 and13 h, respectively. Likewise, the combined ultrasound-thermal treatment configuration studied by Dhar et al. (2012) resulted in increases of 19 – 30% in the methane yield of waste-activated sludge, compared with increases of 15 – 24% and 13 – 19% for single ultrasound and thermal pretreatments, respectively.

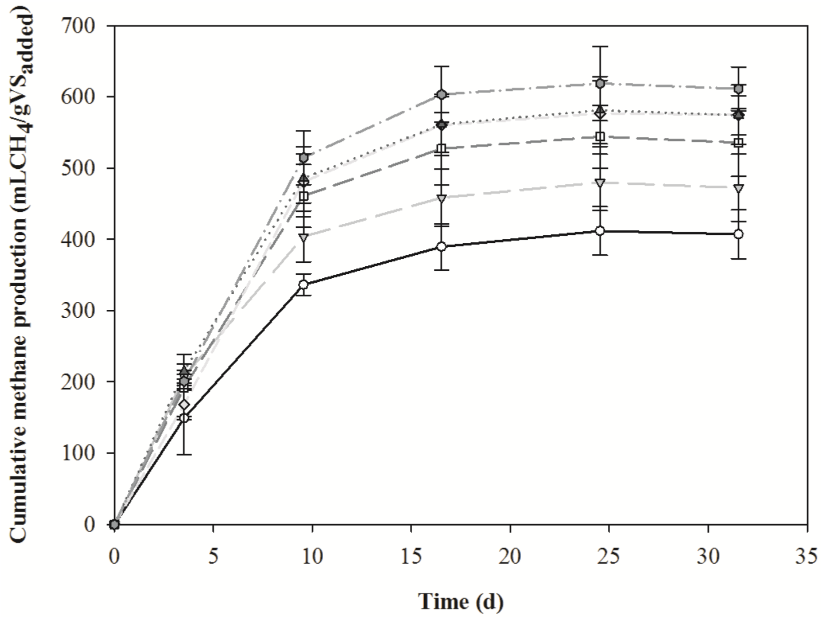

Figure 6. Cumulative methane production during batch digestion of sludge samples subjected at different pretreatment conditions: Raw Sludge; 500 kJ/kgTS, 3 h; 500 kJ/kgTS, 13 h; 15500 kJ/kgTS, 8 h; 30500 kJ/kgTS, 3 h; 30500 kJ/kgTS; 13 h. Average and standard deviation of duplicates.

Methane production showed similar trends for all samples. During the first few days, methane production was similar. After 10 d, differences in productivity were noticed, which were maintained until the end of the assays (Figure 6). Increases in methane concentration in biogas due to pretreatment were observed, in agreement with previous reports (Ferrer et al. 2008a; Dhar et al. 2012; Carvajal et al. 2013). However, these increases were found to be non-significant with respect to the levels in raw sludge ($\alpha = 0.05$).

Table 5 summarizes the experimental results of the batch AD tests and the estimated kinetic constants. As can be observed, all R^2 values were higher than 0.99, which indicated good experimental fits to the theoretical model equation. The R_m values ranged between 126 and 199 mL CH_4/g VS·d, which were comparable with the values reported by Pérez-Elvira et al. (2010) for waste-activated sludge. The maximum methane productivity was 1.3 to 1.8 times higher for the pretreated samples than for raw MSS, which indicated that the sequential pretreatment greatly favored the methane production kinetics in the studied conditions. However, the effects of pretreatment over the digestion lag-phase were divergent, and no evidence of possible inhibition due to substrate pretreatment was observed.

Table 5. Experimental results of the BMP assays (± standard deviation) and adjusted kinetic parameters of modified Gompertz equation (± standard error).

Sample	*ƒ* (%)	BMP ($mLCH_4/gVS$)	BMP increase (%)	CH_4 in biogas (%)	Kinetic parameters			
					P ($mLCH_4/gVS$)	R_m ($mLCH_4/gVS$-d)	λ (d)	R^2
MSS	--	407±35	--	63.5±3.4	404±8	126±15	0.5±0.5	0.996
500 kJ/kgTS; 3h	7.7±0.4	472±47	16	62.3±2.8	468±12	167±28	0.4±0.6	0.994
500 kJ/kgTS; 13h	10.3±0.5	536±48	32	64.2±1.9	536±7	183±16	0.8±0.3	0.998
15500 kJ/kgTS; 8h	12.6±0.7	575±42	41	69.5±3.2	574±5	189±9	1.2±0.2	0.999
30500 kJ/kgTS; 3h	16.0±0.7	574±28	41	66.4±3.4	573±10	189±20	0.6±0.4	0.997
30500 kJ/kgTS; 13h	17.1±1.4	611±31	50	69.2±2.2	613±7	199±14	0.9±0.3	0.999

ƒ: COD solubilization factor; BMP: Experimental methane productivity potential; P: Theoretical methane productivity potential; Rm: Maximum methane production rate; λ: Lag-phase time ; VS: Volatile solids

Table 6. Energy assessment of the pretreatment/anaerobic digestion system.

Pre-treatment conditions		Thermal energy (MWh/d)					Electric energy (MWh/d)				
SE (kJ/kgST)	T (h)	TE_{PT}	TE_{AD}	TE_{BG}	Balance	Δ (%)	EE_{PT}	EE_{AD}	EE_{BG}	Balance	Δ (%)
0	0	0.0	-9.5	+17.0	+7.5	-	0.0	-1.3	+16.0	+14.7	-
500	3	-13.8	-2.2	+19.8	+3.8	-50	-1.6	-1.3	+18.6	+15.7	+7
500	13	-14.0	-2.2	+22.4	+6.3	-17	-1.6	-1.3	+21.0	+18.2	+24
15500	8	-13.9	-2.2	+24.1	+8.0	+6	-48.1	-1.3	+22.6	-26.8	-282
30500	3	-13.8	-2.2	+24.0	+8.1	+7	-94.6	-1.3	+22.6	-73.3	-598
30500	13	-14.0	-2.2	+25.6	+9.4	+25	-94.6	-1.3	+24.0	-71.8	-588

SE: Ultrasound Specific Energy; T: Low temperature thermal hydrolysis Time; TE_{PT}: Thermal energy consumption during pretreatment; TE_{AD}: Thermal energy consumption during AD; TE_{BG}: Thermal energy generated from biogas; EE_{PT}: Electricity consumption during pretreatment; EE_{AD}: Electricity consumption during AD; EE_{BG}: Electricity generated from biogas; Δ: Percent difference in the energy balance compared to the scenario without pretreatment.

The estimated energy balance of the process is presented in Table 6. In terms of thermal energy, the balances of all scenarios were positive, but only pretreatments where ultrasound was applied at 15,500 and 30,500 kJ/kg TS SE led to increased heat recovery from the sludge. However, those conditions also led to negative electricity balances because the energy used during ultrasound far exceeded the amount of energy recoverable as electricity during co-generation. Therefore, only the scenarios where ultrasound was applied at 500 kJ/kg TS SE led to increased energy performance when compared with that recovered in the conventional digestion scenario. This is because the recovered heat was sufficiently high to sustain pretreatment needs and simultaneously increase electrical balance. Therefore, the optimum scenario corresponded to pretreatment of sludge at 500 kJ/kg TS SE and 13 h T, which resulted in a 32% increase in methane yield and 24% higher electricity recovery than conventional AD.

4. CONCLUSIONS

Sequential pretreatment resulted in significant effects on sludge properties and batch AD. Increases of 458 – 1030% and 252 – 674% in the soluble concentrations of carbohydrates and proteins were observed. All independent variable showed significant effects over COD solubilization, with optimal operational conditions at 59.3 kg TS/L SC, 30,500 kJ/kg TS SE and 13 h T. Sequential pretreatment led to increases of up to 50% in methane yield and 1.3 – 1.8 higher maximum methane productivities. Overall, the process results were energetically feasible only when ultrasound was applied at 500 kJ/kg TS SE, achieving up to 24% higher electricity recovery.

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CAPÍTULO V

PROCESS PERFORMANCE AND DIGESTATE QUALITY ASSESSMENT OF ADVANCED ANAEROBIC DIGESTION OF SEWAGE SLUDGE INCLUDING SEQUENTIAL ULTRASOUND – THERMAL (55°C) PRE-TREATMENT

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Process performance and digestate quality assessment of advanced anaerobic digestion of sewage sludge including sequential ultrasound – thermal (55°C) pre-treatment.

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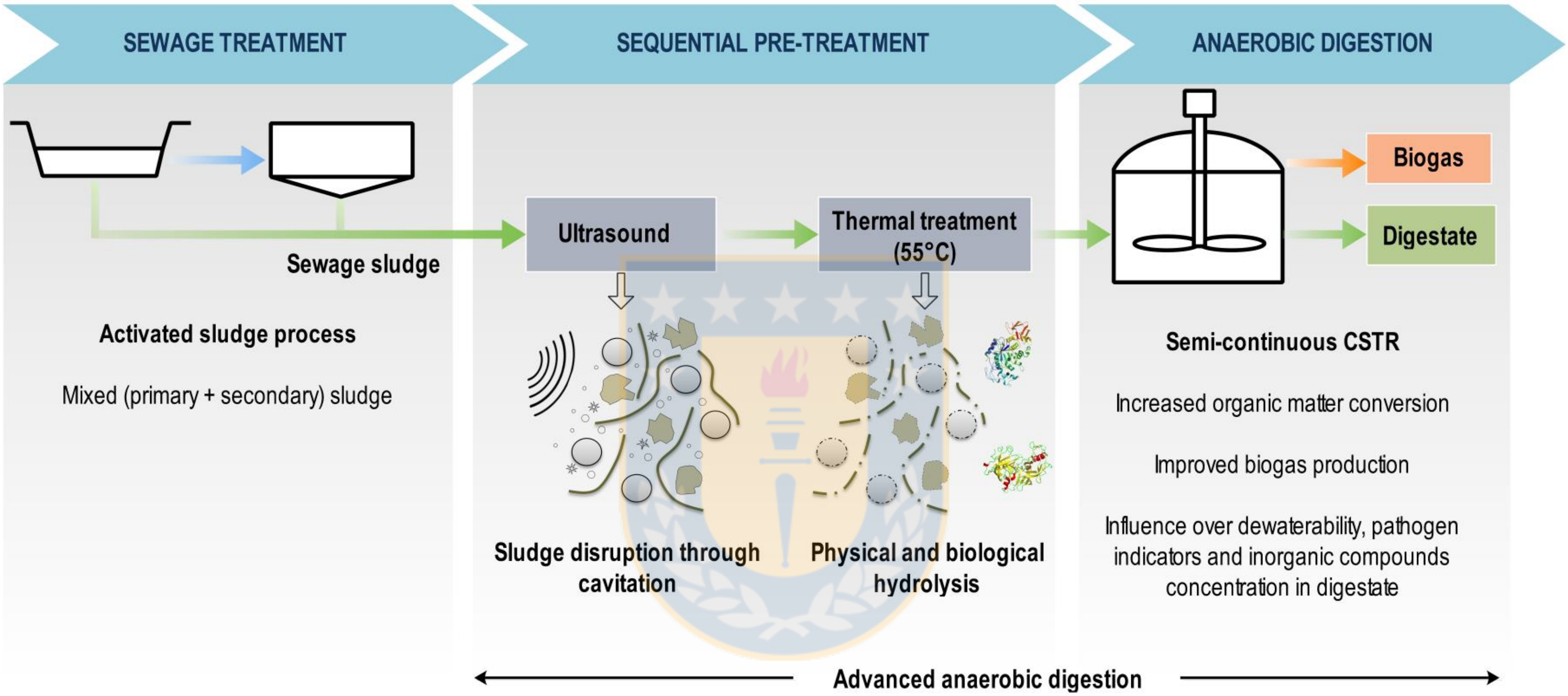
Abstract

The aim of this study was to evaluate the performance and digestate quality of advanced anaerobic digestion of sewage sludge including sequential ultrasound – thermal (55°C) pre-treatment. Both stages of pre-treatment contributed to chemical oxygen demand (COD) solubilization with an overall factor of 11.4 ± 2.2%. Pre-treatment led to 19.1, 24.0 and 29.9% increased methane yields at 30, 15 and 7.5 days solid retention times (SRT), respectively, without affecting process stability or accumulation of intermediaries. Pre-treatment decreased up to 4.2% water recovery from the digestate, but SRT was a more relevant factor controlling dewatering. Advanced digestion showed 2.4 – 3.1 and 1.5 logarithmic removals of coliforms and coliphages, respectively, and up to a 58% increase in the concentration of inorganics in the digestate solids compared to conventional digestion. The COD balance of the process showed that the observed increase in methane production was proportional to the solubilization efficiency and COD removal increase.

Graphical abstract



1. INTRODUCTION

Due to its high costs, potential environmental impacts and social concerns, the management of sludge currently represents one of the most important issues faced by sewage treatment plants (STP) (Lapen et al. 2008; Ruffino et al. 2015). While anaerobic digestion has been widely used for sewage sludge treatment, biogas production and biodegradation during digestion is limited at the hydrolysis step mainly due to the presence of solids and complex organic matter such as extracellular polymeric compounds (Wilson and Novak 2009; Abelleira-Pereira et al. 2015). In response to this limitation, different pre-treatment technologies have been proposed to hydrolyze sludge and improve digestion performance (Neumann et al. 2016).

Recently, the use of combined processes has gained notoriety for hydrolyzing sludge previous to digestion (Dhar et al. 2012; Jang and Ahn 2013) as combined processes have been reported to promote hydrolysis mechanisms that lead to synergistic effects over sludge solubilization and methane yield. Şahinkaya and Sevimli (2013) reported that the combined application of ultrasound and temperature led to up to a 16.8% increase in the disintegration degree of sludge compared to the additive effect of the individual processes, whereas Tian et al. (2015) observed that the increase in methane yield after combined ultrasound and alkaline pre-treatment was 43.2% higher than the value predicted based on the influence of individual pre-treatments.

Particularly, the implementation of sequential ultrasound and thermal pre-treatment has been reported to effectively solubilize sludge and increase its methane yield up to 50% (Dhar et al. 2012; Neumann et al. 2017). This is attributable to the integration of biological and physical phenomena during pre-treatment and could lead up to a 24% increased electricity recovery from sludge depending on the operational conditions (Neumann et al. 2017).

However, while pre-treatments have been mainly oriented towards biogas production improvement, digestate characteristics can also be influenced by their implementation, which is of relevance regarding the feasibility of its disposal alternatives, management costs and the environmental performance of the process (Carballa et al. 2011). Among the parameters that can be affected by pre-treatment are dewaterability, nutrient concentration (<0.1 – 18% of dry weight for N and P in raw sludge), and the presence of pollutants and potential pathogens (10^3–10^6 *E. coli*, 10^5 – 10^6 somatic coliphages and 10^{-2} – 10^2 *Salmonella* per gram of total solids in raw sludge) (Neyens and Baeyens

2003; Levantesi et al. 2015; Neumann et al. 2016). Therefore, the evaluation of the digestate quality is fundamental to providing an integral assessment of the influence of pre-treatment technologies over sewage sludge anaerobic digestion.

In this scenario, the objective of this study was to assess the process performance and digestate quality assessment of advanced anaerobic digestion of sewage sludge including sequential ultrasound – thermal (55°C) pre-treatment.

2. MATERIALS AND METHODS

2.1. Sampling of sludge and the anaerobic inoculum

Anaerobic inoculum and mixed sewage sludge (MSS) samples were obtained from Biobío STP, Concepción, Chile (36° 48' S, 73° 08' W). The inoculum was obtained from the internal recirculation of one of the two 8,000 m^3 sludge digesters at the plant and utilized for the digester start-up. Samples of MSS were obtained after sludge thickening, transported to the laboratory and stored at 4°C with a periodicity of 15 days during the experimental period. This was done to prevent sludge solubilization during storage that could lead to misrepresented results (Bougrier et al. 2007).

2.2. Pre-treatment of sludge

Pre-treatment was performed through the sequential application of ultrasound and thermal treatment. Ultrasound was applied using a UP200ST ultrasonic homogenizer (Hielscher Ultrasonics GmbH, Germany) at 26 kHz and with a specific energy of 2,000 kJ/kgTS. The specific energy was selected based on previous results, and reports indicated that the threshold for sludge disruption in laboratory conditions ranged between 1,000 and 3,000 kJ/kgTS (Bougrier et al. 2005; Neumann et al. 2017). The thermal treatment was performed at 55°C in a Gerhardt Thermoshake incubator (Gerhardt GmbH & Co., Germany) during a period of 8 h and with 70 rpm of continuous agitation. Further information about the pre-treatment experimental setup can be found in our previous study (Neumann et al. 2017).

All sludge samples were characterized before and after pre-treatment in terms of the concentration of solids (total and volatile), total ammonia concentration (TAN), volatile fatty acids (VFA) concentration, pH, electrical conductivity (EC) and chemical oxygen demand (COD). The solubilization efficiency of the pre-treatment was assessed by means of the COD solubilization factor, consisting of the ratio between the observed increase in soluble COD and raw sludge particulate COD (Neumann et al. 2017).

2.3. Digesters operation

Anaerobic digestion was performed in two mesophilic (37°C) lab-scale semi-continuous anaerobic digesters with a 10 L total volume and a 6 L reaction volume. The digesters consisted of cylindrical-shaped acrylic reactors of 32 cm height and 10 cm internal radius with a double wall that allows temperature control through water re-circulation. Mixing of digester contents was achieved using overhead stirrers at a speed of 100 ± 10 rpm. Biogas production in both reactors was measured through the use of a continuous volumetric device and according to Veiga et al. (1990). The system consists of two water columns connected through a hydraulic valve, using a digital counter to register the volume of biogas every time the displaced water from the first column connects two electrodes inside the second column. A schematic representation of the experimental setup used for pre-treatment and anaerobic digestion is presented in Figure 1.

One of the reactors was fed raw (non-pretreated) sludge, which constituted the control reactor of the experiment (CR), whereas the other was fed sludge after the sequential pre-treatment described in 2.2 (pre-treatment reactor; PTR). Both systems were first operated during a start-up and acclimation period of 96 days. During this period, the solid retention time (SRT) was progressively decreased from 100 to 30 days, and the experimental phase was started when stationary state was achieved. The experimental period was performed in three sub-phases of 30 (Phase I), 15 (Phase II) and 7.5 (Phase III) days SRT and controlled through varying the volume of sludge fed daily to the reactors (0.2, 0.4 and 0.8 L, respectively). An equivalent volume of digestate was removed daily from both systems. Experimental sub-phases were operated for a period of 94, 84 and 29 days for the 30, 15 and 7.5 days SRT periods, respectively, corresponding to at least three times the SRT. The average organic loading rate (OLR) for Phases I, II and III was 0.9, 2.1 and 3.6 kgVS/L•d for the CR and 0.9, 2.0 and 3.5 kgVS/L•d for the PTR, respectively.

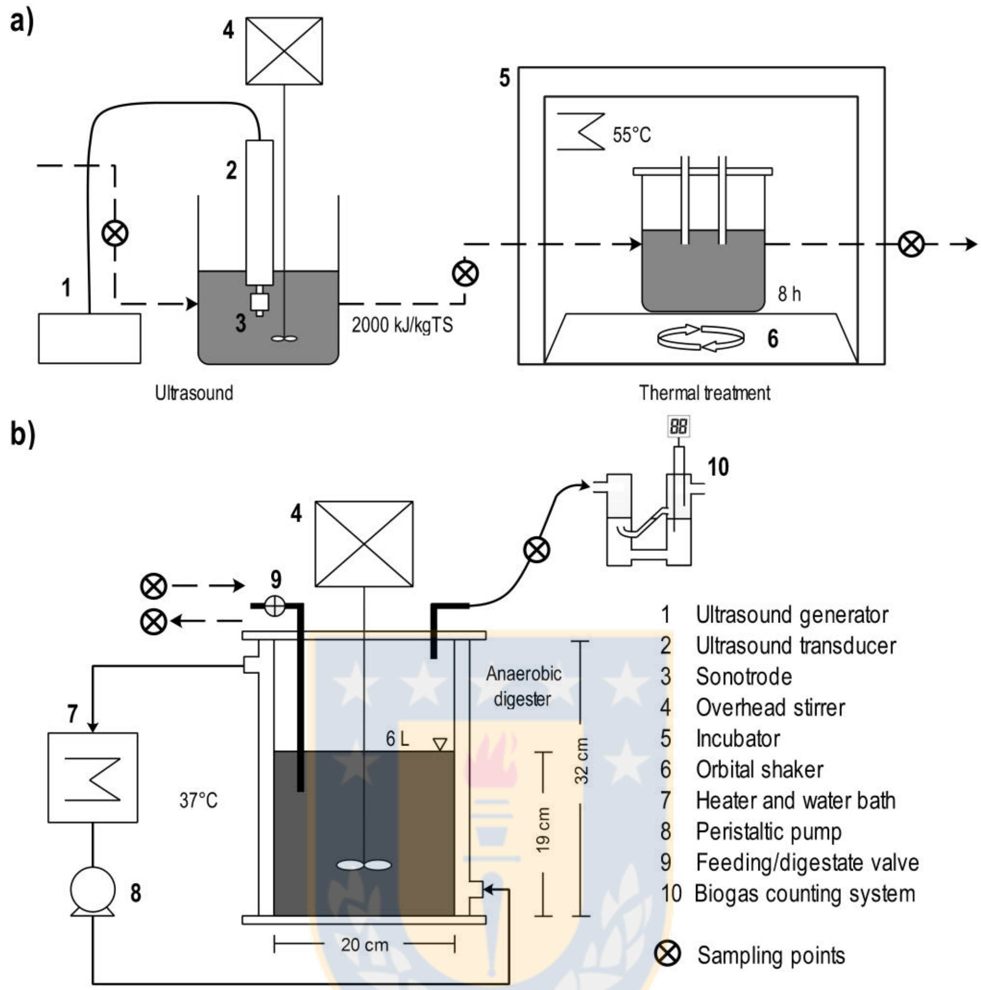


Figure 1. Experimental setup used in laboratory for a) batch pre-treatment of sludge and b) semi-continuous anaerobic digestion.

During reactor operation, biogas production and pH were measured daily, whereas intermediate (IA) and total (TA) alkalinity, COD, solids, and TAN in the digestate were measured 2 – 3 times per week. The biogas composition (CH_4 and CO_2), EC, oxidation-reduction potential (ORP) and VFA concentration of the digesters were measured once per week.

The free ammonia (NH_3-N) concentration was estimated based on the TAN concentration (NH_4^+-N) and considering the temperature (T; K) and pH of the digesters through Equation (1) (El-Mashad et al. 2004).

$$NH_3\text{-N} = (NH_4^+\text{-N})/\left[1 + 10^{-pH}/10^{-(0.1075+2725/T)}\right] \quad (1)$$

The organic matter conversion efficiency during digestion was assessed for the hydrolysis (H), acidogenesis (A) and methanogenesis (M) steps of digestion and according to El-Mashad et al. (2004). as described in Equations (2), (3) and (4), respectively.

$$H\ (\%) = (CH_4\text{-}COD + COD_{S\text{-}E}) / (COD_{T\text{-}I}) \bullet 100 \qquad (2)$$

$$A\ (\%) = (CH_4\text{-}COD + COD_{VFA\text{-}E}) / (COD_{T\text{-}I}) \bullet 100 \qquad (3)$$

$$M\ (\%) = (CH_4\text{-}COD) / (COD_{T\text{-}I}) \bullet 100 \qquad (4)$$

where CH_4-COD: Methane as COD (g)

COD_{S-E}: Soluble COD in the reactor effluent (g)

COD_{T-I}: Total COD in the influent sludge (g)

COD_{VFA-E}: VFA in the reactor effluent expressed as COD (g)

The dewatering characteristics of the digestate from both reactors were studied through centrifugation tests: samples from CR and PTR were subjected to centrifugation at 3,900 rpm in a Sigma 2-6E centrifuge (Sigma Laborzentrifugen GmbH, Germany) for periods of 3 and 10 minutes. Solids recovery (SR) and water recovery (WR) from the digestate were the parameters used to assess the centrifugation efficiency. SR was determined as the ratio between the mass of the total solids in the sludge cake after centrifugation and the total solids in the digestate (Equation (5)), whereas the WR was determined as the ratio between the supernatant mass after centrifugation and the mass of the digestate sample (Equation (6)).

$$SR\ (\%) = [(V_i \bullet TS_S) - (V_s \bullet TSS_s)] / (V_s \bullet TSS_s) \bullet 100 \qquad (5)$$

$$WR\ (\%) = M_s / M_i \bullet 100 \qquad (6)$$

where V_i: Volume of digestate sample (mL)

TS_s: Total solids in digestate sample (mg/mL)

V_s: Volume of supernatant (mL)

TSS_s: Total suspended solids in supernatant (mg/mL)

M_s: Mass of supernatant (g)

M_i: Mass of digestate sample (g)

Samples of the supernatant and sludge cake after the dewatering assays were obtained during the experimental period for both reactors and analyzed in terms of the nutrient (N and P) and metal (As, Cu, Hg, Ni, Pb, Se, and Zn) concentrations. The total and fecal coliforms and somatic coliphage concentrations were also determined in the sludge samples. Somatic coliphages include a wide array of phages from the *Myoviridae*, *Siphoviridae*, *Podoviridae*, and *Microviridae* families (Okafor 2011), and their determination can be used as an indicator of enteric virus contamination due to their similar origin, physical characteristics, environmental persistence and resistance to treatment processes (Cole et al. 2003).

2.4. Analytical methods

The total and soluble COD, TS, TSS and VS concentrations were determined according to Standard Methods for the Examination of Water and Wastewater (APHA, AWWA, WEF, 1998). A UV-VIS Shimadzu UV-1800 Spectrophotometer was used for the COD determination. The soluble fraction of sludge was defined as the liquid obtained after centrifugation and successive filtration through 1.5 μm and 0.7 μm pore diameter filters. The alkalinity was determined through titration to pH 4.3 (TA) and between pH 5.75 and 4.3 (IA) using a Hanna HI255 pH-meter (APHA, AWWA, WEF, 1998).

EC, pH and ORP were determined using a multi-parametric instrument OAKTON PC650 (Vernon Hills, Illinois, USA) with corresponding probes. The ammonia concentration was determined using a Merck-Millipore Spectroquant® photometric test (2.0 - 150 mg/L NH_4-N) using a UV-VIS Spectroquant® Nova 60/Merck photometer.

VFA and biogas composition (CO_2 and CH_4) were measured using a Shimadzu GC 2014 gas chromatograph. Flame ionization and thermal conductivity detectors were used for VFA and biogas analysis, respectively. Further information about the chromatographic method can be found elsewhere (Neumann et al. 2017).

Total and fecal coliforms and somatic coliphages were determined using multiple tubes and double agar-layer methods, respectively (APHA, AWWA, WEF, 1998). Coliforms were expressed as the Most Probable Number (MPN), whereas coliphages were expressed as Plaque Forming Units (PFU). Total Kjeldahl Nitrogen (TKN), total phosphorous (TP) and metal concentrations were determined through the titrimetric (TKN), vanadomolybdo phosphoric acid colorimetric (TP), hydride generation/atomic absorption spectrometry (As and Se), flame atomic absorption spectrometry/direct air-acetylene flame (Cu, Pb, Ni, and Zn) and cold-vapor atomic absorption spectrometry (Hg) methods (APHA, AWWA, WEF, 1998).

2.5. Data analysis

The statistical significance of the differences observed between the results was assessed through a one-way ANOVA or Kruskal–Wallis test for normally and non-normally distributed data, respectively. Pairwise multiple comparisons were performed using the Tukey (normal data) or Dunn´s (non-normal data) methods. The normality was assessed by Shapiro-Wilk tests. The significance of the differences observed in the results was determined in all cases with an α of 0.05 and using the SigmaPlot 11.0 software.

3. RESULTS AND DISCUSSION

3.1. Sludge characterization and pre-treatment influence

Table 1 summarizes the characterized parameters for sludge samples before and after pre-treatment steps (ultrasound and thermal treatment).

Raw MSS showed averages of 29.2 and 53.2 g/L for VS and COD during the experimental period, respectively, with an approximate 1.8 COD to VS ratio. Soluble COD represented approximately 4.2% of the total COD with 40.2% corresponding to VFA. These values are in concordance with a previous study performed using samples of the same origin (Neumann et al. 2017). Average values of 0.29 g NH_4^+-N/L and 1.70 mS/cm were observed for TAN and EC, respectively, and were similar to previous reports from other authors (Borowski and Szopa 2007; Ruffino et al. 2015).

Table 1. Mixed sludge characterization prior to and after pre-treatment.

Parameter	Unit	Sludge sample		
		Raw MSS	MSS after US	MSS after US+TT
pH	-	5.8 ± 0.3	5.8 ± 0.2	5.9 ± 0.2
EC	mS/cm	1.7 ± 0.5	2.0 ± 0.5	2.8 ± 0.6
NH_4^+-N	g/L	0.3 ± 0.2	0.3 ± 0.1	0.6 ± 0.4
Total solids	g/L	40.5 ± 10.6	41.1 ± 12.6	39.7 ± 9.8
Volatile solids	g/L	29.2 ± 6.7	30.1 ± 7.6	29.0 ± 6.5
VS/TS	-	0.7 ± 0.1	0.8 ± 0.1	0.7 ± 0.0
Total COD	g/L	53.2 ± 11.6	55.1 ± 13.4	58.1 ± 13.3
Soluble COD	g/L	2.2 ± 0.9	5.8 ± 1.4	8.0 ± 1.8
f	%	-	7.3 ± 1.3	11.4 ± 2.2
Total VFA	gCOD/L	0.90 ± 0.14	1.00 ± 0.16	0.97 ± 0.13
Acetic acid	g/L	0.17 ± 0.09	0.21 ± 0.08	0.20 ± 0.09
Propionic acid	g/L	0.32 ± 0.08	0.35 ± 0.07	0.35 ± 0.05
Butyric acid	g/L	0.08 ± 0.02	0.09 ± 0.02	0.09 ± 0.02
N-valeric acid	g/L	0.04 ± 0.01	0.05 ± 0.01	0.04 ± 0.01

Average values for all the experimental period ± standard deviation. US: Ultrasound; TT: Thermal Treatment; EC: Electrical Conductivity; VS: Volatile Solids; TS: Total Solids; COD: Chemical Oxygen Demand; *f:* Solubilization Factor; VFA: Volatile Fatty Acids.

Raw MSS showed averages of 29.2 and 53.2 g/L for VS and COD during the experimental period, respectively, with an approximate 1.8 COD to VS ratio. Soluble COD represented approximately 4.2% of the total COD with 40.2% corresponding to VFA. These values are in concordance with a previous study performed using samples of the same origin (Neumann et al. 2017). Average values of 0.29 g NH_4^+-N/L and 1.70 mS/cm were observed for TAN and EC, respectively, and were similar to previous reports from other authors (Borowski and Szopa 2007; Ruffino et al. 2015).

The sequential pre-treatment process resulted in increases of 64, 93 and 256% in conductivity, TAN and soluble COD concentrations, respectively. The total COD, pH and solids (total and volatile) concentrations were not significantly different after pre-treatment (P>0.05). Ultrasound and thermal treatment led to statistically significant increases of 164 and 264% in the soluble COD compared to the raw MSS, respectively (P<0.05), which corresponded to solubilization factors of 7.3±1.3% and 11.4±2.2%. Therefore, both stages of pre-treatment contributed to sludge disruption and solubilization of organic matter in concordance with previous studies performed under similar conditions (Dhar et al. 2012; Şahinkaya and Sevimli 2013; Carvajal et al. 2013). However, only thermal treatment showed statistically significant effects over TAN and EC, and the sequential process only led to a non-statistically significant increase of 8% in total VFA (P>0.05) with similar specific compound profiles for all samples (Table 1). In terms of COD, acetic, propionic, butyric and valeric acid represented on average 21.8, 52.8, 16.6 and 8.8% for the raw sample, 21.9, 52.9, 15.8 and 9.4% for the sample after ultrasonication and 21.1, 54.2, 16.1 and 8.6% for the sample after the sequential pre-treatment, respectively. Previous reports stated that a thermal treatment performed at a low temperature (50 - 70°C) could act as a pre-digestion step for sludge as the biological and enzymatic activities of thermoduric and thermophilic organisms are favored under these conditions (Climent et al. 2007; Yan et al. 2008; Carvajal et al. 2013). Indeed, 1.6 – 4.3 times higher protease/amylase activities have been observed during 55°C thermal treatment of MSS (Neumann et al. 2017). However, while the TAN concentration increased 93% after pre-treatment, the total and individual VFA concentrations were not modified, which suggests that this increase could be related to the physical release of ammonia from bound water in sludge flocs or that the biological transformation of nitrogenated compounds was associated with low VFA yields (Wilson and Novak 2009; Weimer 2011) or the production of non-measured intermediaries (e.g., hexanoic acid).

3.2. Operation and stability of the digestion process

Table 2 summarizes the parameters of digestion operation and the stability for CR and PTR.

Table 2. Operation and stability parameters for the anaerobic digestion systems.

Parameter	Unit	SRT (d)	CR	PTR
OLR	gVS/L•d	30	0.9 ± 0.2	0.9 ± 0.2
		15	2.1 ± 0.8	2.0 ± 0.7
		7.5	3.6 ± 0.6	3.5 ± 0.6
ORP	mV	30	-243.7 ± 7.5	-254.3 ± 12.6
		15	-237.1 ± 32.1	-249.9 ± 28.6
		7.5	-225.5 ± 13.4	-230.0 ± 17.0
pH	-	30	7.4 ± 0.1	7.4 ± 0.1
		15	7.3 ± 0.2	7.4 ± 0.2
		7.5	7.4 ± 0.1	7.4 ± 0.2
EC	mS/cm	30	5.7 ± 0.4	6.1 ± 0.3
		15	6.6 ± 1.0	7.1 ± 1.3
		7.5	5.0 ± 0.1	5.6 ± 0.0
Total VFA	gCOD/L	30	0.28 ± 0.12	0.24 ± 0.10
		15	0.14 ± 0.10	0.10 ± 0.09
		7.5	0.20 ± 0.11	0.18 ± 0.09
IA/TA	-	30	0.22 ± 0.03	0.23 ± 0.04
		15	0.26 ± 0.04	0.25 ± 0.05
		7.5	0.28 ± 0.04	0.25 ± 0.03
NH_4^+-N	g/L	30	0.88 ± 0.06	1.00 ± 0.07
		15	1.11 ± 0.12	1.18 ± 0.18
		7.5	1.01 ± 0.07	1.07 ± 0.07
NH_3-N	mg/L	30	26.6 ± 10.6	30.3 ± 10.0
		15	28.1 ± 4.6	33.7 ± 9.9
		7.5	30.6 ± 6.3	38.8 ± 9.4

SRT: Sludge Retention Time; CR: Control Reactor; PTR: Pre-Treatment Reactor; OLR: Organic Loading Rate; VS: Volatile Solids ORP: Oxidation-Reduction Potential; VFA: Volatile Fatty Acids; COD: Chemical Oxygen Demand; IA: Intermediate Alkalinity; TA: Total Alkalinity.

The observed OLR of both systems was in the conventional range for high-rate mesophilic digestion of sewage sludge (1.6 – 4.8 gVS/L-d) (Tchobanoglous et al. 2003). OLR showed variability during all operational phases, which was associated with changing solids and the COD content of the influent sludge (Figure 2a and 2c). However, average digestate solids (17.1 ± 3.1 and 16.3 ± 3.0 gVS/L for PTR and CR, respectively) and COD (35.6 ± 6.4 and 34.3 ± 6.3 g/L for CR and PTR, respectively) concentrations during all experimental phases showed a more stable trend than the influent as shown in Figure 2b and 2d.

As can be observed in Table 2 and Figure 2b and 2d, the measured ORP (<-200 mV), pH (7.0 – 7.8), total VFA (<300 mg COD/L), and IA total TA alkalinity ratio (<0.35) showed appropriate values for the digestion process (Tchobanoglous et al. 2003; Khanal 2008; Appels et al. 2008a). Both systems showed similar and steady behavior in those parameters under all operational conditions with no significant differences between CR and PTR (P>0.05).

The average TA in the CR and PTR was 3,633±327 and 4,010±380 mg $CaCO_{3\text{-eq}}$/L during Phase I, 4,298±1,133 and 4,895±980 mg $CaCO_{3\text{-eq}}$/L during Phase II, and 2,688±333 and 3,688±377 mg $CaCO_{3\text{-eq}}$/L during Phase III, respectively. Alkalinity showed a 10.4 – 37.2% higher concentration in PTR than CR and with a similar behavior to the TAN concentration (Table 2). This result is expected as ammonia contributes to alkalinity inside digesters due to the formation of ammonium bicarbonate when it reacts with CO_2 (Khanal 2008). PTR showed a 6 – 14% higher TAN concentration and a 7 – 13% higher EC than CR. As can be observed in Figure 3, those parameters showed similar trends after sludge pre-treatment and inside the digesters, which was most likely related to the electrolytic nature of ammonia and its contribution to EC in the aqueous media (Shcherbakov et al. 2009). Similarly, Ruffino et al. (2015) reported that the EC of waste activated sludge (WAS) after thermal pre-treatment at 70 – 90°C was related to the ammonia concentration in the soluble phase. Observed values of TAN and free (FA) ammonia concentrations in both systems were under the inhibitory threshold for anaerobic digestion (Table 2), which ranges between 1.7 – 14 g/L and 100 – 1,450 mg/L for TAN and FA ammonia, respectively (Chen et al. 2008; Yenigün and Demirel 2013). The highest ammonia concentration was related to the observed variability in the influent ammonia concentration (Figure 2), which corresponded to 1.78 gTAN/L and 52.4 gFA/L at day 212 in the PTR.

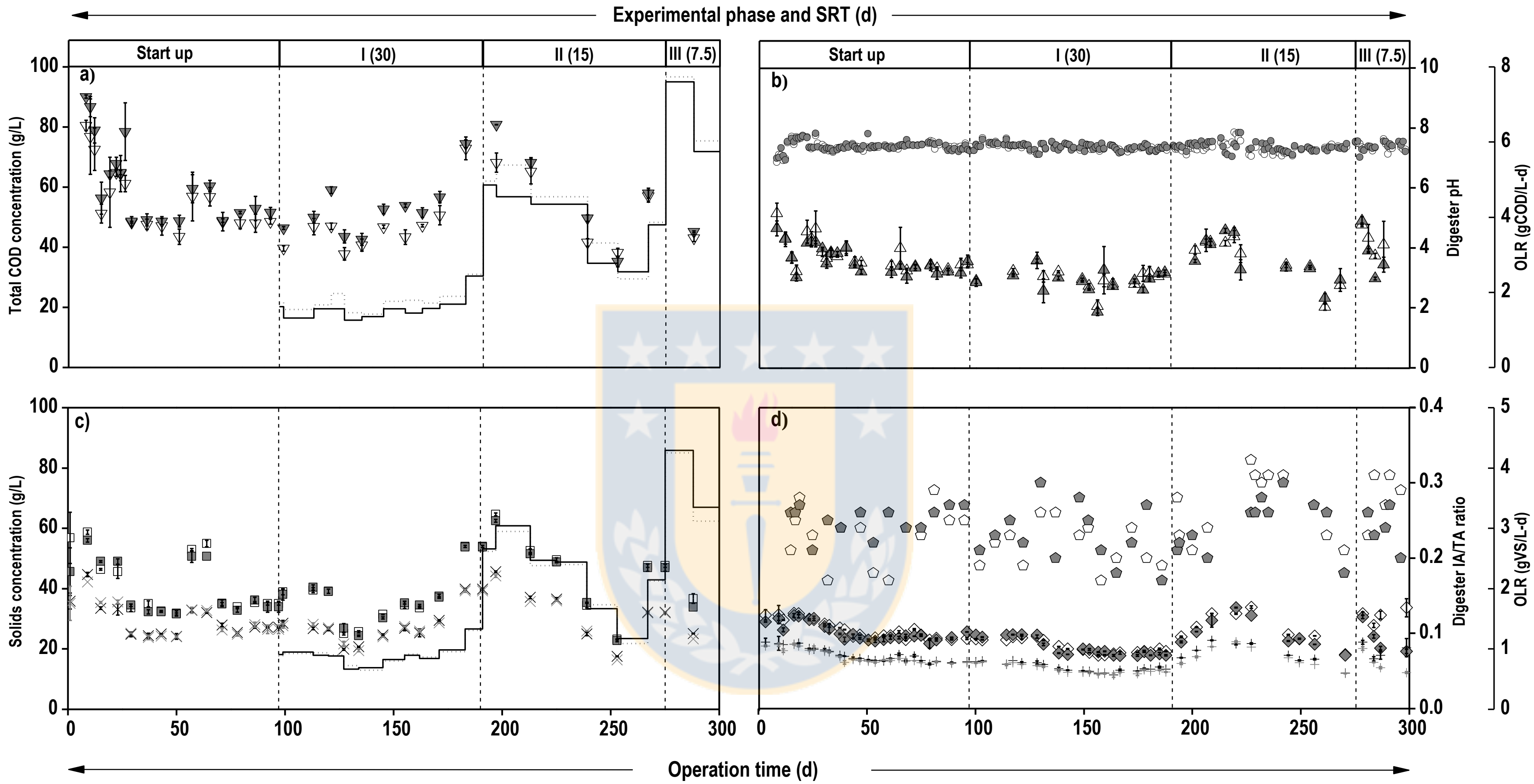


Figure 2. Input/output organic matter concentration and stability indicators during the operation of the digesters. **a)** Total COD concentration in input sludge (▽Raw, ▼ Pre-treated) and corresponding OLR (–CR, --PTR), **b)** Total COD concentration in digestate (△CR, ▲PTR) and reactors pH (○CR, ●PTR), **c)** Total (□Raw, ■Pre-treated) and volatile (×Raw, ×Pre-treated) solids in input sludge and corresponding OLR (–CR, --PTR) and **d)** Total (◇CR, ◆PTR) and volatile (+CR, +PTR) solids in digestate and reactors IA/TA (⬠CR, ⬟PTR).

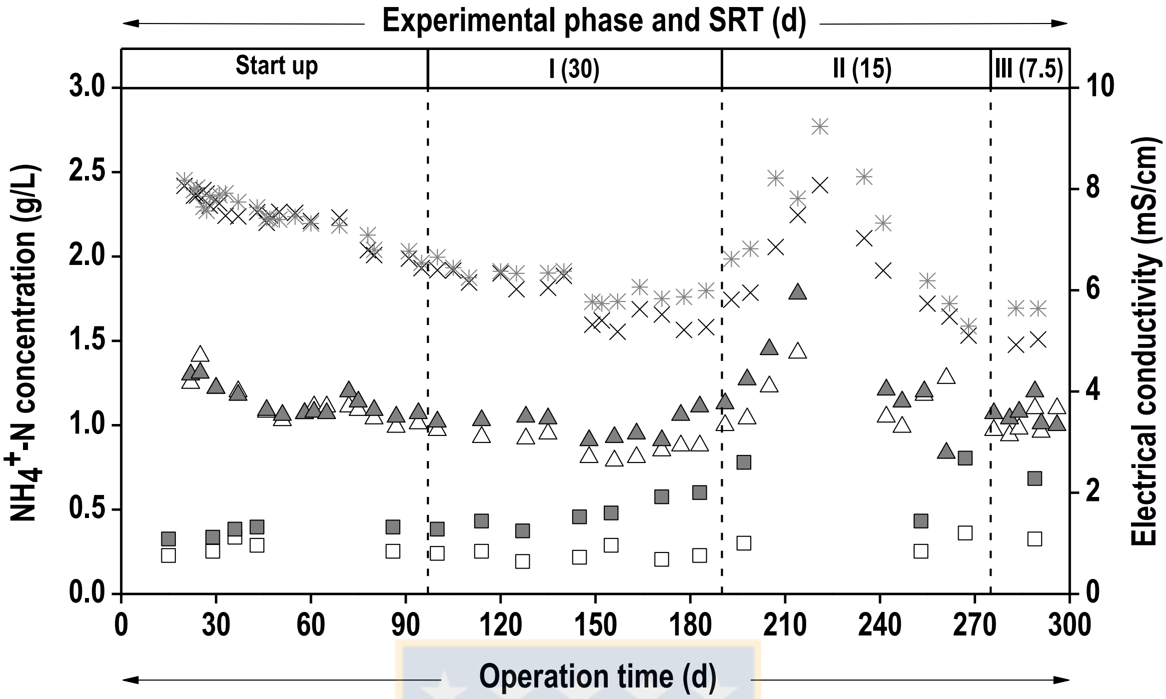


Figure 3. Input sludge NH_4^+-N concentration (□Raw, ■Pre-treated), digestate NH_4^+-N concentration (△CR, ▲PTR) and digestate electrical conductivity (×CR, ✳PTR).

Overall, the sequential pre-treatment did not cause modifications in the operational parameters of digestion that could be related to process instability, including ammonia concentration, pH, IA/TA, ORP and EC. This is important when comparing the process to other pre-treatment technologies, as intensive processes such as thermal hydrolysis at >100°C have been reported to potentially affect biogas production or digestate quality through the generation of non-biodegradable or inhibitory compounds such as ammonia, VFA, long-chain fatty acids and melanoidins (Bougrier et al. 2008; Dwyer et al. 2008; Wett et al. 2010; Lee and Han 2013).

3.3. Digester performance and organic matter conversion efficiency

Figure 4 shows the methane and biogas yields of both digestion systems under all experimental conditions.

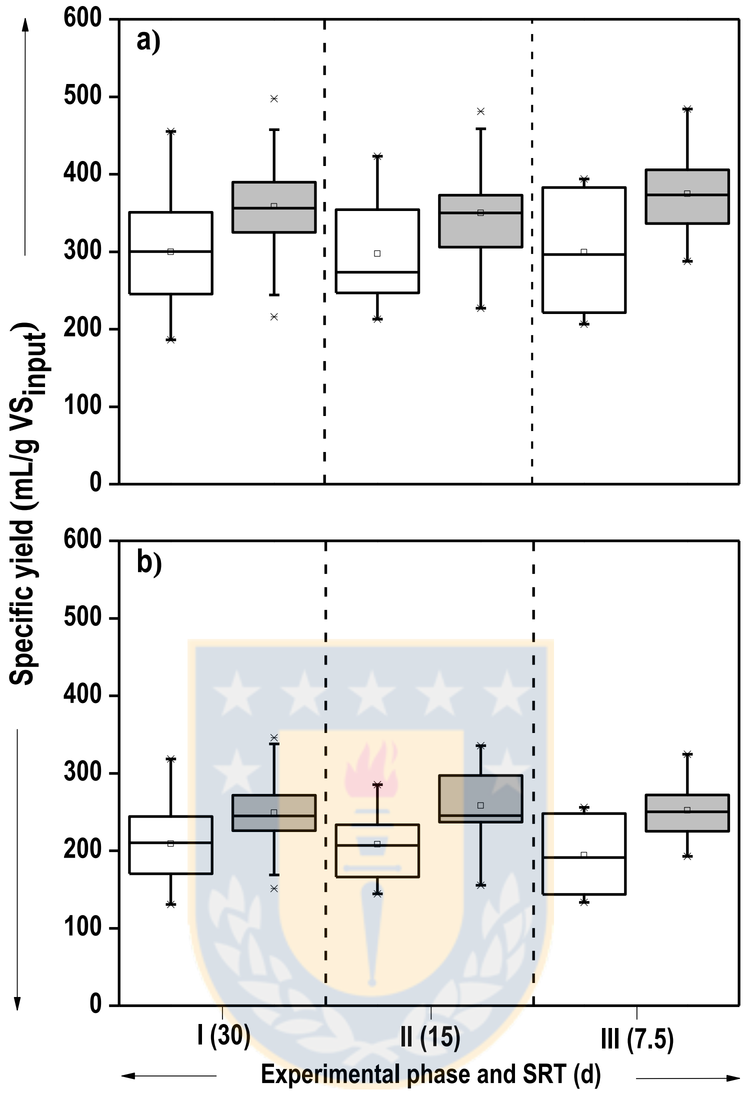


Figure 4. Specific yield of: **a)** Biogas and **b)** Methane (□CR, ■PTR). The central square and horizontal line inside the box represent mean and median values, respectively, while the bottom and top of the box represent the first and third quartiles, respectively. Upper and lower whiskers represent the maximum and minimum observed values, respectively, and points located outside the upper and lower whiskers represent outliers.

The biogas yields were 300 ± 68, 311 ± 61 and 299 ± 77 mL/gVS in CR and 358 ± 62, 377 ± 68 and 375 ± 54 mL/gVS in the PTR during Phases I, II and III, respectively. The methane yields corresponded to 209 ± 48, 208 ± 40 and 194 ± 50 mL/gVS in CR and 249 ± 43, 258 ± 47 and 252 ± 36 mL/Gvs in PTR during Phases I, II and III, respectively. PTR showed statistically significant higher gas production compared to CR under all experimental conditions ($P<0.05$), which corresponds to increases of 19.3 –

25.4% and 19.1 – 29.9% in the biogas and methane yields, respectively. These results are comparable with our previous study (Neumann et al. 2017), which reported a 32% increase in the methane yield of sludge in batch assays when similar pre-treatment conditions were applied. The highest increases observed in biogas (25.4%) and methane (29.9%) yield due to pre-treatment were associated with the 7.5 d SRT experimental period. As pointed by Carrère et al. (2008), one of the main effects of pre-treatments is the increased kinetics of the degradation of sludge with 1.3 to 1.8 higher maximum methane production rates reported in similar conditions to this study (Carvajal et al. 2013; Neumann et al. 2017). Previous reports have stated that the influence of pre-treatment over methane and biogas production is favored at shorter SRT (4 – 7.5 d)(Lin et al. 1997; Neis et al. 2008), which is similar to our study and most likely related to the increased kinetics of digestion. The average methane concentration in biogas was 69.44 ± 1.0, 66.02 ± 1.74 and 67.00 ± 1.75% for the CR and 69.30 ± 0.77, 68.22 ± 1.03 and 67.50 ± 1.08% for the PTR at Phases I, II and III, respectively, with no statistically significant differences due to pre-treatment ($P>0.05$).

A comparison with previous reports from other authors shows mixed results. Using a combined ultrasound (1,000 – 10,000 kJ/kgTS) and thermal (50 – 90°C) pre-treatment, Dhar et al. (2012) achieved 19 – 30% increases in methane yields from WAS in batch assays, whereas Şahinkaya and Sevimli (2013) reported that the sequential application of ultrasound (0.5 – 1.5 W/mL; 0.5 – 10 min) and temperature (60 – 100°C; 60 min) only led to a 14% and 13.6% increase in the biogas and methane yields of WAS in batch conditions, respectively.

Solids and COD removals are presented in Figure 5. The average total solids removal was 39.5 ± 8.5, 35.3 ± 8.5 and 33.4 ± 0.4% for the CR and 40.0 ± 8.4, 38.7 ± 7.1 and 38.2 ± 4.1% for the PTR in Phases I, II and III, respectively, whereas the average volatile solids removal was 46.2 ± 6.8, 40.6 ± 11.1 and 36.8 ± 6.6% for the CR and 47.7 ± 7.1, 43.1 ± 12.0 and 41.1 ± 5.3% for the PTR in Phases I, II and III, respectively. PTR showed an increase of 1.3 – 14.4% in total solids removal and an increase of 3.2 – 11.7% in volatile solids removal compared to CR, but these differences were found to be statistically non-significant ($P>0.05$). Total COD removals were 36.3 ± 10.9, 36.6 ± 11.1 and 31.0 ± 3.3% for CR and 45.8 ± 8.6, 43.0 ± 8.9 and 39.8 ± 8.7% for PTR in Phases I, II and III, respectively. PTR showed statistically significant increases of 17.5 – 28.4% in COD removal compared to CR ($P<0.05$) with the highest difference observed at 7.5 days SRT.

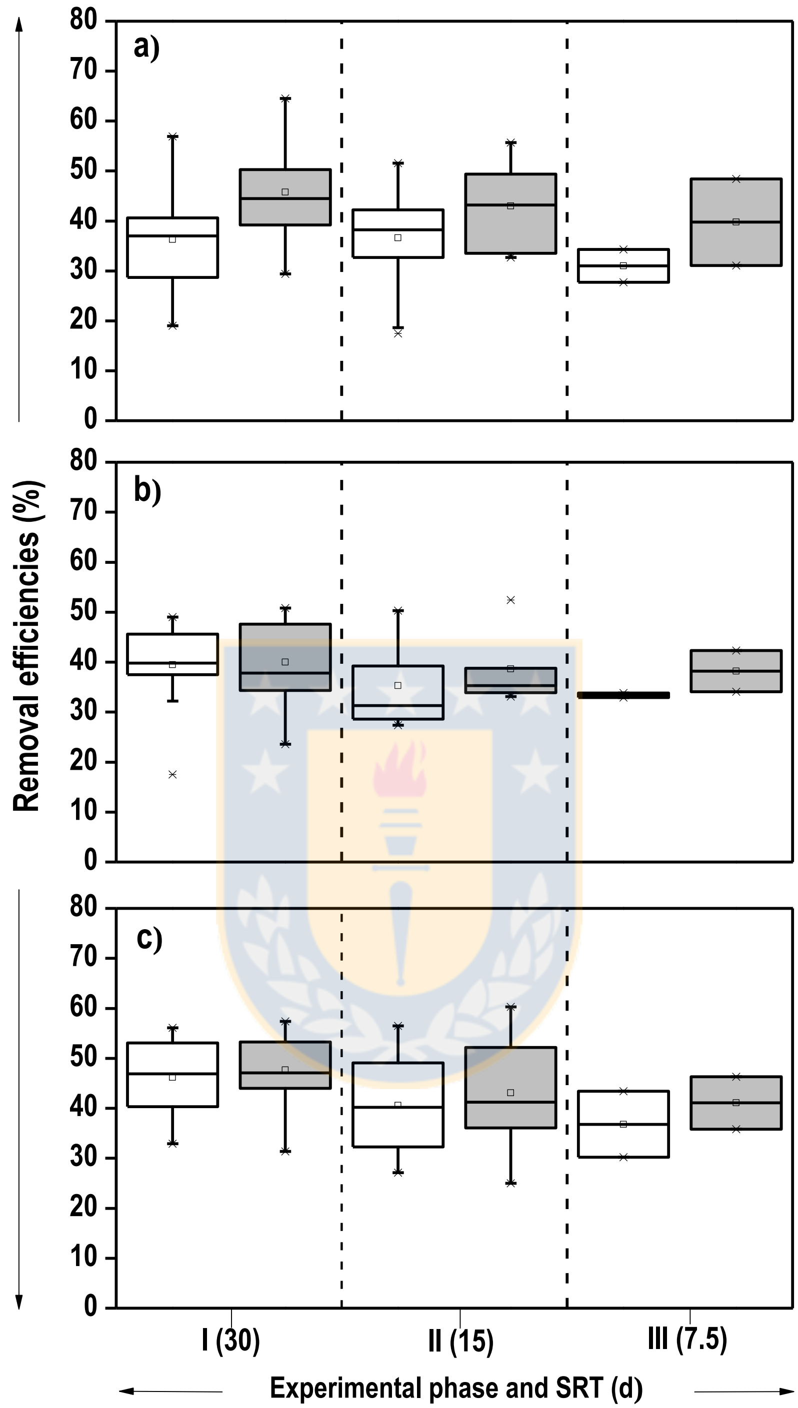


Figure 5. Removal efficiencies of: **a)** COD, **b)** TS and **c)** VS (□CR, ■PTR). The central square and horizontal line inside the box represent mean and median values, respectively, while the bottom and top of the box represent the first and third quartiles, respectively. Upper and lower whiskers represent the maximum and minimum observed values, respectively, and points located outside the upper and lower whiskers represent outliers.

While the pre-treatment resulted in 3.5 times higher soluble COD in the sludge compared to raw MSS, the solids concentration was unaffected by the process (Table 1). Considering that the changes in solids removal during digestion were statistically non-significant, it is possible that the solubilization effect of pre-treatment did not affect the availability and biodegradability of the particulate fraction of MSS, which suggests that solids removal efficiency it is not necessarily related to increased biogas yield caused by pre-treatment.

Table 3 summarizes the conversion of organic matter achieved for the different phases of anaerobic digestion under all experimental conditions.

Table 3. Organic matter conversion efficiency for the different digestion steps in the anaerobic digestion systems.

Digestion phase	Unit	SRT (d)	CR	PTR
Hydrolysis	%	30	38.6 ± 8.4	45.0 ± 8.5
		15	42.0 ± 8.4	51.6 ± 10.2
		7.5	37.5 ± 11.1	47.2 ± 7.2
Acidogenesis	%	30	34.5 ± 8.3	40.8 ± 8.5
		15	37.3 ± 8.3	46.1 ± 10.3
		7.5	33.0 ± 9.4	42.7 ± 5.9
Methanogenesis	%	30	33.9 ± 8.1	40.3 ± 10.1
		15	37.0 ± 10.5	45.9 ± 13.1
		7.5	32.6 ± 9.4	42.4 ± 5.9

SRT: Sludge Retention Time; CR: Control Reactor; PTR: Pre-Treatment reactor.

The conversion of organic matter at the hydrolysis, acetogenesis and methanogenesis steps was 16.6 – 25.9%, 18.3 – 29.4% and 18.9 – 30.1% higher in PTR than CR, respectively. Most of the COD in both systems was effectively transformed to methane as the COD of VFA and other soluble compounds accounted for 0.3 – 0.6% and 4.1 – 4.7% in the CR and 0.2 – 0.5% and 4.2 – 5.5% in the PTR, respectively. The lack of accumulation of soluble COD and VFA inside PTR suggests that digestion is not limited by the acidogenesis or methanogenesis steps as their rate of conversion was sufficient to compensate for the increased soluble COD in the fed sludge. This is further evidence that hydrolysis represents the limiting step during anaerobic digestion of sewage sludge, as stated before (Wilson and Novak 2009; Abelleira-Pereira et al. 2015).

3.4. Digestate characteristics

Table 4 shows the results of the centrifugability assays performed over the CR and PTR digestate.

Table 4. Centrifugability parameters for digestate coming from the anaerobic digestion systems

Parameter	Unit	t (min)		SRT (d)			
				30		15	
				Rank	Average	Rank	Average
WR	%	3	CR	72.0 – 76.3	74.0 ± 2.0	50.0 – 66.0	58.5 ± 7.2
			PTR	68.5 – 73.4	70.9 ± 1.5	44.6 – 63.8	56.4 ± 8.0
		10	CR	79.2 – 80.2	79.7 ± 0.5	63.3 – 74.5	68.6 ± 5.6
			PTR	79.2 – 80.0	79.5 ± 0.4	62.6 – 74.2	68.9 ± 5.4
SR	%	3	CR	93.2 – 98.1	96.5 ± 2.2	97.0 – 98.0	97.3 ± 0.4
			PTR	92.2 – 98.1	96.3 ± 2.7	96.9 – 99.1	98.5 ± 0.9
		10	CR	99.0 – 99.1	99.1 ± 0.1	97.8 – 98.4	98.0 ± 0.2
			PTR	98.6 – 98.7	98.6 ± 0.0	98.2 – 98.9	98.6 ± 0.4

SRT: Sludge Retention Time; t: Centrifugation Time; WR: Water Recovery; SR: Solid Recovery; CR: Control Reactor; PTR: Pre-Treatment Reactor.

The solid recovery ranged between 92.2 and 99.1% for both reactors and it was not affected by either pre-treatment or by SRT (P>0.05). The recovery of water from the digestate ranged between 50.0 and 80.2% for CR and 44.6 and 80.0% for PTR, depending on the reactor SRT and centrifugation time. Pre-treatment caused a statistically significant decrease of 4.2% in water recovery during Phase I at 3 min of centrifugation time (P<0.05). Previous reports stated that pre-treatments such as ultrasound could led to decreased sludge particle size (40% reduction in cut diameter at 1,000 kJ/kgTS) (Bougrier et al. 2005), which could possibly increase the bound water content in sludge due to the higher surface area of particles and affect its dewatering (Pilli et al. 2011). However, when the centrifugation time was increased no significant differences were observed (P>0.05), which suggests that intensive dewatering processes could compensate for the effect of pre-treatment. Decreasing SRT from 30 to 15 days led to 13.3 – 20.5% statistically significant decreases in water recovery in all experimental conditions (P<0.05), which is possibly related to the partial degradation of fine solids and colloids during digestion at this SRT (Braguglia et al. 2010; Wahidunnabi and Eskicioglu 2014). This suggests that SRT is a more significant factor controlling digestate dewaterability than pre-treatment.

Table 5 shows the concentrations of nutrients and metals in both the digestate solids and the supernatant after dewatering.

TKN and TP represented 6.1 – 6.8% and 1.4 – 1.5% of the total solids in the digestate coming from CR and 6.5 – 8.0% and 1.1 – 1.3% of the total solids in the digestate coming from PTR, respectively. Digestion led to increases in the concentration of almost all elements in the sludge solids with values up to 378% higher in digestate solids compared to raw sludge. In most cases, pre-treatment and shorter SRT led to increases (7 – 58%) and decreases (10 – 50%) in the concentration of the studied elements in the digestate solids, respectively. While previous reports have stated that pre-treatment could lead to increased concentrations of up to 6 times of inorganic elements in the soluble phase (Appels et al. 2010), this effect was not consistently observed in the supernatant, and even up to 68% decreases in the concentration of elements, such as Cu and Zn, were observed, which could be related to its precipitation and accumulation as inorganic salts (Carballa et al. 2008).

Table 5. Nutrient and metal concentration in supernatant and solids after dewatering of digestate coming from the anaerobic digestion systems.

	SRT (d)	Input sludge (mg/kg)	CR		PTR	
			Supernatant (mg/L)	Solid (mg/kg)	Supernatant (mg/L)	Solid (mg/kg)
TKN	30	45153	864	68008	949	64798
	15	48773	1044	61326	1046	80812
TP	30	865	163	1399	199	1284
	15	1077	15	1451	11	1145
As	30	7.82	0.01	7.52	0.01	9.63
	15	3.31	0.02	5.47	0.01	4.82
Cu	30	167.0	0.35	288	0.43	455
	15	352.0	0.42	432	0.25	570
Hg	30	<1	<0.001	1.28	<0.001	1.94
	15	1.33	<0.001	1.59	<0.001	1.93
Ni	30	<1	<0.01	<1	<0.01	<1
	15	<1	<0.01	<1	<0.01	<1
Pb	30	<3	<0.03	<3	<0.03	<3
	15	<3	<0.03	<3	<0.03	<3
Se	30	<0.90	<0.005	<0.90	<0.005	<0.90
	15	<0.90	<0.005	<0.90	<0.005	<0.90
Zn	30	147	1.41	656	1.01	702
	15	989	4.72	1087	1.50	1266

SRT: Sludge Retention Time; CR: Control Reactor; PTR: Pre-Treatment Reactor; TKN: Total Kjeldahl Nitrogen

Table 6 shows the assessed pathogen indicators in sludge samples and digestate.

Table 6. Microbiological parameters for input sludge and digestate coming from the anaerobic digestion systems.

	Unit	SRT (d)	Raw Sludge	US Sludge	US+TT Sludge	CR	PTR
Total coliforms	MPN/100 mL	30	$2.00 \cdot 10^{8}$	$1.60 \cdot 10^{8}$	$7.80 \cdot 10^{5}$	$1.65 \cdot 10^{6}$	$8.80 \cdot 10^{5}$
		15				$3.30 \cdot 10^{5}$	$1.70 \cdot 10^{5}$
	MPN/gTS	30	$4.78 \cdot 10^{9}$	$3.85 \cdot 10^{9}$	$1.90 \cdot 10^{7}$	$7.86 \cdot 10^{7}$	$4.21 \cdot 10^{7}$
		15				$1.57 \cdot 10^{7}$	$8.13 \cdot 10^{6}$
Fecal coliforms	MPN/100 mL	30	$2.00 \cdot 10^{8}$	$7.00 \cdot 10^{6}$	$7.80 \cdot 10^{5}$	$9.45 \cdot 10^{5}$	$7.10 \cdot 10^{5}$
		15				$3.30 \cdot 10^{5}$	$1.70 \cdot 10^{5}$
	MPN/gTS	30	$4.78 \cdot 10^{9}$	$1.68 \cdot 10^{8}$	$1.90 \cdot 10^{7}$	$4.50 \cdot 10^{7}$	$3.40 \cdot 10^{7}$
		15				$1.57 \cdot 10^{7}$	$8.13 \cdot 10^{6}$
Somatic coliphages	PFU/100 mL	30	$2.43 \cdot 10^{5}$	$1.54 \cdot 10^{5}$	$2.47 \cdot 10^{4}$	$5.14 \cdot 10^{4}$	$8.40 \cdot 10^{3}$
		15				$6.64 \cdot 10^{4}$	$8.50 \cdot 10^{3}$
	PFU/gTS	30	$5.81 \cdot 10^{6}$	$3.69 \cdot 10^{6}$	$6.01 \cdot 10^{5}$	$2.45 \cdot 10^{6}$	$4.02 \cdot 10^{5}$
		15				$3.16 \cdot 10^{6}$	$4.07 \cdot 10^{5}$

MPN: Most probable number; PFU: Plaque forming units; US Sludge: Sludge after ultrasound application; US+TT Sludge: Sludge after sequential application of ultrasound and thermal treatment.

The presence of coliforms (total and fecal) and somatic coliphages in raw sludge were approximately 10^{9} MNP/gTS and 10^{6} PFU/gTS, respectively, and were similar to previous reports (Levantesi et al. 2015). Sequential pre-treatment led to logarithmic removals ($\log_{rem}$) of 2.4 for coliforms (total and fecal) and 1.0 for somatic coliphages, whereas anaerobic digestion resulted in further removal of the three studied indicators. Conventional digestion led to overall $\log_{rem}$ values of 2.1 – 2.8, 2.3 – 2.8 and 0.6 – 0.7 for total coliforms, fecal coliforms and somatic coliphages, respectively, whereas pre-treatment followed by anaerobic digestion presented overall $\log_{rem}$ values of 2.4 – 3.1 and 1.5 for total/fecal coliforms and somatic coliphages, respectively, which were comparable to other advanced digestion processes (Levantesi et al. 2015).

3.5. COD balance of the process

Figure 6 shows the COD balance for the conventional and advanced digestion processes under all experimental conditions.

During conventional digestion, 32.6 – 37.0% of total input COD was converted to methane. Digestate from this process was composed of 92.1 – 92.9% particulate COD, 6.2 – 7.5% hydrolyzed COD and 0.5 – 0.9% acidized COD. In the case of the advanced digestion system, 40.3 – 45.9% of the input COD was converted to methane and the digestate consisted of 89.5 – 92.1% of particulate COD, 7.0 – 10.2% hydrolyzed COD and 0.4 – 0.8% acidized COD. Pre-treatment resulted in a 6.4 – 9.8 percent point increase in methane COD depending on SRT (Figure 6) and concordant with 10.9 – 11.3% of the total COD transferred to the soluble phase of MSS during pre-treatment. Moreover, COD removal in PTR was 6.4 – 9.5 percent points and 17.5 – 28.4% higher than in CR and in the same order of the observed increase in methane yield during digestion (19.1 – 29.9%). This shows that methane production improvement was proportional to the COD solubilization efficiency of pre-treatment and the associated COD removal increase, which was further evidence that solubilization of organic matter is one of the main mechanisms driving biogas production improvement during anaerobic digestion after pre-treatment.

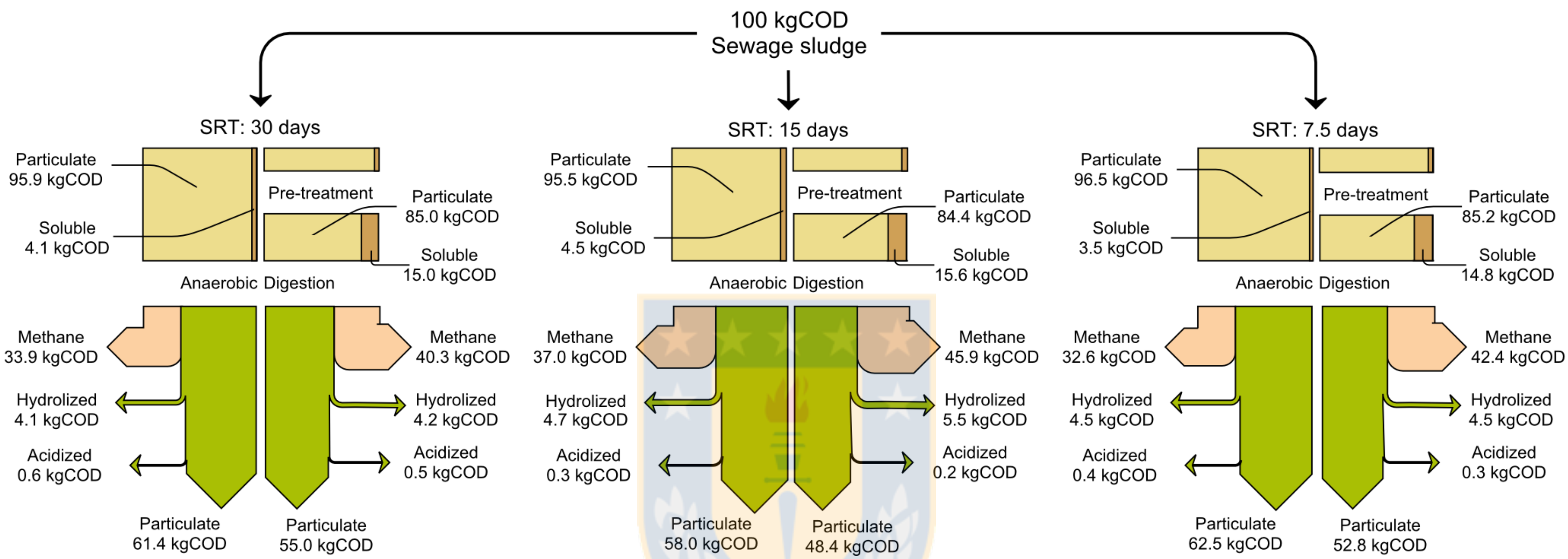


Figure 6. COD balance in both anaerobic reactors during the three different operational phases (■Sludge particulate COD, ■Sludge soluble COD, ■Methane COD and ■Digestate COD).

4. CONCLUSIONS

Sequential ultrasound – thermal pre-treatment resulted in a 19.1 – 29.9% increase in methane yield during sewage sludge anaerobic digestion without affecting the stability of the process or accumulation of intermediaries. Pre-treatment showed up to a 4.2% decrease in water recovery from digestate, but SRT was a more relevant factor controlling dewatering. Advanced digestion showed 2.4 – 3.1 and 1.5 $\log_{rem}$ for coliforms and coliphages, respectively, and pre-treatment caused up to a 58% increase in the concentration of inorganic elements in digestate solids. The COD balance showed that the observed increase in methane production was proportional to the pre-treatment solubilization efficiency of COD.

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CAPÍTULO VI

LIFE CYCLE ASSESSMENT OF MANAGEMENT ALTERNATIVES FOR SLUDGE FROM SEWAGE TREATMENT PLANTS IN CHILE: DOES ADVANCED ANAEROBIC DIGESTION IMPROVE ENVIRONMENTAL PERFORMANCE COMPARED TO CURRENT PRACTICES?

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Life cycle assessment of management alternatives for sludge from sewage treatment plants in Chile: does advanced anaerobic digestion improve environmental performance compared to current practices?

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Abstract

Sludge generation is currently one of the most important issues for sewage treatment plants in Chile. In this work, the life cycle environmental impacts of four sludge management scenarios were studied, focusing on the comparison of current practices and advanced anaerobic digestion (AD) using a sequential pre-treatment (PT). The results show that AD scenarios presented lower potential impacts than lime stabilization scenarios in all assessed categories, including climate change, abiotic depletion, acidification, and eutrophication in terrestrial, marine and freshwater ecosystems. The overall environmental performance of advanced digestion was similar to conventional digestion, with the main difference being a decrease in the climate change potential and an increase in the abiotic depletion potential. Acidification and eutrophication categories showed similar performances in both conventional and advanced AD. The effect of PT in the AD scenarios was related to energy recovery, sludge transport requirements and nutrient loads in the sludge and supernatant after digestate dewatering. Considering the results, PT could be a useful strategy to promote sludge valorization and decrease the environmental burdens of sludge management in Chile compared to the current scenario.

1. INTRODUCTION

During the last decades, sludge management has become a growing issue for wastewater treatment facilities (Yoshida et al. 2013). In Chile, 60% of sewage treatment facilities utilize activated sludge technology (SISS 2016), whose sludge generation rates surpass those of technologies such as sequential batch reactors and extended aeration systems (Vera et al. 2013). Historically, the most utilized sludge disposal strategy in Chile is landfilling, with 55% of the total sludge generated in sewage treatment facilities being disposed either in municipal or industrial wastes landfills (SISS 2011). Comparatively, beneficial land application only represents 9% of total disposed sludge (SISS 2011), causing concern about the sustainability of this strategy in the long term.

Considering stabilization alternatives, anaerobic digestion (AD) represents a preferred alternative due to the production of biogas and digestate that can be used as replacements for conventional energy sources and fertilizers, respectively (Appels et al. 2008a). However, digestion is limited at the hydrolysis step, and consequently, long sludge retention times are necessary, and only partial conversion of organic matter is achieved (Carballa et al. 2011).

The implementation of sludge pre-treatment (PT) prior to digestion has been proposed as a method to improve the efficiency of hydrolysis (Dhar et al. 2012; Carvajal et al. 2013). However, while a wide array of processes have been proposed (Neumann et al. 2016), energy consumption is a barrier to the full-scale implementation of most technologies (Cano et al. 2015). In this scenario, ultrasound and thermal hydrolysis at 50 – 70°C have been proposed as low-energy consumption alternatives for sludge PT (Xie et al. 2007; Carvajal et al. 2013). Both processes have been reported to have significant effects on digestion, as their sequential application can result in increases of up to 50% in the methane yield of sludge (Dhar et al. 2012; Neumann et al. 2017).

While the main objective of PT is increasing biogas production, factors such as energy, raw material consumption and digestate quality could also be affected (Carballa et al. 2011; Neumann et al. 2016). Therefore, the related changes in emissions and other environmental aspects could result in increases in the impacts associated with other steps of sludge management. In this scenario, a suitable tool to estimate these possible trade-offs is Life Cycle Assessment (LCA) (Corominas et al. 2013; Yoshida et al. 2013; Remy et al 2017), a methodology that allows the estimation of the environmental impacts of products, processes and services, potentially including all steps from raw material extraction to waste disposal (Guinée et al. 2011).

Although sludge management and AD have been extensively analyzed using the LCA method (Suh and Rousseaux 2002; Hospido et al. 2005; Hospido et al. 2010; Yoshida et al. 2013), to the best of our knowledge, the literature associated with the assessment of PT is limited. In one of the most extensive studies, Carballa et al. (2011) concluded that mechanical and chemical PT showed better overall environmental performance than other assessed technologies. Mills et al. (2014) reported that thermal hydrolysis improved the environmental and economic performance of sludge digestion, while Gianico et al. (2015) reported that the energetic cost of implementing primary sludge wet oxidation and secondary sludge thermal PT surpassed the benefits of combined heat and power (CHP) generation from biogas, even though the environmental performance of the upgraded facility was similar to that of the conventional plant.

The objective of this study is to compare the life-cycle environmental performance of advanced digestion (i.e., including PT) with current management practices used in Chile. The purpose is to provide insight into the potential consequences or benefits in related environmental impacts associated to PT implementation in the national context, evaluating a potentially feasible technology consisting of the sequential application of ultrasound and thermal hydrolysis at 55°C (Neumann et al. 2017), which has not previously been assessed using LCA.

2. MATERIALS AND METHODS

2.1 Goal, scope and Life Cycle Inventory (LCI) data-sources

The aim of this work is to assess the environmental impacts of sludge management scenarios, focusing on the comparison between advanced AD and common practices in Chile, including chemical (i.e., alkalinization) and biological (i.e., conventional AD) stabilization. Four scenarios were established, where 0a and 0b represents the most common and therefore the "business-as-usual" scenarios:

– Scenario 1 (S_1): AD and agricultural sludge application.
– Scenario 2 (S_2): AD including sequential ultrasound and thermal PT and agricultural sludge application.
– Scenario 0a (S_{0a}): Chemical stabilization using lime and landfilling without electricity recovery from landfill gas.
– Scenario 0b (S_{0b}): Chemical stabilization using lime and landfilling with electricity recovery from landfill gas.

The functional unit (FU) for waste treatment systems can be defined in terms of the products obtained (energy, materials) (Whiting and Azapagic 2014) or treated waste (Suh and Rousseaux 2002; Hospido et al. 2004; Rodriguez-Garcia et al. 2011). As sludge valorization through energy or material recovery is not common across all assessed scenarios, a treatment perspective was selected, and the stabilization of 1 ton of mixed sludge (dry basis) was chosen as the FU (Suh and Rousseaux 2002; Hospido et al. 2005; Mills et al. 2014). All selected scenarios were divided into sub-systems, with the aim of identifying the parameters that influence environmental performance, allowing the proposal of improvement actions when possible (Figure 1).

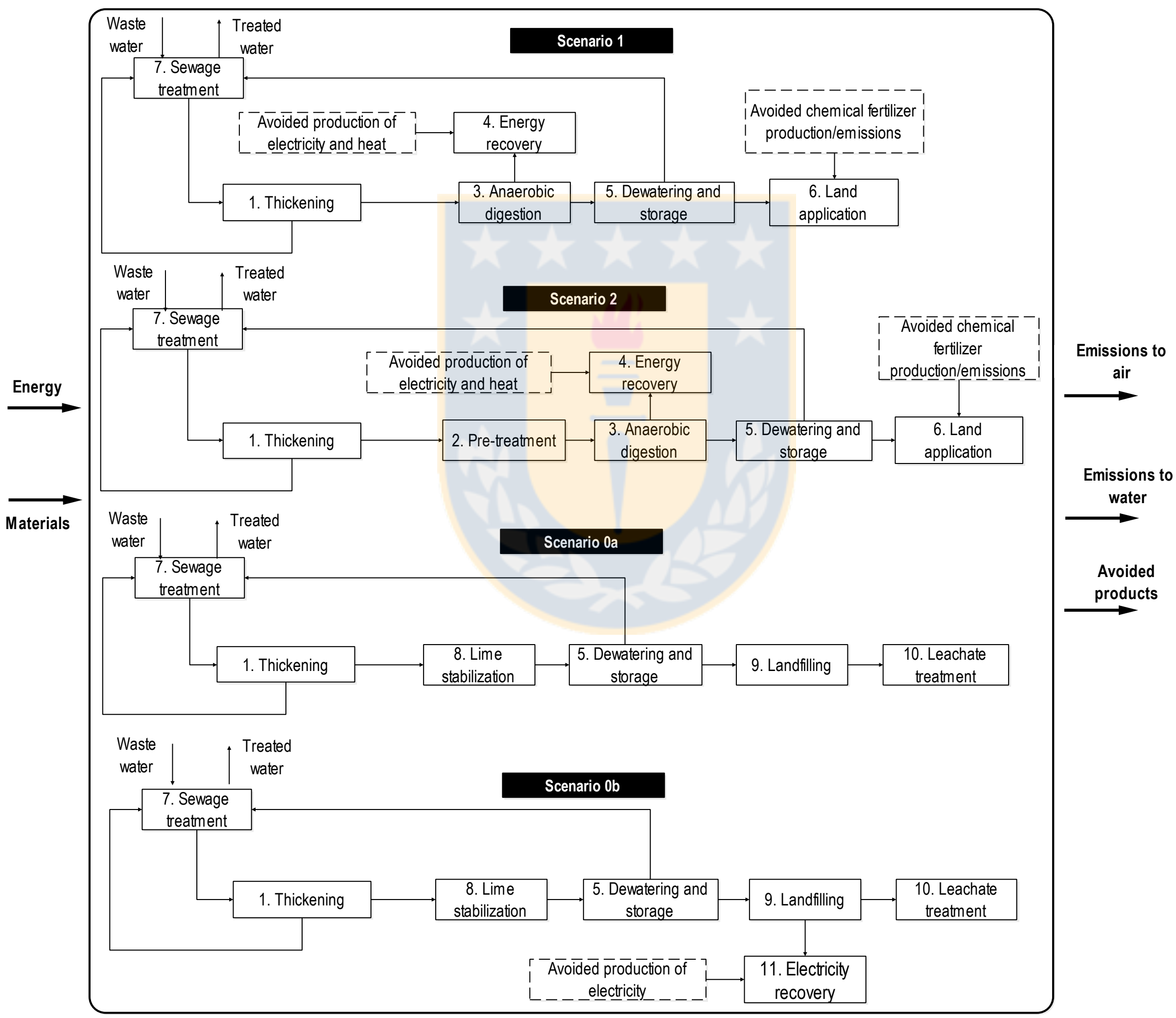

Figure 2. Process subsystems and boundaries. Dashed lines represent avoided products.

Data for the Life Cycle Inventory (LCI) of AD were obtained from the Concepción wastewater treatment plant (WWTP) in central-southern Chile (Neumann et al. 2017) for a period of one year; these data were complemented with laboratory and literature data when required. The influence of PT on digestion performance was assessed in laboratory during a period of ~90 days using two semi-continuous 10-L digesters, one fed with raw sludge and the other with pre-treated sludge. Further details of the laboratory assays can be found in the Supplementary Information. Scenarios 0a and 0b were mainly assessed based on LCI models (Doka 2003a), adapted to the Chilean context when possible. Infrastructure was not included in the assessment, as previous reports state its low contribution to environmental loads, especially in large-scale facilities (Tillman et al. 1998; Lundin et al. 2000). Inputs during the operational stage (i.e., polymers, material for construction of landfill ditches) were included. Detailed information pertaining the literature and experimental parameters used to calculate the LCI is presented in Tables 1 and 2.

Table 1. Parameters used for calculation of the inventory

Parameter	Value	Subsystem	Scenario	Source	Observations
Thickening electricity consumption	4.9 kWh/FU	1	1 – 2 – 0a – 0b	Sylvis et al. (2009)	Default value for thickening equipment in model.
Un-thickened sludge pumping electricity consumption	0.13 kWh/m^3	1	1 – 2 – 0a – 0b	Enconsult (2004)	In agreement with Rodriguez et al. (2014).
Polyacrilamide consumption (secondary thickening)	6.4 kg/FU	1	1 – 2 – 0a – 0b	Plant operation	Mean value from one year operational data. In agreement with Hospido et al. (2005).
Thickened sludge pumping electricity consumption	0.19 kWh/m^3	1 - 2 - 3 - 5	1 – 2 – 0a – 0b	Pirnie (2005)	Average for a sub-metering studio in a full scale WWTP.
Water pumping electricity consumption	0.10 kWh/m^3	1 - 5	1 – 2 – 0a – 0b	Enconsult (2004); Pirnie (2005)	Estimated value based on Enconsult (2004) and Pirnie (2005).
Ultrasound electricity consumption	274 kJ/ kg TS	2	2	Based on data provided by manufacturer	In agreement with data from Pérez-Elvira et al. (2009) for industrial equipment (44 – 360 kJ/kg TS).
Digester and pre-treatment mixing electricity consumption	6.5 W/m^3	2 - 3	1 – 2	Tchobanoglous et al. (2003)	Considering 24 hours of operation.
Specific heat of sludge	4.16 kJ/ºC kg	2 – 3	1 – 2	Silvestre et al. (2015)	Value equal to water, according with Ferrer et al. (2008b).
Ambient temperature	12 °C	2 – 3 – 6	1 – 2	Vera et al. (2013)	Average annual temperature in Concepción, Chile.
Heat transfer coefficient of the reactors wall	1.52 W/m^2-°C	2 – 3	1 – 2	Malina and Pohland (1992)	12'' concrete, 1'' air space and 4'' brick, exposed to air.
Heat transfer coefficient of the reactors cover	3.27 W/m^2-°C	2 – 3	1 – 2	Malina and Pohland (1992)	12'' concrete, exposed to air.
Heat transfer coefficient of the reactors floor	0.62 W/m^2-°C	2 – 3	1 – 2	Malina and Pohland (1992)	12'' concrete, exposed to wet earth.
Internal sludge recirculation in digesters	112 m3/h	3	1 – 2	Plant operation	Mean value, calculated from one year operational data.
Methane yield increase due to pre-treatment	19%	3	2	Laboratory data	Compared to conventional digestion. Increase observed during a ~90 d period. In agreement with Neumann (2017).
Combined heat and power efficiency	46% Electric 49% Thermal	4	1 – 2	Pertl et al. (2010)	In agreement with efficiencies reported by manufacturers of CHP equipment (Cogeneration 2013; Energy 2013).

Table 1. continued

Parameter	Value	Subsystem	Scenario	Source	Observations
Polyacrilamide consumption (dewatering)	2.7 kg/FU	5	1 – 2 – 0a – 0b	Plant operation	Mean value, calculated from one year operational data.
Dewatering electricity consumption	1.6 kWh/m3	5	1 – 2 – 0a – 0b	Unwelt Bundeswamt (2014)	Specific value for centrifugation equipment. In the range of previous reports by Uggetti (2011) and Brown et al. (2010).
Digestate water recovery variation due to pre-treatment	-4.2%	5	2	Laboratory data	Compared to conventional digestion. Mean effect observed on centrifugation tests during a ~90 day operational period.
Wheat nitrogen and phosphorous requirements	162.9 kg N/ha-yr 16.0 kg P/ha-yr	6	1 – 2	Warncke et al. (2004); Dai et al. (2016)	In agreement with Tchobanoglous & Burton (2003) and Johannesson (1999).
Atmospheric nitrogen deposition	6.93 kg N/ha-yr	6	1 – 2	Oyarzun et al. (2002)	NH_4 plus NO_3^- depositions near an agricultural site in south-central Chile
Annual precipitation	967.5 mm/yr	6	1 – 2	Instituto Nacional de Estadistica (2015)	Distributed in seasons according to Brentrup (2001).
N and P biodisponibility	50% N 70% P	6	1 – 2	Bengtsson et al. (1997)	In agreement with Rodriguez et al. (2014).
Lime ($Ca(OH)_2$) dose	120 g/kg TS (primary sludge) 300 g/kg TS (secondary sludge)	8	0a – 0b	Tchobanoglous et al. (2003)	Stabilization according to Chilean legislation (MINSEGPRES 2009).
Electricity consumption during alkalinization	5 kWh/FU	8	0a – 0b	Suh and Rousseaux (2002)	Including mixing and pumping.
Sludge biodegradability during landfilling	60%	9	0a – 0b	Doka (2003a)	Considering a time horizon of 100 years. In agreement with the biodegradability of sludge in anaerobic conditions, according to Tchobanoglous & Burton (2003).

Table 2. Characterization of sludge and supernatant from dewatering

Sample	Parameter	S_1	S_2
Centrifuged digested sludge	$N\text{-}NH_4^+$ (g/kg)[1]	14.0	15.6
	TKN (g/kg)[1]	68.0	64.8
	TP (g/kg)[1]	1.4	1.3
Supernantant	CODs (mg/L)	2,067	2,094
	TSS (mg/L)	978	1011
	$N\text{-}NH_4^+$ (mg/L)	259	134
	TKN (mg/L)	864	949
	TP (mg/L)	163	199

Data obtained during the ~90 day operational period of the laboratory digesters.

[1]Dry basis; TKN: Total Kjeldhal Nitrogen; TP: Total Phosphorous; CODs: Soluble Chemical Oxygen Demand; TSS: Total Suspended Solids

S_1: Scenario 1 (conventional digestion); S_2: Scenario 2 (advanced digestion)

2.2 Biological stabilization subsystems (scenarios 1 and 2)

The subsystems in S_1 and S_2 include the in-plant stabilization operations using AD and the transport and application of sludge to soil as replacements of commercial fertilizers. PT prior to digestion was included in S_2.

2.2.1 Sub-system 1: Thickening

Prior to AD, sludge from wastewater treatment is thickened to reduce its volume. An efficiency of 90% in terms of solids recovery was assumed. Chemical consumption (polyacrylamide) was estimated based on the WWTP operation, and its production was calculated based on the manufacture of acrylonitrile, one of the raw materials used in acrylamide production (Hospido et al. 2005). The supernatant originating from thickeners was assumed to be re-circulated to sewage treatment.

2.2.2 Sub-system 2: Pre-treatment

In S_2, thickened sludge was subjected to the sequential application of ultrasound and thermal treatment at 55°C. The PT was tested in laboratory using a Hielscher UP200ST device with a specific energy corresponding to the disruption threshold for sludge under laboratory conditions (2000 kJ/kg Total Solids; TS) (Bougrier et al. 2005). As industrial-scale devices have lower energy consumption and higher disruption efficiencies than laboratory devices (Zielewicz and Sorys 2008), the specific energy consumption of ultrasound was estimated based on information provided by Ultrawaves GmbH (Hamburg, Germany). Estimation was based on the industrial-device power, treatment flow and the average solids concentration of sludge coming from the assessed WWTP, which gives a value of 274 kJ/kg TS, in agreement with previous reports (see Table 1). Thermal treatment of sludge after ultrasound was performed in a Gerdhardt Thermoshake incubator with a retention time of 8 h. Heat consumption was estimated as the sum of the heat required to increase the sludge temperature and the losses during the process, estimated assuming the use of a cylindrical reactor with heat transfer coefficients corresponding to those of an anaerobic digester (Table 1) (Malina and Pohland 1992). Stirring electricity consumption was estimated based on specific needs per reactor volume, according to sludge retention times. Heat recovery from the output of the PT to the incoming sludge was considered through the use of a sludge-to-sludge heat exchanger (Krugel et al. 1998).

2.2.3 Sub-system 3: Anaerobic digestion

Thermal energy needs for AD were estimated based on the same criteria used for sub-system 2. Biogas production was estimated based on data from the WWTP and modified in S_2 according to the increase observed in laboratory due to PT. CH_4 and CO_2 concentrations in the biogas were measured in laboratory, while N_2, H_2S and NH_3 concentrations were obtained from the literature (Rodriguez-Verde et al. 2014). A 5% loss of total biogas produced was assumed (Hobson 2003), of which 50% was assumed to be emitted directly and the other 50% to exit in the digestate and be emitted during its storage (Cakir and Stenstrom 2005).

2.2.4 Sub-system 4: Electricity and heat recovery

Biogas produced during digestion is used in a CHP system. Energy generation was calculated based on the calorific value of CH_4 (Silvestre et al. 2015). Emissions of NOx, CO_2, CO, CH_4 and N_2O to air due to biogas combustion were estimated based on emission factors (Doka 2003b; De Vries et al. 2012). Electricity generated was assumed to replace electricity supplied by the Interconnected Central Grid of Chile, while heat was assumed to be utilized in its totality to replace heat generated from natural gas. The influence of this last supposition on the results was assessed through a sensitivity analysis, detailed in section 2.4.

2.2.5 Sub-system 5: Dewatering and storage

Dewatering was assumed to be performed in a centrifuge using polyacrylamide. The mass balance in S_1 was estimated based on WWTP data, while the effect of PT on water recovery was evaluated in laboratory and included in the mass balance for S_2. Dewatered sludge and supernatant were characterized, and the latter was assumed to be re-circulated to sewage treatment. After dewatering, sludge is stored in a roofed field open to the atmosphere, where a 5% loss of water due to evaporation was assumed based on information provided by WWTP operators. Emissions during this step correspond to those detailed under section 2.2.3.

2.2.6 Sub-system 6: Land application

After storage, sludge is transported in 16 – 32-metric ton trucks over a distance of 100 km to the application site, modeled using the Ecoinvent v3 process for transport in freight lorries of that capacity (EURO3, Global, Market). Based on Rodriguez-Garcia et al. (2011), it was assumed that sludge replace the use of diammonium phosphate ($(NH_4)_2HPO_4$) as a source of N and P_2O_5 and ammonium sulfate ($(NH_4)_2SO_4$) as a supplementary N source. The sludge application rate was based on the nutrient requirements of wheat, which represents one of the most common crops in Chile (INE 2015).

Non-assimilated N and P were assumed to be emitted to air and to enter water through volatilization and leaching processes. Airborne emissions of NH_3, N_2O and N_2 and water emissions of NO_3^- were estimated based on Brentrup et al. (2001), considering local conditions. Emissions of P were estimated assuming that 2.575% of the applied P was leached as PO_4^{-3} (Doka, 2003b).

2.2.7 Sub-system 7: Sewage treatment

To account for the effect of PT on sewage treatment emissions derived from variations in dewatered supernatant nutrient loads, water treatment was modeled according to Doka (2003b).

2.3 Chemical stabilization subsystems (scenarios 0a and 0b)

Chemical stabilization (i.e. using lime) scenarios included in-plant operations and transport and disposal of stabilized sludge in landfill sites.

2.3.1 Sub-system 1: Thickening

As in S_1 and S_2, sludge from the wastewater treatment was thickened prior to stabilization. The operational parameters used for this sub-system correspond to those used in the digestion scenarios.

2.3.2 Sub-system 8: Lime stabilization

After thickening, sludge is subjected to chemical stabilization using lime. Emissions during alkalinization were calculated based on the ammonia concentration and an estimated molecular formula for sludge based on Houillon and Jolliet (2005): $C_{11.7}H_{18.5}O_{6.1}N$. NH_3 emissions were estimated assuming that all free ammonia present in the sludge was emitted directly to the atmosphere.

2.3.3 Sub-system 5: Dewatering and storage

Efficiency and electricity/chemical consumption of dewatering were assumed equal to S_1. It was estimated that after storage sludge has 70% humidity (Wang et al. 2009), and no emissions were considered in this step as it was assumed they occurred during stabilization.

2.3.4 Sub-system 9: Landfilling

After storage, sludge is transported to landfill sites for disposal; the same truck capacities and distance used for S_1 and S_2 were considered here. Emissions, landfill gas generation and material inputs were estimated based on Doka (2003a). Leachate flow was set at 64 m^3/d, while 40% of the generated gas was assumed to be emitted directly to the atmosphere and the remaining 60% (Bezama et al. 2013) was recovered and used as described in section 2.3.6.

2.3.5 Sub-system 10: Leachate treatment

Leachate generated due to sludge disposal was treated according to Doka (2003b). Direct emissions and electricity consumption were accounted based on leachate characterization.

2.3.6 Sub-system 11: Electricity recovery

Recovered landfill gas is burned as an alternative to avoid direct methane emissions (S_{0a}) or to produce electricity (S_{0b}). Electricity generation in S_4 (E; kWh) was determined using Eq. (1), where P_m represents methane production (m^3/d), LCV is the lower heating value of methane (17,657 BTU/m^3), h represents the hours of operation (21 h/day) and CR is the calorific rate (12,000 BTU/kWh) of internal combustion engines (Colmenares and Santos 2008).

$$E\ (kWh) = \frac{P_m \cdot LCV \cdot h}{CR} \qquad (1)$$

2.4 Life Cycle Impact Assessment (LCIA)

Impact categories were selected based on the correspondence between LCI data and potential environmental impacts and previous reports for sludge management (Corominas et al. 2013; Yoshida et al. 2013). Moreover, the focus was oriented towards categories related to organic matter and nutrients flows, as those are more clearly influenced by the inclusion of PT in the advanced digestion scenario. Categories selected include climate change, abiotic depletion, acidification and eutrophication (terrestrial, freshwater and marine) impact potentials. Recommendations of the International Reference Life Cycle Data System (ILCD) (JRC European commission 2011) were followed for the selection of the assessment methodologies. Detailed information about methodologies can be found Table 3. The impact results were calculated by means of SimaPro 8.0.2 software, using a midpoint approach.

Table 3. Methodologies used for impact assessment

Impact category	Initials	Unit	LCIA method	References
Climate change potential	CCP	kg CO_{2eq}	IPCC	Forster et al. (2007)
Abiotic depletion potential	ADP	kg Sb_{eq}	CML	Guinée (2002)
Acidification potential	AP	$mol_c\ H^+_{eq}$	Accumulated Exceedance	Seppälä et al. (2006)
Terrestrial eutrophication potential	TEP	$mol_c\ N_{eq}$	Accumulated Exceedance	Seppälä et al. (2006)
Freshwater eutrophication potential	FEP	kg P_{eq}	EUTREND model as implemented in ReCiPe	Struijs et al. (2009)
Marine eutrophication potential	MEP	kg N_{eq}	EUTREND model as implemented in ReCiPe	Struijs et al. (2009)

2.5 Sensitivity Analysis

Different types of uncertainty are part of LCA studies, related to inventory parameters, modeling of environmental impacts and scenario choices, among other factors (Huijbregts 2002). In this work, we focused on uncertainty derived from assumptions and estimations made during the LCI phase, and therefore a sensitivity analysis was performed over parameters that showed a significant effect over results. In the base scenario, it was assumed that all carbon present in sewage and the associated emissions were of biological origin. However, the presence of fossil carbon compounds in sewage has been previously reported (Law et al. 2013), which can contribute to greenhouse gasses (GHG) emissions during treatment and sludge management. Therefore, a sensitivity analysis was performed on the presence of fossil carbon in CO_2 emissions, in the range of 0 – 30% of total sludge-related CO_2 emissions.

Moreover, it was also assumed that all heat generated in the CHP unit in S_1 and S_2 could be used to replace heat generated from fossil sources, particularly natural gas. While this scenario is desirable as heat could be used for digester heating or sludge drying in AD plants, it is not always feasible due to technical or economical limitations. Therefore, a sensitivity analysis was performed on the percentage of heat (0 – 100%) from biogas burning that could be used to replace natural gas in S_1 and S_2.

3. RESULTS AND DISCUSSION

Table 4 and Figures 2 to 5 presents the inventory data for the four scenarios. Broadly, AD scenarios (S_1 and S_2) resulted in higher energy consumption, lower emissions and higher energy replacement compared with the chemical stabilization scenarios. PT inclusion in S_2 resulted in higher electricity and heat consumption, emissions and requirements for the transport and disposal of sludge compared to S_1, while it also resulted in a higher replacement of electricity and heat due to the increase in biogas production.

Table 4. Summary of the inventory for the four assessed scenarios. All quantities are referred to the functional unit.

	S_1 (conventional digestion)	S_2 (advanced digestion)	S_{0a} (lime and landfilling)	S_{0b} (lime and landfilling + ER)
Inputs				
Electricity (kWh)	167.0	234.8	97.5	97.5
Heat (kWh)	637.4	649.1	--	--
Polyacrylamide (kg)	9.1	9.1	9.1	9.1
Transport (tkm)	369.4	501.6	333.2	333.2
Lime (kg)	--	--	164.7	164.7
Outputs				
Emissions to air				
CH_4 biogenic (kg)	8.9	10.6	23.7	23.7
CO_2 biogenic (kg)	597.4	712.6	307.7	307.7
H_2S (kg)	0.01	0.01	$9.0 \bullet 10^{-5}$	$9.0 \bullet 10^{-5}$
NH_3 (kg)	0.72	0.85	14.0	14.0
N_2O (kg)	0.17	0.16	0.04	0.04
NO_x (kg)	0.08	0.10	--	--
Emissions to water				
PO_4^{2-} (kg)	27.2	27.6	28.9	28.9
NO_3^- (kg)	264.1	264.5	262.8	262.8
NH_4^+ (kg)	58.0	58.3	60.0	60.0
NO_2 (kg)	3.4	3.4	3.6	3.6
N_{part} (kg)	2.6	2.6	2.7	2.7
Avoided products				
Energy				
Electricity (kWh)	704.5	839.1	--	64.9
Heat (kWh)	750.4	894.8	--	--
Fertilizers				
N (as ammonium sulphate) (kg)	11.5	11.0	--	--
P_2O_5 (as diammonium phosphate) (kg)	1.6	1.4	--	--

ER: Electricity Recovery

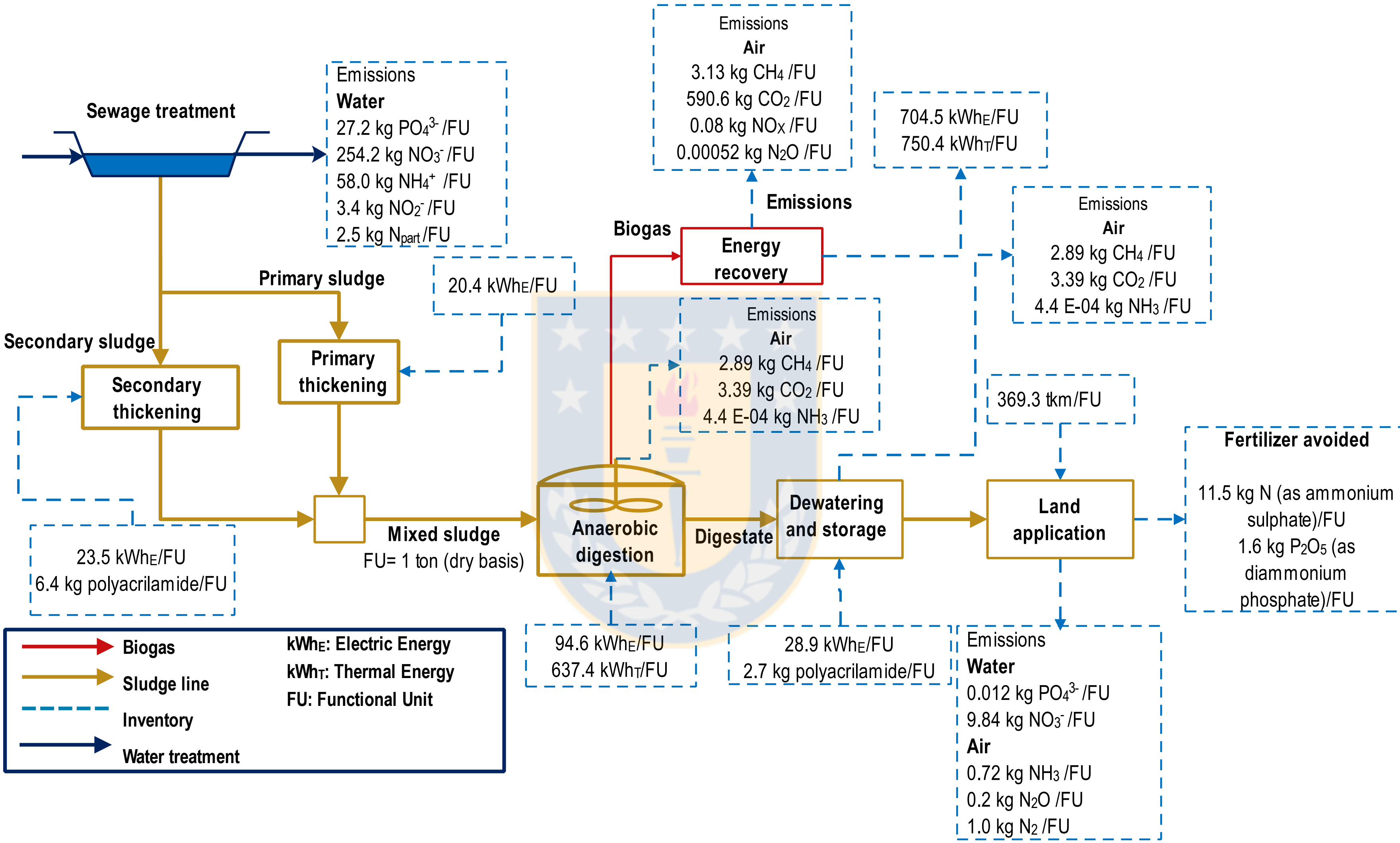

Figure 2. Inventory for Scenario 1

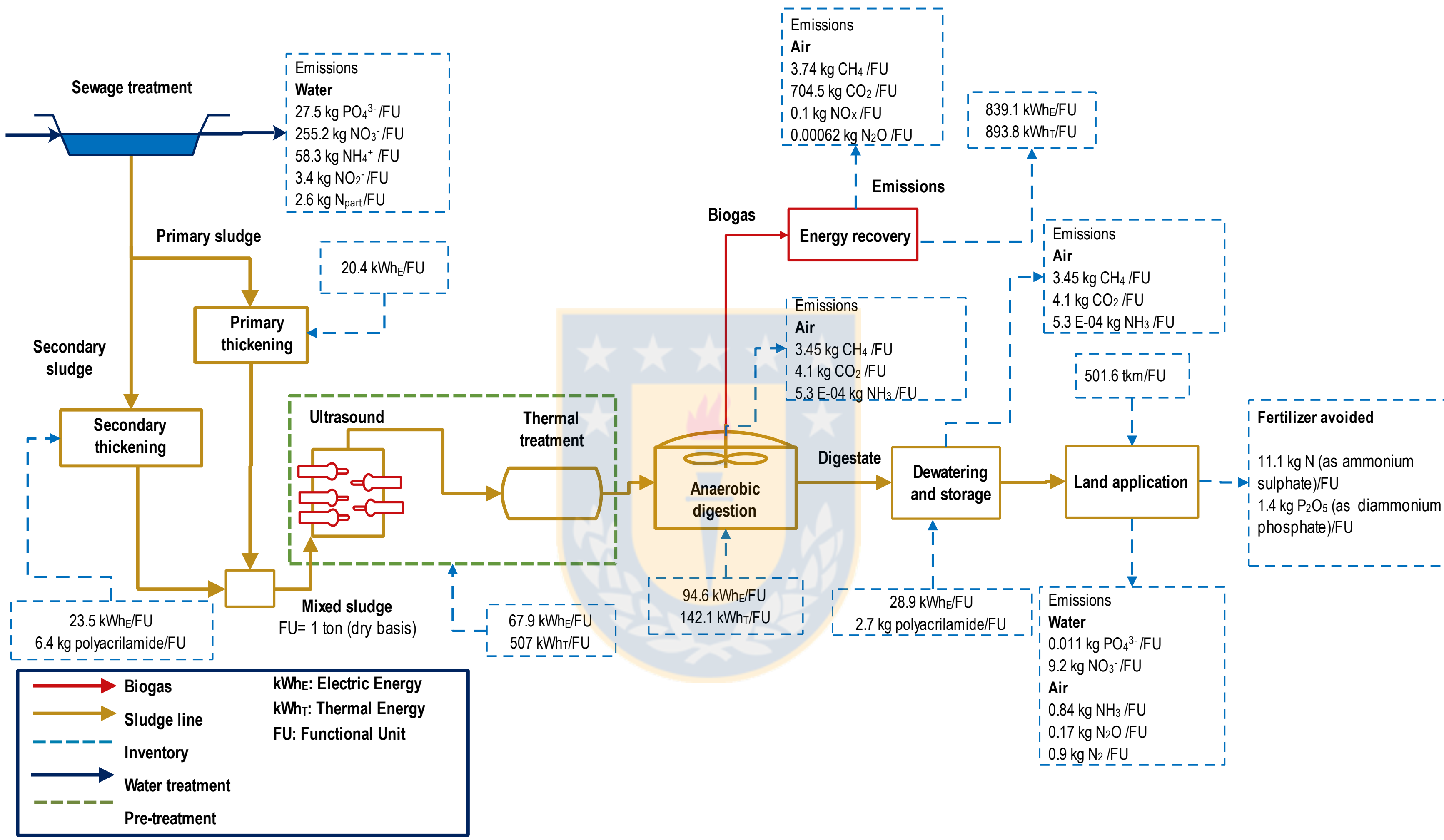

Figure 3. Inventory for Scenario 2

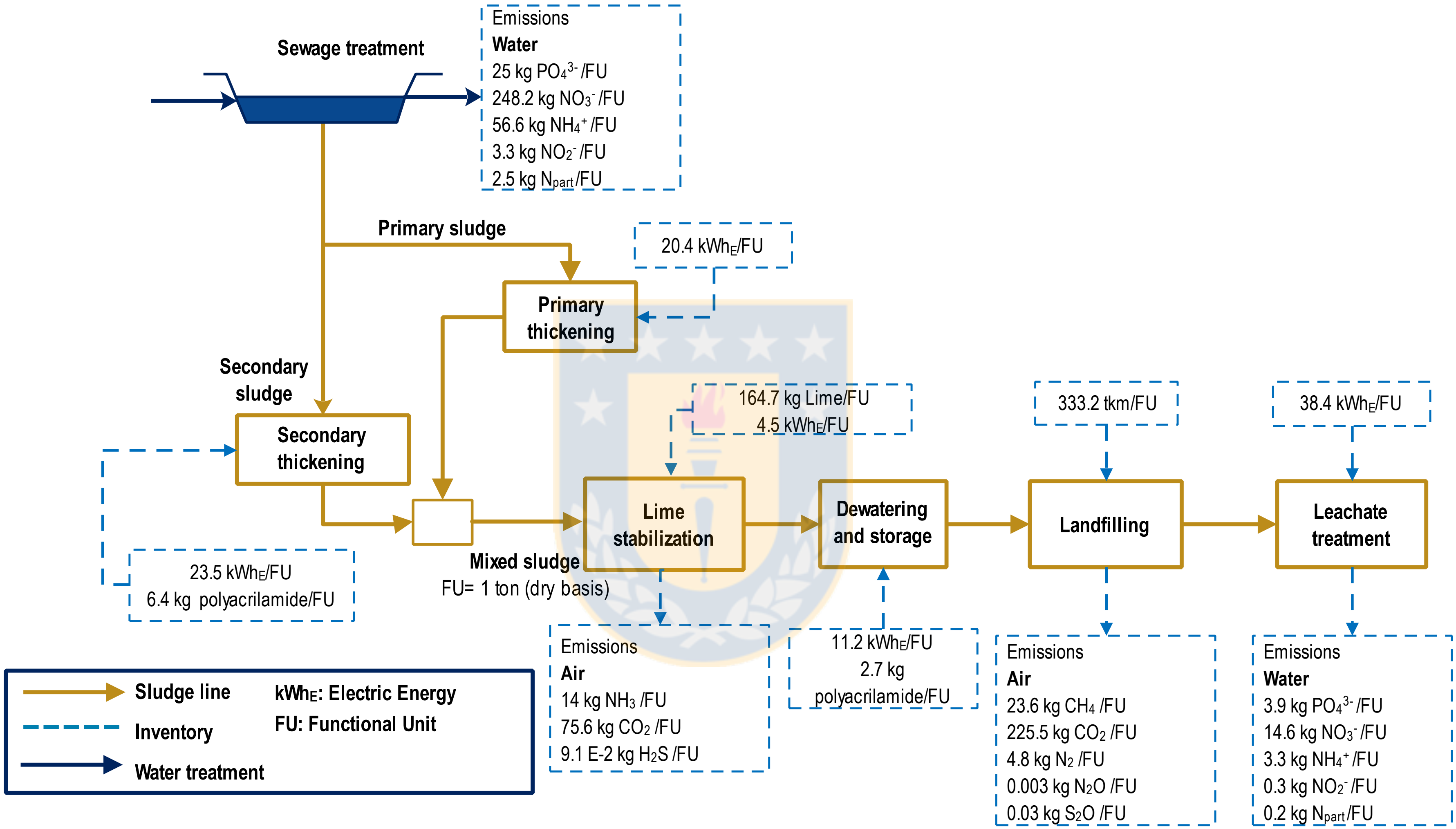

Figure 4. Inventory for Scenario 0a

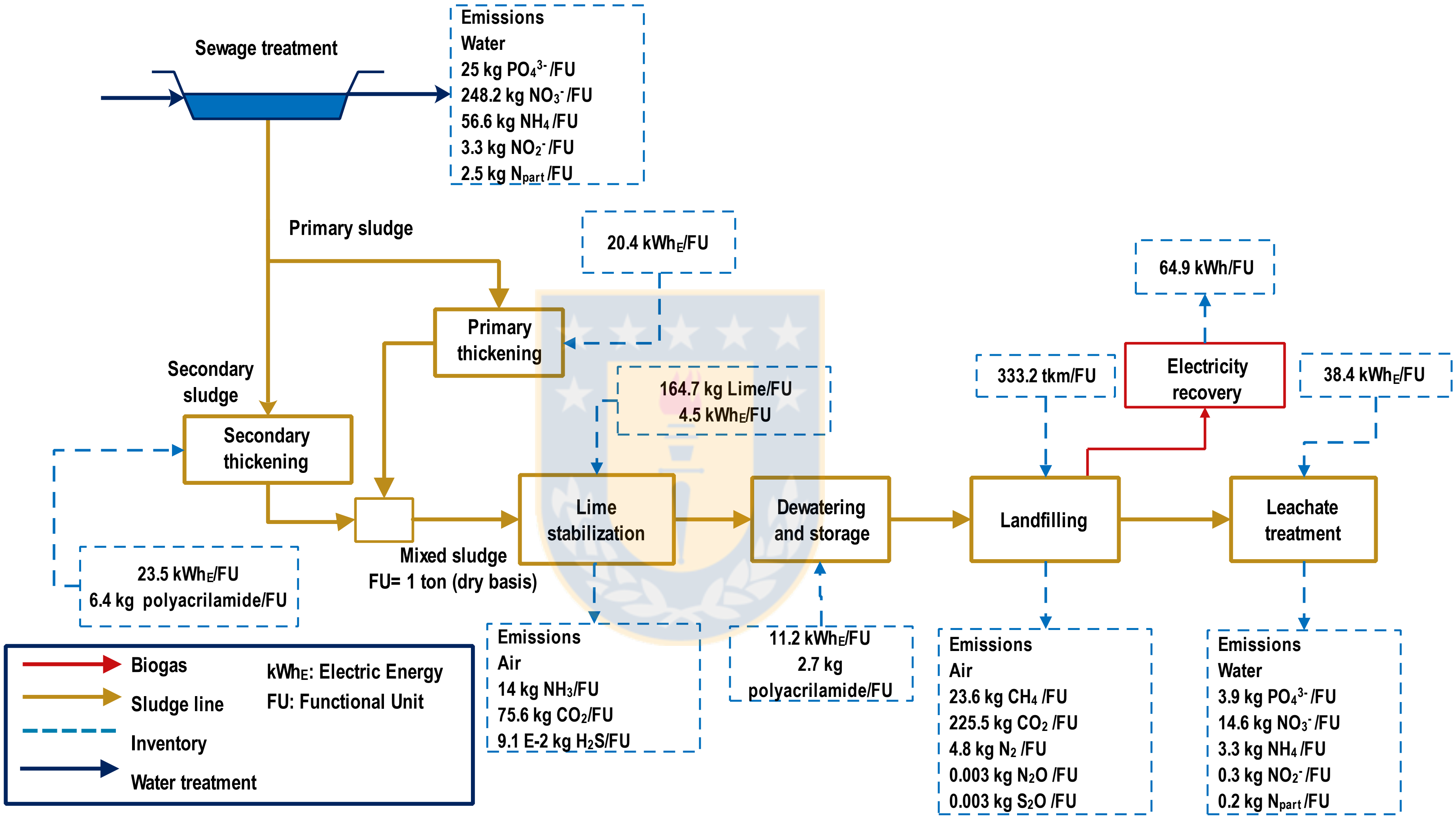

Figure 5. Inventory for Scenario 0b

The environmental impact assessment results are presented in Figure 6, categorized into the different sub-systems and discussed accordingly.

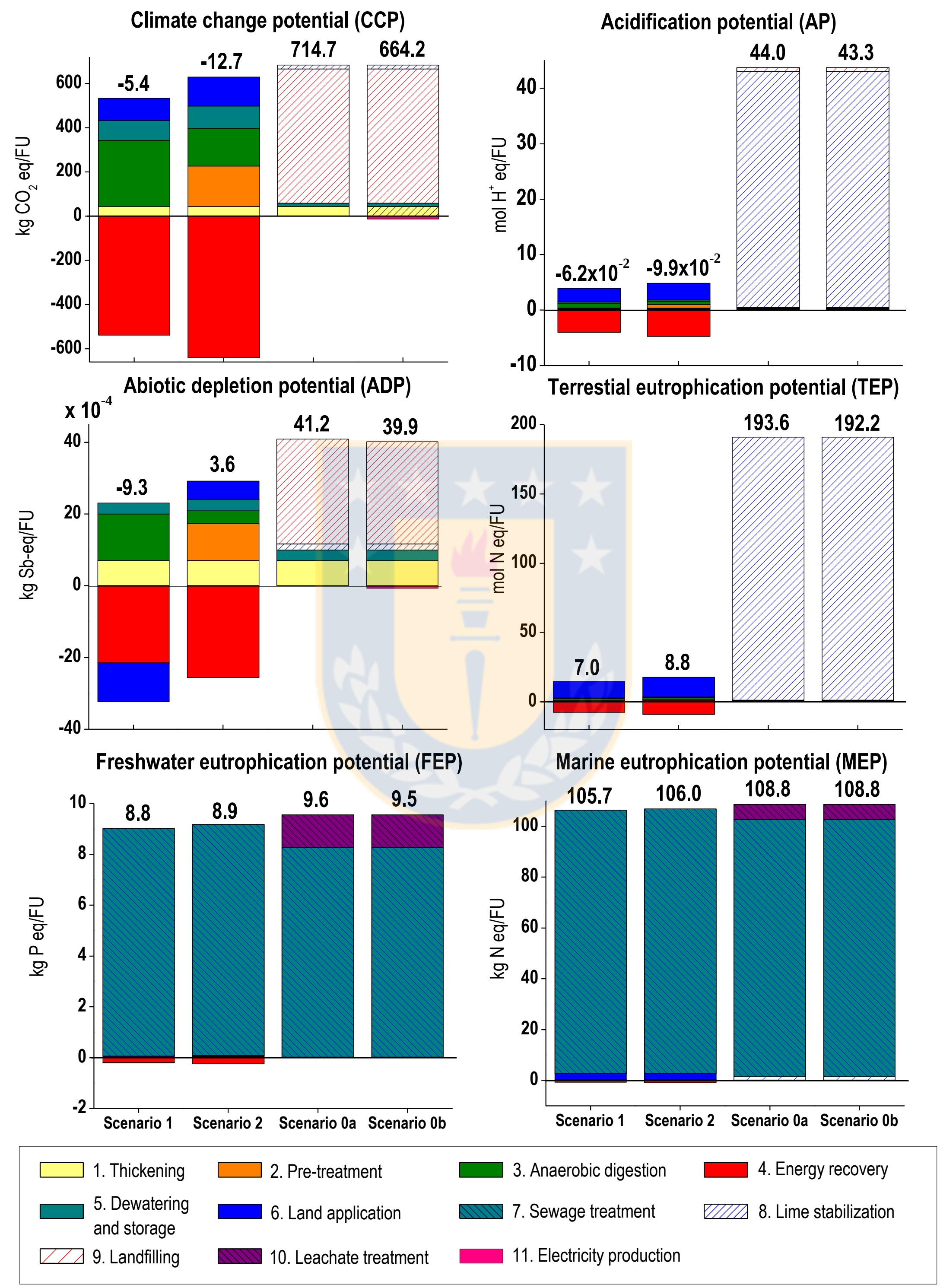

Figure 6. Comparison of the environmental impact for the four scenarios assessed. Values over the bars indicate the net environmental impact for the corresponding scenario.

3.1 Climate change potential

The scenarios that included biological stabilization through AD resulted in lower CCP, as observed in Figure 3 (S_{0a}>S_{0b}>S_1>S_2). The main contributors in S_1 and S_2 were the direct release of CH_4, electricity consumption and chemicals consumed during thickening and dewatering (Figure 2). While PT resulted in increased energy consumption, emissions and requirements for the transport of sludge, the overall CCP was lower than in S_1 due to the greater replacement of electricity and heat. The observed effect on the transport and spreading of sludge was related to the lower water recovery from the digestate (Table 1), comparable to what has been reported previously for similar PT processes (Neumann et al. 2016). Regarding S_{0a} and S_{0b}, the emission of landfill gas was the main contributor to CCP, in accordance with previous reports (Suh and Rousseaux 2002; Bezama et al. 2013). GHG emissions could not be compensated by electricity recovery from landfill gas, which resulted in a CCP reduction of approximately 5% in S_{0b} compared to S_{0a}.

3.2 Abiotic depletion potential

Regarding ADP, S_1 was the only scenario where a net environmental benefit was observed (Figure 3; S_{0a}>S_{0b}>S_2>S_1), associated with the replacement of electricity, heat and commercial fertilizers (Figure 2). In S_2, the replacement of conventional energy sources was higher than in S_1; however, the higher consumption of fossil fuels associated with the transport and spreading of sludge plus the reduced replacement of fertilizers due to the lower concentration and loads of N and P in sludge (Table 2) resulted in an increased ADP.

ADP in S_{0a} and S_{0b} was mostly associated with sludge landfilling, followed by electricity consumption during thickening/dewatering and lime production. The most significant contributor to ADP during landfilling was the use of fossil fuels for transport. The production of electricity in S_{0b} resulted in a 2% reduction in ADP compared to S_{0a}.

3.3 Acidification and terrestrial eutrophication potential

S_1 resulted in the lowest AP and TEP, as observed in Figure 3 (S_{0a}>S_{0b}>S_2>S_1). The incorporation of the PT slightly increased both categories mainly due to emissions during land application, which represented the main contributor in the corresponding scenarios (Figure 2). This was associated with increased NH_3 volatilization due to a higher N-NH_4^+ load in sludge applied to soil (Table 2). The use of management practices oriented toward the efficient use of sludge N in soil could be used to mitigate AP and TEP impacts in those scenarios.

The AP and TEP values for S_{0a} and S_{0b} were more than 700 times higher than those of S_1. This was mostly related to the emission of NH_3 during lime stabilization, representing approximately 98% of the total contribution to both impact categories. The use of odor and NH_3 filters during this step could lead to decreased AP and TEP, in addition to the increased acceptance of WWTPs by the surrounding population.

3.4 Freshwater eutrophication potential

Regarding FEP, S_{0a} and S_{0b} presented higher values than S_1 and S_2, as observed in Figure 3 (S_{0a}>S_{0b}>S_2>S_1). However, as this category was mostly associated with P emissions during sewage treatment (80% of contribution; Figure 2), the differences between scenarios were less than 9%.

The overall effect of PT on FEP was only a 1.3% variation with respect to S_1, mainly due to the increased P concentration and load in the dewatering process supernatant (Table 2). The overall contribution of land application to FEP was negligible for both S_1 and S_2 (<0.03%), which was related to the low mobility of P in soil assumed in this study (Doka 2003b). However, it is important to note that the application of fertilizers such as sludge over a long period of time or with high rates could result in soil oversaturation of P and its release to water bodies (Nair 2014), which can be expected if disposal is the primary goal of sludge land application.

3.5 Marine eutrophication potential

Figure 3 shows that MEP presents the same trend that FEP in terms of scenario performance (S_{0a}>S_{0b}>S_2>S_1) and main contributor (i.e., sewage treatment; Figure 2), with differences of less than ~3% between scenarios. However, NO_3^- emissions from land application in S_1 – S_2 and leachate treatment in S_{0a} – S_{0b} were also relevant. The principal effect of PT was related to an increased N concentration and load in the dewatered supernatant recirculated to sewage treatment (Table 2), which resulted in a negligible ~0.3% variation in MEP in S_2 compared to S_1.

Detailed contribution of sub-systems to all impact categories in the four assessed scenarios is presented in Tables 5 to 8.

Table 5. Contribution of each subsystem to impact categories in Scenario 1.

Impact category	Subsystem						Total
	1	3	4	5	6	7	
CCP ($kgCO_{2eq}/FU$)	43.84	299.23	-539.05	88.94	101.68	0.00	-5.36
ADP ($*10^{-4}$) ($kgSb_{eq}/FU$)	7.01	12.98	-21.49	3.09	-10.87	0.00	-9.28
AP ($*10^{-2}$) ($mol_cH^+_{eq}/FU$)	37.50	86.15	-399.34	21.43	248.10	0.00	-6.16
TEP (mol N_{eq}/FU)	0.86	1.44	-7.55	0.48	11.81	0.00	7.04
FEP (kg N_{eq}/FU)	0.01	0.04	-0.20	0.01	0.00	8.96	8.81
MEP (kg P_{eq}/FU)	0.12	0.14	-0.71	0.06	2.48	103.64	105.73

CCP: Climate change potential; ADP: Abiotic depletion potential; AP: Acidification potential; TEP: Terrestrial eutrophication potential; FEP: Freshwater eutrophication potential; MEP: Marine eutrophication potential.

Table 6. Contribution of each subsystem to impact categories in Scenario 2.

Impact category	Subsystem							Total
	1	2	3	4	5	6	7	
CCP ($kgCO_{2eq}/FU$)	43.84	182.62	170.49	-641.74	101.39	130.76	0.00	-12.65
ADP ($*10^{-4}$) ($kgSb_{eq}/FU$)	7.01	10.25	3.66	-25.59	3.09	5.14	0.00	3.56
AP ($*10^{-2}$) ($mol_cH^+_{eq}/FU$)	37.50	64.64	57.01	-475.26	21.42	304.60	0.00	9.91
TEP (mol N_{eq}/FU)	0.86	1.06	1.10	-8.97	0.48	14.28	0.00	8.81
FEP (kg N_{eq}/FU)	0.01	0.03	0.03	-0.24	0.01	0.00	9.09	8.93
MEP (kg P_{eq}/FU)	0.12	0.10	0.10	-0.84	0.06	2.43	104.04	106.02

CCP: Climate change potential; ADP: Abiotic depletion potential; AP: Acidification potential; TEP: Terrestrial eutrophication potential; FEP: Freshwater eutrophication potential; MEP: Marine eutrophication potential.

Table 7. Contribution of each subsystem to impact categories in Scenario 0a.

Impact category	Subsystem						Total
	1	8	5	9	10	7	
CCP ($kgCO_{2eq}/FU$)	43.84	18.24	14.55	607.07	31.05	0.00	714.74
ADP ($*10^{-4}$) ($kgSb_{eq}/FU$)	7.01	1.70	2.91	29.23	0.40	0.00	41.24
AP ($mol_cH^+_{eq}/FU$)	0.38	42.58	0.12	0.73	0.20	0.00	44.00
TEP (mol Neq/FU)	0.86	189.66	0.29	2.39	0.40	0.00	193.60
FEP (kg N_{eq}/FU)	0.01	0.00	0.00	0.01	1.29	8.26	9.57
MEP (kg P_{eq}/FU)	0.12	1.35	0.05	0.15	5.97	101.19	108.83

CCP: Climate change potential; ADP: Abiotic depletion potential; AP: Acidification potential; TEP: Terrestrial eutrophication potential; FEP: Freshwater eutrophication potential; MEP: Marine eutrophication potential.

Table 8. Contribution of each subsystem to impact categories in Scenario 0b.

Impact category	Subsystem							Total
	1	8	5	9	10	7	11	
CCP ($kgCO_{2eq}/FU$)	43.84	18.24	14.55	569.06	31.05	0.00	-12.53	664.19
ADP ($*10^{-4}$) ($kgSb_{eq}/FU$)	7.01	1.70	2.91	28.55	0.40	0.00	-0.68	39.88
AP ($mol_cH^+_{eq}/FU$)	0.38	42.58	0.12	0.24	0.20	0.00	-0.26	43.26
TEP (mol N_{eq}/FU)	0.86	189.66	0.29	1.71	0.40	0.00	-0.68	192.24
FEP (kg N_{eq}/FU)	0.01	0.00	0.00	-0.01	1.29	8.26	-0.02	9.54
MEP (kg P_{eq}/FU)	0.12	1.35	0.05	0.15	5.97	101.19	-0.06	108.77

CCP: Climate change potential; ADP: Abiotic depletion potential; AP: Acidification potential; TEP: Terrestrial eutrophication potential; FEP: Freshwater eutrophication potential; MEP: Marine eutrophication potential.

3.6 Sensitivity analysis

Table 9 shows the sensitivity analysis performed on the presence of fossil carbon in sludge CO_2 emissions.

Table 9. Sensitivity analysis for fossil carbon presence in sludge-related CO_2 emissions.

	% fossil carbon	$CO_{2\ biogenic}$ (kg/FU)	$CO_{2\ fossil}$ (kg/FU)	CCP (kg CO_{2eq}/FU)	ΔCCP (kg CO_{2eq}/FU)	CCP Slope*
S_1 (conventional digestion)	0	597.4	0.0	-5.4	-	6.0
	10	537.7	59.7	54.4	59.8	
	20	477.9	119.5	114.1	119.5	
	30	418.2	179.2	173.9	179.3	
S_2 (advanced digestion)	0	712.6	0.0	-12.6	-	7.1
	10	641.3	71.3	58.6	71.2	
	20	570.1	142.5	129.9	142.5	
	30	498.8	213.8	201.1	213.7	
S_{0a} (lime and landfilling)	0	307.7	0.0	713.9	-	3.1
	10	276.9	30.8	744.7	30.8	
	20	246.2	61.5	775.5	61.6	
	30	215.4	92.3	806.0	92.1	
S_{0b} (lime and landfilling + ER)	0	307.7	0.0	677.5	-	3.1
	10	276.9	30.8	708.3	30.8	
	20	246.2	61.5	739.1	61.6	
	30	215.4	92.3	769.8	92.3	

* Expressed as $kgCO_{2eq}/FU$ - $\%_{fossilcarbon}$; CCP: Climate change potential; ΔCCP: variation in CCP compared with the base scenario.ER: Electricity Recovery

A higher rate of change was observed for S_2 due to the higher CO_2 emissions associated with biogas leakage and burning. When the fossil carbon presence was higher than 6.3%, CCP in S_2 was higher than in S_1.

Table 10 shows the sensitivity analysis performed on the heat replaced by biogas burning.

Table 10. Sensitivity analysis for the heat replaced by biogas burning in S_1 and S_2.

	% of produced heat used as replacement of natural gas	CCP (kg CO_{2eq}/FU)	ADP (*10^{-4}) (kg Sb_{eq}/FU)	AP (*10^{-2}) (mol$_c$ N_{eq}/FU)
S_1 (conventional digestion)	100	-5.4	-9.3	-6.2
	80	37.4	-6.5	2.7
	60	80.2	-3.6	11.5
	40	123.0	-0.8	20.4
	20	165.8	2.0	29.2
	0	208.6	4.8	38.1
	Slope*	-2.1	-0.14	-0.44
S_2 (advanced digestion)	100	-12.7	3.6	9.9
	80	38.3	6.9	20.4
	60	89.3	10.3	31.0
	40	140.3	14.0	41.5
	20	191.2	17.0	52.0
	0	242.2	20.4	65.3
	Slope*	-2.5	-0.17	-0.55

* Expressed as the reference unit for corresponding impact category per FU and % replaced heat. CCP: Climate change potential; ADP: Abiotic depletion potential; AP: Acidification potential.).

The heat recovery strategy associated with AD was of importance for the CCP, ADP and AP impact categories, and S_2 had the highest slope. S_2 exhibited the highest values for ADP and AP under all conditions, while CCP was the highest for this scenario when less than 82.2% of the produced heat was used to replace the heat from natural gas.

3.7 Overall comparison between scenarios

Figure 7 shows the comparison between the scenarios in terms of their relative impact. From an overall perspective, the utilization of AD followed by land application was the most appropriate alternative, with lower impacts in all selected categories. It is important to note that our results are valid in similar conditions to those assessed, as previous reports show that management strategies and selected impact categories could greatly affect the outcome results of sludge management LCA, and therefore other alternatives could result in even better environmental performance than AD (Yoshida et al. 2013). However, this work illustrates that sludge valorization through energy recovery and land application represents a central aspect of sustainable sludge management, as opposed to practices that consider sludge only as waste (i.e., landfilling). In the alkalinization scenarios, stabilization and landfilling represented the main contributors to environmental impacts, which is in agreement with reports identifying emissions, lime production and the lack of valorization of sludge as important environmental hotspots (Yoshida et al. 2013).

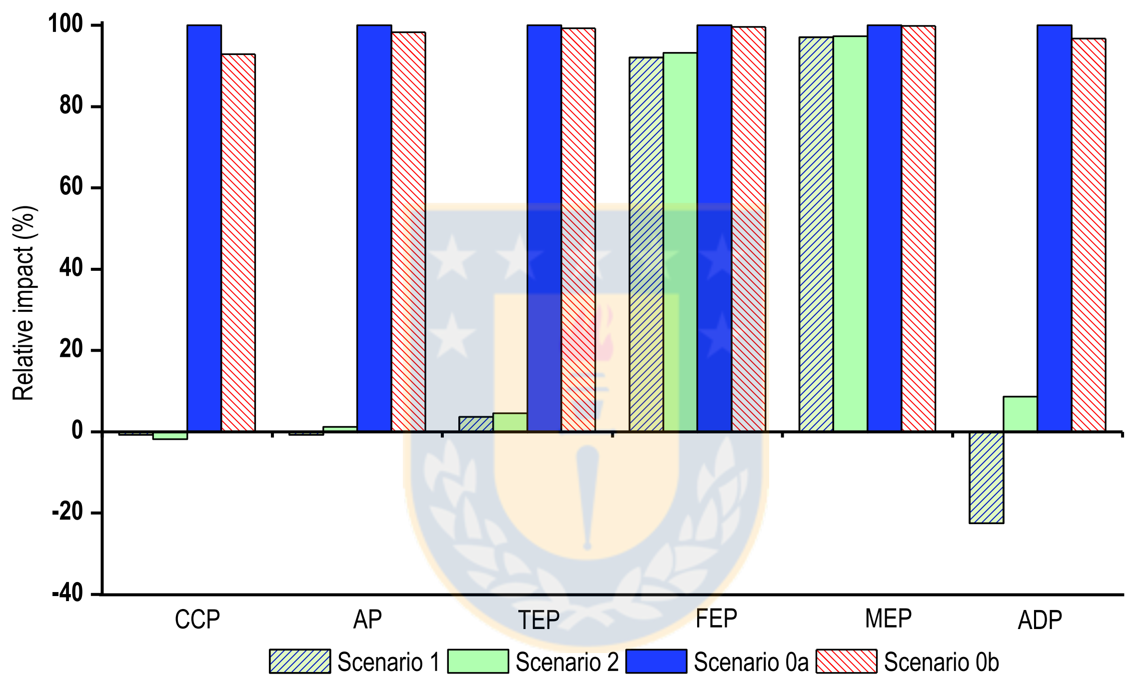

Figure 7. Relative impact of the four scenarios under study, taking the highest value for every category as baseline.

The comparison between advanced and conventional digestion indicates that the burdens associated with PT need to be considered. Sequential PT had positive effects on energy recovery and CCP, but due to the greater needs associated with transport/spreading and the lower replacement of commercial fertilizers, ADP was negatively affected. This was associated with operational effects such as the lower water recovery from the digestate and changes in NH_4^+, N and P concentrations and loads in the sludge and supernatant. These factors also affected the AP, TEP, FEP and MEP impact categories, but the overall values were similar to the conventional digestion scenario. The sensitivity of the results to the assessed parameters should also be accounted when comparing the performance of the different scenarios, as those show different behaviors when modified (Tables 5 and 6).

It is important to note that one main effect of PT on digestion is associated with increased biodegradation kinetics (Carvajal et al. 2013; Neumann et al. 2017). Intensification of the digestion process could lead to smaller digester volumes and decreased capital costs, increasing the attractiveness of the technology for smaller WWTPs. Currently, there are only 6 WWTPs in Chile that use AD for sludge stabilization; these plants treat sewage that exceeds 50,000 person equivalent (SISS 2016). As the studied PT resulted in a similar performance to conventional digestion, this may become an interesting tool for the energetic valorization of sludge in smaller plants, which could led to a decrease in the environmental burdens of sludge management in Chile compared to the current scenario. To further optimize the environmental performance of advanced AD, operational aspects such as organic loading rate and retention time should also be considered prior to its widespread application, as previous reports state their relevance over the life-cycle impacts of AD (Rodriguez-Verde et al. 2014).

Overall, the environmental performance of the advanced digestion scenario was relatively more sensitive to the presence of fossil carbon in sewage and to the effective valorization of the produced heat. This was related to process intensification and the corresponding higher emissions and energy consumption and generation. The chemical stabilization scenarios showed relatively lower sensitivity to the presence of fossil carbon in CO_2 emissions, which was mostly related to its lower contribution compared with leaked methane from landfill sites. However, even the worst-case scenarios of digestion in terms of fossil carbon presence exhibited lower CCP than the best chemical stabilization scenarios.

4. CONCLUSIONS

The combination of AD and the agricultural valorization of digestate exhibited lower potential impacts than the chemical stabilization scenarios in all selected categories. When sequential ultrasound-thermal PT was included, the main effects were a decrease in CCP and an increase in ADP. The influence of PT on digestion performance was related to its effects on energy recovery, transport requirements and nutrient loadings, highlighting the need to assess its performance from a life-cycle perspective. Advanced digestion including the assessed PT showed a similar performance to conventional digestion, but the results were more sensitive to the possible emission of fossil CO_2 and heat valorization strategies. Considering the results, PT can represent an interesting alternative for the implementation of AD in WWTPs lacking sludge valorization strategies, which in the case of Chile, could led to decreased environmental burdens compared to the current scenario.

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CAPÍTULO VII

DISCUSIÓN

1. EFICIENCIA DE SOLUBILIZACIÓN E INFLUENCIA DEL PRE-TRATAMIENTO SOBRE LAS CARACTERÍSTICAS DEL LODO

El primer objetivo específico del estudio fue determinar la influencia del pre-tratamiento secuencial sobre las características del lodo, evaluada tanto mediante ensayos batch (Capítulo IV) como durante la operación de los reactores semi-continuos (Capítulo V). Dentro de los parámetros evaluados se encuentran la solubilización y transformación de la materia orgánica (DQO, carbohidratos, proteínas, AGV, amonio), actividad enzimática hidrolítica (proteasa y amilasa) e indicadores de contaminación por patógenos (coliformes y colifagos).

El lodo sanitario obtenido desde la PTAS Biobío presentó concentraciones de 25.1 – 64.6 g/L sólidos totales, 19.9 – 45.6 g/L sólidos volátiles y 37.8 – 80.5 g/L DQO total durante el periodo experimental. La relación entre DQO total y sólidos volátiles para las muestras fluctuó entre 1.3 y 2.0 gDQO/gSV, con un promedio de 1.8 ± 0.4 gDQO/gSV. Dicha relación es comparativamente más alta que el rango observado en literatura de 1.3 – 1.7 gDQO/gSV (Davidsson & Jansen 2006; Borowski & Szopa 2007; Xie et al. 2007; Montusiewicz et al. 2010), lo que indicaría la presencia en el lodo de compuestos con un bajo estado de oxidación, tales como lípidos y alcoholes (Van Lier et al. 2008). Esto puede estar asociado a la fracción de lodo primario de las muestras (65% de los ST de acuerdo a balances de masa), dado que la presencia de lípidos tiende a ser mayor en estos comparado con lodos secundarios (Wilson & Novak 2009),

Por otra parte, la concentración de amonio en las muestras fue de 0.2 – 0.7 g NH_4^+-N/L, con un promedio de 0.3 ± 0.2 g NH_4^+-N/L, mientras que la conductividad eléctrica fluctuó entre 0.7 y 2.9 mS/cm, con un promedio de 1.7 ± 0.5 mS/cm. Estos valores se encuentran en el mismo orden que reportes previos (Borowski & Szopa 2007; Ruffino et al. 2015). Las tendencias entre estos dos parámetros fueron similares durante la operación de los digestores continuos, y a su vez se asociaron con la variabilidad observada en la concentración de sólidos y DQO del lodo, como puede apreciarse en las Figuras 2 (a y c) y 3 del Capítulo VI.

La Tabla 1 resume el efecto que tuvo el pre-tratamiento secuencial sobre las concentraciones de carbohidratos y proteínas solubles, AGV y amonio en el lodo, además de las actividades de proteasa y amilasa en fase soluble.

Tabla 1. Influencia del pre-tratamiento sobre la concentración soluble de macromoléculas, AGV, amonio y la actividad de proteasa y amilasa en el lodo.

Condiciones experimentales		**Parámetro**					
Ultrasonido (kJ/kgST)	**Tratamiento térmico (h)**	**$CARB_S$ (mg/L)**	**$PROT_S$ (mg/L)**	**AGV (mgDQO/L)**	**Amonio (mg/L)**	**Proteasa (U/mL)**	**Amilasa (U/mL)**
0	0	58	330	671 – 1143	286	0.006	0.106
0	3	310	1087	683	-	0.017	0.278
0	13	305	1456	718	-	0.028	0.347
500	0	69	442	825	-	0.007	0.097
500	3	323	1159	743	-	0.020	0.380
500	13	361	1522	899	-	0.028	0.378
2000	0	-	-	696 – 1146	301	-	-
2000	8	-	-	727 – 1084	555	-	-
15500	0	496	1816	1072	-	0.022	0.296
15500	3	507	2098	740	-	0.024	0.403
15500	13	544	1978	991	-	0.031	0.468
30500	0	579	2504	1248	-	0.029	0.424
30500	3	591	2547	1331	-	0.030	0.510
30500	13	653	2551	1387	-	0.031	0.503

$CARB_S$: Carbohidratos solubles; $PROT_S$: Proteínas solubles; AGV: Ácidos grasos volátiles; DQO: Demanda química de oxígeno.

Como se discutió en el Capítulo IV, el pre-tratamiento secuencial resultó en incrementos de 458 – 1030% y 252 – 674% en la concentración soluble de carbohidratos y proteínas, respectivamente, similar a reportes previos (Dhar et al. 2012). El mayor incremento en la concentración de carbohidratos solubles estaría relacionado con su asociación más débil con los flóculos del lodo y por ende mayor susceptibilidad a la solubilización (Bougrier et al. 2008; Wilson & Novak 2009), además de su menor concentración inicial. De manera similar, las actividades de amilasa y proteasa fueron 1.6 – 3.8 y 1.8 – 4.3 veces más altas después del pre-tratamiento, respectivamente, sin observarse efectos de inactivación y con tendencias similares a estudios previos (Yan et al. 2010). Esto indica que el pre-tratamiento secuencial resulta efectivo para incrementar la actividad hidrolítica endógena del lodo en las condiciones estudiadas, de manera similar a lo señalado por autores como Carvajal et al. (2013), Song & Feng (2011) y Yan et al. (2010).

La concentración total de AGV en el lodo fluctuó entre 671 y 1,143 mgDQO/L. Durante la realización de los ensayos batch, el pre-tratamiento causó incrementos de hasta 107% en la concentración de

AGV, mientras que durante la operación de los digestores se observó un incremento no significativo de 8%. Esta diferencia estaría asociada a la intensidad energética utilizada durante el pre-tratamiento, tal como se aprecia en la Tabla 1. Estudios previos han mostrado que la aplicación de ultrasonido y tratamiento térmico a baja temperatura pueden conllevar incrementos en la concentración de AGV en lodos, pero los resultados resultan dependientes de las condiciones operacionales y del estudio en particular. Si bien Appels et al. (2008) observaron incrementos de 150 – 500% en la concentración de AGV después de la aplicación de ultrasonido (168 – 8180 kJ/kgST), Martín et al. (2015) observaron un incremento de solo 5.5% en la concentración de AGV en lodo mixto al aplicar ultrasonido durante un tiempo de 15 min (>34,000 kJ/gST). De manera similar, Carvajal et al. (2013) observaron que el tratamiento térmico a 55°C resulta en incrementos de hasta ~3 veces en los AGV totales en lodo secundario, pero los resultados dependen de la concentración de sólidos y la presencia o ausencia de oxígeno en el medio. Por otra parte, Ferrer et al. (2008) observaron incrementos en la concentración de AGV en lodos secundarios sólo luego de 9 horas o más de tratamiento a 70°C, lo que atribuyeron a la actividad biológica endógena de los microorganismos.

La concentración de amonio en el lodo pre-tratado fue de 0.3 – 1.7 g NH_4^+-N/L, con un promedio de 0.6 ± 0.4 g NH_4^+-N/L. Esto representa un incremento de un 93% comparado con las muestras de lodo sin pre-tratar, asociado a la etapa de tratamiento térmico. Dado que dicho incremento no se relaciona con cambios en la concentración de AGV, es posible que haya sido causado por fenómenos físicos y no debido a reacciones biológicas fermentativas, como ocurre durante la digestión anaerobia (Gerardi 2003). Similar a los resultados observados, Bougrier et al. (2005) observaron que el principal efecto del ultrasonido (660 – 14,547 kJ/kgST) sobre el nitrógeno orgánico en lodos secundarios fue un 40% de solubilización, sin transformación significativa a amonio.

La Figura 1 resume los resultados obtenidos para el factor de solubilización de DQO en todas las condiciones de pre-tratamiento estudiadas, así como su influencia sobre la conductividad eléctrica, concentración de DQO soluble y amonio y la remoción de coliformes fecales y colifagos somáticos.

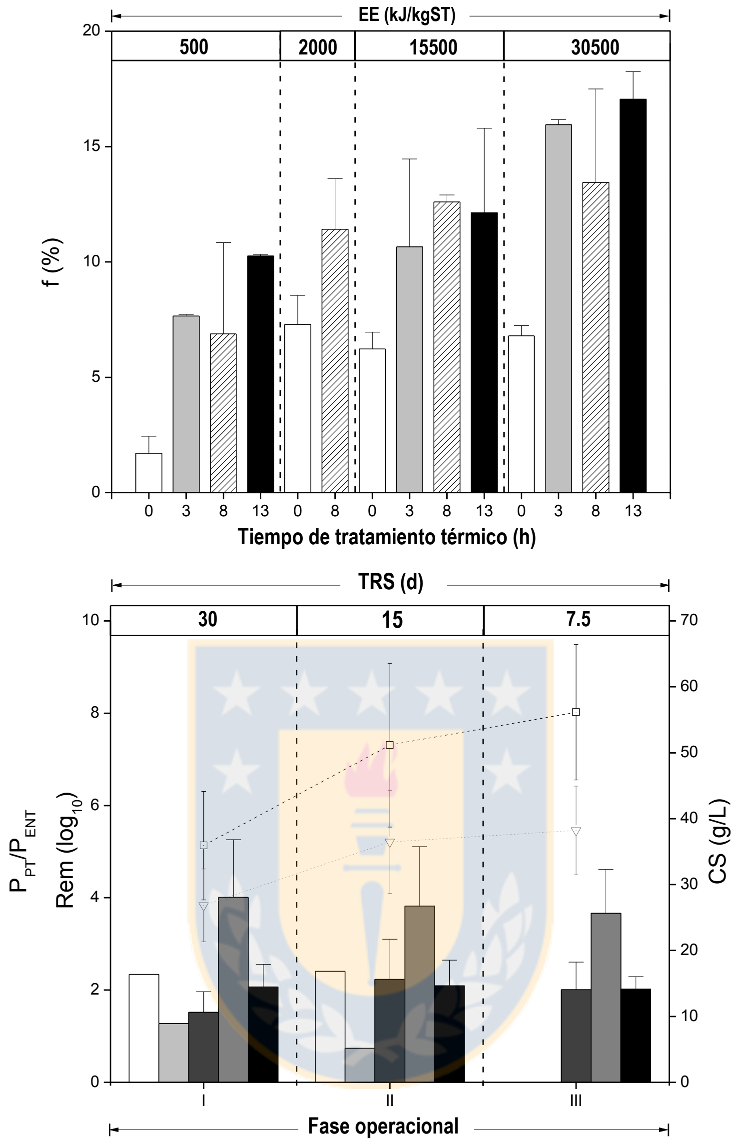

Figura 1. Efectos del pre-tratamiento sobre las características del lodo. a) Factor de solubilización de DQO (f) en función de la energía específica de ultrasonido (EE) y tiempo de tratamiento térmico, b) Remoción de coliformes fecales (□) y colifagos (■), relación entre el lodo pre-tratado y de entrada (P_{PT}/P_{ENT}) en términos de conductividad (■), DQOs (■) y amonio (■), y concentraciones de sólidos (CS) totales (⊟) y volátiles (▽) en el lodo durante las sub-fases del experimento en continuo.

La aplicación de ultrasonido al lodo resultó en factores de solubilización de DQO de 0.8 – 7.4%, mientras que el pre-tratamiento secuencial incrementó la solubilización hasta factores de 3.5 – 17.1%. Todas las variables independientes estudiadas (concentración del lodo, energía específica de ultrasonido y tiempo de tratamiento térmico) ejercieron efectos estadísticamente significativos y correlacionados positivamente con el factor de solubilización. Durante el tratamiento por ultrasonido, la solubilización mostró un comportamiento asintótico con respecto a la energía específica a partir de 15,500 – 23,000 kJ/kgST, mientras que con respecto a la concentración de sólidos se observó un máximo cerca del punto central (Capítulo IV). De manera similar, estudios previos han mostrado que concentraciones de sólidos sobre 3 – 4% resultan negativas para la eficiencia de solubilización del ultrasonido, debido a la atenuación de las ondas en el medio (Show et al. 2007; Pilli et al. 2011). El máximo de solubilización determinado mediante optimización fue de 7.6%, en condiciones de concentración del lodo de 41.8 kgST/L y aplicación de ultrasonido con una energía específica de 26,450 kJ/kgST.

Durante el pre-tratamiento secuencial, la influencia ejercida por la energía específica y el tiempo de tratamiento térmico fueron principalmente lineales, sin mostrar un valor máximo dentro del rango estudiado, mientras que la influencia de la concentración de sólidos presentó un comportamiento asintótico a partir de ~52 gST/L. El valor máximo de f predicho fue de 18.2%, correspondiente a una concentración del lodo de 59.3 kgST/L, ultrasonido con una energía específica de 30,500 kJ/kgST y 13 h de tratamiento térmico. Estudios previos señalan que la concentración de sólidos en el lodo puede favorecer la solubilización durante la aplicación de tratamientos térmicos a temperaturas de 50 – 90°C (Ruffino et al. 2015). En base a los resultados obtenidos, se observa que la integración de ambos procesos no solo permite incrementar el factor de solubilización, si no que permitiría operar con mayores concentraciones de sólidos comparado con procesos de ultrasonido convencional, lo que repercute positivamente en el desempeño energético del proceso (Pérez-Elvira et al. 2010).

El pre-tratamiento secuencial causó remociones logarítmicas de 2.3 a 2.4 en términos de coliformes fecales y 0.7 a 1.3 en términos de colifagos somáticos. Tanto la aplicación de ultrasonido como el tratamiento térmico contribuyeron a la eliminación de dichos indicadores. Reportes previos señalan que la aplicación de ultrasonido a baja frecuencia (~20 kHz) y temperaturas de ≥55°C permiten obtener eliminaciones significativas de coliformes fecales y otros patógenos en lodos (Ruiz-Espinoza et al. 2012; Gao et al. 2014). Los mecanismos de eliminación mediante ultrasonido están principalmente asociados con el esfuerzo de corte generado sobre los microorganismos debido a la implosión de las burbujas generadas durante la cavitación (Gao et al. 2014), mientras que el tratamiento térmico resulta en la inactivación de microorganismos mediante la pérdida de función de la enzimas, ácidos nucleicos, organelos y otras estructuras como la membrana celular debido a su desnaturalización (Nguyen et al. 2006). Por otra parte, después del pre-tratamiento se observaron valores 1.5 - 2.2, 3.7 – 4.0 y 2.0 – 2.1 veces mayores para los parámetros conductividad eléctrica, concentración de DQO soluble y concentración de amonio en el lodo, respectivamente. Si bien durante la operación de los digestores la concentración de sólidos y DQO del lodo varió significativamente, los efectos del pre-tratamiento fueron similares para dichos parámetros durante todas las etapas operacionales.

2. DESEMPEÑO OPERACIONAL DE LA DIGESTIÓN ANAEROBIA AVANZADA INCLUYENDO PRE-TRATAMIENTO SECUENCIAL MEDIANTE ULTRASONIDO Y TEMPERATURA

El siguiente objetivo establecido en la tesis fue determinar la influencia que tiene el pre-tratamiento sobre la digestión anaerobia del lodo, evaluada mediante ensayos batch (Capítulo IV) y semi-continuos (Capítulo VI). Los parámetros evaluados se enfocaron en la cinética del proceso de digestión, la biodegradabilidad anaerobia del lodo, conversión de materia orgánica y generación de biogás/metano. Indicadores del digestado asociados con su capacidad de deshidratabilidad, presencia de indicadores de contaminación por patógenos y elementos inorgánicos regulados en la normativa chilena también fueron evaluados (D.S. 04/09; MINSEGPRES 2009).

Como se discutió en el Capítulo I, la hidrólisis representa la principal limitación durante la digestión anaerobia de lodos provenientes del tratamiento de aguas servidas (Abelleira et al. 2012). La hidrólisis ocurre mediada por enzimas extracelulares excretadas por bacterias fermentativas (Khanal 2008), las que al adherirse a los sólidos actúan sobre la materia orgánica particulada y transfieren los productos de la reacción tales como aminoácidos, monosacáridos y alcoholes a la fase disuelta (Gerardi 2003), desde donde son metabolizados. De esta forma, el grado de solubilización de la materia orgánica obtenido durante el pre-tratamiento ha sido ampliamente utilizado como un indicador para evaluar su eficacia, generalmente en términos de la demanda química de oxígeno (Carlsson et al. 2012).

El pre-tratamiento secuencial mostró efectos tanto sobre la cinética de la digestión anaerobia como sobre el rendimiento de metano. Durante los ensayos batch, se observaron tasas máximas de producción de metano ($mLCH_4/gSV\text{-}d$) 1.3 a 1.8 veces mayores debido a la aplicación del pre-tratamiento, sin efectos significativos sobre la duración de la etapa *lag* (λ; d). De manera similar, Carvajal et al. (2013) reportó tasas máximas de producción de metano hasta 1.2 – 1.3 veces mayores durante la digestión anaerobia de lodo tratado a 55°C (12 h). Durante los ensayos semi-continuos, los mayores incrementos en los rendimientos de metano (29.9%) y biogás (25.4%) fueron observados con el menor tiempo de retención (7.5 días), lo que estaría asociado con la mejora observada en la cinética de degradación debido al pre-tratamiento, similar a lo reportado por otros autores (Lin et al. 1997; Carrère et al. 2008; Neis et al. 2008). El rendimiento de metano incrementó entre 16 a 50% debido a la aplicación del pre-tratamiento, asociado con la intensidad del proceso en términos de la energía específica de ultrasonido y la duración del tratamiento térmico. La Figura 2 muestra la relación observada entre la solubilización de DQO en las muestras de lodo y el rendimiento de metano. Alrededor del 90% de la variabilidad observada en el rendimiento de metano durante los ensayos batch puede explicarse por la solubilización de DQO (r^2 = 0.87). Durante la evaluación semicontinua del proceso de digestión, se observaron incrementos en el rendimiento de biogás y metano proporcionales al factor de solubilización del pre-tratamiento (11.2%). Esto sugiere que el principal mecanismo involucrado en la mejora de la producción de metano es la transferencia de DQO desde la fase particulada a la soluble, y que por ende el factor de solubilización es un parámetro que permite predecir el efecto del pre-tratamiento secuencial sobre la digestión anaerobia.

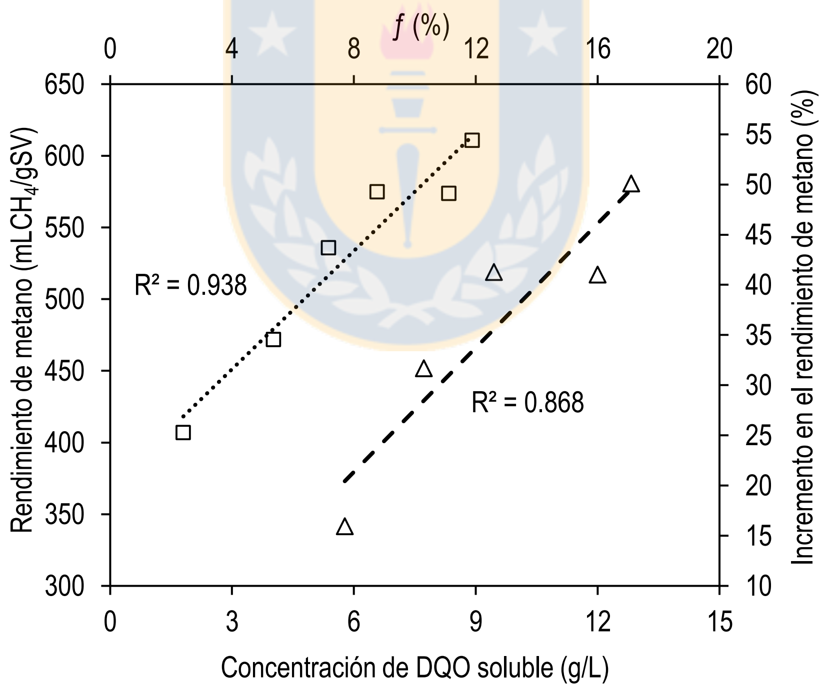

Figura 2. Relación entre la DQO soluble en el lodo y el rendimiento de metano en los ensayos batch. Rendimiento de metano en función de la concentración de DQO soluble (□); Incremento observado en el rendimiento de metano en función del factor de solubilización (△).

La incorporación del pre-tratamiento no resultó en modificaciones significativas en los parámetros operacionales de la digestión anaerobia, incluyendo el potencial de óxido-reducción (<-200 mV), pH (7.0 – 7.8), la concentración de AGV totales (<300 mgDQO/L) y la relación entre alcalinidad parcial y total (<0.35). Si bien la concentración de amonio fue 5.9 – 13.6% mayor en el reactor alimentado con lodo pre-tratado comparado con el control, en todas las condiciones estudiadas esta se mantuvo bajo el rango reportado como inhibitorio (1.7 – 14 gNH_4^+-N/L y 100 – 1,450 mgNH_3-N/L) (Chen et al. 2008; Yenigün & Demirel 2013).

La Tabla 2 resume los principales efectos del pre-tratamiento y su comparación con estudios similares. Durante la evaluación semicontinua del proceso, el pre-tratamiento resultó en incrementos de 19.3 – 25.4% y 19.1 – 29.9% en los rendimientos de biogás y metano, respectivamente, en el mismo orden que el incremento observado en la eliminación de DQO total (17.5 – 28.4%). Esto se asocia con la mayor conversión de DQO durante las etapas de hidrólisis, acidogénesis y metanogénesis, que mostraron incrementos de 6.6 – 25.9%, 18.3 – 29.4% y 18.9 – 30.1%, respectivamente. Debido a que no se observó acumulación de compuestos intermediarios, es posible concluir que la hidrólisis fue la etapa limitante durante la digestión del lodo en las condiciones estudiadas.

Los resultados obtenidos resultan comparables con reportes previos. La aplicación combinada de ultrasonido y tratamiento térmico en condiciones similares (~1,000 – 26,687 kJ/kgST; 50 – 90°C; 30 min – 24 h) ha resultado en factores de solubilización de 12 a 35% e incrementos de 14 – 41% en la producción de biogás, además de hasta 47% mayores remociones de SV. Por otra parte, la implementación de procesos de tratamiento térmico a baja (<100°C) y alta (>100°C) temperatura ha resultado en incrementos de 12 – 36% en términos de la producción de biogás. De manera similar a lo observado en el presente estudio, Ferrer et al. (2008) reportó que el incremento en la producción de metano (27 – 36%) asociado con la implementación de pre-tratamiento a 70°C no se correlaciona con incrementos en la reducción de sólidos, lo que podría indicar que en las condiciones estudiadas el pre-tratamiento no incrementa la biodegradabilidad anaerobia de la fracción particulada del lodo.

Tabla 2. Comparación de los resultados del estudio con sistemas de pre-tratamiento similares

Pre-tratamiento	Escala	Lodo	Condiciones operacionales	Solubilización de DQO	Digestión anaerobia	∆ Producción de biogás	∆ Reducción de sólidos y DQO	Referencias
Ultrasonido-térmico	Laboratorio	Mixto	US: 26 kHz; 500 – 30,500 kJ/kgST TT: 55°C; 3 – 13 h	3.5 – 17.1%	Batch (37°C)	Y_{CH_4}: 16 – 50%	--	Este estudio
					Semi-continua (37°C)	Y_{BG}: 19.3 – 25.4% Y_{CH_4}: 19.1 – 29.9%	DQO: 17.5 – 28.4% SV: 3.2 – 11.7%	
		Secundario	US: 20 kHz; 0.5 – 1.5 W/mL; 0.5 – 10 min TT: 60 – 100°C; 60 min	11.8 – 32.1%	Batch (37°C)	P_{CH_4}: 13.6% P_{BG}: 14%	DQO. 28% SV: 46.5%	Şahinkaya & Sevimli (2013)
			US: 20 kHz; 1,000 – 10,000 kJ/kgSST TT: 50 – 90°C; 30 min	~21 – 35% ~∆DQO_s 5 – 7	Batch (37°C)	Y_{CH_4}: 19 – 30%	--	Dhar et al. (2012)
			US: 24 kHz; 26,687 kJ/kgST TT: 55°C; 24 h	57% (GD)	Batch	Y_{CH_4}: 41%	--	Pérez-Elvira et al. (2010)
Ultrasonido	Laboratorio	Secundario	24 kHz; 0.35 – 1.4 kWh/kgST	2.2 – 9.0% (GD)	Semi-continua (37°C)	Y_{CH_4}: 11.5 – 37.0%	SV: 1.0 – 20.6%	Braguglia et al. (2011)
			24 kHz; 1.4 – 10.8 kWh/kgST	~∆DQO_s 1 – 19	Batch	Y_{BG}: 6 – 42%	--	Pérez-Elvira et al. (2009)
					Semi-continua	PD_{BG}: 37%	DQO: 12 – 38% SV: 10 – 25%	
	Industrial	Mixto	20 kHz; 6kW; 1.5 s; 50 – 300 kWh/d	--	Continua (V: 5,000 m^3)	PD_{BG}: 15 – 58%	SST: 30%	Xie et al. (2007)
Térmico (<100°C)	Laboratorio	Secundario	55°C; 12 – 24 h	29 – 39%	Batch (35°C)	Y_{CH_4}: 16 – 23%	--	Carvajal et al. (2013)
		Mixto	70°C; 9 – 72 h	~∆10 SDV/SV	Batch (55°C)	P_{BG}: 15 – 30%	--	Ferrer et al. (2008)
					Semi-continua (55°C)	Y_{BG}: 27.3 – 36.4%	SV: -25.9 – 10%	
Térmico (>100°C)	Piloto	Secundario/ mixto	170°C; 30 min; 12 bar	--	Continua (mesofílica)	Y_{BG}: 24 – 33%	SV: 25 – 30%	Pérez-Elvira & Fdz-Polanco (2012)
	Laboratorio	Secundario	135 – 190°C; 65 min	34 – 46%	Semi-continua (35°C)	Y_{CH_4}: 12 – 25%	DQO: 11.3 – 22.3% ST: 13.0 – 60.8%	Bougrier et al. (2007)
Enzimático	Laboratorio	Primario/ secundario	6 preparados comerciales incluyendo proteasas, amilasas, celulasas; 0.1 – 0.5%	--	Batch (37°C)	--	SV: 12.8 – 16.3%	Rashed et al. (2010)

DQO; Demanda Química de Oxígeno; DQO_s; Demanda Química de Oxígeno Soluble; ∆: Variación en el parámetro indicado; US: Ultrasonido; TT: Tratamiento térmico; Y_{CH_4}: Rendimiento de metano; Y_{BG}: Rendimiento de biogás; P_{CH_4}: Producción de metano; P_{BG}: Producción de biogás; PD_{BG}: Producción diaria de biogás; SV: Sólidos volátiles; SST: Sólidos suspendidos totales; ST: Sólidos totales; SDV: Sólidos disueltos volátiles; GD: Grado de desintegración de DQO.

Reportes relacionados con la aplicación de procesos de ultrasonido muestran incrementos de 1 a 19 veces en la concentración de DQO soluble y 6 – 58% mayor producción de biogás, en el mismo orden que el presente estudio. Es importante considerar que el ultrasonido es una de las tecnologías de pre-tratamiento de lodos más estudiadas y una de las que ha sido implementada de manera exitosa en plantas de escala industrial (Xie et al. 2007; Neumann et al. 2016). Si bien la evaluación de pre-tratamientos de ultrasonido en laboratorio tiende a resultar en balances energéticos negativos (Pérez-Elvira et al. 2009; Şahinkaya & Sevimli 2013; Neumann et al. 2017), reportes previos indican que la eficiencia de los equipos de ultrasonido utilizados para la disrupción de lodos a escala industrial supera ampliamente a la eficiencia de los equipos utilizados en laboratorio (Zielewicz & Sorys 2008; Cano et al. 2015).

Basándose en los resultados observados en laboratorio, para que el pre-tratamiento secuencial resulte autosustentable energéticamente la energía específica máxima del ultrasonido debe ser del orden de 500 – 2000 kJ/kgST, lo que resulta factible considerando el consumo energético reportado para equipos de escala industrial, cuyo rango es de 44 – 360 kJ/kgST (Pérez-Elvira et al. 2009). Xie et al. (2007) reportaron un incremento de 45% en la producción de biogás en una PTAS en Singapur al aplicar ultrasonido con una energía específica de ~0.1 kWh/kgSST (360 kJ/kgSST), resultando en una relación entre la ganancia neta de energía y el consumo del ultrasonido de 2.5.

En términos de la deshidratabilidad del digestado, se observó que el pre-tratamiento disminuye hasta un 4.2% la recuperación de agua durante los ensayos de centrifugación, dependiendo del tiempo utilizado en el ensayo. Sin embargo, el TRS durante la digestión mostró un efecto más significativo sobre el mismo parámetro (13.3 – 20.5%), lo que indicaría que este factor ejerce un mayor control sobre la deshidratabilidad que la inclusión de pre-tratamiento. En ambos casos, la disminución en la recuperación de agua se debería a la vinculación entre esta y los sólidos finos en el lodo, debido a su mayor área superficial comparado con partículas de mayor tamaño (Braguglia et al. 2010; Pilli et al. 2011; Wahidunnabi & Eskicioglu 2014).

Po otra parte, el pre-tratamiento resultó en un incremento en la remoción de los indicadores de contaminación por patógenos. Durante la digestión convencional, las remociones logarítmicas promedio fueron de 2.5, 2.6 y 0.7 para coliformes totales, coliformes fecales y colifagos somáticos, respectivamente, mientras que durante la digestión avanzada las remociones promedio fueron de 2.8, 2.8 y 1.5, respectivamente. Si bien estos resultados son comparables con procesos de digestión anaerobia avanzada similares (Levantesi et al. 2015), la densidad de coliformes fecales obtenida en el digestado fue de $6.6x10^4$ NMP/gST después de la digestión convencional y $8.5x10^3$ NMP/gST después de la digestión avanzada, ambos sobre el límite legal establecido para biosólidos de Clase A (10^3 NMP/gST; MINSEGPRES 2009). Esto estaría relacionado con la elevada presencia de dichos microorganismos en las muestras de lodo obtenidas desde la PTAS Biobío ($4.8x10^9$ NMP/gST).

El pre-tratamiento resultó además en incrementos de 7 – 58% en la concentración de As, Cu, Hg y Zn en los sólidos del digestado, lo que estaría asociado con la mayor eliminación de materia orgánica durante la digestión anaerobia. Sin embargo, contrario a reportes previos (Appels et al. 2010), el pre-tratamiento no causó incrementos en la concentración de los elementos estudiados en el sobrenadante, lo que podría asociarse con fenómenos de precipitación y acumulación en el digestor (Carballa et al. 2008). Es importante señalar que gran parte de la variabilidad observada en las concentraciones de nutrientes y metales en el digestado se asocian con las concentraciones observadas en las muestras de lodo, en las que se observaron variaciones de hasta 573% entre las distintas fases operacionales.

3. DESEMPEÑO AMBIENTAL DE LA DIGESTIÓN ANAEROBIA AVANZADA INCLUYENDO PRE-TRATAMIENTO SECUENCIAL MEDIANTE ULTRASONIDO Y TEMPERATURA

El tercer objetivo específico de la presente tesis fue evaluar el desempeño ambiental del proceso de digestión anaerobia incluyendo pre-tratamiento (Capítulo VI). Para ello se utilizó como herramienta el ACV, comparando los resultados con 3 escenarios representativos de alternativas de gestión utilizadas actualmente en Chile. Dichos escenarios se diferenciaron en términos de la tecnología de estabilización utilizada y la estrategia de disposición del lodo. En base a información publicada por la Superintendencia de Servicios Sanitarios (SISS 2011), los escenarios base de la evaluación correspondieron al uso de estabilización mediante adición de cal y disposición del lodo en relleno sanitario, considerando alternativamente la quema o recuperación para la generación de electricidad del gas generado en el relleno sanitario. Los escenarios de digestión anaerobia consistieron en la estabilización del lodo mediante digestión convencional o digestión incluyendo el pre-tratamiento secuencial, seguido por la aplicación del digestado en cultivos de trigo como reemplazo de los fertilizantes fosfato diamónico ($(NH_4)_2HPO_4$) y sulfato de amonio ($(NH_4)_2SO_4$).

Los resultados de la evaluación mostraron que los escenarios de digestión anaerobia seguidos por aplicación en suelos agrícolas presentan menores impactos en todas las categorías estudiadas (cambio climático, agotamiento de recursos abióticos, acidificación y eutrofización terrestre, marina y dulceacuícola). Esto es atribuible a la valorización de la energía y nutrientes contenidos en el lodo, que permite el reemplazo de fuentes convencionales de electricidad, energía térmica y fertilizantes (Yoshida et al. 2013). La utilización de digestión anaerobia y aplicación del digestado en el suelo puede resultar en impactos potenciales negativos (impactos evitados) para las categorías cambio climático y agotamiento de recursos abióticos, relacionado en parte con la valorización energética del lodo. Sin embargo, en los escenarios de disposición en relleno sanitario, la recuperación de energía electrica a partir del gas generado en el relleno resultó en una disminución de solo un 5% en el potencial de cambio climático y 2% en el potencial de agotamiento de recursos abióticos.

Por otra parte, los potenciales de acidificación y eutrofización terrestres mostraron comportamientos similares entre los escenarios de digestión anaerobia y entre los escenarios de alcalinización, con valores alrededor de 700 veces mayores en estos últimos. Esta diferencia se asocia principalmente con la emisión de NH_3 durante la estabilización por cal, que representa un 98% de la contribución a ambas categorías. En términos de los potenciales de eutrofización marina y dulceacuícola, todos los escenarios presentaron resultados similares, debido a que alrededor del 80% de la contribución a estos impactos está asociada con el tratamiento del agua servida. La principal diferencia está asociada con la estrategia de disposición del digestado al suelo, pues en los escenarios de aplicación a suelos agrícolas los nutrientes son parcialmente asimilados por los cultivos (Brentrup et al. 2001), mientras que en aquellos en los que el lodo es dispuesto en rellenos sanitarios estos lixivian y son descargados en ecosistemas receptores después de su tratamiento (Doka 2003a).

El pre-tratamiento resultó en dos efectos principales sobre el desempeño ambiental de la gestión del lodo: una disminución en el potencial de cambio climático y un aumento en el potencial de agotamiento de recursos abióticos, asociados con la mayor recuperación de energía que permite el pre-tratamiento y con la mayor demanda para el transporte de lodos, respectivamente. La disminución observada en el potencial de cambio climático resulta sensible a la presencia de carbono fósil en las emisiones de CO_2 del biogás, además de la implementación de estrategias de valorización de la energía térmica obtenida durante la co-generación. Por otra parte, la demanda de transporte y el potencial de agotamiento de recursos abióticos resulta dependiente de la recuperación de agua a partir del digestado, la que se vio influenciada por las condiciones de centrifugación y el TRS durante la digestión.

De manera general, el sistema pre-tratamiento/digestión anaerobia resultó en impactos ambientales potenciales similares a los de la digestión anaerobia convencional. Debido a esto y a que la incorporación del pre-tratamiento permitiría eventualmente extender el uso de la digestión anaerobia a PTAS que actualmente no cuentan con tecnologías de valorización del lodo, su implementación puede resultar en una disminución en las cargas ambientales asociadas a la gestión del lodo en Chile (SISS 2016). Sin embargo, es importante considerar que las condiciones operacionales durante la digestión del lodo y el uso de distintas estrategias de aplicación del digestado puede resultar en modificaciones en los impactos ambientales del ciclo de vida (Rodriguez-Verde et al. 2014). Considerando los criterios evaluados en la presente tesis y las disposiciones consideradas en la legislación chilena para la aplicación de lodos estabilizados en el suelo (DS 04/09; MINSEGPRES 2009), se pueden identificar distintos escenarios (Tabla 3).

Tabla 3. Escenarios de gestión del lodo en base a criterios de operación y aplicación en suelos

Criterios operacionales		Criterios de manejo del lodo		Escenario
Digestión	**TRS (d)**	**Cultivo**	**Tasa de aplicación**	
Convencional	30	Forestal[1]	Cultivos[3]	E1
			Disposición[4]	E2
		Agrícola[2]	Cultivos	E3
			Disposición	E4
	15	Forestal	Cultivos	E5
			Disposición	E6
		Agrícola	Cultivos	E7
			Disposición	E8
Avanzada (incluyendo pre-tratamiento)	30	Forestal	Cultivos	E9
			Disposición	E10
		Agrícola	Cultivos	E11
			Disposición	E12
	15	Forestal	Cultivos	E13
			Disposición	E14
		Agrícola	Cultivos	E15
			Disposición	E16

[1] Asumiendo cultivo de *Pinus radiata* (Webber & Madgwick 1983); [2] Asumiendo cultivo de *Triticum spp* (Warncke and Zandstra 2004; Dai et al. 2016); [3] En base al requerimiento de N del cultivo; [4] Tasa máxima de aplicación permitida por la legislación chilena, 90 ton/ha-año en base seca (MINSEGPRES 2009).

La evaluación de impacto ambiental de dichos escenarios se resume en la Figura 3. Debido a que la reducción del TRS de la digestión desde 30 a 15 días resulta en una mayor disminución sobre la recuperación de agua desde el digestado que la incorporación del pre-tratamiento, los escenarios de digestión anaerobia convencional y avanzada con un TRS de 15 días presentan mayores impactos en las categorías cambio climático, agotamiento de recursos abióticos, acidificación y eutrofización terrestre. Además, la utilización de tasas de aplicación del lodo sobre los requerimientos del cultivo resulta en pérdidas de gran parte de los nutrientes mediante procesos de volatilización y lixiviación, generando incrementos en los potenciales de cambio climático (debido a la mayor emisión de N_2O), acidificación y eutrofización terrestre (debido a la mayor emisión de NH_3) y agotamiento de recursos abióticos (debido al menor reemplazo de fertilizantes comerciales).

A pesar de que el potencial de eutrofización marina se relaciona principalmente con el tratamiento de aguas servidas, la utilización de tasas de aplicación del lodo de acuerdo al máximo permitido por el DS 04/09 resulta en 129 – 143% mayores impactos asociados a dicha etapa, lo que está asociado a la mayor lixiviación de NO_3^-. Aunque estos resultados no fueron observados para la eutrofización dulcecuícola debido a la baja movilidad asumida para el fósforo en el suelo (Doka 2003b), los escenarios cuya tasa de disposición supere los requerimientos del cultivo se asocian con riesgo de sobresaturación del suelo y lixiviación de PO_4^{-3} a cuerpos de agua (Nair 2014), lo que aumentaría el impacto en dicha categoría.

Si bien no se observaron diferencias debido a la disposición del lodo en cultivos agrícolas o forestales, los resultados de este estudio no incluyen la evaluación del impacto por toxicidad debido a la presencia de contaminantes en el digestado. Es esperable que la aplicación de lodos a cultivos posteriormente ingeridos por la población resulte en un mayor impacto en la toxicidad humana (Fantke et al. 2015), pero resulta importante considerar la alta incertidumbre asociada actualmente a la evaluación de la toxicidad de metales y otros contaminantes en en el marco del ACV (JRC European Commission 2011; Fantke et al. 2015).

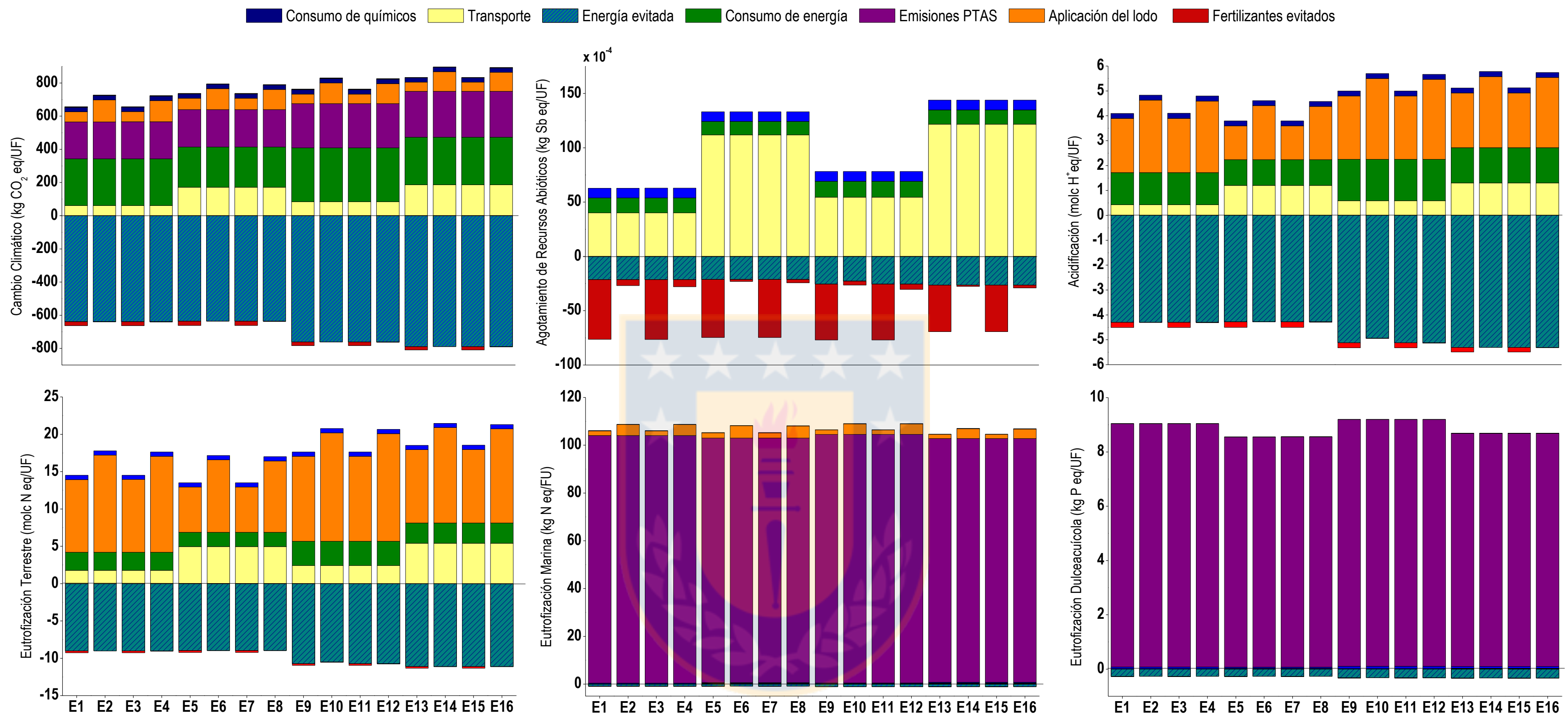

Figura 3. Influencia de criterios operacionales y de gestión del lodo sobre los impactos ambientales de la valorización de lodos mediante digestión anaerobia y aplicación en suelos.

Estos resultados muestran que las estrategias de digestión y manejo del digestado pueden tener un efecto incluso más relevante que la inclusión del pre-tratamiento sobre los impactos ambientales de la gestión del lodo. Considerando que uno de sus objetivos debiese ser disminuir los impactos ambientales incluyendo todas las etapas del ciclo de vida, es importante tomar en consideración que estos dependen tanto de las actividades en PTAS como de la gestión y disposición del digestado, como se puede observar en la Figura 4. Más aún, resulta relevante considerar la influencia que tiene el lodo no estabilizado y por ende el agua servida sobre las características del digestado, tal como se apreció en el Capítulo V de la presente tesis.

Por lo tanto, si bien el uso de tecnologías de valorización energética como la digestión anaerobia es relevante desde el punto de vista económico y ambiental, la implementación de medidas orientadas a disminuir la presencia de contaminantes en los lodos y a optimizar su valorización en suelos constituyen a su vez aspectos de gran relevancia. Dichas medidas pueden incluir mayores exigencias en la normativa de descarga de contaminantes al alcantarillado (D.S. 609/98), programas de educación ambiental a la población y el establecimiento de mejores prácticas para la aplicación de lodos en suelos en el marco del D.S. 04/09, resultando necesario establecer acciones concertadas que involucren a todas las partes interesadas para así disminuir el impacto ambiental asociado a la gestión del lodo.

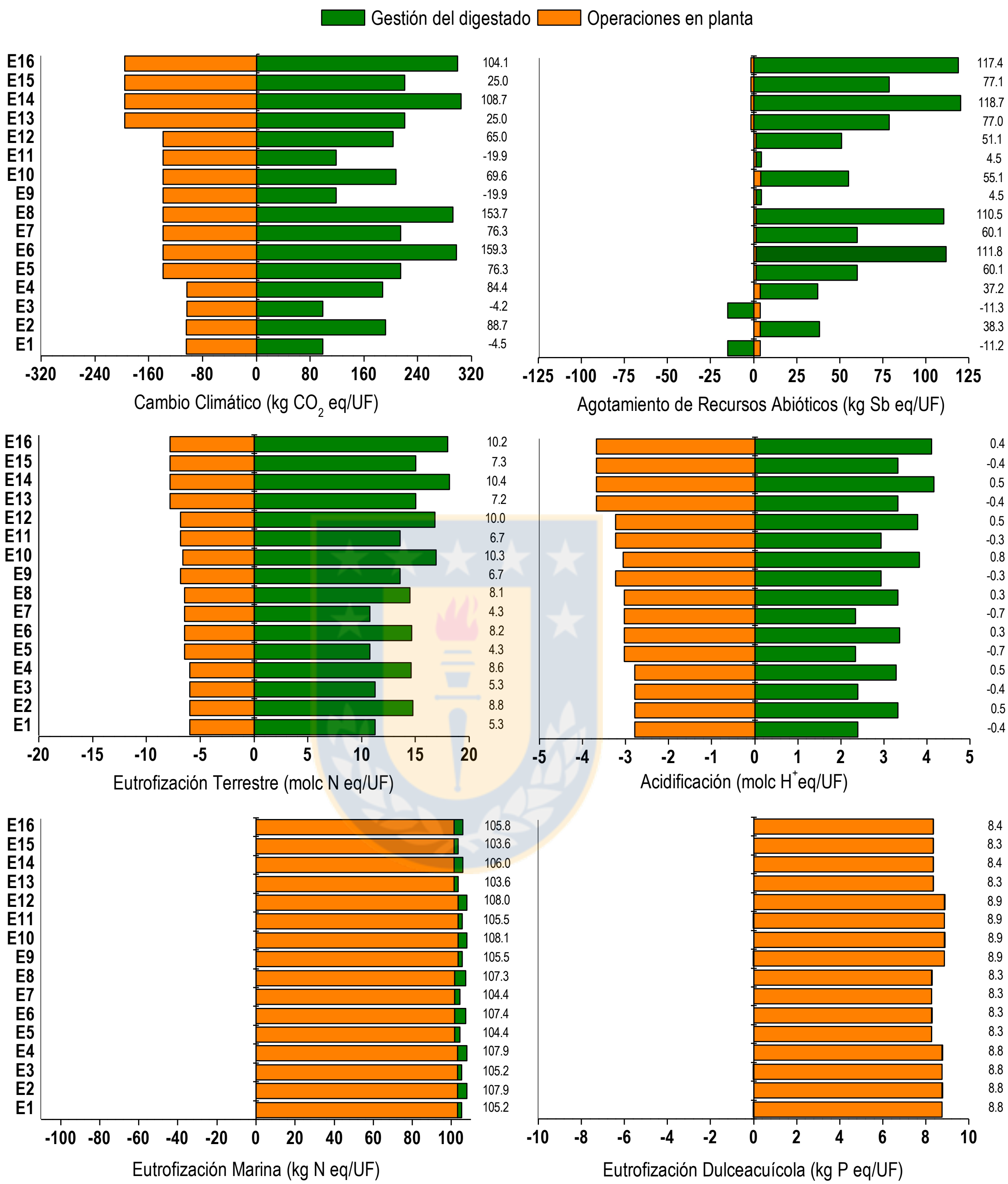

Figura 4. Contribución de las actividades en planta y de manejo del digestado a las categorías de impacto estudiadas bajo distintos escenarios. Los valores a la derecha de cada figura representan el impacto neto de cada escenario.

CAPÍTULO VIII

CONCLUSIONES Y RECOMENDACIONES FINALES

1. CONCLUSIONES

– La evaluación del efecto del pre-tratamiento secuencial sobre las características del lodo mostró una solubilización significativa de la materia orgánica, con incrementos en la concentración soluble de proteínas (252 – 674%), carbohidratos (458 – 1030%) y DQO (f = 3.5 – 17.1%). Además, se observó 1.6 – 3.8 mayor actividad de amilasa y 1.8 – 4.3 mayor actividad de proteasa en el lodo debido al pre-tratamiento. La solubilización de DQO se vio influenciada tanto por la concentración del lodo como por la energía específca del ultrasonido y el tiempo de tratamiento térmico. Si bien la producción de metano durante la digestión anaerobia está directamente relacionada con la solubilización de DQO, el proceso resulta energéticamente factible solo al aplicar ultrasonido con energías específicas de alrededor de 500 – 2000 kJ/kgST en las condiciones estudiadas.

– El pre-tratamiento secuencial resultó en incrementos tanto en la cinética de la digestión anaerobia como en la biodegradabilidad de lodo, con incrementos de 30 – 80% en la tasa máxima de producción de metano y 16 – 50% en el rendimiento específico de metano. Durante la evaluación semi-continua del proceso, se observaron incrementos de 19 – 29% en el rendimiento específico de metano, sin afectar la estabilidad del proceso y manteniendo concentraciones de NH_4^+-N y NH_3-N bajo los rangos de inhibición en todas las condicions experimentales (≤1.8 gNH_4^+-N y ≤53 mgNH_3-N). El mayor incremento fue observado con un TRS de 7.5 días, correspondiente a una carga de 3.6 gSV/L-d y asociado con la mayor cinética de degradación. El incremento observado en el rendimiento de metano durante todas las etapas experimentales resultó proporcional al factor de solubilización del pre-tratamiento (11.2%), lo que sugiere que el principal mecanismo asociado con la mejora en el desempeño operacional de la digestión anaerobia es la transferencia de materia orgánica desde la fase particulada a la soluble durante el pre-tratamiento.

– En términos de la calidad del digestado, el pre-tratamiento resultó en hasta un 4.2% menor recuperación de agua durante la centrifugación. Sin embargo, el TRS ejerce un efecto más significativo sobre dicho parámetro, mostrando disminuciones de 13.3 – 20.5% al reducir el TRS desde 30 a 15 días. El sistema pre-tratamiento/digestión anaerobia permitió remociones logarítmicas de 2.8 para coliformes (totales y fecales) y 1.5 para colifagos somáticos, y se observaron incrementos de hasta un 58% en la concentración de As, Cu, Hg y Zn en los sólidos del digestado debido a la inclusión del pre-tratamiento.

– El desempeño ambiental de la digestión anaerobia incorporando el pre-tratamiento secuencial y valorización del digestado en cultivos fue similar al de la digestión convencional, mostrando menores impactos en todas las categorías estudiadas comparado con escenarios basados en alcalinización y disposición del lodo en relleno sanitario. El principal efecto del pre-tratamiento fue una disminución en el potencial de cambio climático y un aumento en el potencial de agotamiento de recursos abióticos, relacionados con la recuperación de energía y deshidratabilidad del lodo. La intensificación de la digestión anaerobia debido al pre-tratamiento resulta en un escenario más sensible a la presencia de carbono fósil en las emisiones de CO_2 y a la valorización de la energía térmica generado durante la co-generación del biogás. Sin embargo, parámetros tales como el TRS durante la digestión y la tasa de aplicación del lodo al suelo pueden resultar en mayores efectos sobre el desempeño ambiental que la incorporación del pre-tratamiento.

En base a los resultados obtenidos, se acepta la primera hipótesis planteada, debido a que en todas las condiciones estudiadas el pre-tratamiento permitió favorecer la conversión de materia orgánica durante la digestión anaerobia, mejorando el desempeño operacional de la digestión anaerobia al incrementar en al menos un 20% la producción de metano.

Por otra parte, se rechaza la segunda hipótesis planteada, pues los resultados del ACV muestran que el desempeño ambiental del sistema pre-tratamiento/digestión anaerobia fue similar a la digestión anaerobia convencional. Ambos escenarios se vieron influenciados por los supuestos asumidos durante la evaluación, mientras que la selección de criterios operacionales y de gestión tales como el TRS y la tasa de aplicación del digestado al suelo resultan en efectos incluso más relevantes sobre los impactos ambientales estudiados que la incorporación del pre-tratamiento.

2. RECOMENDACIONES FINALES

- Considerando el efecto positivo del pre-tratamiento sobre la cinética y rendimiento de metano durante la digestión anaerobia del lodo, se recomienda evaluar su posible escalamiento en estudios piloto. Para que los resultados presentados en esta tesis resulten replicables, se sugiere profundizar en los mecanismos involucrados en el pre-tratamiento y su efecto sobre la composición y actividad de las comunidades anaerobias de los reactores anaerobios. Es importante señalar que este estudio no incluyó una evaluación económica de la tecnología, factor fundamental para evaluar su factibilidad y que debiese ser incluído en estudios futuros.
- Por otra parte, se recomienda evaluar en mayor detalle el efecto del pre-tratamiento sobre la calidad del digestado. En términos de la deshidratabilidad, esto puede incluir: a) evaluación de distintas tecnologías y parámetros operacionales de deshidratación, b) el uso de polímeros como ayuda a la

deshidratabilidad bajo distintas condiciones, y c) la influencia del pre-tratamiento sobre el tamaño de partícula y su relación con los parámetros de deshidratabilidad. Además, se sugiere evaluar con mayor detalle el efecto del pre-tratamiento sobre la presencia de patógenos y contaminantes orgánicos e inorgánicos en el lodo. Finalmente, se sugiere evaluar la influencia del proceso sobre el grado de estabilidad de la materia orgánica y calidad del digestado, incluyendo eventualmente la evaluación de: a) concentración y biodisponibilidad de N y P, b) presencia de ácidos fúlvicos y húmicos, y c) posibles efectos de fitotoxicidad y crecimiento en cultivos.

– Debido a que la incorporación del pre-tratamiento resultó en un desempeño ambiental similar a la digestión convencional, su implementación puede ser una herramienta de interés para extender el uso de la digestión anaerobia a PTAS que no cuentan con la tecnología y así disminuir las cargas ambientales asociadas a la gestión del lodo en Chile. Sin embargo, se sugiere profundizar en los aspectos relacionados con el uso del digestado en el suelo, incluyendo una mayor comprensión del efecto de las tasas de aplicación sobre la lixiviación de PO_4^{3-}, la evaluación de los impactos potenciales de toxicidad humana y ecotoxicidad y evaluaciones del impacto por contaminación microbiológica. Para esto, puede ser necesaria la integración del ACV con herramientas tales como la Evaluación de Riesgo, lo que permitiría obtener resultados de mayor alcance y certidumbre como apoyo a la toma de desiciones.

CAPÍTULO IX

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ANEXO I

HITOS Y PRODUCTOS DE LA TESIS

Proyectos de investigación

Proyecto PAI-CONICYT Folio 2014-781413004: "Evaluación del pre-tratamiento de lodos sanitarios mediante hidrólisis enzimática asistida: influencia sobre el proceso de digestión anaerobia y su desempeño ambiental". Concurso Nacional de Tesis de Doctorado en la Empresa 2014, Programa de Atracción e Inserción de Capital Humano Avanzado de CONICYT. Institución patrocinante: Essbío S.A. Investigador Responsable: Patricio Neumann. Profesor Patrocinante: Dra. Gladys Vidal.

Pasantías internacionales

Universidad de Santiago de Compostela (España), Junio – Julio 2016. Grupo de Ingeniería Ambiental y Bioprocesos, Departamento de Ingeniería Química. Dra. Almudena Hospido. Objetivo: Evaluación ambiental de escenarios de gestión y valorización energética de lodos sanitarios. Financiamiento: Beca Doctorado Nacional CONICYT 21130054-2013.

Publicaciones en revistas indexadas

1. **Neumann P.**, Barriga F., Álvarez C., González Z., Vidal, G. Process performance and digestate quality assessment of advanced anaerobic digestion of sewage sludge including sequential ultrasound – thermal (55°C) pre-treatment. *Bioresource Technology* (enviada).
2. Cartes J., **Neumann P.**, Hospido A., Vidal G. Life cycle assessment of management alternatives for sludge from sewage treatment plants in Chile: does advanced anaerobic digestion improve environmental performance compared to current practices?. *Journal of Material Cycles and Waste Management* (en evaluación).
3. **Neumann P.**, González Z., Vidal G. 2017. Sequential ultrasound and low-temperature thermal pretreatment: process optimization and influence on sewage sludge solubilization, enzyme activity and anaerobic digestion. *Bioresource Technology*, 234, 178 – 187.
4. **Neumann P.**, Pesante S., Venegas M., Vidal G. 2016. Developments in pre-treatment methods to improve anaerobic digestion of sewage sludge. *Reviews in Environmental Science and Bio/Technology*, 15 (2):173–211.

Presentaciones en congresos internacionales

1. **Neumann P.**, Cartes J., Hospido A., Vidal G. 2017. Life-cycle environmental performance of advanced anaerobic digestion of sewage sludge including sequential ultrasound and low-

temperature (55°C) thermal pre-treatment. VII Conferencia Internacional de Análisis de Ciclo de Vida en Latinoamérica. Medellín, Colombia.

2. **Neumann P.**, Del Río C., González Z. and Vidal G. 2016. Improved energy recovery during sludge anaerobic digestion by sequential ultrasound and incubation pre-treatment. 2nd IWA Conference on Holistic Sludge Management. Malmö, Suecia.
3. Cartes J., **Neumann P.**, Del Río C., González Z., Vidal G. 2016. Energetic and environmental performance of different scenarios of advanced anaerobic digestion of sewage sludge. 10th ISEB Conference. Barcelona, España.
4. **Neumann P.**, Del Río C., González Z., Vidal G. 2016. Evaluation of sequential ultrasound-incubation pre-treatment influence over sewage sludge by surface response methodology. 10th ISEB Conference. Barcelona, España.
5. **Neumann P.**, Del Río C. y Vidal G. 2015. Solubilisation and enzyme activity stimulation during sludge pre-treatment for anaerobic digestion. 14th World Congress on Anaerobic Digestion. Viña del Mar, Chile.

Presentaciones en congresos nacionales

1. Barriga F., **Neumann P.**, Álvarez C., Vidal G. 2017. Efecto del pre-tratamiento secuencial mediante ultrasonido e hidrólisis térmica a 55°C sobre el desempeño de la digestión anaerobia de lodos sanitarios. XX Congreso Chileno de Ingeniería Química. Santiago, Chile.
2. Cartes J., **Neumann P.**, González Z., Vidal G. 2016. Alternativas de gestión energética y ambiental en digestión anaeróbica avanzada de biosólidos sanitarios. Segundo Congreso Nacional en Gestión Integrada: Innovación y sustentabilidad. Concepción, Chile.
3. **Neumann P.**, Venegas M., Vidal G. 2014. Estrategias de optimización de la hidrólisis enzimática durante la digestión anaerobia de lodos sanitarios. XIX Congreso Chileno de Ingeniería Química. Concepción, Chile.
4. **Neumann P.**, Pesante S., Venegas M., Vidal G. 2013. Tecnologías para la reducción y valorización de biosólidos sanitarios orientadas a la sustentabilidad ambiental. Workshop Internacional y Taller Nacional Valorización de Residuos: Oportunidad para la Innovación, Pucón, Chile.

ANEXO II

PORTADA DE LOS ARTÍCULOS PUBLICADOS

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REVIEW PAPER

Developments in pre-treatment methods to improve anaerobic digestion of sewage sludge

P. Neumann · S. Pesante · M. Venegas · G. Vidal

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Abstract During wastewater treatment, most organic matter is transferred to a solid phase commonly known as sludge or biosolids. The high cost of sludge management and the growing interest in alternative energy sources have prompted proposals for different strategies to optimize biogas production during anaerobic sludge treatment. Because of the high solid content and complex structure of sludge-derived organic matter, methane production during digestion is limited at the hydrolysis step. Therefore, large digester volume and long retention times of over 20 days are necessary to achieve adequate stabilization. Pre-treatments can be used to hydrolyze sludge and consequently improve biogas production, solids removal and sludge quality after digestion. This paper reviews the main pre-treatment processes, with emphasis on the most recent developments. An overview of the different technologies is presented, discussing their effects on sludge properties and anaerobic digestion. Future challenges and concerns related to pre-treatment assessment and implementation are also addressed.

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Keywords Sewage sludge · Hydrolysis · Pre-treatment · Biogas production · Biosolids · Anaerobic digestion

Abbreviations

AD	Anaerobic digestion
ATH	Advanced thermal hydrolysis
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
CST	Capillary suction time
DD	Disintegration degree
DMDO	Dimethyldioxirane
DOC	Dissolved organic carbon
DS	Dry solids
EDC	Endocrine disrupting compounds
EPS	Extracellular polymeric substances
F/I	Feed/inoculum ratio
FC	Fecal coliforms
GRS	Growth rate of solubilization
HE	Helminth eggs
HPH	High pressure homogenization
MW	Microwave
ODS	Organic dry solids
OLR	Organic loading rate
OM	Organic matter
OUR	Oxygen uptake rate
PAA	Peracetic acid
POMS	Peroxymonosulfate
PT	Pre-treatment
SBOD	Soluble biochemical oxygen demand

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Sequential ultrasound and low-temperature thermal pretreatment: Process optimization and influence on sewage sludge solubilization, enzyme activity and anaerobic digestion

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HIGHLIGHTS

- Sequential ultrasound and thermal pretreatment of sewage sludge was assessed.
- Pretreatment led to solubilization and increased enzyme activity in sewage sludge.
- Optimal COD solubilization was obtained at 59.3 kg TS/L, 30,500 kJ/kg TS and 13 h.
- Methane yield and maximum production rate were significantly increased.
- Pretreatment increased electricity recovery from sludge up to 24%.

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ABSTRACT

The influence of sequential ultrasound and low-temperature (55 °C) thermal pretreatment on sewage sludge solubilization, enzyme activity and anaerobic digestion was assessed. The pretreatment led to significant increases of 427–1030% and 230–674% in the soluble concentrations of carbohydrates and proteins, respectively, and 1.6–4.3 times higher enzymatic activities in the soluble phase of the sludge. Optimal conditions for chemical oxygen demand solubilization were determined at 59.3 kg/L total solids (TS) concentration, 30,500 kJ/kg TS specific energy and 13 h thermal treatment time using response surface methodology. The methane yield after pretreatment increased up to 50% compared with the raw sewage sludge, whereas the maximum methane production rate was 1.3–1.8 times higher. An energy assessment showed that the increased methane yield compensated for energy consumption only under conditions where 500 kJ/kg TS specific energy was used for ultrasound, with up to 24% higher electricity recovery.

1. Introduction

Concerns regarding increasing sludge generation in wastewater treatment plants (WWTPs) have increased. During 2012, the annual generation of sludge from sewage treatment facilities in Europe was approximately 10.0×10^6 tons (dry matter basis), whereas in China, sludge generation was over 6.0×10^6 tons (Eurostat, 2016; Zhang et al., 2016). The situation in Chile has not been different, with an estimated sludge generation of 300 ton/day during 2010 (Celis et al., 2008). In this scenario, sludge valorization through the recovery of energy and nutrients represents a fundamental step toward developing sustainable WWTPs.

Anaerobic digestion (AD) is an environmentally friendly alternative for sludge stabilization. AD processes significantly reduce odor, pathogens and organic matter (Appels et al., 2008a). Moreover, biogases with significant percentages of methane (60–70% CH_4) and nutrient-rich digestates are obtained during digestion, which can be utilized as energy sources and commercial fertilizers, respectively (Carballa et al., 2011).

Modern WWTPs have integrated the benefits of AD; however, a few noteworthy AD performance drawbacks exist. Low performance rates are typically observed during the hydrolysis of organic matter in sewage sludge, which includes solids, flocs, extracellular

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Process performance and digestate quality assessment of advanced anaerobic digestion of sewage sludge including sequential ultrasound – thermal (55°C) pre-treatment

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Abstract

The aim of this study was to evaluate the performance and digestate quality of advanced anaerobic digestion of sewage sludge including sequential ultrasound – thermal (55°C) pre-treatment. Both stages of pre-treatment contributed to chemical oxygen demand (COD) solubilization with an overall factor of 11.4 ± 2.2%. Pre-treatment led to 19.1, 24.0 and 29.9% increased methane yields at 30, 15 and 7.5 days solid retention times (SRT), respectively, without affecting process stability or accumulation of intermediaries. Pre-treatment decreased up to 4.2% water recovery from the digestate, but SRT was a more relevant factor controlling dewatering. Advanced digestion showed 2.4 – 3.1 and 1.5 logarithmic removals of coliforms and coliphages, respectively, and up to a 58% increase in the concentration of inorganics in the digestate solids compared to conventional digestion. The COD balance of the process showed that the observed increase in methane production was proportional to the solubilization efficiency and COD removal increase.

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Keywords: anaerobic digestion; sewage sludge; ultrasound; thermal treatment; digestate

Original article

Life cycle assessment of management alternatives for sludge from sewage treatment plants in Chile: does advanced anaerobic digestion improve environmental performance compared to current practices?

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ABSTRACT

Sludge generation is currently one of the most important issues for sewage treatment plants in Chile. In this work, the life cycle environmental impacts of four sludge management scenarios were studied, focusing on the comparison of current practices and advanced anaerobic digestion (AD) using a sequential pre-treatment (PT). The results show that AD scenarios presented lower potential impacts than lime stabilization scenarios in all assessed categories, including climate change, abiotic depletion, acidification, and eutrophication in terrestrial, marine and freshwater ecosystems. The overall environmental performance of advanced digestion was similar to conventional digestion, with the main difference being a decrease in the climate change potential and an increase in the abiotic depletion potential. Acidification and eutrophication categories showed similar performances in both conventional and advanced AD. The effect of PT in the AD scenarios was related to energy recovery, sludge transport requirements and nutrient loads in the sludge and supernatant after digestate dewatering. Considering the results, PT could be a useful strategy to promote sludge valorization and decrease the environmental burdens of sludge management in Chile compared to the current scenario.

Keywords: Life cycle assessment, sludge management, pre-treatment, anaerobic digestion.