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A Review of Wet Air Oxidation and Thermal Hydrolysis Technologies in Sludge Treatment

Kevin Hii[a], Saeid Baroutian[b,c], Raj Parthasarathy[a], Daniel J. Gapes[c] and Nicky Eshtiaghi[a,*]

[a] *School of Civil, Environmental and Chemical Engineering, RMIT University, 3001, Melbourne, Australia*

[b] *Department of Chemical & Material Engineering, Faculty of Engineering, The University of Auckland, Private Bag 92019, Auckland, New Zealand*

[c] *Scion, 49 Sala Street, Rotorua 3010, New Zealand*

Abstract

With rapid world population growth and strict environmental regulations, increasingly large volumes of sludge are being produced in today's wastewater treatment plants (WWTP) with limited disposal routes. Sludge treatment has become an essential process in WWTP, representing 50% of operational costs. Sludge destruction and resource recovery technologies are therefore of great ongoing interest. Hydrothermal processing uses unique characteristics of water at elevated temperatures and pressures to deconstruct organic and inorganic components of sludge. It can be broadly categorized into wet oxidation (oxidative) and thermal hydrolysis (non-oxidative). While wet air oxidation (WAO) can be used for the final sludge destruction and also potentially producing industrially useful by-products such as acetic acid, thermal hydrolysis (TH) is mainly used as a pre-treatment method to improve the efficiency of anaerobic digestion. This paper reviews current hydrothermal technologies, roles of wet air oxidation and thermal hydrolysis in sludge treatment, and challenges faced by these technologies.

Keywords: Thermal hydrolysis; wet air oxidation; wastewater sludge; hydrothermal processing; sludge treatment

* Corresponding author: Tel.: + (61 3) 9925 9554, Email *address:* nicky.eshtiaghi@rmit.edu.au

1. Introduction

Today, rapid world population growth has increased the volume of sewage sludge produced from wastewater treatment plants (WWTP) whilst strict environmental regulations have limited their disposal (Eshtiaghi et al., 2013). The treatment of sludge has therefore become an essential part of today's WWTPs representing up to 50% of operational costs (Kroiss, 2004; Neyens and Baeyens, 2003; Spinosa and Vesilind 2001). As such, methods for sludge destruction and resource recovery are of ongoing interest. In sludge treatment, processing techniques which utilize the principles behind hydrothermal processing have been implemented for different purposes and accomplished different outcomes in the treatment line. Although these methods have achieved varying degrees of success, their relative simplicity and ease of implementation still make them attractive enough to further be investigated for improvement.

Hydrothermal processing refers to technologies involving reactions carried out in an aqueous solvent at elevated temperatures and pressures. This can not only degrade the waste but also potentially produce industrially useful by-products. Since the necessary reactions can be completed in the water phase, the need for removing water from the waste prior to processing is avoided (Baroutian et al., 2013a). Hydrothermal technologies in sludge treatment can be broadly categorized into two main groups, oxidative techniques and non-oxidative techniques. Catalysts and chemicals may or may not be involved in both cases but the main difference between the techniques is the presence of oxidative agents and subsequently the end-products achieved (Strong et al., 2011). Wet air oxidation (WAO) is representative of the oxidative techniques, and it is usually carried out at high temperatures (>200 °C) in the presence of an oxidant. Non-oxidative techniques, such as thermal hydrolysis (TH), are usually undertaken at a lower temperature range (100 °C – 200 °C) without the addition of oxidants. Although these technologies can appear anywhere on the sludge treatment line, TH is normally used as a pre-treatment step before anaerobic digestion

(AD) whereas WAO is used towards the end of the treatment line as a means of final sludge destruction. Although it is a well-proven process for sludge treatment, AD suffers from low efficiency associated with a rate-limiting hydrolysis reaction (Appels et al., 2008). By implementing TH pre-treatment, this hydrolysis step is effectively carried out in a separate reactor under optimal conditions provided by the TH process. Using high temperatures and pressures, the complex molecular compounds and cellular content of sewage sludge is broken down. This releases intracellular content and water, thus making the sludge more digestible. As a result, the digestion efficiency and biogas production during AD is improved. This is particularly effective when treating waste activated sludge that contains bacterial cells, which are not easily biodegradable (Chen et al., 2012). Waste activated sludge is known to be difficult to dewater (Neyens and Baeyens, 2003). Therefore, TH would also help for dewatering of waste activated sludge.

Whereas TH is mainly used as pre-treatment in the sludge treatment line, WAO can be used as the final step in complete sludge destruction. Wet air oxidation works by oxidizing organic and inorganic substances in an aqueous solution using air or oxygen, which is achievable at high temperatures and pressures. The result is that these substances are either broken down into simpler components or converted into water and carbon dioxide with complete oxidation. The technology is comparable with incineration other than the fact that it is completed in the aqueous phase, making it very useful for wastes which are too dilute for incineration, such as sewage sludge. In contrast to incineration however, harmful emissions such as nitrous oxides (NO_x) are not released and WAO can be used to treat toxic waste components. Furthermore, since the extent of oxidation is controlled by the severity of operating conditions, the WAO can also be controlled to produce useful intermediate products such as acetic acid (Strong et al., 2011).

In the past decade, WAO and TH processes in waste treatment have been reviewed by different authors. For example, the WAO process has been reviewed for the treatment of aqueous wastes and industrial wastes by Debellefontaine and Foussard (2000) which covered topics including its history, industrial examples and reactor design. Similarly, Zou et al. (2007) have also reviewed WAO for waste treatment, covering topics such as catalysts and design. Appels et al. (2008) reviewed anaerobic digestion and briefly reviewed TH as a pre-treatment process. Carerre et al. (2010) also reviewed pre-treatment processes used to improve anaerobic digestion and presented TH as one of the methods. In addition, there are some useful review papers on different aspects of hydrothermal processing techniques (Table 1). However, no work has attempted to compare TH and WAO as hydrothermal processes implemented in sludge treatment. This paper presents an overview of the emergence and development of hydrothermal technologies specifically in the field of sludge treatment. In particular TH and WAO are compared, showcasing their fundamental differences in terms of process mechanisms, goals and end-products.

2. Hydrothermal processing

The principles behind hydrothermal technologies have long been utilized in many fields and applications besides waste treatment. The term “hydrothermal reactions” has been defined as “any heterogeneous chemical reaction in the presence of a solvent (whether aqueous or non-aqueous) above room temperature and at pressures greater than 1 atm in a closed system (Byrappa and Yoshimura, 2001). However in the context of this review, hydrothermal treatment generally refers to processes involving reactions carried out in water facilitated by high temperatures and high pressures conditions.

In sludge treatment, hydrothermal processing has four main goals: (i) enhancing anaerobic digestion process, (ii) degrading and removing organic compounds, (iii) reducing waste mass and volume and (iv) recovering valuable compounds (Baroutian et al., 2013a). Water plays an important role in hydrothermal sludge treatment where it not only acts as solvent for the sludge contents but is also a main reactant for the hydrolysis of the organic compounds in sludge (Toor et al., 2011; Brunner, 2009). At the high temperature and high pressure conditions usually employed in hydrothermal processes, water has a high reactivity and is able to break the chemical bonds in complex molecules and convert them into simpler compounds. This is known as hydrolysis and follows the following reaction (Brunner 2009):

$$A - B + H - OH \rightarrow A - H + B - OH \quad (1)$$

The main steps in WWTPs are generally a pre-treatment followed by primary and secondary treatment. During pre-treatment, coarse particles are separated from wastewater by screening. Primary sludge is produced in primary treatment when heavy compounds are settled by gravity in a primary settler. Secondary treatment involves biological treatment and produces a sludge which is highly organic and contains large amounts of microorganisms. The activated sludge process is the most popular method for secondary treatment and produces excess sludge known as waste activated sludge (WAS), which is an aquatic culture of bacteria and other living organisms. It also contains extracellular polymeric substances (EPS) produced by microorganisms in the sludge. The EPS are three-dimensional, gel-like, highly hydrated and often charged biofilm matrices that can be used to accumulate the microorganisms and cells into aggregates known as flocs. The term EPS is generally used to describe a variety of classes of macromolecules found to occur on the cell surface of the microorganisms. These compounds include polysaccharides, proteins, nucleic acids and lipids (Neyens et al., 2004). The EPS found in WAS are predominantly composed of proteins, which may have originated from proteins released from lysed cells and entrapped exoenzymes (Liu and Fang, 2003). Following secondary treatment, the mixture of primary sludge and WAS are usually treated in anaerobic digesters before disposal and digested sludge is produced during this digestion process. Wastewater sludge is thus a suspension composed of 1 to 5% of the solid waste products generated as a net result of the wastewater treatment process. It is characterized by non-degraded organics, excess bacterial populations and some minerals. The moisture content in sludge is generally very high (75 – 90 wt%) and the dry matter contains 30 – 40 wt% carbon (Bernardi et al., 2010).

Extracellular polymeric substances have been found to bind large volumes of water, making WAS especially difficult to dewater, and meaning sludge volumes cannot be reduced easily. Hydrothermal treatments are able to break down the structure of EPS to liberate bound water and destroy cell walls thus releasing cell contents in the sludge. These changes improve the dewaterability of the sludge and make it more susceptible to anaerobic digestion, and the treated sludge is also sterilized (Neyens and Baeyens, 2003). Hydrothermal technologies for waste treatment emerged more than 50 years ago with the development of the WAO process for treatment of paper mill liquors. An early technology, named the Zimmerman process or Zimpro®, used air at high pressure to cause combustion of organic compounds suspended or dissolved in water. Almost all (95%) of organic matter was removed at temperatures up to 300 °C and at pressures up to 175 bar. The main products were carbon dioxide, nitrogen, ammonia, ash and small amounts of acetic acid. A modified version of this process which operated at lower temperatures (<200 °C) was later used to treat municipal sludge. This process, called low pressure oxidation, involved very little oxidation and is in fact more similar to TH processes (Camacho et al., 2008). However, many plants faced issues with corrosion and high energy costs, and eventually closed down (Odegaard, 2004; Debellefontaine and Foussard, 2000).

A thermal hydrolysis concept can also be found during the 1960s in the form of the Porteous process, which involved applying heat treatment to sludge to improve its dewaterability before incineration (Camacho et al., 2008). The Porteous process operated at higher temperatures (200 °C) than today's thermal hydrolysis processes and resulted in an end product which could be dewatered to 40 – 60% solids content without the aid of chemicals (Hecht and Duvall, 1975). However, technical problems, issues with odor and economic factors have also led to most plants to shut down (Kepp et al., 2000).

The more recent thermal hydrolysis processes developed by Cambi were a result of research work which showed advantages of operating at lower temperatures (150 – 200 °C). The resulting processes were designed around an optimum temperature of 170 °C which gave the best compromise between improved dewaterability at higher temperatures and better digestibility at lower temperatures. Cambi TH processes are the most widely used TH processes at present (Maugans and Ellis, 2002; Camacho et al., 2008).

The main difference between WAO and TH is that oxidation reactions are desired in WAO processes whereas they are not necessary in TH processes; oxidation is achieved by the addition of an appropriate oxidant such as oxygen gas or hydrogen peroxide. The TH process is largely used as a pre-treatment for other processes in the sludge treatment line for its ability to alter sludge properties. As oxidation is an ultimate method for the organic waste destruction, it is typically used as one of the final processes in the sludge treatment line. Typical setups for TH and WAO are illustrated in Figure 1(a) and (b).

3. Wet air oxidation (WAO)

Wet oxidation or wet air oxidation technologies were first commercialized for the production of artificial vanilla flavoring and later for the destruction of paper-mill sludge and biological sludge. Today, the application of this technology has expanded – most successfully for treatment of industrial wastes such as the caustic solution from scrubbing towers, and for treatment of powdered activated carbon (Maugans and Ellis, 2002). Other applications include the production of useful products such as acetic acid (Shanableh, 2000), biofuel from microalgae (Alba et al., 2011) and synthesis of methyl methacrylate (Giudici & Maugans, 2000).

The WAO process can be defined as "the oxidation of organic and inorganic substances in an aqueous solution or suspension by means of oxygen or air at elevated temperatures and pressures either in the presence or absence of catalysts" (Zou et al., 2007). The main reactions are similar to incineration, and any substance that can be incinerated can be oxidized in water via WAO. The WAO process is therefore ideal for treating waste liquors, slurries and sludge where the organic matter is very high in concentration compared to water. Another benefit of the WAO process is that nitrous oxide, sulfur dioxide, hydrochloric acid, dioxins, furans, and fly ash are not generated. The WAO process is capable of up 99%

conversion of toxic organics to harmless end products. For compounds which are not completely oxidized, intermediate compounds representing up to a quarter of the original mass of the organic matter are formed, such as small carboxylic acids.

Typical conditions for WAO are temperatures between 150 - 320 °C, at 20 – 150 bar and with a residence time 15 – 120 minutes. The type of application is usually determined by the range of temperatures used. Low temperature oxidation (100 – 200 °C) is used for thermal conditioning of municipal and paper industry sludge, whereas medium temperature (200 – 260 °C) oxidation is typically used for treatment of ethylene spent-caustics and some other industrial wastes, as well as for regeneration of powdered activated carbon used in wastewater treatment. Higher temperatures (260 – 320 °C) are used for sludge destruction and treatment of industrial wastewaters including organic industrial wastes such as pharmaceutical wastes and solvents. At the higher end of this temperature range, complete destruction of municipal, pulp and paper and other organic sludge is expected (Giudici & Maugans, 2000). This high temperature range is within the sub-critical region for water where the solubility of salts is reduced. Precipitated salts may be the cause of the corrosion that was a problem for early Zimpro sludge treatment operations. The process of WAO must be undertaken in the aqueous phase so high pressures are required to maintain water as a liquid. Pressurization also increases the concentration of dissolved oxygen and thus increases the oxidation rate (Debellefontaine & Foussard, 2000).

3.1. Kinetics and mechanisms of WAO

The composition of sewage sludge can vary greatly but the main components are carbohydrates, proteins and lipids. The first stage in the WAO of sludge involves a large proportion of the insoluble organic content being converted into simpler soluble organics compounds (sugars, amino acids, fatty acids, etc.). The smaller molecules are then oxidized into easily biodegradable and oxygenated products (carbon dioxide, inorganic salts and water) (Bernardi et al., 2010). This conversion is achieved through a number of hydrolysis and oxidation reactions occurring in series. These series of reactions are propagated by an organic radical obtained through oxidation of C-H bonds. The organic radicals produced are able to oxidize all organic compounds that contain hydrogen via hydrogen abstraction. The organic compounds are gradually decomposed into more stable intermediates which are finally oxidized to carbon dioxide and water. The overall reaction rate slows down as the easily oxidized compounds are gradually removed and acetic acid and other stable intermediates are formed (Imteaz & Shanableh, 2004).

To simplify the reaction mechanism for WAO, it can be assumed that the destruction of sludge proceeds via two pathways – it can proceed either directly or indirectly. In the direct pathway, all initial relatively unstable intermediates in sludge come into direct contact with oxygen and are converted into carbon dioxide. In the indirect pathway, these initial relatively unstable intermediates first undergo hydrolysis to form relatively refractory intermediates such as acetic acid. These intermediates are later oxidized into carbon dioxide. Based on this simplified reaction scheme, Li (1991) developed a generalized kinetic model for WAO of organic compounds where production of an intermediate such as acetic acid was considered to be the rate-limiting step. The overall reaction rate can be calculated according to a general model (Equation 1), which is true when describing the global reaction rate of any elementary chemical reaction (Debellefontaine and Foussard, 2000; Li et al., 1991). However, sludge contains a complex mixture of compounds. Through the series of reactions involved in WAO, some of the organic compounds are fully oxidized, whereas some are transformed to intermediate products of lower reactivity.

The generalized kinetic model of Li et al. (1991) is given in Equation 2, which describes the change in concentration of organic compounds over time. The concentrations for A and B can be expressed in terms of total organic carbon (TOC), chemical oxygen demand (COD), or total oxygen demand (TOD). This model takes into account the formation and destruction of rate-controlling intermediates, based on the 2-pathway reaction scheme described previously. It was decided that the global rate for WAO depended on the formation rate of final oxidation products as well as the formation and destruction rates of low-reactivity intermediates. This was due to the relatively high activation energies of these intermediates, which are represented by acetic acid, methanol and ethanol.

$$r_c = k_0 e^{-\frac{E}{RT}} C_i \left(C_{O_2}\right)^b$$

(2)

$$\frac{(A+B)}{(A+B)_0} = \frac{k_2}{k_1+k_2-k_3} e^{-k_3 t} + \frac{k_1-k_3}{k_1+k_2-k_3} e^{-(k_1+k_2)^t}$$

(3)

$$k_i = k_{0,i} e^{-\frac{E_i}{RT}} \left(C_{O_2}\right)^{b_i}$$

(4)

where

r_c = Rate of chemical reaction

k_0 = Pre-exponential factor for the rate of a reaction

E =Activation energy (k/Jmol)

R = Ideal gas constant (8.3145 J/mol.K)

T = Temperature (K)

C_i = Concentration of organic substrate where i represents the i^{th} substrate (mol/L)

C_{O_2} = Concentration of dissolved oxygen (mol/L)

t = Time (s)

b = Partial order of the reaction with respect to the oxidant

A = Concentration of all initial and intermediate organic compounds other than acetic acid

B = Concentration of acetic acid

k_i = Rate constant for the reaction of a specific compound, i (i = 1, 2, or 3)

Imteaz and Shanableh (2004) have developed a model for the WAO of wastewater sludge using a simplified first-order reaction scheme. The proposed alternative WAO reaction model aimed to present a more convenient method to describe the oxidation of sludge. Instead of describing the WAO process in terms of oxidation of unstable and stable compounds, the authors simplified the reaction scheme in terms of solubilisation and oxidation of all the COD in sludge. Here, it is assumed that the destruction of COD ~~biosolids may~~ proceeds via a single pathway involving two reaction steps. Any solid COD in the sludge must first solubilize via hydrolysis before it can come into contact with the oxidants and finally oxidize. The global reaction model proposed is shown in Equation 4:

$$\frac{d(X+Y)}{dt} = -ke^{-\frac{E}{RT}}(X+Y)^m(\mathbf{O})^n \tag{5}$$

where

(X + Y)	= total COD
O	= concentration of oxidant
m	= order of reaction with respect to organic reactant
n	= order of reaction with respect to oxidant

Both models presented here are suitable for describing the WAO process. The model proposed by Li et al. (1991) is more representative of the kinetics of WAO processes. However it is more complex and requires good understanding of the contents of treated sludge, which may sometimes be impractical. On the other hand, the model proposed by Imteaz and Shanableh (2004) is much simpler but gave some inconsistent predictions in terms of effluent COD.

Several other models have also been proposed however, they are will not be described in detail for the purpose of this review. An early study on WAO of sewage sludge by Ploos van Amstel and Rietema (1973) produced a model which could be used for the design of large scale reactors. This model assumed that the sludge consisted of three groups of components which were of high reactivity, intermediate reactivity and no reactivity at all. The effect of hydrolysis on the overall conversion was neglected and the reactions were assumed to be first order. When the model results compared to the results obtained from a large scale WAO installation (200 tons per day of dry sludge), the model predicted a COD reduction value with 1% error compared to the actual value.

Verenich et al. (2002; 2003) have developed a lumped kinetic model for WAO treatment of organic wastewater. The mechanism proposed considered the degradation of organics into end products. The refractory compounds were considered to undergo two parallel reactions. The first one would lead to the formation of oxidation end-products and the second one would lead to organic compounds, which are degraded to biologically oxidizible large molecules. These large molecules will undergo further transformation into smaller biodegradable compounds which are finally be oxidized into end products.

3.2. WAO treatment conditions

Wet air oxidation processes typically take place at temperatures between 150 – 320 °C and pressures 20 – 150 bar. Researchers have considered supercritical water technologies as a part of WAO technologies (Fytlili and Zabaniotou, 2008; He et al., 2008; Zou et al., 2007) or as an alternative (Bermejo and Cocero, 2006). Fytlili and Zabanioutou, (2008) described the WAO process as "occurring in two distinctive regimes", with the first occurring at sub-critical conditions for water (below 374 °C temperature and 100 bar pressure) and the second occurring at supercritical conditions for water (above 374 °C temperature and 220 bar pressure).

Maugan and Ellis (2002) divided the typical range of WAO temperatures used for various applications, into low (100 – 200 °C), medium (200 – 260 °C) and high (260 – 320 °C). The high temperature range is commonly used for sludge destruction and industrial wastewater treatment. The range of low temperatures is used for sludge-conditioning purposes. However oxidation is unlikely to occur at low temperatures and these processes are, in fact, thermal hydrolysis processes. The WAO process typically becomes energetically self-sufficient at medium and high temperature ranges.

It has been noted that COD reduction in sludge is primarily a function of temperature and the type of sludge being treated. Up to 20% variation in COD reduction can be identified between primary, secondary and digested sludge when treated under a given reaction temperature, whilst secondary sludge was found to be most resistant to oxidation (Lendormi et al. 2001). Many researchers have highlighted the influence of temperature and reaction time on the performance of WAO (Baroutian et al., 2013b; Chung et al., 2009; Lendormi et al., 2001; Shanableh, 2000). Shanableh (2000) reported that COD removal from the sludge increased as temperature increased in the range of 280 – 460 °C, with 67 – 97% COD reduction achievable. The author noted that COD removal was also dependent on reaction time. However, COD removal was limited to 85% at temperatures below 300 °C (sub-critical water oxidation) even after 1 hour of reaction time. This was due to the generation of thermally resistant by-products, mainly acetic acid and ammonia, at the lower temperatures. At supercritical conditions however, COD removal above 99.9% was possible within 10 minutes of reaction time at 450 °C temperature. Similarly, Lendormi et al. (2001) reported that at temperatures of 240 °C, COD reduction is limited to 70% whereas COD removal efficiencies greater than 80% is achievable at 300 °C without the addition of catalysts.

More recently, Chung et al. (2009) investigated the effects of operational conditions on sludge degradation and organic acids formation. Reaction time and temperature was again found to be important factors affecting liquefaction of volatile solids. The degradation efficiency of sludge and formation of organic acids was improved with longer reaction time and higher temperatures. The high temperatures accelerate sludge dissolution whereas high pressures increased the solubility of the oxidizing agents, such as oxygen – both of which speed up sludge liquefaction. The authors found optimal conditions to be 240 °C temperatures, 60 bar pressure and 30 minutes reaction time.

Baroutian et al., (2013b) examined individual and interactive effects of process variables on the degradation of fermented municipal sludge during wet oxidation. It was found that temperature has the most significant effect on degradation rate throughout. During the near completion stage, the interaction of temperature and oxygen ratio had significant effect on sludge degradation.

In recent years, work has been done on developing wet oxidation under milder conditions and lower pressure (Abe et al., 2013; Abe et al., 2011). Wet air oxidation treatment at 150 °C temperature, 10 bar pressure and 2 hours reaction was able to give a 62% volatile suspended solids (VSS) removal efficiency. This lower pressure WAO process was considered as a sludge pre-treatment process to improve the sludge characteristics for anaerobic digestion. Studies suggested that an excessive concentration of oxygen used in the reaction led to production of recalcitrant soluble organics and toxic compounds and can reduce gas production in anaerobic digestion (Abe et al., 2013). Typically, catalysts will lower reaction temperatures and pressures to be used to achieve the same results as those achieved without catalysts in WAO processes. Refractory compounds such as acetic acid and ammonia also become more susceptible to oxidation (Luck, 1999). Catalytic wet oxidation techniques are beyond the scope of this paper.

3.3. Impact of WAO on sludge digestion efficiency

The Zimpro® process was the first commercial WAO process and several large WAO plants were built in the early 1960s for the treatment of municipal sludge to either improve the dewaterability of sludge or to achieve complete oxidation in the sludge. More than 130 Zimpro® units had been installed around the US and Europe. Most of these were used for conditioning sludge by partially oxidizing the organic fractions such that the sludge flocs are broken to release bound water. Sludge conditioning was performed at 210 – 240 °C, whereas for sludge destruction temperatures of 250 – 270 °C at 85 – 120 bar pressures were used; air was the usual oxidant used (Luck, 1999). Information regarding more recent applications of WAO sludge technologies is relatively scarce despite it often being mentioned for sludge treatment. Some examples of results achieved via WAO are provided in Table 2.

Lendormi et al. (2001) studied the application of WAO for treatment of municipal sewage sludge in tests carried out a pilot scale plant. Chemical oxygen demand removal efficiency greater than 80% was achieved at 300 °C without the use of catalysts. However it was found that at lower temperatures around 240 °C, the process produced foam which impaired the reactor operation. The lower temperatures also generated compounds that are resistant to oxidation.

Genç et al. (2002) investigated WAO for pre-treatment of digested and secondary sludge before aerobic digestion and its effect on the sludge biodegradability. Hydrogen peroxide was used as the oxidant with copper and manganese salts used as catalysts. Temperatures of 120 °C at 2 bar pressure were used to solubilize the sludge organics. The liquid phase organics concentration, measured in terms of total organic carbon (TOC) was found to increase by 16.5 % after 10 minutes, whereas an increase of 66% was achieved after 120 minutes of treatment. The biodegradability was not changed for digested sludge but was increased for activated sludge. The final solids volume was also reduced by 80% after treatment.

Zhu et al. (2004) investigated the digestion of mixture of primary and surplus sludge using wet oxidation without catalysts. WAO experiments were carried out in an autoclave at 250°C temperature and holding times ranging between 30 to 120 minutes. The volatile suspended solids (VSS) digestion efficiency was around 94-96%. However, the product liquid contained large amounts of organic matter content.

Strong et al. (2011) compared WAO to thermal hydrolysis processes as a pre-treatment for mesophilic anaerobic digestion on a mixture of primary and secondary sludge. Wet air oxidation of Sludge was carried out in a high pressure reactor at 220 °C temperature, 20 bar pressure and 2 hours reaction time. Volatile suspended solids destruction of 93% and total suspended solids (TSS) destruction of 83% was achieved. The soluble COD found in the product was lower compared to that found in thermal hydrolysis due to the oxidation of these solubilized compounds under WAO. The production of acetic acid was also found to be greater in WAO than thermal hydrolysis.

Abe et al. (2011) compared several pre-treatment methods to improve thermophilic digestion of residual sludge including low pressure wet oxidation. Wet air oxidation experiments were carried out in an autoclave for 2 hours with oxygen supplied in amounts corresponding to 0 – 120% of the theoretical oxygen required for oxidizing the carbon content of the sludge. Volatile suspended solids removal efficiencies of 62% at 150 °C and 94% at 250 °C temperature were achievable and this can be increased when the oxygen supply was increased.

Abe (2013) compared the effectiveness of thermal treatment to WAO under mild conditions for the pre-treatment of secondary sludge before thermophilic anaerobic digestion. Wet air oxidation was carried out in an autoclave under 150 °C temperatures and at 5 – 14 bar pressure for 2 hours. The treatment achieved 77% VSS digestion efficiency and the gas production was highest at 150 °C treatment with 40% of theoretical oxygen supplied.

3.4. Production of useful by-products in WAO

It is well known that the WAO process is able to produce chemical products such as volatile fatty acids (VFA), mainly acetic acid, which can be recovered for use. The production of acetic acid using WAO at sub-critical conditions was investigated by Shanableh (2000) for use as the organic reactants necessary in denitrification processes in WWTPs. The WAO effectively hydrolyses sludge solids but achieves incomplete oxidation of the organic components. This produced COD-rich liquors containing 10% wt/wt acetate, which accounted for up to 80% of soluble COD. Strong et al. (2011) using WAO process at 220 °C was able to obtain a slightly higher production of acetic acid (15% wt/wt). Chung et al. (2009) determined that the formation of organic acids increased with reaction temperature. More organic acids were formed as intermediates when the reaction temperature increases. Acetic acid production increased by four times as temperature was increased from 180 °C to 240°C, at 40 minute reaction time.

He et al. (2008) undertook a comprehensive review on resource recovery from organic wastes using hydrothermal treatment. The author described the mechanism for the formation of various compounds from hydrothermal processing of organic wastes. Acetic acid was identified as the main intermediate product. Jin et al. (2005) suggested a two-step process to improve acetic acid production which consisted both of a hydrothermal reaction process in the absence of oxygen and a reaction process with oxidant supplied afterward. In the first step, the formation of furans is accelerated as the oxidation of these compounds leads to large amounts of acetic acid. In the second step, these furans are further converted to acetic acid by oxidation with fresh supplies of oxygen. The acetic acid obtained was of a high purity.

Aggrey et al. (2011) developed a two-stage hydrothermal process based on the two-step concept proposed by Jin et al. (2005) which is a series combination of TH and WAO processes operated at the same reaction temperature of 220 °C. This process was specifically developed with the intention of maximizing acetic acid production and it was compared to TH at 140 °C and WAO at 220 °C. The WAO process achieved yield and purity of acetic acid of 12% and 38% respectively. On the other hand, the two-stage process achieved 8% yield and purity of 25%.

These works highlight the potential of using WAO to produce acetic acid from sludge. The production of useful chemical products may become an incentive for the implementation of WAO processing in sludge treatment, as research continues on the conditions which affect the production of acetic acid in WAO processing of sludge.

3.5. Commercial examples of WAO

Currently, few examples of commercial WAO plants are operational for the treatment of sludge as many of the early plants have shut down due to commercial reasons and technical issues. Debellefontaine (2000) gave an overview of some of the earlier facilities which were made up of technologies such as the Loprox ®, Zimpro ®, Athos™ and VerTech processes.

The Athos process by Veolia Water (Veolia, 2013) is one of the main WAO sludge treatment technologies currently provided commercially. The process operates at temperatures between 250-300 °C, using air or pure oxygen as the oxidant. The process is claimed to produce mineral products, clean gas emissions, and biodegradable liquids. Reference plants are available in Belgium, Italy and France.

Chauzy et al. (2010) reported that he Athos process was in use in a WWTP in North Brussels, Belgium. It is used as a final sludge-destruction process located in the sludge treatment line after the anaerobic digestion of sludge, which was pre-treated by thermal hydrolysis. The process is exothermic and becomes energetically self-sufficient after start-up. The process was also designed so that it was integrated into the plant's energy recovery scheme where the heat produced from WAO is used to produce hot water used to heat buildings and to operate dryer plate filter.

3.6. Supercritical water technologies

Supercritical water oxidation (SCWO) is basically an evolution of the WAO process where the operating temperature is increased beyond the critical temperature of water. However, because supercritical water behaves very differently to sub-critical water, many of the reactions and mechanisms in SCWO would be different from WAO. The SCWO process has been used for the treatment of various wastes (Brunner, 2009) including sludge, but for the moment in-depth review of SCWO technologies are outside the scope of this paper. Nevertheless SCWO is showing promise and is being continually developed for application in sludge treatment.

Cabeza et al. (2013) gives one example of SCWO process used in sewage sludge treatment. Here the destruction of sludge was achieved by SCWO in a hydrothermal flame regime, where at operating temperatures above autoignition temperature, the SCWO reaction proceeds in the form of flames. Reaction times can be as little as in the order of milliseconds and the process does not emit hazardous gases, unlike incineration. Furthermore, this technology can successfully achieve destruction of ammonia, which cannot be achieved via WAO alone.

On the other hand, supercritical water gasification (SCWG) is another process similar to SCWO except it occurs in the absence of oxygen, and hence does not involve oxidation. Water splitting, steam reforming, and water-gas shift reactions are the main reactions involved in SCWG. This process has been applied to treat primary sewage sludge (Wilkinson et al., 2012), which results in a vapour product containing water, carbon dioxide, methane and hydrogen. However, the technology is energy intensive compared to traditional AD sludge treatment processes.

4. Thermal hydrolysis

Thermal hydrolysis and related heat treatment processes have long been used in sludge treatment, although for different purposes. Traditionally, sludge from wastewater treatment processes were simply dewatered and disposed immediately. Thermal hydrolysis was originally used for conditioning the sludge and improving its dewaterability. Early research on TH processes began as early as the 1970s aimed at improving the settleability and filterability of sludge by altering the sludge's physical characteristics. Thermal hydrolysis was found to destroy the structural integrity of microbes in the sludge and cause the lysis of cell walls, which released cell contents. Higher temperatures and treatment times were found to destroy more cell walls and insoluble proteins could also be broken down into more soluble amino acids. Later, it was realized that combining thermal pre-treatment with anaerobic digestion could potentially improve biogas production and remove odour. Early tests on both the laboratory and pilot-scale showed good results. Anaerobic digestion has today become a promising method for sludge treatment and TH is an important pre-treatment method to improve the efficiency of the process, especially for the digestion of WAS. Essentially, under high temperature conditions (130 – 200 °C), a hydrolysis reaction occurs to break down complex molecules in sludge into simpler compounds. This results in the improved bioavailability of sludge contents for AD (Strong et al., 2011; Li & Noike, 1992).

4.1. Kinetics and mechanism of thermal hydrolysis

The TH process relates to the thermal decomposition of the sludge contents without the occurrence of oxidation and solid matter becomes soluble. Takamatsu et al. (1970) presented one of the earliest work in establishing a mathematical model to describe thermal decomposition of WAS. Because sludge is composed of very complex compounds, the mathematical model proposed represents the thermal decomposition reaction in terms of four components. These take into account the solid matter, soluble matter (evaporative and non-evaporative) and water. Experiments were carried out on WAS in an autoclave at temperatures 170 - 250 °C, and pressures 60 – 130 bar and without introducing oxygen. The COD in the solids were found to decrease and in the soluble matter, COD was increased. The total COD in the sludge however remained unchanged.

The reactions occurring during thermal decomposition were described by Takamatsu et al. (1970) in terms of solubilisation of solid matter into soluble evaporative matter and soluble non-evaporative matter. The differentiation between evaporative and non-evaporative matter was only relevant within the context of the author's experiment due to limitations in experimental procedure. Evaporative matter was described as matter lost during drying at 120 °C temperature.

Based on the assumption that the rate constants are of the Arrhenius type, the mathematical models for thermal decomposition based on changes in weight was given as:

$$\frac{dA_{wt}}{dt} = -\left(0.37e^{-\frac{249}{T}} + 0.319e^{-\frac{500}{T}}\right)(1 - \xi)A_{Wt} \quad (6)$$

$$\frac{dB_{Wt}}{dt} = 0.37e^{-\frac{249}{T}}.(1 - \xi).A_{Wt} - \left(1800e^{-\frac{4600}{T}}.B_{Wt}\right) + 0.55e^{\frac{-1260}{T}}.C_{Wt}$$

(7)

$$C_{Wt} = [\![(A]\!]_{Wt} + B_{Wt})_{init.} - A_{Wt} - B_{Wt} \quad (8)$$

where

$\xi = [\![(A]\!]_{Wt} + B_{Wt})_{init.}(-0.00457 \times T - 2.323)$;

T = Temperature (K)

$(A_{wt} + B_{wt})_{init.}$ = Initial weight of total solids

and A_{wt}, B_{wt}, C_{wt} are the weights of components A (solid matter), B (Soluble non-evaporative matter), and C (soluble evaporative matter) in mg/kg-total-sludge.

In their review on subcritical hydrothermal technologies, Toor et al. (2011) have identified a large number of studies on the reaction pathways of components typically found in biomass such as sewage sludge. These components include carbohydrates, lignin, protein and lipids. Based on individual studies on the degradation mechanisms of these components, a basic reaction mechanism in subcritical water was described. The first step of reaction involves depolymerisation of the sludge molecules. This was followed by decomposition of the resultant monomers via cleavage, dehydration, decarboxylization and deamination. The reactive fragments produced are then recombined. Since sludge is a complex waste with varying compositions, the parameters affecting the reaction rates of each individual component in sludge will likely affect the kinetics of the overall process and should be taken into consideration. For example the authors identified that the hydrolysis of carbohydrates are rapid under hydrothermal conditions, although the hydrolysis rates vary between different types of carbohydrates.

More recently, Imbierowicz and Chacuk (2012) developed a lumped kinetic model for WAS thermohydrolysis which suggested that during heating of WAS, two parallel first-order reactions would occur. The first one related to the thermal destruction and solubilisation of sludge particles to organic carbon while the second parallel reaction produced a new solid phase, which may further decomposed into carbon dioxide gas. It was found that reaction temperatures strongly impacted the decrease in the concentration of organic carbon in the solid phase as well as solubilisation of particulate organic matter.

4.2. TH treatment conditions

Table 2 presents the outcomes of TH sludge treatment under associated treatment conditions. Similar to WAO, treatment time and temperature are the most important parameters which determine the performance of the TH process. Several researchers have performed work over the last few decades to determine the effect of temperature and reaction time on WAS thermal treatment and the best conditions for the process. Most studies have agreed that the optimal range of temperature lies between 160 – 180 °C to achieve increased methane yield in subsequent anaerobic digestion (AD), but at higher temperatures the biodegradability of sludge is reduced sharply (Bougrier et al., 2008).

Li and Noike (1992) investigated the effect of TH pre-treatment on the degradation of WAS in anaerobic digestion in batch and continuous experiments. The pre-treatment temperature ranged between 62 – 175 °C with treatment times between 15 – 60 minutes. It was found that solubilisation generally increased as temperature was increased. More precisely, the solubilisation of carbohydrate and protein were found to increase as the treatment temperature increased from 120 °C to 175 °C. At a given temperature carbohydrate had greatest solubilisation, followed by protein and lipid. This showed that the degree of solubilisation achieved is dependent on the kinds of organic compounds present in WAS. Furthermore, the COD removal efficiency from WAS greatly increased with thermal pre-treatment and increased with temperature between 120 – 170 °C. Above 170 °C, the COD removal efficiency was found to decrease, indicating that an optima of 170 °C. The author concluded that for a sludge treatment system comprised of TH before anaerobic digestion, the optimal time for TH was between 30 – 60 minutes for increasing methane production from WAS. A reaction temperature between 150 – 175 °C improved anaerobic degradability of WAS and methane production. Furthermore, the retention time necessary for anaerobic digestion can be reduced.

Similarly, Carrere et al. (2010) notes that most studies report optimum TH temperatures between 160 – 180 °C under treatment times of 30 – 60 minutes. Treatment times of 1 minute were also possible in this temperature range (Dohányos et al., 2004) while treatment at much lower temperatures (70 °C) will require up to several days (Gavala et al., 2003, Ferrer et al., 2010). Dwyer et al. (2008) also finds that above 150 °C, no increase in methane production resulted despite increased solubilisation. Treatment temperatures above 170 – 190 °C in fact decrease the biodegradability of sludge.

Recently, Donoso-Bravo et al. (2011) studied the influence of TH reaction time on sewage sludge composition and anaerobic digestion performance. Pre-treatment time was varied between 0 to 30 minutes under treatment temperature of 170 °C. The hydrolysis time was concluded to result in very small improvements with regards to sludge solubilisation but greatly improves its dewaterability.

4.3. Effect of TH on biogas production

Increased methane and biogas production from anaerobic digestion is the primary goal of TH processes in sludge treatment today because not only are the resources in sludge being recovered, but the energy which can be produced from the increased methane can be used to make the TH process energetically neutral. This means that identifying the factors which affect methane yield through TH is of great interest.

Haug et al. (1978) finds that for WAS, gas production from anaerobic digestion increases as TH pretreatment temperatures increased up to 175 °C. At 100 °C, methane production was increased 14% whereas at 175 °C, up to 70% increase could be expected. Above this temperature, inhibitory materials are produced which reduced gas production. For WAS, it was particularly evident that after TH pre-treatment at 175 °C, the sludge contained toxic materials which reduced gas production in anaerobic digestion. This toxicity can be overcome by feeding a diluted sludge containing only 4% solids. Increased methane production was also accompanied by increased VSS reduction. For primary sludge, TH pre-treatment did not increase methane production significantly. Li and Noike (1992) also found that the gas production increased after TH pre-treatment but the gas production rate decreased with increasing retention time in the anaerobic digester. The gas production increased with increasing temperature between 120 – 170 °C but decreased slightly at 175 °C. The increase of gas production was nearly double for pre-treatment temperatures between 150 – 175 °C.

More recently, Pérez-Elvira et al. (2008) studied TH and anaerobic digestion under mesophilic conditions in a pilot-scale study. Pre-treatment temperatures of 170 °C and reaction time of 30 minutes was used to give a 40% increase in biogas production under half the residence time in anaerobic digestion. In another study pilot-scale study combining TH with mesophilic anaerobic digestion, Pérez-Elvira and Fdz-Polanco (2012) reported a 33% biogas production increase under 17 days residence time. Even at half this residence time, the biogas production was still 24% greater compared to conventional anaerobic digestion. Qiao et al. (2011) investigated the biogas production using different wastes in the lab-scale using hydrothermal pre-treatment at 170 °C temperature and 1 hour reaction time. The biogas production increased 67.8% for municipal sewage sludge after hydrothermal treatment. Wilson et al. (2011) reported biogas production increase between 24 – 59% after thermal pre-treatment at temperatures 150 – 170 °C and 5 – 8 bar pressure when compared with conventional mesophilic anaerobic digestion.

Most researchers generally agree that an optimum temperature for TH lies somewhere around 175 °C, without the addition of catalysts, to increase the solubilisation of sludge solids and to improve the digestibility of the sludge. Temperatures above this would have inhibitory effects in terms of digestibility and biogas production.

4.4. Energy requirement of TH

Thermal hydrolysis processes generally require an input of energy to maintain the reaction temperatures whereas WAO which is exothermic and becomes auto-thermal at high enough temperatures. In many cases, this energy requirement will impact on the implementation of TH processes in sludge treatment systems. This energy requirement needs to be overcome by the increased rate of biogas production by implementing TH pre-treatment. Careful design of the system to recover excess heat will also be necessary for the TH process to be implemented economically. Haug (1978) performed energy balances for TH and an anaerobic digestion system to treat WAS and mixed primary/secondary sludge. In case of WAS, a 70% increase in gas production rate was expected and required in this system to obtain a net energy production when an anaerobic digestion followed TH pre-treatment. A thorough energy balance study was also carried out by Pérez-Elvira et al. (2008), which considered different configurations of the TH and anaerobic digestion system as well as different options for energy integration. Without implementing an energy integration scheme, it was found that the feed concentration of sludge must be increased (from 3% to 7% total solids) in order to produce enough biogas in the system for the process to become energetically self-sufficient. An energy integration scheme which considered heat recovery from the flash vapor outlet of the TH reactor can lower the required feed concentration. It was also found out that only TH of WAS is beneficial rather than the mixture of primary sludge and WAS to be pre-treated using TH. This scheme can help a 30% increase in biogas production to achieve net energy production.

4.5. Commercial examples of TH

Currently, Cambi, a Norwegian company and French company, Veolia Water are the main companies providing TH technologies for sludge treatment. The Cambi process treats sludge under pressure (4.5 bar) at temperatures between 150 – 180 °C and improves both the digestibility and dewaterability of sludge but avoids issues with corrosion and refractory compounds encountered in higher temperature processes. Sludge is first dewatered to 17% dry solids before it is heated using recycled steam. The reaction time is up to 30 minutes and after reaction, the treated sludge is flashed into a flash tank. This technology has been implemented in a large number of wastewater treatment plants globally and especially in Europe.

Veolia Water also provides continuous and batch systems of TH processes combined with anaerobic digestion. These are marketed under the names of Exelys™ and Biothelys™ respectively and currently, one prototype plant is operating in France using reaction temperature 165 °C, 9 bar pressure and reaction time up to 30 minutes.

5. Upcoming technologies

Many interesting technologies based on the hydrothermal concept are continually being developed for application in sewage sludge treatment. Some of these incorporate ideas from both TH and WAO, blurring the lines between oxidative and non-oxidative hydrothermal processes. One such technology is the advanced thermal hydrolysis (ATH) concept developed by Abelleira et. al (2012). The ATH process can fundamentally be viewed as a modification of the TH process which combines TH with hydrogen peroxide addition. Hydrogen peroxide is a powerful oxidant, and when combined with steam injection used in TH causes a synergistic effect which achieves desirable sludge treatment effects. Like in TH, the ATH process achieves solubilisation of sludge solids and improves sludge dewaterability. However, both solubilisation and dewaterability are markedly better in the ATH process, with solubilisation up to twice as much improved. Furthermore, organic matter removal is achievable due to oxidation reactions occurring (85 - 92% organic matter removal at 170 °C, and stoichiometric hydrogen peroxide dosage). This means ATH process can also potentially be used as a final destruction method, similar to WAO. However, if used as a pre-treatment process to AD, the methane production is not necessarily improved and in some cases decreased. Therefore, further research is required to determine the operating conditions which facilitate methane production. ATH is nonetheless a very promising technology as it operates under relatively mild conditions compared to TH and WAO without the addition of catalysts and still achieves comparable results.

On the other hand, a hydrothermal treatment concept has been used to convert sludge into solid residues (Escala et. al 2013; Shi et al., 2013). This hydrothermal treatment involves heating sludge in a water medium up to temperatures of 210 °C and allowing buildup of saturation pressure. Under these conditions the sludge is broken down over a number of reactions including hydrolysis, dehydration, decarboxylation, polymerization and aromitisation. The result is a solid residue, water, and carbon dioxide. The solid residue (hydrochar) can be used as a solid fuel or use as a soil amendment for agricultural application. These technologies are more or less similar to TH although they operate at higher temperatures and generally longer reaction times. These technologies are intended as final solutions for sludge treatment rather for improvement of current sludge treatment lines.

6. Future work

Hydrothermal processing technologies have been shown to provide significant benefits and improvements to existing sludge treatment methods. Thermal hydrolysis greatly enhances anaerobic digestion with potential to increase biogas production by 40% at a half the residence time (Perez-Elvira et al. 2008). The rheological characteristics of sludge are also improved and dewatering is enhanced (Ahn et al., 2008; Chauzy et al. 2007). On the other hand, WAO is a very effective sludge reduction process which can also be used to convert wastewater sludge into useful products.

However, both TH and WAO are energy-intensive processes which may make them economically infeasible for sludge treatment. Further work should be focused on methods to make them less energy-intensive. Several research works such as those by Pérez-Elvira and Fdz-Polanco (2012) have investigated ways to integrate these processes into the overall sludge treatment line that optimizes the recycling of excess heat. This was done by looking at different configurations of the processes within the overall treatment process. This will be especially useful for WAO processes since the oxidation reactions are exothermic and the excess heat can be recovered for use elsewhere.

Thermal hydrolysis has been implemented commercially successfully, however further work needs to be done on describing the process and reaction kinetics. This can help to further optimize the process which may lead to increased biogas yields and reduced energy requirements.

Wet air oxidation has historically suffered from issues with corrosion at high operating temperatures. Catalytic WAO may be investigated in detail to help solve this issue by allowing milder operating conditions. The production of acetic acid has also shown potential benefit for further commercial development of WAO. Further work on maximizing acetic acid production following Jin et al.'s study (2005) would be beneficial.

7. Conclusion

Hydrothermal technologies involving high temperature and high pressure reactions in water play increasingly substantial roles in sludge treatment. Wet air oxidation (oxidative) is mainly used for final sludge destruction whereas TH (non-oxidative) is used as a pre-treatment method to improve subsequent sludge treatment processes. The optimal TH temperature range is between 170 - 180°C, increasing biogas production by 40%. The TH and WAO processes have been reviewed with regards to their development in sludge treatment, reaction kinetics, commercial examples, operational specifics and unique characteristics. Differences and similarities between both processes were presented. Future works for improving both processes were recommended.

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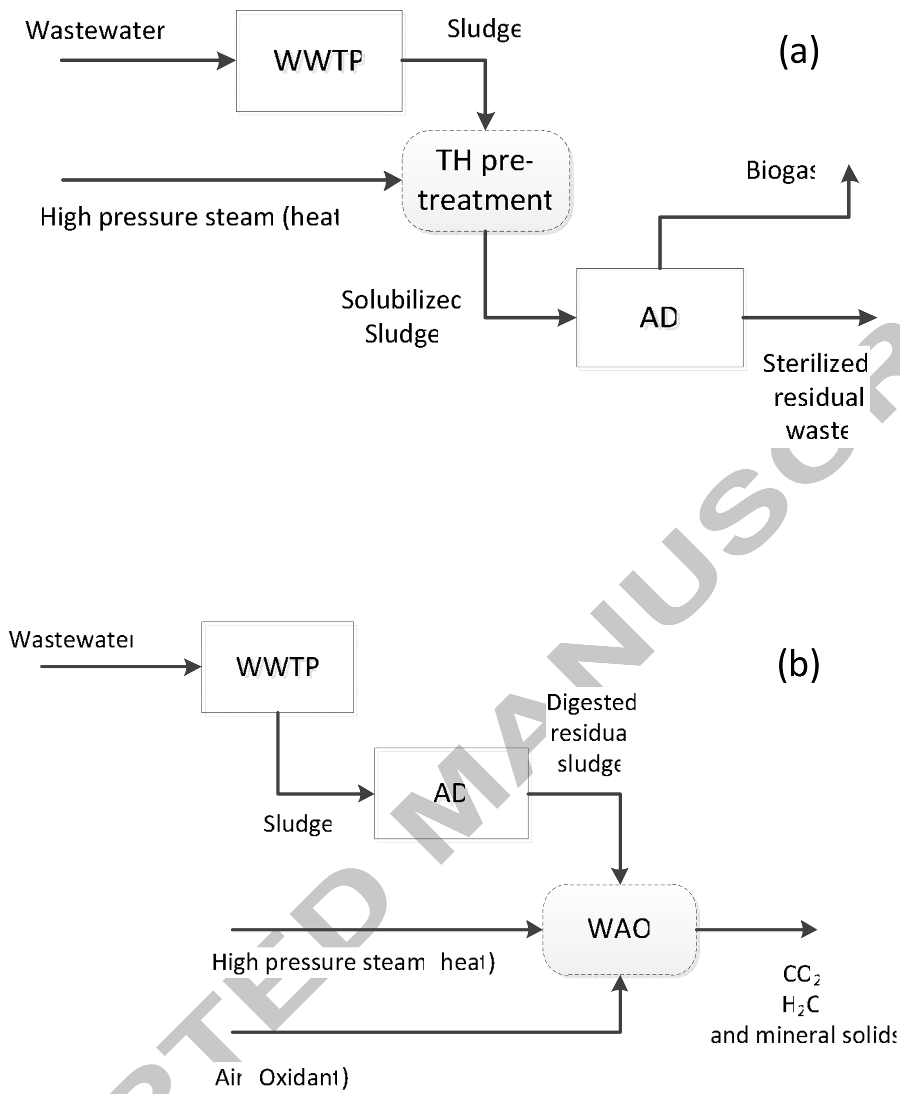
Table titles

Table 1. Reviews on non-catalytic wet oxidation (WO) and thermal hydrolysis (TH) Published from 1995 to 2013

Table 2. Typical conditions of wet air oxidation and thermal hydrolysis in sludge treatment and their impacts

Figure captions

Fig. 1. Typical configuration of thermal hydrolysis (a) and wet air oxidation (b) in a sludge treatment line


Wastewater
WWTP
Sludge
(a)
TH pre-treatment
High pressure steam (heat
Biogas
Solubilized Sludge
AD
Sterilized residual waste
Wastewater
WWTP
(b)
Digested residual sludge
AD
Sludge
WAO
High pressure steam heat)
Air Oxidant)
and mineral solids

Reference	Technology		Review highlights	Review gaps; More work required on the following area:
	WAO	TH		
Mishra et al., 1995	X		Industrial applications and miscellaneous applications.	Sludge treatment; Process parameters.
Debellefontaine et al., 1996	X		Mechanisms of Oxygen transfer, its solubility and balance.	Sludge and biological wastes; WAO chemistry.
Foussard et al., 1997	X		Process development challenges.	
Luck, 1999	X		Technical features of various commercial processes; Advantages of catalytic WO.	Non-catalytic WAO.
Imamura, 1999	X		Correlations study on reactivity with carbon content.	Sludge and biological wastes.
Kolaczkowski et al., 1999	X		Kinetics and mass transfer; Industrial applications.	Process parameters.
Debellefontaine & Foussard, 2000	X		Kinetics and mass transfer; Reactor design; Industrial examples mainly in Europe.	Non-European facilities.
Zarycki & Imbierowicz, 2001	X		Mathematical modelling; Industrial applications.	Mass transfer as a controlling phenomenon.
Maugans & Ellis, 2002	X		Process commercialization and commercial examples.	Technical aspects.
Oliviero et al., 2003	X		WAO of toxic nitrogen-containing compounds.	Nitrogenous compounds produced in WWTPs.
Neyens & Baeyens, 2003		X	Optimum treatment conditions.	Technical aspects and chemistry.
Bhargava et al., 2006	X		Chemistry and mechanisms of WAO.	Non-catalytic WAO of municipal sludge; Hydrolysis reactions during WO treatment
He et al., 2008	X	X	Production of useful chemicals via hydrothermal processing.	WAO and TH reactions.
Berardinelli et al., 2008	X		Catalytic and non-catalytic WAO.	Chemistry and technical aspects.
Zhu et al., 2011		X	WAO reaction mechanisms.	
Luan et al., 2012	X		Mechanism and kinetics of WAO; Treatment of refractory pollutants.	Sludge treatment.
Kang et al., 2013	X		Production of value-added chemicals from Lignin	Process chemistry.
Tyagi & Lo, 2013	X	X	Resource recovery from sludge; Major factors affecting processes; Advantages and drawbacks of processes.	Technical and chemical aspects of the processes; Major focus not on hydrothermal treatment.

Treatment method	Treatment conditions	Treated Material	Outcome	Reference
WAO	240 – 300 °C 50 – 110 bar O_2 oxidant 30 – 76 min	WAS	83% COD reduction at 300 °C temperature.	Lendormi et al. (2001)
	120 °C 2 bar H_2O_2 oxidant Cu catalyst 10 – 120 min	Mixed primary and activated sludge	16.5 % - 66% increase in liquid phase TOC.	Genç et al. (2002)
	250 °C 30 – 120 bar O_2 oxidant 20 – 120 min	WAS	94 – 96% VSS digestion efficiency; high organic matter content in liquid product.	Zhu et al. (2004)
	150 – 250 °C 10 – 80 bar O_2 oxidant 120 min	WAS	62% VSS removal efficiency at 150 °C and 94% VSS removal efficiency at 250 °C.	Abe et al. (2011)
	220 °C 20 bar Air oxidant 120 min	Mixed primary and secondary sludge	93% VSS destruction; 83% TSS destruction.	Strong et al. (2011)
	150 °C 5 – 14 bar O_2 oxidant 120 min	WAS	77% VSS digestion efficiency at 150°C and 40% theoretical oxygen.	Abe et al. (2013)
TH	62 – 175°C Vapour pressure 15 – 120 min	WAS	Doubled biogas production for temperatures 150 – 175 °C; >60% COD removal efficiency	Li & Noike (1992)
	170 °C 8 bar 60 seconds	WAS mixed with digested sludge	35 – 49% increased methane yield	Dohányos et al. (2004)
	170 °C Vapour pressure 30 min	WAS	Increased biogas production by 40% in half the residence time in mesophilic anaerobic digestion.	Pérez-Elvira et al. (2008)
	170 °C Vapour pressure 0 – 30 min	WAS	50 -75% carbohydrate solubilisation; hydrolysis time greatly improves dewaterability but not solubilisation	Donoso-Bravo et al. (2011)
	170 °C Vapour pressure 60 min	WAS	68% increased biogas production.	Qiao et al. (2011)
	150 – 170 °C 30 min 5 – 8 bar	WAS	24 – 59% increased biogas production in mesophilic anaerobic digestion.	Wilson et al. (2011)
	170 °C Vapour pressure 30 min	WAS	33% increased biogas production time in mesophilic anaerobic digestion.	Pérez-Elvira and Fdz-Polanco (2012)

Highlights:

- Thermal hydrolysis and wet air oxidation enhances sludge treatment processes.
- TH is a pre-treatment for anaerobic digestion and improves biogas production.
- WAO is a means of final sludge destruction and can achieve 99% organics removal.
- WAO can also be used to convert sludge into useful chemical like acetic acid.