

Wet oxidation of sewage sludge: full-scale experience and process modeling

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Abstract Nowadays, sewage sludge management represents one of the most important issues in wastewater treatment. Within the European project “ROUTES,” wet oxidation (WO) was proposed for sludge minimization. Four different types of sludge were treated in an industrial WO plant: (1) municipal primary sludge (chemical oxygen demand COD: 73.0 g/L; volatile suspended solid VSS: 44.1 g/L); (2) secondary sludge from an industrial wastewater treatment plant (WWTP) without primary sedimentation (COD: 71.8 g/L; VSS: 34.2 g/L); (3) secondary sludge from a mixed municipal and industrial WWTP without primary sedimentation (COD: 61.9 g/L; VSS: 38.7 g/L); and (4) mixed primary (70 %) and secondary (30 %) municipal sludge (COD: 81.2 g/L; VSS: 40.6 g/L). The effect of process parameters (temperature, reaction time, oxygen dosage) on WO performance was investigated. Depending on operating conditions, VSS and COD removal efficiency varied in the range 80–97 % and 43–71 %, respectively. A correlation between process efficiency and the initial VSS/TSS (total suspended solids) ratio was highlighted. Furthermore, a mathematical model of WO process for simulating VSS and COD profiles was developed.

Keywords Chemical oxygen demand · Kinetic constants · Mathematical model · Operating conditions · Process performance · Sludge minimization · Volatile suspended solid · Wet oxidation

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Introduction

Nowadays, sewage sludge treatment and disposal represent increasingly stringent issues in biological wastewater treatment plants (WWTPs) control; therefore, sludge handling is of great concern, both for scientists and technicians responsible for WWTPs management. The growing interest on these themes is demonstrated by the recent European (EU) research financing policies: as an example, the ROUTES (Novel processing routes for effective sewage sludge management-<http://www.eu-routes.org>) and END-O-SLUDG (Wastewater transformed for good-<http://www.end-o-sludg.eu>) projects can be mentioned. Due to the difficulty in finding appropriate sludge treatment and disposal methods and to the high costs associated to these operations, different technologies have been developed for sludge minimization (Liu and Tay 2001; Wei et al. 2003; Pérez-Elvira et al. 2006; Foladori et al. 2010; Uma Rani et al. 2014; Veera Lakshmi et al. 2014). A review of the many technical solutions proposed for sludge reduction is presented in Foladori et al. (2010): the methods are based on physical, mechanical, chemical, thermal, and biological treatments, and they can be integrated in wastewater or sludge handling units. The most common techniques are based on cell lysis-cryptic growth: enzymatic hydrolysis, mechanical and thermal treatment, chemical and thermochemical hydrolysis, ultrasound treatment, oxidation with ozone or other oxidants, and electrical treatment can be mentioned in this category. Other techniques for sludge reduction are based on uncoupled metabolism, microbial predation, endogenous metabolism, and hydrothermal oxidation. Among hydrothermal oxidation methods, wet oxidation (WO) was proposed as an alternative solution to conventional incineration. Even though all these techniques have been investigated, sludge minimization represents still an open issue: actually, while some processes are already applied in full-scale plants (e.g., mechanical-chemical and thermochemical treatment, sonication, wet air oxidation, oxidation with ozone, side

stream anaerobic treatment), other solutions are still under research (e.g., predation by protozoa and metazoa, sludge freezing and thawing, and irradiation with gamma waves). Table 1 shows a comparison of the sludge reduction efficiencies obtained by the more commonly applied technologies: these values were reported in the work by Foladori et al. (2010).

WO consists in the oxidation of organic and inorganic pollutants at high temperature (150–360 °C) and pressure (30–250 bar) by means of oxygen as oxidizing agent (Bertanza and Zanaboni 2011; Chung et al. 2009). The liquid phase is maintained by high pressure which also improves the oxidation rate by increasing dissolved oxygen concentration (Chung et al. 2009). As a consequence of the enhanced contact between molecular oxygen and the matter to be treated, pollutants are effectively converted to carbon dioxide, water, and intermediate oxidation products (low molecular weight organic compounds, such as acetic and propionic acid as reported in Debellefontaine and Foussard 2000).

WO technology is well-known: it was proposed 100 years ago for the treatment of both high strength industrial wastewaters and sewage sludge (Strehlenert 1911; Zimmermann 1958; van Amstel JJAP 1971; Ploos Van Amstel and Rietema 1973; Devlin and Harris 1984; Seiler 1987; Foussard et al. 1989; Joglekar et al. 1991; Debellefontaine et al. 1996; Duprez et al. 1996; Schmidt and Thomsen 1998; Debellefontaine et al. 1999; Khan et al. 1999; Luck 1999; Zerva et al. 2003). Today, 200 wet oxidation full-scale plants are operating around the world for the treatment of industrial wastewaters (Roy et al. 2010): it is, for instance, the case of pharmaceutical, chemical (synthesis processes), textile dyeing, petrochemical, iron and steel industry, pulp and paper mill black liquor wastes, spent caustic scrubbing liquids, cyanide/nitrile bearing wastes such as acrylonitrile plant wastewater, and streams rich in ammonia and phenol (Mishra et al. 1995; Debellefontaine and Foussard 2000; Hung et al. 2003; Goi

et al. 2004; Stüber et al. 2005; Quintanilla et al. 2006; Sung-Chul and Dong-Keun 2006; Collado et al. 2012).

The number of recent publications confirms the renewed interest in WO process: many studies have investigated wet oxidation, at lab scale, as a technology for excess sludge treatment (Chung et al. 2009; Yang et al. 2010; Abe et al. 2011; Gielen et al. 2011; Strong et al. 2011; Baroutian et al. 2013), and conceptual and mathematical models have been proposed for both industrial wastewaters and sewage sludge (Li et al. 1991; Luck 1996; Deiber et al. 1997; Lopez Bernal et al. 1999; Luck 1999; Zhang and Chuang 1999; Debellefontaine and Foussard 2000; Larachi et al. 2001; Sanchez-Oneto et al. 2004; Lopes et al. 2007; Mucha and Zarzycki 2008).

While many recent publications deal with the treatment at lab/pilot scale of a single type of sludge, experiences at industrial scale under real conditions and with different types of sludge are rarely described in the scientific literature. This paper concerns an experimentation conducted in a full-scale WO plant where four different types of sludge were treated: the influence of sludge origin and operating conditions (temperature, reaction time, and oxygen supply) on process performance was investigated. Moreover, a conceptual and mathematical model was developed and calibrated on experimental results. The kinetic constants determined through the mathematical simulations allow the calculation of WO performance under different process conditions and for different initial VSS/TSS ratios (volatile suspended solid (VSS), total suspended solid (TSS)), despite the sludge origin.

Materials and methods

Sludge characteristics

The following four types of sludge were submitted to WO:

1. Primary sludge from a municipal WWTP (hereinafter marked with “A”);
2. Secondary sludge from an industrial WWTP which is not provided with primary sedimentation (hereinafter marked with “B”);
3. Secondary sludge from a mixed municipal and industrial WWTP which is not provided with primary sedimentation (hereinafter marked with “C”);
4. Mixed primary (70 %) and secondary (30 %) sludge from a municipal WWTP (hereinafter marked with “D”).

Main characteristics of these four types of sludge are reported in Table 2: Chemical oxygen demand (COD) and VSS/TSS ratio varied in the ranges 61.9–81.2 g/L and 0.60–0.75, respectively. As expected, the majority of total COD (85–95 %) was in the particulate form (data not shown). Sludge

Table 1 Comparison of the sludge reduction efficiency obtained by different technologies (Foladori et al. 2010)

Technology	Sludge reduction [%]
Aerobic digestion	<30 (VSS)
Anaerobic digestion	30–50 (VSS)
Mechanical disintegration—stirred ball mills	12–14 (VS)
Ultrasonic disintegration	4.5–12.2 (VS)
Ozonation	8.9–32, 59 (TSS)
Digestion with alternating aerobic/anoxic/anaerobic conditions	<10
Thermophilic anaerobic digestion	40–45 (VSS), 30 (TSS)

The data indicated in the table should be considered carefully, because the ranges indicated originate from various experiences reported in the literature which are not always aimed to economic viability, but often aimed to evaluate the highest performance of the technique. VSS = volatile suspended solid; VS = volatile solid; TSS = total suspended solid

Table 2 Main characteristics of the different types of sludge submitted to WO. Number, mean, median and standard deviation values are reported for the following parameters: COD, BOD₅, TSS, VSS, TKN (total kjeldahl nitrogen) and pH

Sludge	Statistic	COD [g/L]	BOD ₅ [g/L]	TSS [g/L]	VSS [g/L]	TKN [g/L]	pH [-]
A	Mean	73.0	21.1	71.8	44.1	2.9	9.1
	Median	72.9	21.2	74.6	44.3	2.9	9.5
	Std. dev.	4.0	1.8	7.2	4.2	0.09	0.88
	<i>n.</i>	18	18	18	18	18	18
B	Mean	71.8	23.1	51.0	34.2	4.8	9.4
	Median	71.3	22.7	51.6	34.3	4.8	9.4
	Std. Dev.	3.3	1.1	3.3	3.8	0.09	0.05
	<i>n.</i>	21	21	21	21	21	21
C	Mean	61.9	17.8	51.8	38.7	4.3	7.6
	Median	62.0	17.2	51.8	38.9	4.2	7.4
	Std. dev.	2.2	2.0	3.3	3.4	0.09	0.55
	<i>n.</i>	21	21	21	21	21	21
D	Mean	81.2	27.1	67.5	40.6	3.0	11.8
	Median	82.0	26.8	66.9	40.2	3.0	11.8
	Std. dev.	3.4	1.6	3.4	3.5	0.17	0.18
	<i>n.</i>	21	21	21	21	21	21

differences (e.g., in terms of VSS/TSS ratio, nitrogen concentration etc.) are mainly due to their origin that, as stated above, are quite different as far as WWTP scheme (presence/absence of primary sedimentation or denitrification section etc.) and type of wastewater (domestic, industrial, etc.) is concerned.

Wet oxidation industrial scale plant and treatment conditions

The full-scale WO plant used for the experimental activity is the DUAL TOP® (temperature, oxygen, pressure) plant, which is located in 3V Green Eagle Environmental Center, in which different WO plants operate for the treatment of both wastewaters and wastewaters plus sludge (Slavik et al. 2013). The plant consists of a reactor (volume=2,670 L), built in different special alloys in order to avoid corrosion issues, operating in continuous mode that can reasonably be assimilated to a continuous-flow stirred tank reactor (CFSTR, as proved by temperature measurements, data not shown). This plant usually works at temperatures of about 240–250 °C, pressures of about 50–55 bar, and reaction times of about 40–80 min. From an initial COD of about 20–100 g/L, the industrial scale WO plant operates a mean COD removal of about 70 % (up to 85 %) and a VSS mean removal of about 96–98 %. For the experimental activity here described, the WO plant operated with only sludge at a solid content of 5–7 %. Figure 1 represents a schematic of the WO industrial plant. The sludge fed to the reactor is preheated by means of vapor recycled from flash tanks. In the reactor, pure oxygen and further vapor are added upstream in order to reach the desired treatment conditions. In Fig. 2, some details of the WO plant are shown.

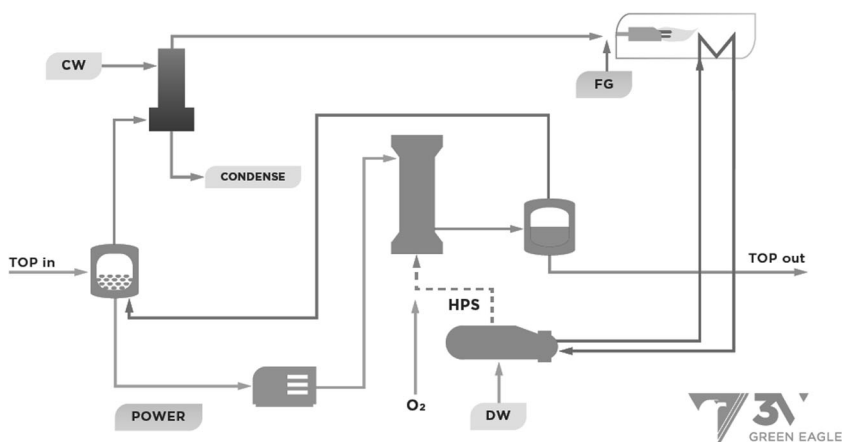
The WO plant is characterized by the following outflows:

- Liquid outflow: biodegradable wastewater fed to the subsequent biological WWTP, which consists of a main liquid effluent and a secondary effluent from vapor condense;
- Gas outflow: the wet oxidation process produces low gaseous emission (mainly CO₂, N₂, and O₂ in excess), without fly ashes. Reaction gases from WO are cooled, washed, and used as secondary air into the heater to recover the oxygen in excess as comburent;
- Residue outflow: the residue that leaves the plant is suspended in the liquid effluent and it is recovered by conventional decantation and filtration. This is a mostly inorganic material that can be converted into a primary-secondary material by recycling the heat produced during the process for the residue drying, avoiding the disposal of the residue in landfill. This material (TOP® filler) obtained the CE mark as filler according to UNI EN 13043 “Aggregates for bituminous mixtures and surface treatment for roads, airfields and other trafficked areas.”

The following different sets of operating conditions were tested for each kind of sludge:

- Temperature (*T*) 250 and 225 °C (reaction time=60 min; oxygen dosage with respect to initial COD=75 %)—operating condition *n.* 1 and 2, respectively;
- Reaction time (*t_r*) 60, 40, 70, and 100 min (*T*=250 °C; oxygen dosage with respect to initial COD=75 %)—operating condition *n.* 1, 3, 4, and 5, respectively;
- Oxygen dosage 75, 65, and 85 % with respect to initial COD (*T*=250 °C; *t_r*=60 min)—operating condition *n.* 1, 6, and 7, respectively.

Fig. 1 Schematic of WO industrial plant (CW clean water, DW demineralized water, HPS high pressure steam, FG fuel gas, Slavik et al. 2013)



The operating conditions investigated are on average limiting conditions, allowing to observe process performance variation according to changes in operating parameters; moreover, the identified ranges were set also to take into account real-scale plant requirements.

Three streams were submitted to analysis: the influent sludge (“IN”), the main liquid effluent (“OUT”), and the secondary liquid effluent (“Condensate”). Three samples were taken for each stream during the steady-state phase. Results are expressed as the average of these three samples, and plant efficiencies are calculated according to the vapor fluxes and internal recycles. COD, biological oxygen demand (BOD₅), TSS, VSS, and total Kjeldahl nitrogen (TKN) were determined according to Italian standards (APAT-IRSA/CNR 2003).

Process modeling

WO reaction kinetic can be described by the following equation (Debellefontaine and Foussard 2000):

$$\frac{dC}{dt} = k' e^{-\frac{E}{RT}} C^\alpha (O_2)^\beta \tag{1}$$

where

- C* Organic matter concentration
- k'* Pre-exponential factor
- E* Activation energy
- R* Gas constant
- T* Reaction absolute temperature
- α Reaction order with respect to organic matter concentration
- O₂* Oxygen concentration
- β Reaction order with respect to oxygen concentration.

Kinetic is usually first-order with respect to the organic matter concentration while reaction order is generally between 0.4 and 1 as far as oxygen concentration is concerned (Debellefontaine and Foussard 2000).

During WO, many reactions occur and the global velocity depends on the formation rate of final products and the formation and destruction rate of intermediate products. Sewage sludge is a complex mixture of compounds, and this model is not able to describe the observed rate in such a complex matrix. For this reason, different generalized lumped kinetic models (GLKM) were used in the scientific literature to

Fig. 2 Details of 3V Green Eagle WO plant

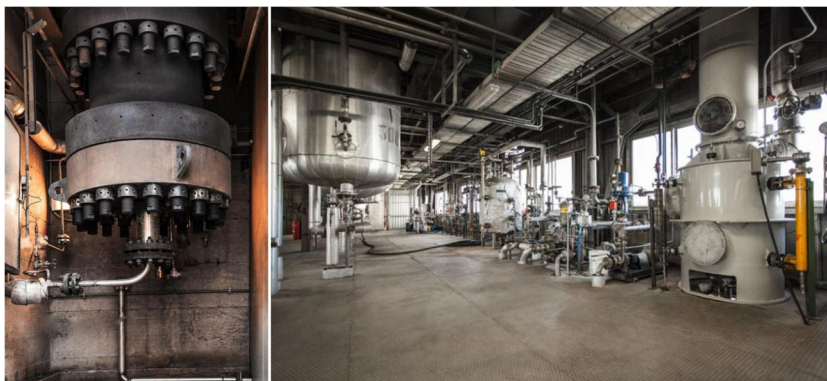
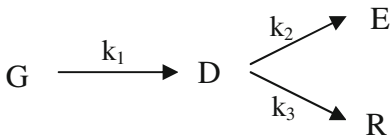
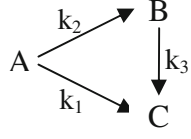
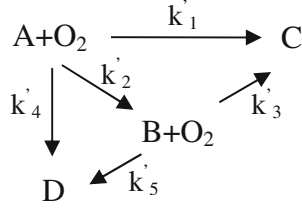
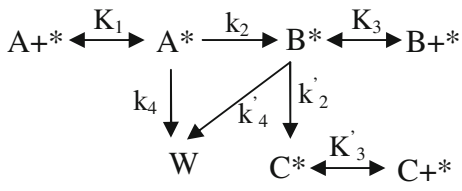
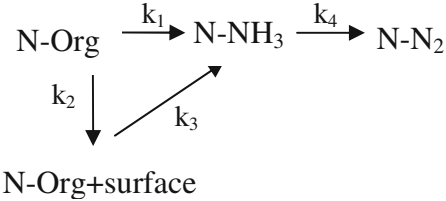
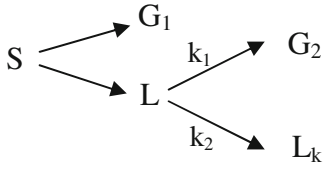


Table 3 Examples of generalized lumped kinetic models (GLKM) used to describe the reaction mechanisms (k_i =rate constants) during WO process (Bertanza and Zanaboni 2011)

Kinetic model	Bibliographic references
	<p><i>G</i>: oil and greases <i>D</i>: degradable compounds (soluble in water) <i>E</i>: CO₂ and H₂O <i>R</i>: short-chain organic acids</p>
	<p><i>A</i>: initial instable compounds <i>B</i>: intermediates hard to oxidize (e.g., acetic acid) <i>C</i>: final products (CO₂ and H₂O)</p>
	<p><i>A</i>: easily degradable compounds <i>B</i>: intermediates hard to oxidize (e.g., acetic acid) <i>C</i>: final products (CO₂ and H₂O) <i>D</i>: non oxidable substances.</p>
	<p><i>A</i>: initial compounds (e.g., phenols) <i>B</i>: oxidized intermediates <i>C</i>: final products <i>W</i>: carbonaceous residues (adsorbed onto catalyst)</p>
	<p><i>N-Org</i>: organic nitrogen <i>N-Org+surface</i>: organic nitrogen on catalyst surface <i>N-NH₃</i>: ammonia nitrogen <i>N-N₂</i>: molecular nitrogen</p>
	<p><i>S</i>: solid fraction <i>G₁</i>: gaseous fraction <i>L</i>: liquid fraction <i>G₂</i>: gaseous fraction <i>L_k</i>: compounds with a low molecular weight, hard to be chemically oxidized</p>

describe reaction mechanisms during WO process, as shown in Table 3 (Bertanza and Zanaboni 2011).

The conceptual framework of the model adopted in the present study is represented in Fig. 3.

According to this model, the following transformations occur during WO:

- Particulate organic compounds (S) are transformed into liquid intermediate products (L₁);
- A fraction of the dissolved organic substance is mineralized to gaseous compounds (G), while the other one is transformed into low molecular weight organic liquid residues (L₂, e.g., acetic and propionic acids).

The model consists in the following set of equations, assuming first-order kinetics with respect to the organic components S, L₁, and L₂ (symbols in square brackets represent concentrations):

$$\frac{d[S]}{dt} = -k_1[S][O_2]^\beta \tag{2}$$

$$\frac{d[L_1]}{dt} = (k_1[S] - (k_2 + k_3)[L_1])[O_2]^\beta \tag{3}$$

$$\frac{d[L_2]}{dt} = k_3[L_1][O_2]^\beta \tag{4}$$

$$\frac{d[G]}{dt} = k_2[L_1][O_2]^\beta \tag{5}$$

where $k_i = k'_i e^{-\frac{E_i}{RT}}$ is the rate constant of reaction (i), k'_i is the pre-exponential factor, E_i is the activation energy, R is the gas constant, T is the reaction absolute temperature, and β is the reaction order with respect to oxygen concentration $[O_2]$.

A CFSTR configuration was assumed for integration of Eqs. (2)–(5); in this case, oxygen concentration is constant

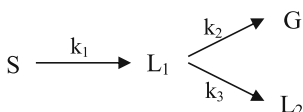


Fig. 3 Conceptual framework of the kinetic model adopted in the present study

(due to continuous supply), and, under the hypothesis of steady-state conditions, we obtain

$$[S(t)] = \frac{[S(0)]}{1 + k_1[O_2]^\beta \theta} \tag{6}$$

$$[L_1(t)] = \frac{1}{(k_2 + k_3)[O_2]^\beta \theta + 1} \left[L_1(0) + k_1[O_2]^\beta \theta S(t) \right] \tag{7}$$

$$[L_2(t)] = L_2(0) + k_3[O_2]^\beta \theta L_1(t) \tag{8}$$

where

$[S(0)]$ Initial particulate organic substance concentration

$[S(t)]$ Particulate organic substance concentration at time t

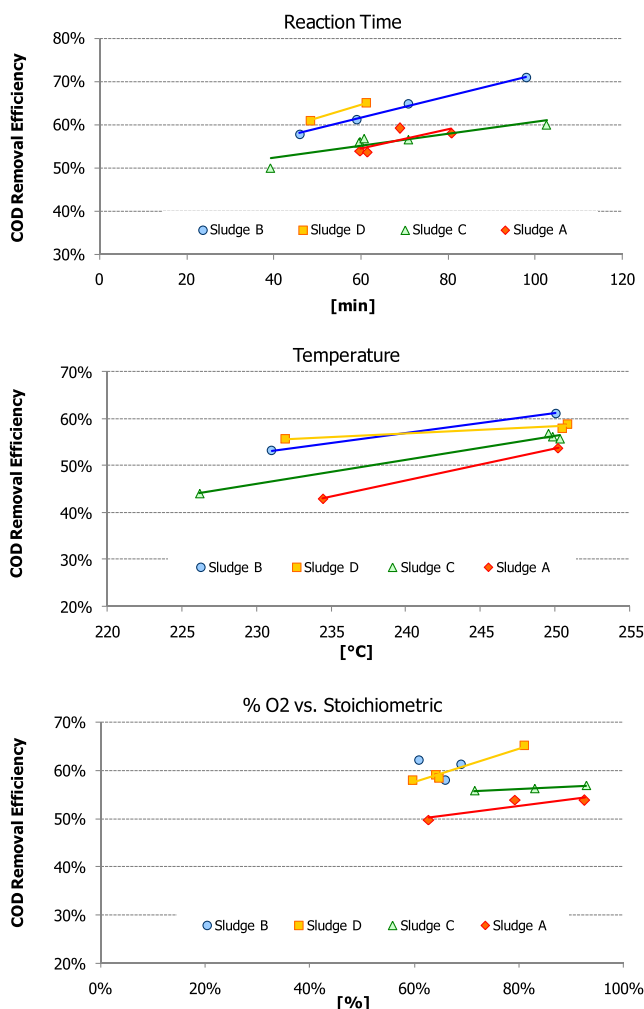


Fig. 4 Effect of operating conditions (reaction time, temperature, and oxygen dosage) on COD removal efficiency

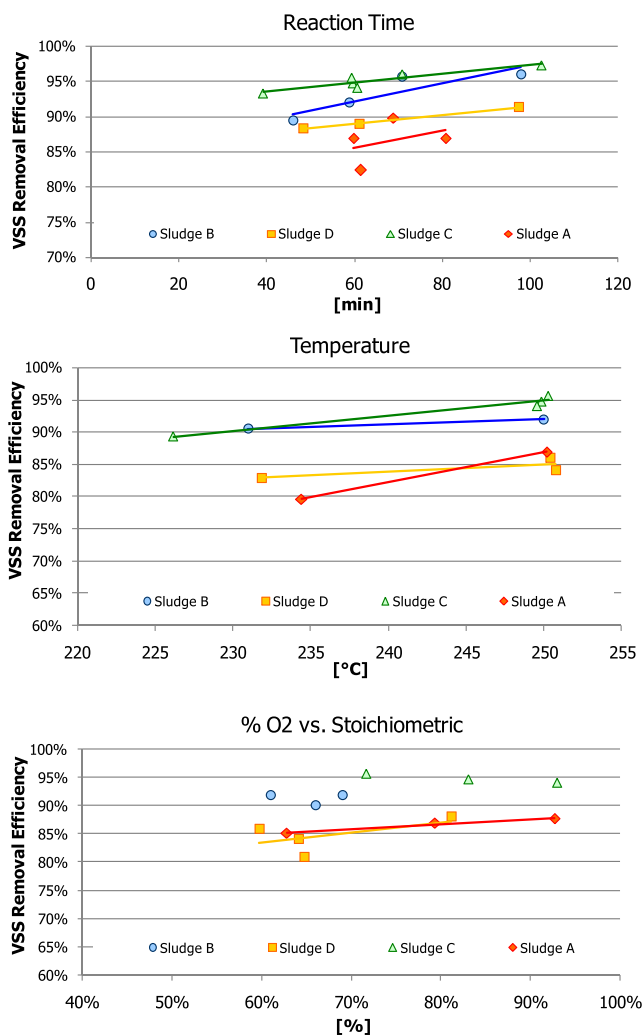


Fig. 5 Effect of operating conditions (reaction time, temperature, and oxygen dosage) on VSS removal efficiency

$[L_1(0)]$, Initial dissolved organic substance concentration (first and second component)
 $[L_2(0)]$, Dissolved organic substance concentration at time t (first and second component)
 $[L_1(t)]$,
 $[L_2(t)]$
 k_i Kinetic constant of reaction i ($k_i = k'_i e^{-\frac{E_i}{RT}}$)
 θ Hydraulic reaction time

The mathematical model was calibrated using the experimental results of industrial scale tests according to the following procedure: initial fractionation of total COD was set based on soluble COD (assumed as accounting for the component $L_1(0)$, $L_2(0)$ being set at zero) and particulate COD ($S(0)$). Equation (6) was then applied, so as to determine k_1 and β by the least square method related to the difference between the measured and calculated VSS concentrations. The obtained values were used in Eqs. (7) and (8) which account for soluble COD concentration ($[L_1] + [L_2]$). The remaining constants (k_2 and k_3) were determined by the least square method referred to the difference between measured and calculated total COD concentration ($[S] + [L_1] + [L_2]$). In order to apply Eqs. (6)–(8), oxygen concentration appraisal was necessary. Since a CFSTR configuration and steady-state conditions were assumed, oxygen concentration in the reactor was considered equal to the residual one after WO treatment. The residual oxygen concentration was calculated as the difference between the initial concentration and removed COD.

Results and discussion

Industrial scale tests

Results of WO tests on the four different types of sludge showed that COD and VSS removal efficiency varied in the

Table 4 COD and VSS removal efficiency as a function of operating condition and type of sludge

Parameter to be studied	Planned operating condition no.	Set of operating conditions	Sludge A		Sludge B		Sludge C		Sludge D	
			η COD [%]	η VSS [%]	η COD [%]	η VSS [%]	η COD [%]	η VSS [%]	η COD [%]	η VSS [%]
Temperature	1	250 °C, 60 min, 75 % O ₂	53.8	86.9	61.2	91.9	56.1	94.7	59.0	84.0
	2	225 °C, 60 min, 75 % O ₂	43.0	79.6	53.2	90.5	44.1	89.3	55.7	82.9
Reaction time	3	250 °C, 40 min, 75 % O ₂	– ^a	– ^a	57.8	89.4	49.9	93.4	61.0	88.3
	4	250 °C, 70 min, 75 % O ₂	59.1	89.8	64.7	95.6	56.5	96.1	58.3 ^b	80.8 ^b
	5	250 °C, 100 min, 75 % O ₂	58.0	87.0	70.8	96.0	59.9	97.3	62.9 ^b	91.4 ^b
Oxygen dosage	6	250 °C, 60 min, 65 % O ₂	49.6	85.1	62.0	91.8	55.8	95.6	57.9	86.0
	7	250 °C, 60 min, 85 % O ₂	53.6	87.6	57.8	90.1	56.8	94.1	65.0	88.9

^a Test not performed

^b During these tests, aimed at assessing the effect of reaction time, oxygen supply resulted as a limiting factor due to an initial influent COD underestimation

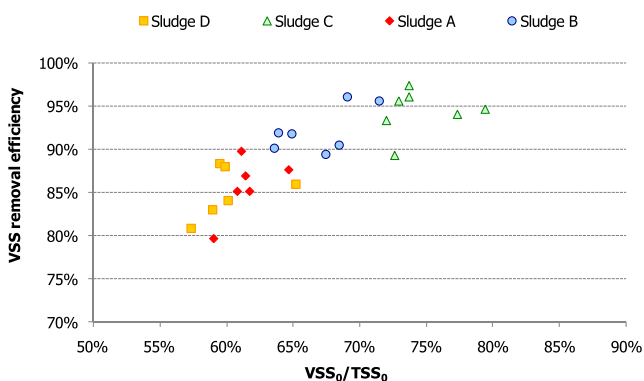


Fig. 6 VSS removal efficiency as a function of the influent VSS/TSS ratio

range 43–71 % and 80–97 %, respectively, according to different operating conditions (on average limiting conditions) and sludge origin. These results agree with similar studies output (Chung et al. 2009; Baroutian et al. 2013; Hii et al. 2014). According to Lendormi et al. (2001), the COD reduction efficiency is limited to 70 % at a temperature of 240 °C. Results of the experimental studies have to be considered according to the initial COD concentration: in fact, in case of sludge B, the COD removal efficiencies varied from 53 to 71 %. As far as VSS removal is concerned, an efficiency of 93 % was reported by Strong et al. (2011) at 220 °C, 20 bar, and 2-h reaction time. Accordingly, Abe et al. (2011) obtained a VSS abatement of 94 % at 250 °C and 2-h reaction time. During the WO process, the ammonia load can be significantly removed by means of selective catalytic oxidation (Hung et al. 2003). Therefore, as expected for a non-catalytic WO process, a low TKN abatement was observed: an average value of 20 % was measured for sludge A, B, and D while sludge C exhibited a lower efficiency (<5 %).

The effect of WO on biodegradability was assessed taking into account the BOD₅/COD ratio: considering the average value of the seven operating limiting conditions for the four

different types of sludge, the biodegradability index increased from about 0.3 (raw sludge) to about 0.5 (after WO). The aerobic biodegradability of the WO effluent is well known (Kawabata and Urano 1985; Debellefontaine and Foussard 2000). Moreover, the high biodegradability of the WO effluent is also confirmed by its different potential use (Hii et al. 2014): Strong et al. (2011) used successfully the effluent from WO of biological sludge as carbon source for the denitrification process; WO produces useful by-products (Hii et al. 2014) and the VFA-rich wet oxidation effluent may be used as a substrate for biopolymer production (Shanableh 2000); moreover, WO results suitable as a pre-treatment for sludge and biowaste anaerobic digestion in order to improve biogas production (Abe et al. 2011; Lissens et al. 2004).

Moreover, the effect of operating conditions on process performance was analyzed: on the whole, two different temperatures, four reaction times, and three oxygen dosages were tested.

Figures 4 and 5 show the results related to COD and VSS removal efficiency, respectively: reaction times and temperatures fitted quite well the planned operating conditions to be tested, while some differences were observed as far as oxygen dosage is concerned, since oxygen dosage was set according to instantaneous measurements taken from the feeding tank during the test, that could be slightly different with respect to the actual COD fed to the reactor during the whole full-scale test.

Table 4 summarizes the outcomes of the seven different sets of operating conditions that were tested for each kind of sludge.

Test results showed the dependence of all the investigated parameters on removal efficiencies. Actually, both COD and VSS abatement increased with reaction time and temperature. Few exceptions occur in Table 4, mainly due to the fact that the actual operating conditions may in some cases slightly differ from the planned ones; however, these data were

Fig. 7 Volatile suspended solid profiles (VSS/VSS₀) for different kinds of sludge: experimental data and model simulations (T=250 °C)

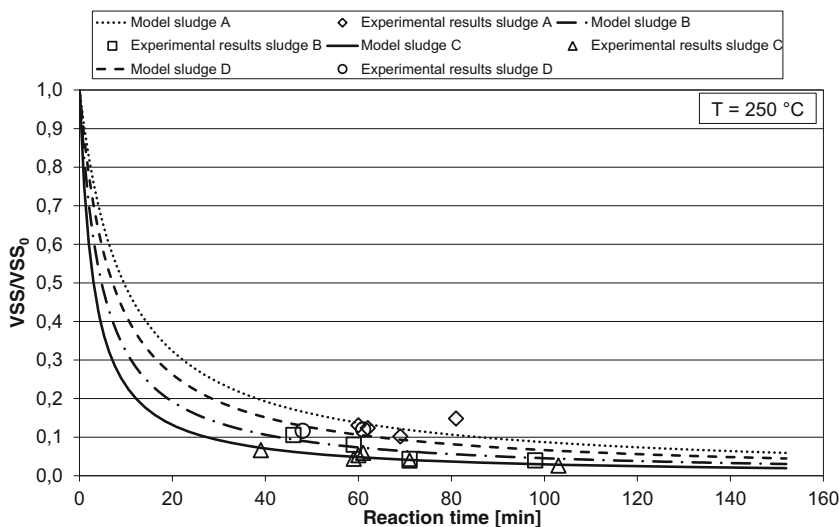
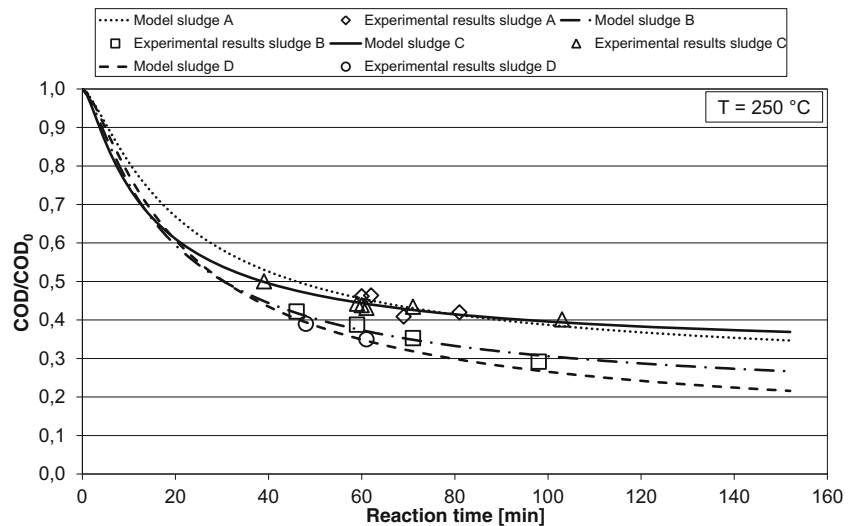


Fig. 8 Total organic substance profiles (COD/COD_0) for different kinds of sludge: experimental data and model simulations ($T=250\text{ }^\circ\text{C}$)



used in the elaboration as well, according to the respective operating condition value and limiting factor. Considering sludge C, as an example, COD removal varied from 50 to 60 % and from 44 to 56 % depending on reaction time (from 40 to 100 min) and temperature (from 225 to 250 °C), respectively. Simultaneously, VSS abatement increased from 93 to 97 % and from 89 to 95 % as a function of reaction time (from 40 to 100 min) and temperature (from 225 to 250 °C), respectively.

According to Lendormi et al. (2001), COD removal was limited to 70 % at a temperature of 240 °C, while the efficiency rose up to 80 % with higher reaction temperature (300 °C). Chung et al. (2009) investigated the influence of reaction time and temperature on process performance: after 10 min of reaction, a COD abatement of 25 and 35 % was observed at temperature of 220 and 240 °C, respectively; by increasing reaction time up to

80 min, the COD removal raised up to 58 % ($T=220\text{ }^\circ\text{C}$) and 67 % ($T=240\text{ }^\circ\text{C}$).

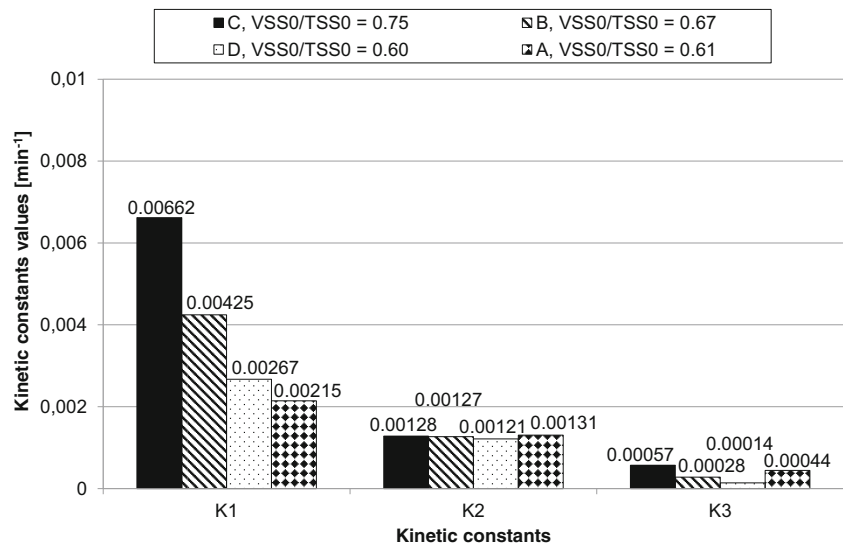
As far as VSS removal is concerned, Abe et al. (2011) observed an increase from 62 to 94 % at reaction temperature of 150 and 250 °C, respectively.

Also, considering oxygen dosage, a slight influence on WO performance was observed (see in particular COD removal efficiency in Fig. 4).

These results confirmed the outcomes obtained from lab tests conducted within the European project ROUTES (data not shown, paper in preparation) and are in a good agreement with results presented in recent literature (Chung et al. 2009).

Finally, the influence of sludge origin was analyzed considering the correlation (Fig. 6) between the VSS removal efficiency and the initial VSS/TSS ratio (VSS_0/TSS_0): sludges characterized by higher VSS_0/TSS_0 ratios showed higher VSS removal efficiencies.

Fig. 9 Kinetic constant values obtained from WO process modeling for the four different types of sludge tested at full scale ($\beta=0.4$)



Process modeling

Figure 7 shows the results of modeling the VSS trend during WO conducted at a temperature of 250 °C. In general, the different types of sludge have the same trend and the variability among them decreases at higher reaction times: this is due to the similarity of bulk composition (reaction products) as the reaction proceeds, despite the initial characteristics of the treated substrate. After 60 min, VSS/VSS₀ ratio is in the range 5–14 %, while after 150 min, it is always lower than 10 % and in particular, it varies between 2 and 6 %. Furthermore, the highest VSS₀/TSS₀ ratio corresponds to the highest VSS removal efficiency (sludge C, VSS₀/TSS₀=75 %) and vice versa (sludge D, VSS₀/TSS₀=60 %), with the exception of sludge A that actually showed a VSS₀/TSS₀ value quite similar to sludge D.

Figure 8 shows COD-simulated profiles for WO reaction at 250 °C: even in this case, there is a good correspondence between experimental data and model results. After 150 min, the COD/COD₀ ratio is always lower than 40 % and in particular, it varies between 22 and 37 %: sludges A and C have a higher residual COD/COD₀ ratio.

Figure 9 represents the comparison among kinetic constants of the different types of sludge: the transformation of the particulate organic compounds (S) into liquid intermediate products (L₁) is the predominant reaction. Moreover, it can be observed that, except for sludge A (as previously observed), higher kinetic constant values were obtained for sludges with higher VSS₀/TSS₀ ratios.

Conclusions

Wet oxidation tests were performed at industrial scale on four different types of sludge in order to study the effect of process conditions on WO efficiency: according to literature, all the parameters investigated (i.e., temperature, reaction time, and oxygen dosage) influence the process performance. Depending on operating conditions (on average limiting conditions—*T*, 225–250 °C; *t_r*, 40–100 min; oxygen dosage, 65–85 % with respect to initial COD) and sludge origin, VSS and COD removal efficiency varied between 80–97 % and 43–71 %, respectively. While with other sludge treatment technologies the VSS removal efficiency is in the range 5–50 %, a VSS abatement up to 99 % can be reached by WO: with this respect, WO can be compared to incineration. Despite the different sludge origin and initial VSS content, the average value of BOD₅/COD ratio after the treatment was about 0.5. A positive correlation between the VSS removal efficiency and the VSS₀/TSS₀ ratio was highlighted for all the sludges.

A mathematical model was proposed for both VSS and COD transformation during WO treatment. The model was

calibrated with full-scale experimental results, and kinetic constants, depending on VSS₀/TSS₀, were obtained.

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References

- Abe N, Tang YQ, Iwamura M, Ohta H, Morimura S, Kida K (2011) Development of an efficient process for the treatment of residual sludge discharged from an anaerobic digester in a sewage treatment plant. *Bioresour Technol* 102:7641–7644
- APAT-IRSA/CNR (2003) Analytical methods for water quality control. APAT Handbooks and Guidelines 29/2003, Rome (in Italian)
- Baroutian S, Smit AM, Gapes DJ (2013) Relative influence of process variables during non-catalytic wet oxidation of municipal sludge. *Bioresour Technol* 148:605–610
- Bertanza G, Zanaboni S (2011) Wet oxidation of sewage sludge. In: Belgiorno V, Naddeo V, Rizzo L (ed) *Water, wastewater and soil treatment by Advanced Oxidation Processes (AOPs)*, 1st edn. ASTER onlus ed., pp 227–240
- Chung J, Lee M, Ahn J, Bae W, Lee YW, Shim H (2009) Effect of operational conditions on sludge degradation and organic acids formation in low-critical wet air oxidation. *J Hazard Mater* 162: 10–16
- Collado S, Laca A, Diaz M (2012) Decision criteria for the selection of wet oxidation and conventional biological treatment. *J Environ Manag* 102:65–70
- Debellefontaine H, Foussard JN (2000) Wet air oxidation for the treatment of industrial wastes. Chemical aspects, reactor design and industrial applications in Europe. *Waste Manag* 20(1):15–25
- Debellefontaine H, Chakchouk M, Foussard JN, Tisso D, Striolo P (1996) Treatment of organic aqueous wastes, wet air oxidation and wet peroxide oxidation. *Environ Pollut* 92(2):155–164
- Debellefontaine H, Crispel S, Reilhac P, Perie F, Foussard JN (1999) Wet air oxidation (WAO) for treatment of industrial wastewater and domestic sludge. Design of bubble column reactors. *Chem Eng Sci* 54:4953–4959
- Deiber G, Foussard JN, Debellefontaine H (1997) Removal of nitrogenous compounds by catalytic wet air oxidation. Kinetic study. *Environ Pollut* 96(3):311–319
- Devlin HR, Harris IJ (1984) Mechanism of the oxidation of aqueous phenol with dissolved oxygen. *Ind Eng Chem Fundam* 23:387–392
- Duprez D, Delanoe F, Barbier J Jr, Isnard P, Blanchard G (1996) Catalytic oxidation of organic compounds in aqueous media. *Catal Today* 29: 317–322
- Foladori P, Andreottola G, Zigliio G (2010) Sludge reduction technologies in wastewater treatment plants. IWA Publishing, London
- Foussard JN, Debellefontaine H, Besombes VJ (1989) Effective elimination of organic liquid wastes: wet air oxidation. *Environ Eng* 115: 367
- Gielen GJH, Love SR, Lei RJ, Gapes DJ, Strong PJ, McGrouther KG, Stuthridge TR (2011) Wet oxidation technology—a potential biosolids management alternative. *IPENZ Trans* 2
- Goi D, De Leitenburg C, Trovarelli A, Dolcetti G (2004) Catalytic wet-oxidation of a mixed liquid waste: COD and AOX abatement. *Environ Technol* 25(12):1397–1403
- Hii K, Baroutian S, Parthasarathy R, Gapes DJ, Eshtiaghi N (2014) A review of wet air oxidation and thermal hydrolysis technologies in sludge treatment. *Bioresour Technol* 155:289–299

- Hung CM, Lou JC, Lin CH (2003) Wet air oxidation of aqueous ammonia solution catalyzed by composite metal oxide. *Environ Eng Sci* 20(6):547–556
- Joglekar HS, Samant SD, Joshi JB (1991) Kinetics of wet oxidation of phenol and substituted phenols. *Water Res* 25(2):135–145
- Kawabata N, Urano H (1985) Improvement of biodegradability of organic compounds by wet oxidation. *Mem Fac Eng Des Kyoto Inst Technol Ser Sci Technol* 34:64–71
- Khan Y, Anderson GK, Elliott DJ (1999) Wet oxidation of activated sludge. *Water Res* 33(7):1681–1687
- Larachi F, Iliuta I, Belkacemi K (2001) Catalytic wet air oxidation with a deactivating catalyst analysis of fixed and sparged three-phase reactors. *Catal Today* 64(3–4):309–320
- Lendormi T, Prevot C, Doppenberg F, Foussard J, Debellefontaine H (2001) Subcritical wet oxidation of municipal sewage sludge: comparison of batch and continuous experiments. *Water Sci Technol* 44(5):161–169
- Li L, Chen P, Gilkoyna EF (1991) Generalized kinetic model for wet oxidation of organic compounds. *AIChE J* 37(11):1687–1697
- Lissens G, Thomsen AB, De Baere L, Verstraete W, Ahring BK (2004) Thermal wet oxidation improves anaerobic biodegradability of raw and digested biowaste. *Environ Sci Technol* 38:3418–3424
- Liu Y, Tay JH (2001) Strategy for minimization of excess sludge production from the activated sludge process. *Biotechnol Adv* 19:97–107
- Lopes RJG, Silva AMT, Quinta-Ferreira RM (2007) Screening of catalysts and effect of temperature for kinetic degradation studies of aromatic compounds during wet oxidation. *Appl Catal B* 73(1–2):193–202
- Lopez Bernal J, Portela JR, Nebot E, Martinez de la Ossa E (1999) Wet air oxidation of oily wastes generated aboard ships: kinetic modeling. *J Hazard Mater* 67(1):61–73
- Luck F (1996) A review of industrial catalytic wet air oxidation processes. *Catal Today* 27(1–2):195–202
- Luck F (1999) Wet air oxidation, past, present and future. *Catal Today* 53:81–91
- Mishra VS, Mahajani VV, Joshi JB (1995) Wet air oxidation. *Ind Eng Chem Res* 34:2–48
- Mucha J, Zarzycki R (2008) Analysis of wet oxidation process after initial thermohydrolysis of excess sewage sludge. *Water Res* 42:3025–3032
- Pérez-Elvira SI, Nieto D, Fdz-Polanco F (2006) Sludge minimisation technologies. *Environ Sci Biotechnol* 5:375–398
- Ploos van Amstel JJA, Rietema K (1973) Wet-air oxidation of sewage sludge part II: the oxidation of real sludges. *Chem Ing Tech* 45:1205–1211
- Quintanilla A, Casas JA, Zazo JA, Mohedano AF, Rodríguez JJ (2006) Wet air oxidation of phenol at mild conditions with a Fe/activated carbon catalyst. *Appl Catal B Environ* 62:115–120
- Roy S, Vashishtha M, Saroha AK (2010) Catalytic wet air oxidation of oxalic acid using platinum catalyst in bubble column reactor: a review. *J Eng Sci Technol Rev* 3(1):95–107
- Sanchez-Oneto J, Portela JR, Nebot E, Martinez de la Ossa EJ (2004) Wet air oxidation of long-chain carboxylic acids. *Chem Eng J* 100(1–3):43–50
- Schmidt AS, Thomsen AB (1998) Optimization of wet oxidation pre-treatment of wheat straw. *Bioresour Technol* 64(2):139–151
- Seiler GS (1987) Twenty five years of sludge management by wet oxidation. *Sludge Manag Ser* 17:100–105
- Shanableh A (2000) Production of useful organic matter from sludge hydrothermal treatment. *Water Res* 34(3):945–951
- Slavik E, Galessi R, Salvetti R, Bertanza G (2013) Experiences of sludge treatment by wet oxidation. In: Mininni G (ed) *Effective sewage sludge management—minimization, recycling of materials, enhanced stabilization, disposal after recovery*, 1st edn., CNR Quaderni de “La ricerca scientifica” n. 120, Rome, pp.111–130
- Strehlenert RW (1911) Swed Patent 34:941
- Strong PJ, McDonald B, Gapes DJ (2011) Combined thermochemical and fermentative destruction of municipal biosolids: a comparison between thermal hydrolysis and wet oxidative pre-treatment. *Bioresour Technol* 102(9):5520–5527
- Stüber F, Font J, Fortuny A, Bengoa C, Eftaxias A, Fabregat A (2005) Carbon materials and catalytic wet air oxidation of organic pollutants in wastewater. *Top Catal* 33(1–4):3–50
- Sung-Chul K, Dong-Keun L (2006) Catalytic wet peroxide oxidation of dyehouse effluents with Cu/Al₂O₃ and copper plate. *Stud Surf Sci Catal* 159:393–396
- Uma Rani R, Adish Kumar S, Kaliappan S, Yeom I-T, Rajesh Banu J (2014) Enhancing the anaerobic digestion potential of dairy waste activated sludge by two step sono-alkalization pretreatment. *Ultrason Sonochem* 21:1065–1074
- Ploos van Amstel JJAP (1971) The oxidation of sewage sludge in the liquid water phase at elevated temperatures and pressures (wet-air oxidation). PhD thesis, Eindhoven University of Technology, Netherlands
- Veera Lakshmi M, Merrylin J, Kavitha S, Adish Kumar S, Rajesh Banu J, Yeom I-T (2014) Solubilization of municipal sewage waste activated sludge by novel lytic bacterial strains. *Environ Sci Pollut Res* 21:2733–2743
- Wei Y, Van Houten RT, Borger AR, Eikelboom DH, Fan Y (2003) Minimization of excess sludge production for biological wastewater treatment. *Water Res* 37(18):4453–4467
- Yang X, Wang X, Wang L (2010) Transferring of components and energy output in industrial sewage sludge disposal by thermal pretreatment and two-phase anaerobic process. *Bioresour Technol* 101:2580–2584
- Zerva C, Peschos Z, Pouloupoulos SG, Philippopoulos CJ (2003) Treatment of industrial oily wastewaters by wet oxidation. *J Hazard Mater* 97:257–265
- Zhang Q, Chuang KT (1999) Lumped kinetic model for catalytic wet oxidation of organic compound in industrial wastewater. *AIChE J* 45(1):145–150
- Zimmermann FJ (1958) New waste disposal process. *Chem Eng* 25:117–120

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