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Wet oxidation of sewage sludge from municipal and industrial WWTPs

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ABSTRACT

In the last years, sewage sludge management turned out to be a topic of great interest due to the increasing sludge production and the high cost of sludge treatment and disposal. In this context, several methods are being studied for sewage sludge minimization: among them, wet oxidation (WO) was proposed as an effective hydrothermal oxidation based technology. The aim of this work, carried out within the European project "ROUTES," was the assessment of the influence of sludge composition on process performance: for this purpose, seven different types of sewage sludge were submitted to WO tests at lab scale. Moreover, each operating condition (temperature, reaction time, and initial oxygen pressure) was varied so as to highlight the effect of process parameters on oxidation efficiency; this was essentially evaluated in terms of chemical oxygen demand (COD), volatile suspended solid (VSS) and total suspended solid (TSS) reduction. COD and VSS abatement varied in the ranges 44–85%, 71–99% depending on reaction time (15–120 min) and 22–79%, 54–99% as a function of temperature (200–250˚C), respectively. Furthermore, by comparing WO tests results of the seven types of sludge obtained under the same treatment conditions (temperature = 250˚C and reaction time = 60 min), it was highlighted that VSS and COD removal efficiency can be correlated to the initial VSS/TSS ratio.

Keywords: Process performance; Sludge minimization; VSS/TSS

1. Introduction

Nowadays, the stringent requirements in force in the European Union (EU) make sludge handling a crucial issue for the management of wastewater treatment plants (WWTPs): therefore, some projects on this theme were supported by the European Community (see, among the others: ROUTES novel processing routes for effective sewage sludge management—[1], END-O-SLUDG wastewater transformed for good—[2]). Actually, sludge treatment and disposal can account for up to 60% of WWTPs operating expenditure (OPEX) [3–5]. Moreover, excess sludge production, which for EU-27 resulted in a total amount of about 9.6 million tons dry solids (DS) in 2010 [6], is expected to exceed 13 million DS in 2020 [7]. For this

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reason, the development of technologies aiming at sewage sludge minimization represents a topic of great interest: in this context, different techniques have been studied to be applied either to wastewater or sludge treatment units. Sludge minimization can be achieved through biological, thermal, physical, chemical, or mechanical methods based on cell lysis-cryptic growth, uncoupled metabolism, microbial predation, endogenous metabolism, or hydrothermal oxidation [8]. Some of these technologies are still at the research level (e.g. predation by protozoa and metazoa, sludge freezing and thawing, and irradiation with gamma waves), while, for others, full-scale applications already exist (e.g. mechanical and thermochemical treatments, sonication, wet air oxidation). Wet oxidation (WO) was proposed as an effective hydrothermal oxidation based technology and full-scale facilities are in operation for the treatment of both sewage sludge and high strength wastewaters [9–13].

WO consists of the oxidation of organic compounds into CO_2, H_2O, and hetero-atom dissolved ions, along with smaller molecules such as short-chain carboxylic acids [14]. The process occurs in the liquid phase at high temperature (150–325˚C) and pressure (10–200 atm) with the use of an oxygen-containing gas, usually air [10].

Some recent works investigated WO process, proving the interest of the scientific community in this technology [10,11], [15–19]: in these cases, WO performance was assessed at lab scale on a single type of sludge. As for authors' knowledge, experimental studies related to the treatment of different types of sludge are rarely reported in the scientific literature.

The aim of this work, carried out within the ROUTES project, was the assessment of the influence of sludge composition on process performance: for this purpose, seven different types of sewage sludge were submitted to WO tests at lab scale. Moreover, each operating condition (temperature, reaction time, and initial oxygen pressure) was varied so as to highlight the effect of process parameters on oxidation efficiency; this was essentially evaluated in terms of chemical oxygen demand (COD), volatile suspended solid (VSS) and total suspended solid (TSS) reduction.

Other techno-economic aspects of WO were not considered in this paper because they are deeply investigated by the authors in recent publications [13,20].

2. Materials and methods

2.1. Sludge characteristics

Seven different types of sludge were submitted to WO tests:

(1) Primary sludge from a municipal conventional activated sludge plant (hereinafter marked with "A");
(2) primary sludge from a septic tank treating domestic wastewater (hereinafter marked with "B");
(3) secondary sludge from an industrial WWTP which is not provided with primary sedimentation (hereinafter marked with "C");
(4) secondary sludge from a mixed municipal and industrial WWTP which is not provided with primary sedimentation (hereinafter marked with "D");
(5) secondary sludge from a municipal WWTP provided with primary settling (hereinafter marked with "E");
(6) activated sludge from a thermophilic high strength wastewater treatment plant (hereinafter marked with "F"); and
(7) chemical–physical sludge from an industrial high strength wastewater treatment plant (hereinafter marked with "G").

Table 1 reports the main characteristics of the seven sludges: COD, Total Kjeldahl Nitrogen (TKN) and VSS/TSS ratio varied in the range 32.3–86.0 g/L, 0.6–5.9 g/L, and 0.28–0.77, respectively. The choice of the different types of sludge was carried out in order to cover the widest range of influent VSS (and COD) concentrations. Actually, it is well known that the typical VSS/TSS ratio for municipal stabilized sludge falls within the range 60–70%. Therefore, the sludge samples tested during this research, while including typical municipal sludge, were taken by both urban and industrial WWTPs. On the other hand, more diluted types of sludge (much lower VSS/TSS ratio) were not examined because it is of common knowledge that WO is self-sustaining in case COD is within the range 20–200 g/L [21,22].

2.2. WO pilot plant

WO tests were carried out in a continuously stirred autoclave built in special alloys (ASME SB 564 N 10 276, V = 1.75 L), operated in batch mode [23]. The maximum tolerable temperature and pressure are 350˚C and 200 bar, respectively. The reactor is equipped with an electric heating jacket, an internal water cooling system to control reaction temperature, a system for pressure control, and a mechanical stirrer. Plant is supervised by means of an electric control panel.

Table 1
Main characteristics of the different types of sludge submitted to WO tests

Sludge (#)	COD (mg/L)	TKN (mg/L)	VSS (mg/L)	TSS (mg/L)	VSS/TSS (–)	NVSS (mg/L)	Moisture content (%)	pH (–)
A	76,808	2,408	34,780	45,780	0.76	11,000	94.9	4.8
B	44,577	2,058	27,240	73,860	0.37	46,620	92.4	7.3
C	74,300	5,712	56,500	74,300	0.76	17,800	92.2	7.4
D	86,000	5,880	63,000	82,000	0.77	19,000	91.8	7.0
E	57,000	3,410	44,000	80,000	0.55	36,000	92.0	7.0
F	32,300	2,070	20,868	73,829	0.28	52,961	92.0	7.4
G	51,300	601	31,710	81,140	0.39	49,430	91.4	10.4

Note: VSS—volatile suspended solids; TSS—total suspended solids; and NVSS—non-volatile suspended solids.

2.3. Treatment conditions and characterization of the residual sludge after WO

The following different sets of operating conditions were tested for each sludge: (a) temperature (T): 200, 225, and 250˚C (reaction time = 60 min; stoichiometric oxygen initial partial pressure; initial TSS = 8%); (b) reaction time (tr): 15, 30, 45, 60, and 120 min (T = 250˚C; stoichiometric oxygen initial partial pressure; initial TSS = 8%). For sludge *C*, a wider range of operating conditions was investigated: temperature, oxygen initial partial pressure, and initial TSS were varied in the range 180–300˚C, 15–44 atm, and 4–10%, respectively. Each test took about one day for sludge and equipment preparation, execution of the experiment, sampling, plant cleaning, and sample processing for analyses.

The sludge was characterized in terms of COD, biochemical oxygen demand (BOD_5), TSS, and VSS. Analyses were performed according to Italian standards [24].

3. Results and discussion

Tables 2 and 3 report the results of WO tests in terms of COD and VSS removal efficiency as a function of reaction time and temperature, respectively. As expected, higher reaction time and temperature resulted in a higher removal efficiency of both COD and VSS for all the seven samples. In particular, COD and VSS abatement varied in the ranges 44–85% and 71–99%, respectively, by increasing the reaction time (t_r) from 15′ up to 120′ (T = 250˚C); and the increase of temperature from 200 to 250˚C (t_r = 60 min) led to a variation of COD and VSS removal efficiency in the ranges 22–79% and 54–99%, respectively.

These results confirmed the outcomes of previous literature studies [10–12,16,18,19,25–28]. According to [25], 80% COD removal can be achieved after 30 min at a temperature of 300˚C [28] found out that COD abatement is limited to 85% if treatment temperature is kept below 300˚C [27] assessed WO performance in terms of total organic carbon (TOC) reduction: TOC removal efficiency varied in the range 30–43% after

Table 2
COD and VSS removal efficiency (%) as a function of reaction time (t_r). Treatment conditions: temperature—250˚C; stoichiometric oxygen initial partial pressure; initial TSS—8%

Sludge (#)	t_r = 15′		t_r = 30′		t_r = 45′		t_r = 60′		t_r = 120′	
	η_{COD}	η_{VSS}	η_{COD}	η_{VSS}	η_{COD}	η_{VSS}	η_{COD}	η_{VSS}	η_{COD}	η_{VSS}
A	72	98	75	98	79	98	79	99	81	99
B	60	75	66	85	67	87	69	89	74	93
C	59	93	71	96	75	96	80	96	85	98
D	54	94	67	94	71	96	74	98	81	99
E	44	73	59	82	64	85	68	86	74	86
F	44	84	57	85	62	88	67	88	75	88
G	47	71	51	78	65	82	66	83	82	93

Note: The shady numbers represent, respectively, the minimum and maximum COD and VSS removal efficiency obtained during the tests.

Table 3
COD and VSS removal efficiency (%) as a function of temperature (*T*). Treatment conditions: reaction time—60 min; stoichiometric oxygen initial partial pressure; initial TSS—8%

Sludge (#)	$T = 200$ ˚C		$T = 225$ ˚C		$T = 250$ ˚C	
	η_{COD}	η_{VSS}	η_{COD}	η_{VSS}	η_{COD}	η_{VSS}
A	59	92	69	98	79	99
B	51	82	59	89	69	91
C	54	86	54	90	69	95
D	61	90	61	95	74	98
E	44	66	59	78	68	86
F	22	73	52	79	67	83
G	34	54	60	76	66	83

Note: The shady numbers represent, respectively, the minimum and maximum COD and VSS removal efficiency obtained during the tests.

1 h, as a function of reaction temperature (from 200 to 220˚C). In [10] it was observed that, after 80 min of reaction, COD removal improved from 43 to 67% by increasing temperature from 200 to 240˚C. As far as VSS is concerned, [16] and [18] obtained a reduction of 94 and 93% at temperature of 250˚C and 220˚C, respectively. WO full-scale tests carried out within the ROUTES project showed that COD and VSS abatement varied in the range 43–71% and 80–97%, respectively, according to different operating conditions [12].

In order to assess the influence of sludge composition on process performance, results obtained by submitting the seven samples to WO under the same treatment conditions ($T = 250$˚C; $t_r = 60$ min) were compared.

TSS removal efficiency (Fig. 1) is strongly dependent on the initial volatile solids content (VSS_0), despite the different origin and characteristics of the tested sludge: the higher the initial volatile solids content, the higher the TSS removal. VSS and COD removal efficiency can be correlated to initial VSS/TSS ratio, as well. Actually, the correlation between solids and COD abatement and initial VSS content may be, at least partially, due to the kinetic effect of oxygen concentration: COD oxidation reaction is reported to be 0.4–1 order with respect to oxygen concentration [29]. As shown in Table 4, the VSS_0/TSS_0 ratio is proportional to influent COD concentration. Oxygen supply was based on stoichiometric requirement, that is on initial COD concentration: the higher the initial COD concentration, the higher the oxygen concentration and, consequently, the reaction rate.

In addition to kinetic factors, also physical limitations can be supposed to affect somehow COD removal efficiency: when sludge is characterized by a low initial VSS/TSS ratio, reagents (COD and oxygen) are scarcely available to each other due to the massive presence of inorganic solids.

Based on these results, the correlation between VSS (and COD) abatement and initial VSS/TSS ratio reported in Fig. 1 can be used for the approximate prediction of WO process performance of a given sludge, instead of conducting WO tests, which require expensive experimental devices and are quite time-consuming.

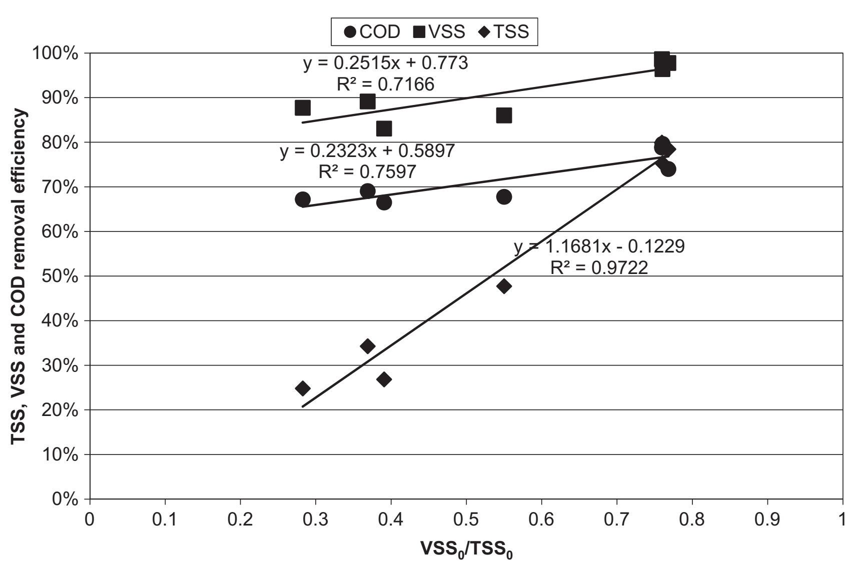

Fig. 1. Correlation between initial VSS/TSS ratio and WO performance (rated as COD, VSS, and TSS removal efficiency) for the seven types of sludge (operating conditions: $T = 250$˚C, $t_r = 60$ min, pO_2 initial = depending on the type of sludge, TSS = 8%).

Table 4
Influent COD concentration (COD_{in}), VSS/TSS ratio (VSS_0/TSS_0), and oxygen partial pressure (pO_2) for the seven types of sludge submitted to WO tests

Sludge	COD_{in} (mg/L)	VSS_0/TSS_0 (%)	$pO_{2\ in}$ (atm)
D	86,000	77	25
A	76,808	76	20
C	74,300	76	22
E	57,000	55	14
G	51,300	40	13
B	44,577	37	11
F	32,300	28	8

4. Conclusions

In this work, WO lab-scale tests were carried out on seven different types of sludge. As a general outcome, it was shown that COD and VSS abatement varies in a wide range (22–85% and 54–99%, respectively) depending on reaction time and temperature (tested intervals: 15–120 min and 200–250°C, respectively). This is in agreement with literature data. Furthermore, by comparing WO results obtained for the seven types of sludge, it was highlighted that VSS and COD removal efficiency can be correlated to initial VSS/TSS ratio: the higher the initial VSS/TSS ratio, the higher the WO process performance. This is a valuable result for practical purposes: the proposed correlation can be used for calculating expected results when submitting a given sludge to WO, based on its VSS/TSS ratio. This permits avoiding expensive and time-consuming experimental tests, at least in case a rough estimation of WO performance is required.

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