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Wet Oxidation of sewage sludge: a mathematical model for estimating the performance based on the VSS/TSS ratio

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HIGHLIGHTS

- A kinetic model of Wet Oxidation was proposed for a set of six types of sludge.
- Primary, secondary and mixed sludge from both urban and industrial WWTP was used.
- Kinetic constants values were correlated to the sludge VSS/TSS ratio.
- WO performance can now be predicted based on simple parameters (VSS, TSS).

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ABSTRACT

Wet Oxidation (WO) models are generally employed for reactor design, thus WO modeling is a topic of great interest. Indeed, WO is one of the different technologies studied for sludge minimization and treatment, which represent crucial aspects in the management of wastewater treatment plants (WWTP). Different Generalized Lumped Kinetic Models (GLKM) for sewage sludge WO were proposed in the literature for describing the complex transformations occurring in the process. Usually, works are related to a single type of sludge and, consequently, kinetic constants cannot be used for different case studies. In the present paper an alternative approach has been followed. A mathematical model was proposed and identified on a set of six different types of sludge (primary, secondary and mixed sludge from both urban and industrial WWTP). Kinetic parameters were determined for the different types of sludge with the non-linear least-squares method. In general, the predicted COD values obtained with the estimated kinetic constants closely fit experimental data: the mean absolute error associated with total (dissolved) COD is 3.2% (3.7%) and 10% (17%), respectively for the best and worst case. Kinetic constants values were finally correlated to the sludge VSS/TSS ratio (VSS = Volatile Suspended Solids; TSS = Total Suspended Solids) in order to provide a tool for a gross estimation of WO kinetic parameters, for a given sludge, relying on simple analytical measurement (VSS and TSS), commonly available at every WWTP.

1. Introduction

Sewage sludge handling exerts a strong impact on municipal wastewater treatment sector due both to the increasing amount produced as a consequence of the stringent legislative requirements and to the high cost for its final disposal [1]. Wet Oxidation (WO) is one of the numerous technologies that have been studied for sludge minimization and treatment. In this hydrothermal process, organic and oxidizable inorganic components are degraded in the liquid phase at high temperature and pressure with the use of air or oxygen. Typical operating conditions are: temperature = 150–320 °C, pressure = 20–150 bar, reaction time = 15–120 min [2]. Mild treatment conditions are generally adopted for sludge treatment, so that organics are partially converted to biodegradable intermediates with the production of carbon dioxide, water and inorganic salts, and avoiding generation of harmful emissions (i.e., CO, NO_x, SO_x, HCl, dioxins, furans, fly ash, etc.). Refractory compounds, such as ammonium and carboxylic acids of low molecular weight (i.e., acetic and propionic acids), methanol, ethanol and acetic aldehyde are formed during the process [3,4]. Due to the high temperature, pathogens are destroyed, so that sterilization is achieved.

Recently, WO of sewage sludge was investigated at lab scale [5–9] and its techno-economic and environmental sustainability

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was assessed [10]. WO modeling also represents a topic of great interest, as confirmed by the number of recent publications, models being generally used for reactor design [2–4,11,12].

Even though full-scale applications are present around the world, the process is not yet completely understood due to the complexity of the transformations involved. Indeed, different types of chemical reactions occur (i.e., hydrolysis, auto-oxidation, heterolytic/hemolytic cleavage, decarboxylation, etc. – [13]) following a very complicated pathway. Moreover, liquid, solid and gas phases are simultaneously involved, which makes nearly impossible the detailed process description. Some studies were carried out on pure compounds (i.e., phenol – [14]) but even in this case the reaction pathways were not completely understood for the above reasons.

Particularly in case of sewage sludge, which is a complex and heterogeneous matrix, a great number of compounds is involved into the process. Therefore, as an alternative approach to a detailed microscale description, certain lumped parameters such as COD or TOC can be profitably referred to. Researchers, in effect, developed different Generalized Lumped Kinetic Models (GLKM) for sewage sludge WO [3,12,15–17]. First order reactions were assumed in the model proposed by [15] and the organic matter was attributed three different levels of reactivity (high, intermediate and nihil, respectively). [16] considered the organics as grouped in three lumps: the first one (A) was supposed to undergo two parallel reactions leading to the formation of intermediate (second group, B) and final (third group, C) products, respectively. Further oxidation of lump B to lump C was also postulated. [3] proposed two different kinetic models for the two fractions (liquid and solid) of sewage sludge that was previously submitted to thermal hydrolysis. The liquid fraction was supposed to decompose into a gas and a liquid final product, while the solid fraction was supposed to be transformed in both a gas and an intermediate liquid product, the latter being subsequently degraded in a gas and a final liquid product.

To the best of authors' knowledge, unfortunately, literature results are "sludge-specific", so that the mathematical models and related kinetic constants cannot be used for a generic sludge which is different from the one used for the model design.

In this work, a WO kinetic model was proposed and identified on a set of six different types of sludge: primary, secondary and mixed sludge from both urban and industrial wastewater treatment plants (WWTP) were selected in order to cover the widest range of characteristics. Based on the results of tens of experimental tests, kinetic constants were determined for the different types of sludge and their values were finally correlated with the sludge VSS/TSS ratio (VSS = Volatile Suspended Solids; TSS = Total Suspended Solids). The aim of our research was to provide a tool for a gross estimation of WO performance, for a given sludge, just based on those simple parameters (VSS and TSS) that are commonly available at every WWTP: a simple and cheap analysis would be sufficient, in this way, instead of performing expensive and time-consuming (and "sludge-specific") WO lab tests.

2. Material and methods

2.1. Sludge characteristics and WO lab tests

The mathematical model was developed based on experimental results of tens of WO lab tests, carried out on the following six different types of sludge and published elsewhere [8]: 1) activated sludge from a thermophilic high strength wastewater treatment plant (henceforth sludge "A"); 2) primary sludge from a septic tank treating domestic wastewater (henceforth sludge "B"); 3) chemical–physical sludge from an industrial high strength wastewater treatment plant (henceforth sludge "C"); 4) secondary sludge from a municipal WWTP provided with primary settling (henceforth sludge "D"); 5) secondary sludge from an industrial WWTP which is not provided with primary sedimentation (henceforth sludge "E"); 6) secondary sludge from a mixed municipal and industrial WWTP which is not provided with primary sedimentation (henceforth sludge "F"). As reported in Table 1, influent Chemical Oxygen Demand (COD) and initial VSS/TSS ratio varied in the range 32.3–86.0 g/L and 0.28–0.77, respectively, thus representing a wide range of typical sludge characteristics.

WO tests were carried out in a continuously stirred autoclave operated in batch mode. A manometer was installed in the upper part of the autoclave for oxygen partial pressure measurement. Oxygen was introduced in the initial phase and then it was consumed while the reactions occurred. This operation mode could lead to oxygen transport limitation. For this reason, in order to avoid this issue, an excess initial oxygen partial pressure was introduced with respect to oxidizable COD. A stirring velocity of 750 rpm was chosen so as to limit mass transfer resistance and simultaneously promote oxygen sparging into the liquid phase, as suggested by [18,19]. In addition, in order to limit the possible negative effect related to the presence of a high solid content, the TSS concentration in the sludge submitted to WO was fixed to 8%: from preliminary tests performed at different TSS concentrations (data not shown), no negative effect was observed with a concentration lower than 10%. Moreover, the strong WO treatment conditions (high temperature and pressure) contribute themselves to the minimization of the oxygen transport limitation: the gas phase mass transfer resistance is negligible at high temperatures as a consequence of the high oxygen diffusivity in the gas phase and low oxygen solubility in the liquid phase [18].

Lab tests were conducted under variable treatment conditions, in terms of reaction temperature and residence time. For each sludge, the following ranges of reaction temperature (T) and residence time were investigated: 200–250 °C (reaction time = 60 min; stoichiometric oxygen initial partial pressure; initial TSS = 8%); 15–120 min (T = 250 °C; stoichiometric oxygen initial partial pressure; initial TSS = 8%). For sludge E, temperature, oxygen initial partial pressure, and initial TSS were varied in a wider range (180–300 °C, 15–44 atm, and 4–10%, respectively). Table 2 reports the list of the operating conditions tested for each sludge and subsequently used for mathematical modeling.

Further details concerning the aforementioned sludge characteristics, the pilot plant apparatus and experimental results are thoroughly reported and discussed in [8].

2.2. WO mathematical model

The organic substrate submitted to non-catalytic WO undergoes exothermic reactions, which rate can be described by Eq. (1) [20].

$$\frac{d[C(t)]}{dt} = k' e^{-\frac{E}{RT}} [C(t)]^{\alpha} [O_2(t)]^{\beta} \tag{1}$$

Table 1

COD and initial VSS/TSS ratio for the six different types of sludge submitted to WO lab tests.

Sludge #	COD [mg/L]	VSS/TSS [–]
A	32,300 ± 4,845	0.28
B	44,577 ± 6,687	0.37
C	51,300 ± 7,695	0.39
D	57,000 ± 8,550	0.55
E	74,300 ± 11,145	0.76
F	86,000 ± 12,900	0.77