Wet oxidation of activated sludge: Transformations and mechanisms

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Wet oxidation (WO) is an interesting alternative for the solubilization and mineralization of activated sludge. The effects of different temperatures (160–200 °C) and pressures (4–8 MPa), on the evolution of chemical composition and rheological characteristics of a thickened activated sludge during WO are analyzed in this work. Soluble COD increases initially to a maximum and then diminishes, while the apparent viscosity of the mixture falls continuously throughout the experiment. Based on the experimental evolution of the compositions and rheological characteristics of the sludge, a mechanism consisting of two stages in series is proposed. Initially, the solid organic compounds are solubilized following a pseudo-second order kinetic model with respect to solid COD. After that, the solubilized COD was oxidized, showing a pseudofirst kinetic order, by two parallel pathways: the complete mineralization of the organic matter and the formation of highly refractory COD. Kinetic parameters of the model, including the activation energies are mentioned, with good global fitting to the experiments described.

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1. Introduction

Sludge management is one of the main problems in municipal wastewater treatment plants (WWTPs), due to the large amount of sludge generated during the treatment process and the costs associated with its disposal. Sludge generation in these systems is an inevitable inconvenience and the difficulty of dehydrating it is a serious problem.

In order to achieve sludge with lower moisture content, it is necessary to conduct pre-treatment processes for modifying the structure of the flocs, causing the breakdown of the bacterial cells and the release of their content. The cytoplasm of cells released by hydrolysis is rich in dissolved organic compounds that can be used to improve the efficiency of a subsequent biological degradation process or can be oxidized directly using oxidation processes.

Various techniques have been studied for years to find a viable alternative for the sludge management. Some of these techniques such as thermal hydrolysis, mechanical and alkali treatments increase the solubilization of organic matter through partial or total destruction of the cellular structures of the bacteria. Other techniques include the use of oxidizing agents, which allow both the solubilization of organic matter and a significant COD (chemical oxygen demand) reduction. Among these, the most common include ozonation, Fenton oxidation and wet oxidation (WO) (Carrère et al., 2010).

So, Dewil et al. (2007) studied three different peroxidation treatments of a secondary sludge using Fenton, peroxymonosulphate and dimethyldioxirane. The results showed an improvement in the production of biogas with the three treatments, however, the dimethyldioxirane was the most effective increasing the biogas production by a factor of 2.5. Weemaes et al. (2000) determined a reduction of up to 38% of the organic matter after the ozonation of sludge and an improvement of the biogas production by a factor of 1.8 at ozone dose of 0.1 g O_3/g COD. Appels et al. (2011) studied the use of peracetic acid for the disintegration of sewage sludge. The results showed an increase of soluble organic material, favouring the production of biogas for low doses but having a negative effect at high doses.

Moreover, the WO process has been adapted for the treatment of sewage sludge as an alternative to incineration (Lin et al., 1996). Organic solids present in the sludge are oxidized in aqueous phase by injecting air or oxygen in a reactor designed to operate at elevated temperatures and pressures. Operating conditions usually include temperatures between 160 and 300 °C and pressures between 2 and 20 MPa. The products obtained are inorganic salts, carbon dioxide and water when the oxidation is complete or simple forms of biodegradable compounds when it is partial (Abelleira et al., 2012; Collado et al., 2012; Chung et al., 2009). Carboxylic acids of low molecular weight (mainly acetic acid) are formed as intermediate products during the WO of organic compounds (Inamura, 1999; Genç et al., 2002). These are known to have a high resistance to oxidation by WO, more severe conditions being necessary to achieve complete oxidation (Shende and Mahajani, 1997). The degree of oxidation is mainly a function of temperature, oxygen partial pressure, residence time and pollutant oxidisability (He et al., 2008; Padoley et al., 2012). The individual and interactive effect of the reaction temperature, oxygen to biomass ratio and mixing intensity during the WO of sludge have been examined by Baroutian et al. (2013).

Two kinds of reactions occur during the WO process, a solubilization effect caused by thermal hydrolysis and oxidation, which takes place in series or in parallel, depending on the oxygen supply (Mucha and Zarzycki, 2008). The use of this technology achieves a sludge that settles and can be filtered more easily (Khan et al., 1999), and also reduces the organic load.

Generally, WO is used as a pre-treatment step in which the sludge is solubilized and the soluble fraction is partially oxidized, yielding biodegradable products and the COD being reduced. Therefore, a subsequent biological treatment is necessary in order to complete the mineralization of the effluent (Mishra et al., 1995).

In order to improve the degradation rate, the addition of catalysts during the sludge WO has also been studied by several authors (Bernardi et al., 2010). The use of catalyst causes that refractory compounds are more susceptible to oxidation and allows the selection of milder operating conditions (Hii et al., 2014). Nevertheless, the need for a subsequent operation for the recovery of the catalyst must be considered, in order to avoid a negative impact on the environment (Collyer, 1995).

Most of the studies have reported that the chemical reaction of WO chiefly proceeds via free radical reactions (Luan et al., in press). However, different types of chemical reactions that can cause/lead to oxidation of organic compounds under WO treatment include auto-oxidation (free radical reactions involving oxygen), heterolytic/homolytic cleavage (oxidative or non-oxidative thermal degradation), hydrolysis, decarboxylation, alkoxide formation followed by subsequent oxidation (alkaline solution), and carbanion formation followed by subsequent oxidation (alkaline solution) (Bhargava et al., 2006).

The reaction kinetics for sludge subjected to WO has been addressed by some researchers. Li et al. (1991) proposed a generalized kinetic model for WO of organic compounds based on three groups of organic substances. This model includes all initial and intermediate organic compounds (group A), that can be directly oxidized to the end products (group C) or form refractory intermediates represented by acetic acid (group B) that are also oxidized to form the end products (group C). This model was successfully applied in the WO of an activated sludge, providing a good fit with the experimental data. Nevertheless, it has been mentioned that this model includes an excess of adjustable parameters and this may be the reason for its good fit when it is applied to the WO of different types of compounds (Zhang and Chuang, 1999).

Mucha and Zarzycki (2008) studied the kinetics for a sludge that had previously been thermally hydrolyzed and separated into two fractions (solid and liquid), which were subsequently submitted separately to WO. They proposed a model for each oxidized fraction. For the liquid phase, two reaction pathways were suggested in which a gas and a liquid, this latter formed by compounds resistant to oxidation, were obtained as final products. In the case of the solid phase, they propose an initial decomposition that gives a gas product and an intermediate liquid product, which in turn is decomposed to more gas product and a final liquid product. In the oxidation of the intermediate liquid, the kinetic constants obtained from the WO of the liquid phase are used, assuming that the kinetics in this phase are the same.

The rheological behaviour of the sludge is an important property to consider, since its viscosity affects operations such as pumping, the hydrodynamics of bioreactors and the transfer of oxygen. For this reason rheology studies are considered to be important for improving management in wastewater treatment plants, for example for the calculation of pressure losses during transport in the pipes, the selection of pumps and for the design of aeration systems (Ratkovich et al., 2013; Seyssiecq et al., 2003).

It has been suggested by several authors that the concentration of suspended solids has an exponential relationship with the viscosity of the sludge (Mori et al., 2006; Tixier et al., 2003). At high concentrations of solids, the space between the structural units of suspension smaller, leading to stronger inter-particle interactions and hence the higher apparent viscosity of sludge (Eshtiaghi et al., 2013). The use of pre-treatment techniques, which allow a reduction in the solids content, generated a positive effect on the viscosity of the sludge. In a previous work (Urrea et al., 2014) the effect of thermal hydrolysis on rheological properties of an activated sludge was investigated, concluding that the reduction in the amount and size of the particles and polymers caused a decrease in the interaction between them. This, in turn, favoured the flow and caused a decrease in the apparent viscosity.

The aim of this work is to analyse the effects of temperature and pressure on the wet oxidation of an activated sludge, following the evolution of the chemical and rheological characteristics of the sludge. After discussion of the results, a model is presented to describe the kinetics of the reactions.

2. Material and methods

2.1. Experimental setup

The tests were performed with thickened activated sludge from a municipal WWTP in Asturias, Spain. This sludge had the following characteristics (mean values): total suspended solids (TSS) 32.25 g/L, total chemical oxygen demand (TCOD) 34,018 mg/L, soluble chemical oxygen demand (SCOD) 1797 mg/L and pH of 6.95.

The experimental equipment used was composed of a PARR series 4520 reactor of one litre, equipped with a stirrer with two propellers to maintain continuous mixing of the solid phase and liquid. A gas humidifier, formed by a steel tank of two litres, through which the gas was passed before it was introduced into the reactor, was used. A proportional integral differential controller handled the reactor and humidifier temperatures and the gas flow. As a safety condition, both the reactor and the humidifier were filled to 70% of their capacities.

Initially, the reactor was charged with sludge and preheated to 70 °C. Once this value was reached, the desired operating values of temperature and pressure were fixed. The pressure was adjusted through a backpressure controller located at the end of the gas line.

The stirrer speed was adjusted to 500 rpm for all the experiments and the feed gas was pure oxygen, which was introduced from the start of the preheating period, maintaining a fixed flow rate of 1200 mL/min for all experiments.