Journal of Environmental Management 206 (2018) 284–290

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Sludge hydrothermal treatments. Oxidising atmosphere effects on biopolymers and physical properties

José L. Urrea, Manuel García, Sergio Collado, Paula Oulego, Mario Díaz*

Department of Chemical and Environmental Engineering, University of Oviedo, C/ Julián Clavería s/n, E-33071 Oviedo, Spain

ARTICLE INFO

Article history:
Received 19 July 2017
Received in revised form
15 September 2017
Accepted 21 October 2017

Keywords:
Oxidation state
Proteins
Settleability
Size distribution
Thermal hydrolysis
Wet oxidation

ABSTRACT

In this work, the role of an oxidising atmosphere during the hydrothermal treatment of an activated sludge at 160 °C and 40 bar, was determined. The composition and molecular weight sizes of the soluble biopolymers generated during the sludge treatment in presence (wet oxidation “WO”) or absence (thermal hydrolysis “TH”) of oxygen were compared. Likewise, the characteristics of organic material, settleability, colour and pH of the treated sludge during both treatments were analysed. The thermal treatment in presence of oxygen provided better results in terms of solubilisation, settleability and mineralisation. WO initially favoured a more intense cellular lysis, causing a higher degree of solubilisation than that achieved by TH. Either in presence or absence of oxygen, thermal treatments caused a marked worsening of the settleability of the sludge. However, the degradation of biopolymers during WO led subsequently to an improvement of the settleability properties for longer reaction times. Both treatments caused a fast solubilisation of biopolymers at the beginning by effect of the release of extracellular and intracellular material from sludge. Subsequently, the presence of oxygen produced a significant decrease in the concentration of those biopolymers. In contrast, the proteins were the only one biopolymer that was degraded during TH.

1. Introduction

Sewage sludge is an inevitable by-product in wastewater treatment plants (WWTP), which management is very complicated due to the high volumes generated and its high water content. Current sewage sludge treatment and disposal methods, such as landfilling, incineration and gasification require drying the sludge, a costly pre-treatment step, and/or risk contaminating the environment (Silva et al., 2016).

In this regard, hydrothermal processing has progressively been recognised as an attractive alternative for the sludge management during the last years. Hydrothermal treatments refer to technologies involving reactions carried out in an aqueous solvent at elevated temperatures and pressures, under inert (thermal hydrolysis) or oxidising (wet oxidation) atmospheres. Both wet oxidation (WO) and thermal hydrolysis (TH) allow the breakage of floc structure by means of solubilisation and degradation of EPS and cellular lysis (Hii et al., 2014).

The potential of hydrothermal treatments to improve the sludge management, as well as, the differences of results achieved with both techniques, have been addressed by some researchers. For instance, Baroutian et al. (2013) studied the effect of WO and TH to degrade wood extractive compounds from pulp mill sludge, such as: phenolic compounds, phytosterols, fatty acids and resin acids. They concluded that although both techniques were effective to reduce the total solid content of pulp mill sludge, the degradation of wood extractives was faster and more complete when WO was applied. Moreover, Yousefifar et al. (2017) studied and compared the effect of oxidative and non-oxidative hydrothermal processes (180–260 °C) on cellulose, which was used as a model compound of organic solid wastes. These authors found that to low temperatures, the capacity of solid degradation and solubilisation of organic matter for both techniques was similar. However, WO showed a major efficiency of solubilisation when higher temperatures of treatment were applied.

In sludge treatment, hydrothermal processing has traditionally had three main goals: the enhancement of a subsequent anaerobic digestion process, the reduction of the solid COD and/or the reduction of waste mass and volume (Barber, 2016; Chung et al., 2009; Genç et al., 2002; Khan et al., 1999). These approaches explain why, although the literature about sludge thermal

* Corresponding author.
E-mail address: mariodiaz@uniovi.es (M. Díaz).

https://doi.org/10.1016/j.jenvman.2017.10.043
0301-4797/

treatments is abundant, the vast majority of these studies are only focused on the measurement of degrees of solubilisation and mineralisation, biodegradability indexes and/or biochemical methane potentials before and after treatment (Abe et al., 2011; Strong et al., 2011; Urrea et al., 2015). Nevertheless, information about the effects of thermal treatments on the composition or on other properties of the hydrolysed sludge is very scarce or does not even exist. As example, thermal treatments involve the release of high amounts of polymeric substances into the bulk medium during the cellular lysis, whose composition, concentration and molecular size will vary with the reaction time, especially under an oxidising atmosphere (Hii et al., 2014; Urrea et al., 2016). Evidently, information about the composition and properties of these biopolymers would be very interesting in order to design the following step of treatment of the hydrolysed sludge. For instance, fouling in membrane bioreactors is greatly affected by the protein and carbohydrates contents as well as their molecular sizes (Judd, 2011). In a similar way, the composition of soluble biopolymers in the medium also has effect on its viscosity, the settleability and wettability of the remaining solids or the biodegradability and chemical properties of the supernatant (Liu et al., 2013; Martins et al., 2011; Ruiz-Hernando et al., 2015; Wang et al., 2014; Zhang et al., 2015). Moreover, taking into account that sewage sludge consists of 61% proteins and 11% carbohydrates (Chen et al., 2007), this gives rise to the following question: is it possible to obtain valuable products from the sludge by means of thermal treatments? Obviously, the first step to answer this question is to know the products obtained and the mechanisms involved in their formation.

Nevertheless, as it was previously mentioned, information about composition and properties of the products formed during thermal treatments (soluble biopolymers, mainly) are very scarce and deals only with TH processes. Thus, Ramirez et al. (2009) pointed out that soluble proteins, carbohydrates and lipids concentrations increased with increasing temperature for a fixed time and that proteins were released easier than carbohydrates from the VSS. However, Bougrier et al. (2008) and Li and Noike (1992) indicated that carbohydrates were more hydrolysable than proteins, and proteins more hydrolysable than lipids in turn. For temperatures ranging from 130 °C to 220 °C, soluble carbohydrates concentration decreased due to reactions between them or with soluble proteins (Bougrier et al., 2008; Ramirez et al., 2009). In the case of proteins, Xue et al. (2015) observed that the rise in their concentration with temperature is accompanied by an increase in the ammonia nitrogen concentration. Bougrier et al. (2008) and Donoso-Bravo et al. (2011) concluded that volatile fatty acids are produced by lipid degradation instead of by protein decomposition. Yin et al. (2015) studied the time and temperature dependence of soluble proteins and carbohydrates and ammoniacal nitrogen, and found that at 220–300 °C, soluble proteins and carbohydrates went through a maximum with the reaction time, and that the higher the temperature, the lower the time at which the maximum appear. At this point, it is important to stress that, although information about the composition of soluble biopolymer during the sludge TH is available, there is no studies dealing with the properties of these biopolymers, such as their molecular weight size.

Regarding the WO of sludge, the majority of the works about this technique are exclusively focused on volatile fatty acids, which are the main chemicals generated by WO of biomass (He et al., 2008; Hii et al., 2014), and specially, on acetic acid, whose concentrations usually exceed those of the other acids. In fact, no studies on the effects of the WO on the composition of soluble biopolymers have been found. Regarding the properties of these polymers, to the best of our knowledge, there is only a work, corresponding to our research group, in which the molecular weight distribution of the solubilised matter during a WO treatment was determined by size exclusion chromatography (Urrea et al., 2016).

Therefore, based on the foregoing, the aim of this work is to study and compare, for the first time, the effects of hydrothermal treatments (TH and WO) on the composition and molecular weight sizes of the soluble biopolymers generated during the treatment as well as on the “classical” parameters of solubilisation, mineralisation and settleability.

2. Material and methods

2.1. Sludge samples

The activated sludge employed in the experiments was obtained from a municipal wastewater treatment plant of the region (Asturias-Spain). The sludge was extracted of a unit of thickening by flotation and stored at 4 °C until its subsequent use. The characteristics of the sludge were as follow: total suspended solids (TSS): 31.9 g/L, volatile suspended solids (VSS): 26.5 g/L, sludge volume index (SVI): 31 mL/g, total chemical oxygen demand (TCOD): 37,200 mg O_2/L, soluble chemical oxygen demand (SCOD): 200 mg O_2/L, soluble total organic carbon (soluble TOC) 400 mg C/L, initial pH: 6.5, soluble protein: 181 mg/L, soluble humic acids: 281 mg/L and soluble carbohydrates: 82 mg/L.

2.2. Experimental setup

The experiments of TH or WO were carried out in a PARR series 4520 reactor with a propeller stirrer (500 rpm). Oxygen (WO) or nitrogen (TH) previously conditioned in a humidifier, were fed since the beginning of the experiment to a constant flow rate of 1.2 L/min. Pressure was adjusted through a backpressure controller located at the end of the gas line, whilst the reactor temperature and the oxygen flow were regulated by means of PID controllers. The operating conditions stablished to carry out the reaction were 160 °C and 40 bar. Eight samples were taken at different times of reaction. The first one was withdrawn when 100 °C were reached in the reactor (45 min). The following samples were extracted periodically from minute 67, when the operating conditions were reached, to the end of the treatment (187 min).

2.3. Analytical methods

The analysis corresponding to total suspended solids (TSS), volatile suspended solids (VSS), fixed suspended solids (FSS), chemical oxygen demand (COD), sludge volume index (SVI) and pH were performed according to Standard Methods (APHA, 1998).

In order to quantify the biopolymers solubilisation, their concentrations were measured by the following colorimetric methods: proteins and humic acids by the modified Lowry method (Frolund et al., 1995), using BSA and humic acids as standards, respectively, and carbohydrates by the Dubois method (Dubois et al., 1956), employing glucose as standard. UV-VIS scans from 190 to 900 nm were performed for supernatants employing a T80 UV/VIS spectrophotometer (PG Instruments Ltd). The colour of the soluble samples was determined by means of the colour number (CN), which is defined according to equation (1) (Tizaoui et al., 2007).

$$CN = \frac{SAC_{436}^2 + SAC_{525}^2 + SAC_{620}^2}{SAC_{436} + SAC_{525} + SAC_{620}} \quad (1)$$

where SAC_i corresponds to the spectral absorption coefficient at a wavelength of i nanometers.

Soluble total organic carbon (TOC) was measured using a TOC analyser (Shimadzu TOC-VCSH, Japan). The mean oxidation number of organic carbon (MOC) was calculated from equation (2) (Vogel