Science of the Total Environment 584–585 (2017) 921–934

Contents lists available at ScienceDirect

Science of the Total Environment

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

Review

Valuable compounds from sewage sludge by thermal hydrolysis and wet oxidation. A review

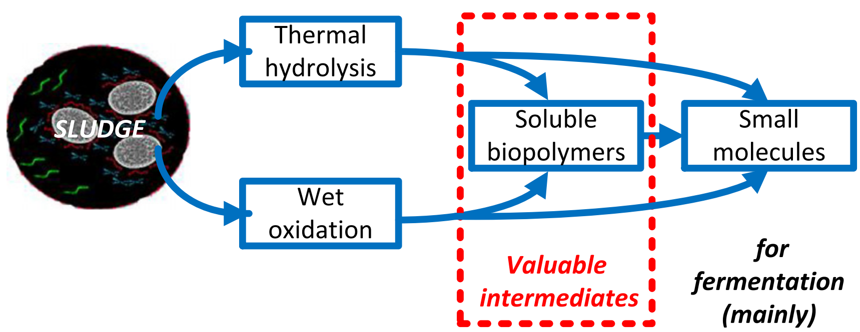
Octavio Suárez-Iglesias, José Luis Urrea, Paula Oulego, Sergio Collado, Mario Díaz *

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

HIGHLIGHTS

- Thermal hydrolysis solubilizes proteins, carbohydrates, lipids and phosphorus
- Wet oxidation mainly produces soluble volatile fatty acids.
- Temperature, reaction time and type of sludge determined the obtained products.
- There is a lack of product characterization and absence of economic evaluations.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 September 2016
Received in revised form 19 January 2017
Accepted 20 January 2017
Available online 8 February 2017

Editor: D. Barcelo

Keywords:
Biopolymers
Resource production
Sewage sludge
Solubilization
Thermal hydrolysis
Wet oxidation

ABSTRACT

Sewage sludge is considered a costly waste, whose benefit has received a lot of attention for decades. In this sense, a variety of promising technologies, such as thermal hydrolysis and wet oxidation, are currently employed. Thermal hydrolysis is used as a pretreatment step ahead of anaerobic digestion processes and wet oxidation is intended for the solubilization and partial oxidation of the sludge. Such processes could be utilized for solubilizing polysaccharides, lipids, fragments of them and phosphorus (thermal hydrolysis) or for generating carboxylic acids (wet oxidation). This article compiles the available information on the production of valuable chemicals by these techniques and comments on their main features. Temperature, reaction duration times and sludge characteristics influence the experimental results significantly, but only the first two variables have been thoroughly studied. For thermal hydrolysis, a rise of temperature led to an increase in the solubilized biomolecules, but also to a greater decomposition of proteins and undesirable reactions of carbohydrates with themselves or with proteins. At constant temperature, the amounts of substances that can be recovered tend to become time independent after several minutes. Diluted and activated sludges seem to be more readily hydrolyzable than the thickened and primary ones. For wet oxidation, the dependence of the production of carboxylic acids with

Abbreviations: Carb, carbohydrates; col, colloidal; DKN, dissolved Kjeldahl nitrogen; DOC, dissolved organic carbon; DON, dissolved organic nitrogen; HTC, hydrothermal carbonization; HTG, hydrothermal gasification; HTL, hydrothermal liquefaction; Lip, lipids; PCOD, particulate chemical oxygen demand; Prot, proteins; TH, thermal hydrolysis; SBOD, soluble biochemical oxygen demand; sCarb, soluble carbohydrates; SCOD, soluble chemical oxygen demand; SCWO, supercritical wet oxidation; sLip, soluble lipids; sProt, soluble proteins; SubCWO, subcritical wet oxidation; TBOD, total biochemical oxygen demand; TCarb, total carbohydrates; TCOD, total chemical oxygen demand; TDS, total dissolved solids; TKN, total Kjeldahl nitrogen; TLip, total lipids; TOC, total organic carbon; TON, total organic nitrogen; TP, total phosphorus; TProt, total proteins; TS, total solids; TSS, total suspended solids; TVS, total volatile solids; VDS, volatile dissolved solids; VFA, volatile fatty acids; VSS, volatile suspended solids; WO, wet oxidation; WWTP, wastewater treatment plant.

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

http://dx.doi.org/10.1016/j.scitotenv.2017.01.140

temperature and time is not simple: their concentration can increase, decrease or go through a maximum. At high temperatures, acetic acid is the main carboxylic acid obtained. Concentrated, fermented and secondary sludge seem to be more suitable for yielding higher amounts of acid than diluted, undigested and primary ones.

Contents

1. Introduction

Sewage sludge is a broad term that refers to several aqueous suspensions of solids generated during the decontamination of the influents to Wastewater Treatment Plants (WWTP). Sewage sludge is called "primary" if it comes from the primary treatment (mechanical processes, such as gravitational settling and air flotation, which separate heavy solids and oils from the raw wastewater) and "secondary" if it is mainly comprised of microorganisms from the biological treatment that follows the primary one (where microbial activity removes suspended and dissolved organic matter, but also causes an increase in the amount of biomass, which has to be purged). Table 1 sums up some characteristics of both suspensions (Li and Noike, 1992; Metcalf and Eddy Inc. et al., 2003; Bougrier et al., 2008). Additionally, a "tertiary sludge" can be originated, if further purification of the effluent from the secondary treatment is required (e.g., elimination of specific nutrients as phosphorus or nitrogen). Due to the growing environmental concerns over the last decades, new WWTPs have been built and part of the existing ones have been upgraded (Ødegaard, 2004; Rulkens, 2004), leading to a significant rise of the global sewage sludge production.

Although the operating conditions of the biological treatment can be adapted to accumulate polyhydroxyalkanoates in the microorganisms (Chua et al., 2003) or to produce aerobic granular sludge, which can be utilized as a source of biodegradable plastics or as adsorbent (Zhang et al., 2016), the WWTPs are reluctant to modify these conditions, if the overall performance of the plant is good. In this sense, it is more desirable: i) to deposit the residual sludge in landfills, ii) to use it as fertilizer/soil conditioner, or, instead of giving it a final destination, iii) to use it for the production of energy or valuable compounds (Ødegaard et al., 2002). This last alternative refers to a variety of processes, such as anaerobic digestion (Appels et al., 2008), pyrolysis and gasification (Manara and Zabaniotou, 2012), mono-incineration and co-combustion (Werther and Ogada, 1999) and hydrothermal methods (Hii et al., 2014). Anaerobic digestion produces biogas, pyrolysis and gasification transform the sludge into fuel, incineration and combustion allow for the recovery of energy by means of heat exchangers, and hydrothermal methods generate energy, chemicals and gases (Rulkens, 2008; Tyagi and Lo, 2013). Unfortunately, the decreasing capacities of landfills, the scarcity of appropriate regions to construct new sites, the legal limitations applied to landfilling, the necessity of stabilizing the sludge (due to its poor physical nature) and the presence of heavy metals and other toxic organics in it, make options i) and ii) troublesome (Werther and Ogada, 1999). Anaerobic fermentation is widely used, but it is a slow process, which requires large reactors and can be easily inhibited by organics present in the sludge or generated during the digestion (Anjum et al., 2016). Besides, pyrolysis, gasification, incineration and combustion require extensive drying of the material, with the subsequent high energy costs (Libra et al., 2011; Xue et al., 2015a).

Table 1
General characteristics of primary and secondary sludge.

Parameter	Primary sludge	Secondary sludge
Total solids (% TS)	2.0–8.0	0.83–3.3
Organic solids (% TS)	60–80	59–88
Grease, fats and lipids (% TS)	13–65	2–12
Protein (% TS)	20–30	32–41
Nitrogen (N, % TS)	1.5–4.0	2.4–5.0
Phosphorus (P, % TS)	0.17–0.6	0.6–2.3
Cellulose (% TS)	8.0–15.0	n.a.[a]
Carbohydrates (% TS)	n.a.[a]	6.1–9.8
pH	5.0–8.0	6.5–8.0
Organic acids (mg/L as acetic acid)	200–2000	16–1700

[a] n.a. not available.

Hydrothermal technologies can be defined as those performed in dense water at elevated temperatures and pressures, namely, above 100 °C and 0.101 MPa (Byrappa and Yoshimura, 2013), and are categorized into oxidative and non-oxidative techniques (Hii et al., 2014). The first ones are carried out in oxidative atmospheres (air, oxygen or hydrogen peroxide), and are generically called wet oxidations (WO): subcritical wet oxidation (SubCWO) is performed below the supercritical point of water, whereas supercritical wet oxidation (SCWO) if performed above it. The second ones are implemented in inert atmospheres and comprise thermal hydrolysis (TH), hydrothermal carbonization (HTC), hydrothermal liquefaction (HTL) and hydrothermal gasification (HTG). HTC, HTL and HTG lead to the production of solid, liquid and gaseous fuels, like pyrolysis and gasification, but are advantageous in that there is no need to dry the resulting sludge before processing it. TH usually ranges from 100 to 180 °C at the saturation pressures, and is commonly employed as pretreatment for the anaerobic treatment of activated sludge (Foladori et al., 2010). Since most of the organic substances in this sludge are in the particulate form and only a small percentage of them are dissolved, they are not readily available for digestion. TH breaks particles and microbial cells, releasing either their content, which allows a better fermentation, or the bond water, which improves the sludge dewaterability. It also decomposes lipids (Lip), proteins (Prot) and carbohydrates (Carb) into lighter molecules, as schematically represented in Fig. 1. HTC is operated at 180–220 °C (saturation pressures between 1.0 and 2.32 MPa, respectively), and mainly generates a coal called hydrochar, together with minor amounts of liquid biocrude and gas (Ekpo et al., 2016; Matsumura, 2016; Wagner and Pruss, 2002). HTL works at higher temperatures (up to 370 °C,