Journal of Environmental Management 188 (2017) 203–211

Contents lists available at ScienceDirect

Journal of Environmental Management

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

Research article

Sludge from paper mill effluent treatment as raw material to produce carbon adsorbents: An alternative waste management strategy

Guilaine Jaria [a, 1], Carla Patrícia Silva [a, 1], Catarina I.A. Ferreira [a], Marta Otero [b], Vânia Calisto [a, *]

[a] Department of Chemistry and CESAM (Centre for Environmental and Marine Studies), University of Aveiro, Campus de Santiago, 3810-193, Aveiro, Portugal
[b] Department of Applied Chemistry and Physics, IMARENABIO, University of Léon, Campus de Vegazana, Léon, Spain

ARTICLE INFO

Article history:
Received 30 September 2016
Received in revised form
25 November 2016
Accepted 3 December 2016
Available online 14 December 2016

Keywords:
Waste valorization
Circular economy
Alternative adsorbents
Carbon materials
Environment
Pyrolysis

ABSTRACT

Pulp and paper industry produces massive amounts of sludge from wastewater treatment, which constitute an enormous environmental challenge. A possible management option is the conversion of sludge into carbon-based adsorbents to be applied in water remediation. For such utilization it is important to investigate if sludge is a consistent raw material originating reproducible final materials (either over time or from different manufacturing processes), which is the main goal of this work. For that purpose, different primary (PS) and biological sludge (BS) batches from two factories with different operation modes were sampled and subjected to pyrolysis (P materials) and to pyrolysis followed by acid washing (PW materials). All the materials were characterized by proximate analysis, total organic carbon (TOC) and inorganic carbon (IC), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and N_2 adsorption isotherms (specific surface area (S_{BET})and porosity determination). Sludge from the two factories proved to have distinct physicochemical properties, mainly in what concerns IC. After pyrolysis, the washing step was essential to reduce IC and to considerably increase S_{BET}, yet with high impact in the final production yield. Among the materials here produced, PW materials from PS were those having the highest S_{BET} values (387–488 $m^2\ g^{-1}$). Overall, it was found that precursors from different factories might originate final materials with distinct characteristics, being essential to take into account this source of variability when considering paper mill sludge as a raw material. Nevertheless, for PS, low variability was found between batches, which points out to the reliability of such residues to be used as precursors of carbon adsorbents.

1. Introduction

Pulp and paper industry is considered to be one of the most important industrial segments in the world. The enormous water requirements of this industry result in the generation of huge volumes of wastewater (on average, in a typical paper mill, between 1.5 and 60 m^3 of effluent is generated for each ton of paper) (Adhikari and Bhattacharyya, 2015; Soucy et al., 2014). As a consequence of the effluent treatment, a large quantity of sludge is produced, which represents a massive environmental burden. Biological (BS) and primary sludge (PS) are amongst the produced solid wastes and their properties depend on the manufacturing process, namely wood preparation, pulp and paper manufacture, chemical recovery, recycled paper processing and wastewater treatment (Buruberri et al., 2015; Monte et al., 2009; Pervaiz and Sain, 2015; Vochozka et al., 2016). On average, a total of 40–50 kg of dry sludge is produced for each ton of paper, 70% of which is PS and 30% is BS (Bajpai, 2015).

In recent years, and considering that environmental legislation is increasingly stringent, the pulp and paper industry has been facing some challenges with respect to the management of the resulting wastes. This aspect has to be linked to economic aspects in order to apply feasible solutions for waste management/valorization (Buruberri et al., 2015; Kamali and Khodaparast, 2015; Pervaiz and Sain, 2015). In the case of sludge from wastewater treatment, management options include incineration (approximately 19% of sludge is incinerated on-site) for energy recovery, land application to enhance soil fertility on agricultural and forest areas and

* Corresponding author.
E-mail address: vania.calisto@ua.pt (V. Calisto).
[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.jenvman.2016.12.004
0301-4797/

production of ethanol (Bajpai, 2015; Likon and Trebše, 2012; Pervaiz and Sain, 2015). However, the most common practice has always been the landfill disposal of sludge (Likon and Trebše, 2012; Pervaiz and Sain, 2015). Landfills can be owned and operated by the industry itself or can be independently maintained, requiring a payment from the mills. In any case, landfills should comply with the requirements of the European Landfill Directive (1999/31/EC) (Likon and Trebše, 2012). Nevertheless, landfilling is not recommended and is being discouraged since it causes environmental problems related with leaching and greenhouse gas production (Reckamp et al., 2014). The Confederation of European Paper Industries (CEPI) supports a complete ban of landfilling and incineration in the European Union in agreement with the Waste Framework Directive (2008/98/EC) which lays down some basic waste management principles, prioritizing recycling over energy recovery and disposal. Also, the European Commission Roadmap to a Resource Efficient Europe (COM (2011) 571) foresees the sustainability of the Europe's economy by 2050, proposing milestones to be reached by 2020 in which waste will be managed as a resource and energy recovery will be limited to non-recyclable materials (CEPI, 2016; European Commission, 2016a, 2016b). Therefore, sustainable practices must be developed, involving the valorization of wastes, by using them as raw materials for distinct purposes (Buruberri et al., 2015). In this context, some innovative approaches for the conversion of sludge from the paper industry into new materials have been explored in the past two decades. Promising innovations include the use of such sludge as heat insulation material, paper and wood adhesive, dried mixture for use as pesticides or fertilizers carriers in agriculture and as building material (Buruberri et al., 2015; Likon and Trebše, 2012; Pervaiz and Sain, 2015). Also, given the carbonaceous nature of paper mill sludge, their conversion into activated carbon with application on water remediation has been proposed by several authors (*e.g.* Devi and Saroha, 2014; Ferreira et al., 2016a; Khalili et al., 2000; Khalili et al., 2002; Pirzadeh and Ghoreyshi, 2014; Reckamp et al., 2014). This conversion, besides reducing the environmental problems associated with the disposal of wastes, also enhances wastewater treatment by using materials from industrial waste itself, and helps the preservation of naturally-existing resources usually applied in the production of activated carbons (Khalili et al., 2002). Adsorbents originated from paper mill sludge have already been applied in the adsorption of phenolic compounds (Devi and Saroha, 2014, 2015; Masomi et al., 2015; Pirzadeh and Ghoreyshi, 2014), dyes (Auta and Hameed, 2014; Li et al., 2011), heavy metals (Battaglia et al., 2003) or pharmaceuticals (Calisto et al., 2014, 2015; Ferreira et al., 2015; Ferreira et al., 2016b; Jaria et al., 2015) from contaminated waters.

There is a relationship between the properties of an adsorbent material and its effectiveness (*i.e.* enhanced adsorption capacity), these characteristics being importantly determined by the used precursor and the production process (Gonzalez et al., 1995; Namazi et al., 2010). Therefore, in order to evaluate the appropriateness of pulp and paper mill sludge as precursor for the production of carbon adsorbents, it is essential to know if these wastes are a consistent and reliable raw material, guaranteeing the repeatability of the final product through time. However, no attention is given to this aspect when studying the production of alternative adsorbents from pulp and paper mill sludge (and other residues in general) – as far as authors know, there are no studies concerning this subject.

This work aimed to assess, for the very first time, the consistency of carbon adsorbents produced by the pyrolysis of sludge from the paper industry. With this purpose, four PS and BS batches collected from two factories with different operation characteristics were used in this work. Moreover, in order to conclude about the potential of the obtained materials as adsorbents, key physicochemical properties were determined and the influence of the raw materials on these properties evaluated. All the materials (raw sludge and resulting carbons) were characterized by proximate analysis, N_2 adsorption isotherms (specific surface area (S_{BET}) and porosity determination), total organic carbon (TOC) and inorganic carbon (IC) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR).

2. Experimental section

2.1. Factory description and sludge production

Sludge from two paper industries, hereafter named Factory 1 (F1) and Factory 2 (F2), were used in this work. Both factories use a kraft elemental chlorine free (ECD) pulp production process and operate using *Eucalyptus globulus* wood. Factory 1 has more than 6 decades of existence and was the first one, worldwide, to produce paper pulp from eucalyptus wood by the kraft process. Its production reaches about 320,000 tons of bleached pulp per year, while the Factory 2 production reaches approximately 570,000 tons of bleached eucalyptus kraft pulp and 800,000 tons of uncoated woodfree (UWF) printing paper. Therefore, Factory 2 combines the production of pulp and paper, while Factory 1 produces only pulp.

On average, in both factories, PS and BS are produced at a rate of 20 and 10 kg per ton of air dried pulp, respectively. These solid wastes are generated during the effluent treatment. PS results from fibers rejected after the cooking/digestion of the pulp and losses of fibers and other solids which occur when liquid effluents are involved (for example, washing and bleaching). The composition of PS is very similar to the pulp, consisting essentially of organic matter (mostly composed of fibrous materials) (Calisto et al., 2014; Soucy et al., 2014). After primary treatment, the remaining suspended solids are then submitted to bacterial digestion, under aerobic conditions, which generates BS. Some studies indicate that this type of sludge may have lignin in its composition and no cellulose or hemicelluloses; therefore, BS is considered to be constituted mostly by biomass (after dehydration) (Calisto et al., 2014; Soucy et al., 2014). This process generates a large amount of sludge due to the microbial growth. However, the generated volume of BS is lower than that of PS since most of the heavy, fibrous and/or inorganic solids are removed during the primary treatment (Monte et al., 2009).

2.2. Sludge collection and conditioning

PS and BS were collected four times from each F1 and F2 in campaigns separated by 15 days from each other. After collection, PS and BS were firstly dried at room temperature, followed by a 24 h period at 105 °C in an oven. BS was grinded with a mortar grinder and sieved (the 0.5–1.0 mm fraction was used in this work). In the case of PS, a blade mill was used after drying, resulting in an extremely light net of fibrous material that was not possible to sieve.

Sludge samples are referred as F1PS1, F1PS2, F1PS3 and F1PS4, for the four PS batches from Factory 1 (F1PS); F2PS1, F2PS2, F2PS3 and F2PS4, for the four PS batches from Factory 2 (F2PS). An equivalent nomenclature was defined for BS samples, using, for example, F1BS1 for the first batch of BS from Factory 1.

2.3. Carbon adsorbents production

2.3.1. Pyrolysis

After sludge collection and conditioning, PS and BS samples were separately pyrolysed into porcelain crucibles in a muffle