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Production of adsorbents by pyrolysis of paper mill sludge and application on the removal of citalopram from water

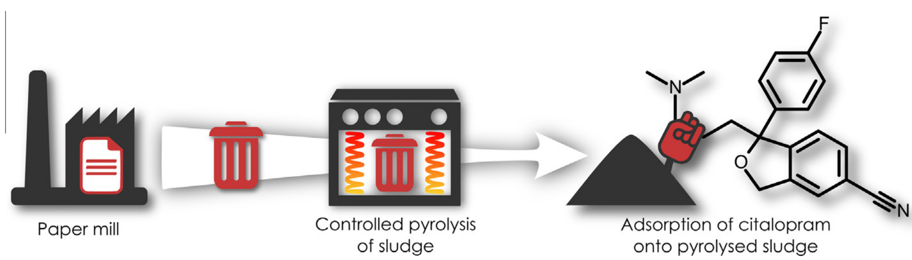
Vânia Calisto [a,*], Catarina I.A. Ferreira [a], Sérgio M. Santos [b], María Victoria Gil [c], Marta Otero [d], Valdemar I. Esteves [a]

[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 Chemistry and CICECO (Centre for Research in Ceramics and Composite Materials), University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal
[c] Instituto Nacional del Carbón, INCAR-CSIC, Apartado 73, 33080 Oviedo, Spain
[d] Department of Applied Chemistry and Physics, IMARENABIO, University of Léon, Campus de Vegazana, Léon, Spain

HIGHLIGHTS

- Pyrolysis was applied for adsorbent production for paper mill residues valorization.
- Pyrolysed paper mill sludge was tested for the removal of an antidepressant from water.
- Adsorbents were produced by environmentally friendly methods without activation steps.
- Primary sludge resulted in higher porous and efficient adsorbents than biological sludge.
- Best results were obtained for primary sludge pyrolysed at 800 °C for 150 min.

GRAPHICAL ABSTRACT



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ABSTRACT

This work describes the production of alternative adsorbents from industrial residues and their application for the removal of a highly consumed antidepressant (citalopram) from water. The adsorbents were produced by pyrolysis of both primary and biological paper mill sludge at different temperatures and residence times. The original sludge and the produced chars were fully characterized by elemental and proximate analyses, total organic carbon, specific surface area (BET), N_2 isotherms, FTIR, ^{13}C and ^{1}H solid state NMR and SEM. Batch kinetic and equilibrium experiments were carried out to describe the adsorption of citalopram onto the produced materials. The fastest kinetics and the highest adsorption capacity were obtained using primary sludge pyrolysed at 800 °C during 150 min. The use of pyrolysed paper mill sludge for the remediation of contaminated waters might constitute an interesting application for the valorization of those wastes.

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1. Introduction

Paper mill sludge is produced in the order of eleven million tons per year only by European mills (Monte et al., 2009). The use of pulp and paper production sub-products is quite dependable on the legislation applied in each country; however, in general, main applications include energy recovery, disposal on landfills and

* Corresponding author. Tel.: +351 234401408.
E-mail address: vania.calisto@ua.pt (V. Calisto).

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composting (CEPI, 2004). Taking into account that some of those traditional disposal options are being progressively restricted, the management of these wastes in an economically and environmentally acceptable manner is a critical issue for the mills. Hence, from a sustainable point of view, it is necessary to develop innovative handling strategies that maximize recovery of useful materials and/or energy and that also allow the minimization of such wastes (Stoica et al., 2009). Taking into account that these residues are derived from natural resources (wood) and are a result of controlled and well known processes, their use as raw materials in other industries has been increasing (such as cement, brick and tile manufacturing), in opposition to the most conventional applications referred above (CEPI, 2004).

The contamination of sewage treatment plant's (STPs) effluents with pharmaceuticals is well documented and considered to be generalized and, consequently, the discharge of those effluents is pointed out to be the primary source of pharmaceutically active ingredients into the environment (Kinney et al., 2006; Jelic et al., 2011). Taking into account the scarcity of potable water resources that the world has been facing and the need to maintain an unpolluted environment, it is of the utmost importance to develop effective strategies that mitigate this continuous contamination. Considering the need of applying those removal strategies at large scales, economically feasible and high-efficient low-cost strategies ought to be a priority (Chong et al., 2010). For pharmaceuticals, the most promising results are usually obtained with advanced treatment methods such as advanced oxidation processes (ozonation, Fenton, photo-Fenton), reverse osmosis and membrane bio-reactors (Silva et al., 2012). These methods have the major drawback of being cost consuming and, in some cases, resulting on the formation of undesirable by-products (such as nitrosamines, formaldehyde, chlorinated products) (Chong et al., 2010; Margot et al., 2013; Rivera-Utrilla et al., 2013). In this context, removal by adsorption onto solid matrices is a very promising option due to its effectiveness and versatility. Activated carbons (in powdered and granular forms) are the most frequently used adsorbents and, in general, result in very satisfactory removal rates (Aksu and Tunç, 2005; Yu et al., 2008, 2009). However, using commercial activated carbons is quite expensive (Aksu and Tunç, 2005). As a consequence, there are various works reported in the literature describing the production (and subsequent application) of alternative low-cost adsorbents produced by pyrolysis, generally combined with chemical or physical activation of industrial wastes (Yao et al., 2012), sewage sludge (Smith et al., 2009) and agricultural residues (Mohan et al., 2014; Ioannidou and Zabaniotou, 2007; Antunes et al., 2012), to mention a few. Yet, until now, very few studies reported the production of adsorbents using paper mill sludge (Devi and Saroha, 2014; Khalili et al., 2002; Li et al., 2011) and there are no data describing the use of primary sludge, in particular.

In this work, primary and biological paper mill sludge is used for the production of alternative adsorbents. The main goal is to obtain a carbon with high adsorption capacity using cheap and environmentally friendly production methods (without employing chemical or physical activation) and, simultaneously, to propose a new way to valorize this industrial sub-product. The produced adsorbents are here applied on the removal of the antidepressant citalopram from water which is, to the best of our knowledge, the first description of an application of paper sludge derived adsorbents to the adsorption of a pharmaceutical. The antidepressant citalopram was selected for this study due to its high consuming patterns (caused by the large prevalence of stress related conditions and mental diseases (OECD, 2011)), the frequency of occurrence in the environment and its ability to interfere in the regulation of behavior and neuro-endocrine signaling of aquatic non-target organisms (Calisto and Esteves, 2009).

2. Methods

2.1. Chemicals

Citalopram hydrochloride (>98%) was purchased from TCI Europe. All chemicals used for capillary electrophoresis were of analytical grade: sodium dodecylsulphate (SDS, 99%, for electrophoresis, Sigma Aldrich), hexadimethrine bromide (polybrene, Sigma Aldrich), sodium chloride, ethylvanillin (99%, Sigma Aldrich), sodium tetraborate (Riedel-de Haën), sodium hydroxide (Fluka). All solutions were prepared using ultra-pure water, obtained from a Milli-Q Millipore system (Milli-Q plus 185).

2.2. Adsorbent materials

Primary (PS) and biological paper mill sludge (BS) were provided by a mill which employs the kraft ECD (elemental chlorine free) pulp production process. The mill operates exclusively with eucalyptus wood (*Eucalyptus globulus*). On average, PS and BS are produced at a rate of 20 and 10 kg per ton of air dried pulp, respectively. The PS results from fibers rejected after the cooking/digestion pulping step and losses of fibers and other solids which occur when liquid effluents are involved (for example, washing and bleaching); the composition of the PS is very similar to the pulp, consisting essentially of organic matter (fibers). After primary treatment, the effluent is then submitted to biological treatment: the BS is essentially biomass (after dehydration) that results from the action of microorganisms, under aerobic conditions, which are meant to reduce the organic matter content of the effluent.

After collection, PS and BS were dried at room temperature for several days, followed by a 24 h period at 60 °C in an oven. BS was then grinded with a mortar grinder and separated by grain size (<0.18 mm and between 0.18 and 0.5 mm, referred as 0.18 mm and 0.5 mm, respectively). The same procedure was not applied to PS due to its particular physical characteristics: it was not effectively grinded by a mortar grinder; instead, a blade mill was used, resulting in an extremely light net of fibrous material, impossible to sieve.

PS and BS were then pyrolysed into porcelain crucibles using a muffle (Nüve, series MF 106, Turkey). The pyrolysis was carried out at a heating rate of 10 °C min^{-1}, under N_2 saturated atmosphere (N_2 flow of 0.5 dm^3 min^{-1}). The final pyrolysis temperature and residence time was varied in order to evaluate the influence of those parameters in the adsorption capacity of the material. The temperatures were chosen according to the mass losses observed in the thermogravimetric analysis (see Sections 2.3.1 and 3.1 and Fig. S1 of Supporting Information (SI)). Accordingly, PS and BS were pyrolysed at 315 °C for 150 min (PS315-150 and BS315-150), at 600 °C for 10 min (PS600-10 and BS600-10), at 800 °C for 10 min (PS800-10 and BS800-10) and finally PS was also pyrolysed at 800 °C for 150 min (PS800-150). After the pyrolysis, the pyrolysed sludge was maintained inside the muffle until the temperature reached room temperature; the nitrogen stream was continuously applied during the cooling step.

Apart from the paper mill sludge based adsorbents, and given that, to the best of our knowledge, there are no data in the literature on the adsorptive removal of citalopram, the commercial powdered activated carbon PULSORB FG4 (PBFG4), provided by Chemviron Carbon, was used for comparison purposes.

2.3. Materials characterization

2.3.1. Thermogravimetric analysis

Thermal characterization of PS and BS was carried out by thermogravimetric (TG) analysis and derivative thermogravimetric

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