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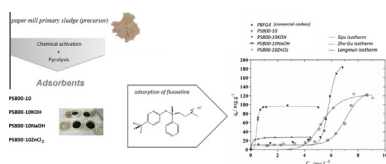
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## Removal of fluoxetine from water by adsorbent materials produced from paper mill sludge

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## GRAPHICAL ABSTRACT



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## ABSTRACT

In this work, three adsorbents were produced by using as precursor primary paper mill sludge and applying KOH, NaOH or ZnCl<sub>2</sub> as chemical activating agents (PS800-10KOH, PS800-10NaOH and PS800-10ZnCl<sub>2</sub>) and subjected to pyrolysis. The produced materials were tested for removal of fluoxetine from water, reported as one of the most persistent pharmaceuticals in the aquatic environment. Also, primary sludge pyrolysed under the same conditions but without activation (PS800-10) and a commercial activated carbon (PBF4) were studied for comparison. Physical and chemical properties of the materials were determined and adsorption kinetic and equilibrium studies were performed in batch experiments. Equilibrium studies allowed testing the capacity of the produced materials for adsorb fluoxetine-HCl, showing no apparent correlation between the S<sub>BET</sub> areas and the adsorption capacities of the materials. The maximum adsorption capacity (mg g<sup>-1</sup>) was of 191.6 ± 4.8 for PS800-10KOH; 136.6 ± 9.6 for PS800-10NaOH; 28.4 ± 0.3 for PS800-10ZnCl<sub>2</sub>; 120.4 ± 2.5 for PS800-10 and 96.2 ± 1.0 for PBF4. It was demonstrated that many factors influence the removal of fluoxetine from solution and that the surface area is not the main factor in the process. Also the activation process did not enhance the properties of the produced materials.

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## 1. Introduction

Carbon materials, namely activated carbons (AC), have crucial industrial roles in the treatment processes like the ones used for wastewater treatment. Their applicability is due to their high adsorptive capacities, being a good alternative to other treatment methods such as flocculation, chlorination, biodegradation, oxidation by ozone, and ion exchange resins [1–3]. In fact, adsorptive treatment by activated carbon has been pointed as a most appro-

priate technology for the removal of emerging contaminants from water [4]. A main advantage of adsorptive treatments for the treatment of water containing emerging contaminants is that transformation products, which may be even more dangerous than the parent compounds, are not generated.

The general main characteristics required for a good AC are a high surface area, and therefore, a high microporosity, high percentage in carbon content and low ash content [5–8]. Nevertheless, commercial AC are expensive materials and are needed in relatively high amounts when applied at large scale [6,9]. One of the factors affecting the price of AC is the starting material used for

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their production. Among them, lignocellulosic materials, which have low inorganic and relatively high volatile contents, are considered good precursors of AC [10]. Lignocellulosic materials have three main components: hemicellulose, cellulose and lignin, each of them having a contribution for the development of microporosity throughout the production of AC [11]. Some examples of lignocellulosic precursors referred in literature are coconut shell, fruit stones, olive waste and pine wood [3,10,11]. On the other hand, the production process of pulp and paper industry generates large amounts of lignocellulosic wastes, particularly sludge from wastewater treatments, which require adequate disposal methods [12]. Therefore, these residues could be an interesting and cheap precursor for producing AC, which utilization would mean the valorisation of an industrial residue.

Chemical activation is a simple process that has been proven to increase the porosity during the pyrolysis of lignocellulosic materials [13], potassium hydroxide, sodium hydroxide and zinc chloride being among the most commonly used activating agents. Although the process of chemical activation is not quite understood, it is believed that these chemicals may act like a template for the development of microporosity [3].

In this work, and for the very first time, adsorbent materials were produced by chemical activation of primary sludge (PS) from a paper mill industry. The produced materials were characterized in terms of total organic carbon analysis (TOC), Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR), proximate and ultimate analyses, scanning electron microscopy (SEM), Hg porosimetry, BET surface area and point of zero charge (PZC). Then, the adsorption rate and capacity of the produced materials was determined for fluoxetine, which is an antidepressant of the Selective Serotonin Reuptake Inhibitor (SSRI) class. Fluoxetine, whose most popular trade name is Prozac, is an organic compound considered an emerging pollutant and has been detected in the environment in the range between  $\text{ng L}^{-1}$  and  $\mu\text{g L}^{-1}$  [1,14]. Although this range of concentration is not acutely toxic for humans, synergic, addictive effects or accumulation can occur [1]. Also, fluoxetine was reported as being one of the most persistent pharmaceuticals from the SSRI group, even after some treatments such as chlorination, being also reported as recalcitrant [15].

## 2. Materials and methods

### 2.1. Chemicals

Fluoxetine-HCl (>98%) was purchased from TCI Europe. For the chemical activation the chemicals were: potassium hydroxide (99.5%, Fluka), sodium hydroxide (99.3%, José Manuel Gomes dos Santos, Portugal) and zinc chloride (98%, Riedel-de Haën).

For capillary electrophoresis a 20 mM sodium tetraborate (Riedel-de Haën) buffer solution was used as background electrolyte and 0.1 M sodium hydroxide (99.3%, José Manuel Gomes dos Santos, Portugal).

For the determination of zero point charge 1.0 M HCl (37%, Panreac), 1.0 M sodium hydroxide (99.3%, José Manuel Gomes dos Santos, Portugal) and 0.1 M sodium chloride ( $\geq 99.5\%$ , Fluka) solutions were prepared.

All solutions were prepared using ultra-pure water, obtained from a Milli-Q Millipore system (Milli-Q plus 185).

### 2.2. Preparation and characterization of adsorbent materials

#### 2.2.1. Impregnation and pyrolysis conditions

For the production of the adsorbent materials, primary sludge (PS) from paper mill industry was used as precursor. This sludge is obtained from a mill kraft pulp with an elemental chlorine free production process, which uses, as raw material, eucalyptus wood

(*Eucalyptus globulus*). PS was dried at room temperature followed by a 24 h period at 60 °C in an oven and then it was grinded with a blade mill [16].

The chemical agents used for activation were potassium hydroxide, sodium hydroxide and zinc chloride in the ratio 1:1 (w/w) [17]. For the preparation of each adsorbent a sample of about 60 g of primary sludge was weighted and impregnated with 60 g of the chemical agent dissolved in 480 mL of ultra-pure water. The impregnated material was placed in polypropylene tubes and agitated at 80 rpm for 24 h at  $25.0 \pm 0.1$  °C and dried for 48 h in a weak air stream atmosphere. The activated sludge was then placed in porcelain crucibles for pyrolysis which was carried out under inert environment (nitrogen flow) at 800 °C with a heating rate of  $10$  °C  $\text{min}^{-1}$  and with 10 min of residence time. After pyrolysis, the hydroxide AC were washed with distilled water until neutral pH and the carbon activated with zinc chloride was washed with 500 mL of HCl 1.2 M followed by distilled water until neutral pH. The washing procedures were adapted from Hayashi et al. [18] and Khalili et al. [19], respectively. Subsequently, the samples were dried in an oven at 105 °C for 24 h and crushed mechanically. According to the preparation conditions, the produced materials were named as PS800-10KOH, PS800-10NaOH and PS800-10ZnCl<sub>2</sub>, corresponding to primary sludge pyrolysed at 800 °C for 10 min impregnated with KOH, NaOH and ZnCl<sub>2</sub>, respectively. The same pyrolysis conditions were also applied to the primary sludge without activation and the resultant char was named PS800-10.

Later, in order to test the effects of HCl washing, PS800-10NaOH was washed with a 1.2 M HCl solution followed by water until neutral pH. This material was dried in an oven for 24 h at 105 °C and named PS800-10NaOH-HCl.

#### 2.2.2. Characterization of the adsorbent materials: FTIR-ATR, TOC, proximate and ultimate analyses, BET surface area, Hg porosimetry and SEM

The characterization of the adsorbents included the qualitative analysis of the carbon functional groups. The FTIR-ATR (Fourier transform infrared spectroscopy with attenuated total reflectance) spectra were obtained through a Shimadzu-IRAffinity-1, using an attenuated total reflectance (ATR) module, with a nitrogen purge. The measurements were recorded in the range of 600–4000  $\text{cm}^{-1}$ , 4.0 of resolution, 128 scans and with atmosphere and background correction.

Total organic carbon (TOC) was calculated by difference between the total carbon (TC) content and inorganic carbon (IC) content, that were determined through a TOC analyzer (TOC-VCPh Shimadzu, solid sample module SSM-5000A).

For complementing the latter analysis, proximate and ultimate analyses were performed. Proximate analysis was performed in a LECO TGA-601 automatic analyzer. There were employed standard methods to determine the moisture (UNE 32002), volatile matter (UNE 32019) and ash content (UNE 32004). The fixed carbon was determined as the remaining fraction after ash and volatile matter (at dry basis) determination. Ultimate analysis were performed in a LECO CHNS-932 analyzer, determining the content in C, H, N, S and O in the samples. The oxygen content was calculated by difference between 100% and the percentages of C, H, N, S and ash. Elemental contents were all corrected considering moisture content of the samples in order to present them at a dry basis.

Specific surface area ( $S_{\text{BET}}$ ) and scanning electron microscopy (SEM) were obtained for the physical characterization of the carbons. The N<sub>2</sub> adsorption isotherm at  $-196$  °C was analyzed on a Micromeritics ASAP2420 apparatus in order to determine BET surface area, total pore volume ( $V_p$ ), micropore volume ( $W_0$ ) and average micropore width ( $L$ ). The Dubinin-Asthakov (DA) method [20] was applied to the N<sub>2</sub> adsorption isotherms in the relative pressure range 0.01–0.1 in order to obtain the corresponding micropore vol-

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