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An adsorbent with a high adsorption capacity obtained from the cellulose sludge of industrial residues

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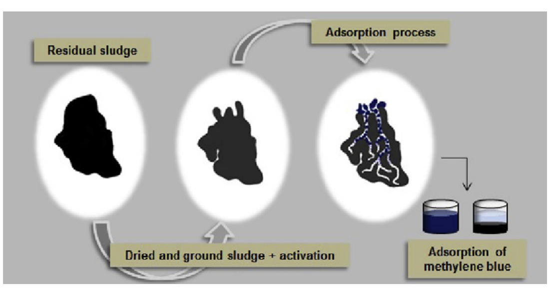
GRAPHICAL ABSTRACT

Residual cellulose sludge, after being dried and ground, was chemically activated with 42.5% (v/v) phosphoric acid at 85 °C for 1 h and charred, and the adsorption properties of the coals were evaluated by kinetic experiments with methylene blue.



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ABSTRACT

One of the major problems in effluent treatment plants of the cellulose and paper industry is the large amount of residual sludge generated. Therefore, this industry is trying to develop new methods to treat such residues and to use them as new products, such as adsorbents. In this regard, the objective of this work was to develop an adsorbent using the raw activated sludge generated by the cellulose and paper industry. The activated cellulose sludge, after being dried, was chemically activated with 42.5% (v/v) phosphoric acid at 85 °C for 1 h and was charred at 500 °C, 600 °C and 700 °C for 2 h. The efficiency of the obtained adsorbent materials was evaluated using kinetic tests with methylene blue solutions. Using the adsorption kinetics, it was verified that the three adsorbents showed the capacity to adsorb dye, and the adsorbent obtained at a temperature of 600 °C showed the highest adsorption capacity of 107.1 mg g^{-1}. The kinetic model that best fit the experimental data was pseudo-second order. The Langmuir-Freudlich isotherm adequately described the experimental data. As a result, the cellulose sludge generated by the cellulose and paper industries could be used as an adsorbent.

1. Introduction

Over the past decade, the paper manufacturing industries have produced large volumes of cellulose sludge. Consequently, new

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options/methods for the treatment and use of this waste are important and necessary to define the appropriate destination of these materials (Filippis et al., 2013). Nolasco et al. (2000) stated that the primary sludge and the activated sludge represent 17% of the total volume of the waste produced by the paper industries (Nolasco et al., 2000). The cellulose sludge of the industrial processes are removed periodically and conducted to environmental landfills (Hojamberdiev et al., 2008a; Gottumukkala et al., 2016) or for uses as agricultural fertilizers (Mäkela et al., 2012; Ríos et al., 2012) or in the construction of embankments (Taramian et al., 2007; Asquini et al., 2008; Buruberri et al., 2015).

The chemical composition of this sludge is complex, and its reuse is difficult. The sludge contains short fibers of cellulose, paints, dyes and others chemical additives. However, this residue has a high concentration of carbon that can be transformed into an adsorption material at low cost and with high efficiency using chemical and physical activation processes (Bhatnagar and Sillanpaa, 2010; Hofman and Pietrzak, 2012). The transformation of industrial sludge in absorbent materials is a possible use of cellulose sludge because the cost associated with the treatment processes and the storage of these wastes are reduced (Khalili et al., 2002).

Adsorbent materials from the sludge can be produced according to two activation steps: i) the physical activation of the cellulose sludge by an oxidative or water vapor treatment (Lanlan and Qin, 2006; Zanin and Figueiredo, 2009) to increase the pore sizes; and ii) the chemical activation of coal with $FeCl_3$ (Asquini et al., 2008), $FeSO_4$ and H_2O_2 (Buruberri et al., 2015), $ZnCl_2$ and H_2SO_4 (Ríos et al., 2012; Bhatnagar and Sillanpaa, 2010) H_3PO_4 (Hofman and Pietrzak, 2012; Khalili et al., 2002) or $ZnCl_2$ in atmospheres of N_2 (Saka et al., 2012). With these procedures, the pore size and the surface area of the coal particles are increased, and some chemical functional groups are incorporated into the adsorbent material to make the material more active in adsorption processes (Hofman and Pietrzak, 2012; Gautam et al., 2014; Colpani, 2012; Dural et al., 2011).

CO treatment is not “oxidative”. I would still insist on saying “oxidative or water vapor treatment” or “CO, CO2 or water vapor treatment”.

Adsorption processes are efficient and easy to apply to remove many compounds in aqueous solutions (Oliveira and Franca, 2008). Activated coal is used to purify water and industrial effluents and to remove recalcitrant and bio-accumulative materials, such as aromatics compounds, dyes and heavy metals (Chatzopoulos and Irvine, 1993; Kanawade and Gaikwad, 2011).

The conventional active coals have a high efficiency of adsorption, but their production is very expensive (Zhang et al., 2005). Therefore, many methods have been developed to produce adsorbents with an equivalent or better adsorption capacity but with cheaper manufacturing processes (Gonçalves et al., 2007; Auta and Hameed, 2011; Pavan et al., 2014).

The adsorbent capacity of many types of adsorbent materials has been studied to remove dyes in aqueous solutions. For example, the capacities of the seed powder of papaya (Pavan et al., 2014), coffee waste (Brum et al., 2008), ceramic clays and residues of construction (Conceição et al., 2013), orange, banana or pineapple peels (Velmurugan et al., 2011; Mohammed et al., 2014) and others have been probed. Beer yeast has been applied as an adsorbent of mercury, chrome and nickel, and the residues of yeast processes and orange peel have been applied to adsorb lead. Rice husk ash is an adsorbent of zinc, and the sugarcane bagasse is an adsorbent of chrome (Gautam et al., 2014). The sludge from the treatment of vegetable oil residues has been applied as an adsorbent of copper and lead (Zaini et al., 2014).

The sludge from the treatment of the effluent of the paper and cellulose industries can be utilized as fuels for the co-generation of electricity (Borges et al., 2008) and as treatments of soils because of its chemical, physical and biological characteristics (Andrade et al., 2003). These residues can be incorporated into ceramics materials (Brum et al., 2008; Conceição et al., 2013; Velmurugan et al., 2011; Mohammed et al., 2014; Zaini et al., 2014) and can be used to produce grouts (Zanella, 2011; Kim et al., 2009).

The sludge from paper and cellulose manufacturing can be utilized to produce adsorbent materials. Hojamberdiev et al. (2008a,b) applied a thermal treatment to the sludge, and the material obtained was able to remove phosphate compounds (Hojamberdiev et al., 2008b). Calace et al. (2002) applied the activated sludge to remove phenolic compounds (Calace et al., 2002). Bhatnagar et al. (2007) investigated the adsorbent processes of the activated sludge after its thermal treatment at 500 °C against anionic dyes in aqueous solutions. The adsorption capacity was 62.3 mg g^{-1} (Suctu and Akkurt, 2009). Jaria et al. (2015) produced an adsorbent applying primary sludge as precursor (Jaria et al., 2015). The sludge was chemically treated and submitted to a pyrolysis process. The adsorbent materials were tested for the removal of fluoxetine in an aqueous solution and had an adsorption capacity of 191.6 mg g^{-1}.

For the production of activated coal from the cellulose sludge, many variables should be considered. The physical and chemical characteristics of the precursor materials, the type of the activation agent of the coal, the pH used, the time and activation temperature are important information to obtain a coal with high adsorption capacities (Velghe et al., 2012). Therefore, in this work, the authors developed a coal adsorbent material utilizing cellulose sludge from the manufacturing of paper and cellulose as the precursor. The size of the particles of the adsorbent was determined, and a morphological study was completed. The adsorbent capacity of the coal was determined from the complete adsorptions kinetic studies and equilibrium isotherms with methylene blue solutions.

2. Experimental procedures

2.1. Cellulose residues

The cellulose sludge applied for the production of the adsorbent was obtained from the manufacturing processes of cellulose at the Celulose Irani S.A./Vargem Bonita/SC/BR. The cellulose sludge was dried in an oven (Quimis – model Q-317M52) with a controlled temperature of 105 °C for 24 h. The humidity content of the sludge, the fixed solids and volatile solids were determined according to the methodology of the Standard Methods for Examination of Water and Wastewater (AWWA, 1995).

Once dried, the residue was crushed in a laboratory mill (Tecnal – model TE-625) and sifted using a set of vibrating screens (Bertel – model 4181). The granulometric analysis was performed according to the standard NBR 7181 (ABNT, 1984) with a screen set of 35–200 mesh (500 μm–74 μm). The fractions with a grain size of less than 149 μm (100 mesh) were utilized for the studies. The powder residues were analyzed using X-ray Fluorescence Spectrometry in helium flux (200 mL min^{-1}).

2.2. Chemical activation of the cellulose sludge

The chemical activation of the cellulose sludge was conducted in a solution containing phosphoric acid (Vetec – 85%) and distilled water in a proportion of 1:1 (v/v), according to the methodology proposed by Colpani (2012). The activation processes were carried out in a 500 ml Erlenmeyer flask containing 150 ml of acid solution and 30 g of sludge. The activation processes were completed in a shaker (Logen Scientific – model LS 4500) at 65 rpm for 1 h at 85 °C.

After the activation processes with phosphoric acid, the active