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Mesoporous carbon derived from a biopolymer and a clay: Preparation, characterization and application for an organochlorine pesticide adsorption



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ABSTRACT

The production of carbon-based materials is a field of intense scientific research due to the diversity of potential applications that this kind of material presents. In this paper, it is reported the synthesis of porous carbonaceous material (PCM) based on the pyrolysis at 850 °C of a composite made of Laponite (commercially available synthetic clay) and Cassava starch, followed by clay removal through acid digestion. The Laponite presence influenced the structural order and textural properties of the pyrolytic carbon formed. After pyrolysis and acid digestion of clay, it was obtained a material with a partial graphitic structure containing majorly sp² bounded carbon atoms, that has almost twice the specific surface area and up to 20 times more mesopore volume than the carbonaceous material obtained without the clay. The adsorbent potential of PCM was evaluated by adsorption of Dicamba, an organochlorine pesticide, from aqueous solutions. The PCM exhibits a high Dicamba removal efficiency, with a maximum adsorption capacity of 251.9 mg g⁻¹ related to a pseudo-second-order kinetic adsorption model with a strong pH dependence.

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1. Introduction

The growing demand for multifunctional materials has encouraged the scientific community to investigate the production of new carbon-based materials such as fullerenes, nanotubes, nanostructured porous carbon and carbon nanofibers [1–6]. These solids can exhibit high specific surface area, mechanical strength, heat resistance, electrical conductivity, among others properties [7–11], which allow the application of these materials as catalysts, catalyst supports, modified electrodes, fuel cells, supercapacitors and adsorbents [12–21]. Some types of carbon materials are obtained by using an inorganic template, which allows the control of

the structure. These materials are known as *nanostructured porous carbons*. By removing the template, by acid digestion for example, after carbonization/graphitization of the organic precursor, it gives rise to a porous carbon structure that is the inverse replica of template, named as *carbon replicas* [22–26]. Considering only the universe of inorganic templates, they can be classified in two types of templates: the endotemplates, such as silica particles of defined shape and the exotemplates, composed of porous structures such as zeolites, clays and mesoporous silica [25–38].

Smectite clays, such as montmorillonite, saponite, and hectorite, are highlighted inorganic templates for the carbon materials synthesis due to their structural and chemical properties and lower cost compared to the other porous inorganic templates [30,35–38]. Kyotani et al. were the forerunners in producing highly oriented graphite using acrylonitrile as carbon source and the

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montmorillonite clay as template [35]. The acrylonitrile interleaved in the interlayer spacing of montmorillonite was polymerized to poly(acrylonitrile) by using γ irradiation and then the material was heated to 700 °C under N_2 atmosphere for carbonization. The carbon material was obtained after acid digestion of the template and thermal treatments at different temperatures up to 2800 °C.

Among clays, a synthetic hectorite, known as Laponite, is an interesting material to be used as template for mesoporous carbons synthesis, since it is available on the market at costs lower than mesoporous silicas, has a high phase purity and is composed of small-sized particles that are easy to exfoliate in water medium. The hectorite layered structure is composed of three-sheet layers, wherein each layer consists of two outer sheets built up by tetrahedral $[-SiO_4]-$ units and one internal central sheet built up by $[-MgO_6]-$ octahedral units. The isomorphous substitution of magnesium ions in the internal central sheet by lithium ions results in a positive charge deficiency in the layers; the electrical neutrality is achieved by the intercalation of water solvated cations between adjacent layers. The hectorite general chemical composition is $M_{x/n}^+[Mg_{6-x}Li_x][Si_8]O_{20}(OH)_4 \cdot nH_2O$, where M^+ represents a monovalent metal cation and x corresponds to the degree of isomorphous substitution (typically between 0.5 and 1.3). The scheme of the Laponite structure is shown in Fig. 1.

The Laponite used in this work has sodium ions between the layers, x equal to 0.7, estimated surface area of 370 $m^2 g^{-1}$, particles with a disk-like shape and dimensions of about 25–30 nm of diameter and 1 nm of thickness [39].

Different organic sources have been used as precursor to carbon materials such as alcohols, ionic surfactants, polymers, disaccharides and biopolymers [40–43]. Biopolymers are an interesting choice of carbon precursors due to their renewable origin [44]. Among the various existing ones, the cassava starch derived from *Manihot esculenta crantz* stands out as an attractive option because it is produced in large quantities at low cost. Cassava plantations require low treatment of the planted area, have high resistance to pests and the highest yield per acreage, which are particularities usually not seen in other crops [45].

The starch structure consists basically of two types of polysaccharides, amylose and amylopectin [46]. The ratio between these polysaccharides in the structure differs depending on the cassava variety, but it is usually between 20% and 80%, respectively. Amylose (Fig. 2a) is a linear molecule composed of D -glucose units linked by $\alpha(1 \rightarrow 4)$ glycosidic bonds, while amylopectin (Fig. 2b) is a highly branched molecule composed of D -glucose units linked at $\alpha(1 \rightarrow 4)$ and $\alpha(1 \rightarrow 6)$ glycosidic bonds at the branching points.

The present paper deals with the synthesis and characterization of a porous carbonaceous material (abbreviated PCM) produced

from sodium hectorite and cassava starch through an easily applied procedure. The materials produced were characterized by a series of techniques, among which were powder X-ray diffraction (XRD), thermogravimetry coupled with mass spectrometry (TGA-MS) photoelectron spectroscopic analysis (XPS), scanning and transmission electron microscopies (SEM, TEM), medium-sized pore distribution and zeta potential analysis. The adsorptive properties of the produced PCM was evaluated in the removal of Dicamba (3,6-dichloro-methoxybenzoic acid) from aqueous solution. This herbicide has high potential for genetic toxicity and it is widely used in agriculture for the controlling of broadleaf weeds [47]. Due to its high water solubility and low volatility, it is easily leached to the environment, polluting water bodies.

2. Experimental

All reagents used in this work were analytical grade and used as received. The sodium hectorite Laponite RD (Lap) was provided from Laporte Industries (UK). The pesticide Dicamba Pestanal[®] was purchased from Sigma–Aldrich. The cassava starch (Cas) was purchased from the Amafil[®] Company (Brazil).

2.1. Preparation of the porous carbonaceous material

The biomass-based porous carbonaceous material (PCM) was obtained by the pyrolysis of a mixture of cassava starch (Cas) and the synthetic Laponite clay (Lap). The simplified chart of the procedure is shown in Fig. 3. Initially 10 g of commercial cassava starch were mixed with 200 mL of deionized water and then heated at 80 °C for 2 h, under continuous stirring, until the formation of a homogeneous gel-like system. In another container, 10 g of Laponite were added to 200 mL of deionized water and the suspension was kept at 80 °C under stirring for 2 h. Then the Cas solution were mixed to the Lap suspension and kept under stirring and heat at 80 °C for additional 2 h. The obtained gel containing Cas and Lap in a 1:1 mass proportion was dried in an oven at 65 °C and grinded to produce a powdered material, named as Cas-Lap composite. The Cas-Lap was calcined at 850 °C, under nitrogen atmosphere at a flow rate of 150 $cm^3 min^{-1}$, for 4 h to produce the clay-templated carbon (CTC). This material was successively treated with 1 L of a 6 mol L^{-1} HCl solution for 72 h, followed by centrifugation and washing with 2 L of deionized water and, then 0.5 L of a 40% (v/v) HF solution for another 72 h, in order to solubilize the clay framework and produce the porous carbonaceous material (PCM). The isolated PCM was centrifuged, washed with deionized water and dried in an oven at 100 °C. For comparison purposes, the same procedure was repeated but Laponite clay was not added in order to evaluate its real role in the carbon properties. The carbonaceous material isolated in the absence of clay template was abbreviated CM.

2.2. Dicamba adsorption studies

2.2.1. Sorbate solutions and concentration analysis

The adsorption studies with PCM were performed with the pesticide Dicamba as adsorbate. A prepared stock aqueous Dicamba solution (1000 $mg L^{-1}$) was subsequent diluted to adsorption studies. The Dicamba concentration remaining in the supernatant was spectrophotometrically determined by UV–Vis analyses.

2.2.2. Study on the influence of pH and temperature on Dicamba adsorption

Suspensions were prepared by adding 10 mg of the PCM in 20 mL of 250 $mg L^{-1}$ Dicamba solutions. To study the pH influence, the suspensions pH values were adjusted in 2.00 and 11.00 range

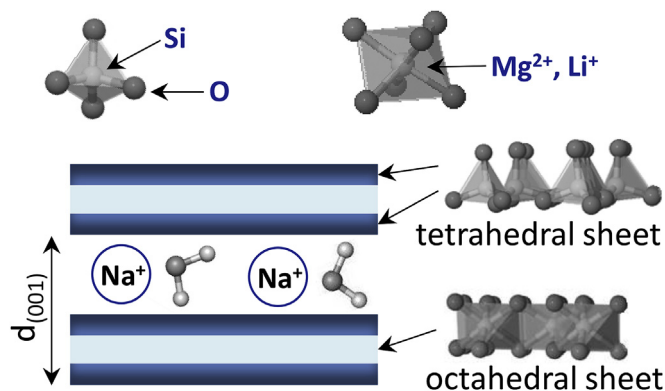


Fig. 1. Scheme of the hectorite structure in the Na⁺ form.

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