



Adsorption of caffeine on mesoporous activated carbon fibers prepared from pineapple plant leaves



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ABSTRACT

The present work reports the preparation of activated carbon fibers (ACFs) from pineapple plant leaves, and its application on caffeine (CFN) removal from aqueous solution. The preparation procedure was carried out using the H_3PO_4 as activating agent and slow pyrolysis under N_2 atmosphere. The characterization of materials was performed from the N_2 adsorption and desorption isotherms, scanning electron microscopy (SEM), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Raman spectroscopy, Boehm titration and pH_{pzc} method. ACFs showed high BET surface area value ($S_{BET} = 1031 \text{ m}^2 \text{ g}^{-1}$), well-developed mesoporous structure (mesopore volume of $1.27 \text{ cm}^3 \text{ g}^{-1}$) and pores with average diameter (D_M) of 5.87 nm. Additionally, ACFs showed features of fibrous material with predominance of acid groups on its surface. Adsorption studies indicated that the pseudo-second order kinetic and Langmuir isotherm models were that best fitted to the experimental data. The monolayer adsorption capacity was found to be 155.50 mg g^{-1} . thermodynamic studies revealed that adsorption process is spontaneous, exothermic and occurs preferably via physisorption. The pineapple leaves are an efficient precursor for preparation of ACFs, which were successfully applied as adsorbent material for removal of caffeine from the aqueous solutions.

1. Introduction

The development of new technologies and products are responsible for improving the population's life quality. However, the final disposal of products resulting from industrial and sewage treatment systems, when not properly treated, can cause environmental contamination and interfere directly in the life of living beings. In recent years, studies have shown a concern related to the environmental impacts caused by the presence of new compounds with unknown effects in wastewaters, groundwater and surface water (Liu et al., 2016).

Emerging contaminants comprise compounds and/or microorganisms whose presence has recently been detected in the environment, and their effects on biota and society are uncertain (Naidu et al., 2016). Among the various existing emergent contaminants, there may be mentioned the compounds from the pharmaceutical, personal care, veterinary, food additive and agrochemical products (Matamoros et al., 2016a). Caffeine (CFN) is an alkaloid used as cardiac, cerebral and respiratory stimulant and it can also be employed as additive in drugs for increase the analgesic effect (Buerge et al., 2003). CFN is found in teas, coffees, soft drinks, chocolate and some kinds of candies (Buerge

et al., 2012), and its average consumption per people is around 200 mg per day (Chrościńska-Krawczyk et al., 2011). The CFN, when ingested, is metabolized by human body, however about 1–10% is excreted by urine (Thorn et al., 2012). Several works have reported CFN as an emerging contaminant (Matamoros et al., 2016a, 2016b). In addition, it is a resilient compound and its presence in the water bodies indicate the disposal of domestic wastewaters (anthropogenic pollutant), i.e., it is an indicative of the presence of other contaminants, which were not monitored, but they can present risks to the environment (Buerge et al., 2003).

The industrial and domestic wastewater treatment systems usually employ biological (activated sludges), physical (adsorption, filtration, flocculation, etc.) and chemical processes (coagulation and electrolysis), which can be inefficient on removal of some compounds (Naidu et al., 2016). Thus, there is great interest and need to establish new treatment methods to completely remove the wastewater pollutants. Recently, new technologies have been reported, including bioreactors with membranes (Holloway et al., 2016) and advanced oxidation processes (Cheng et al., 2016), however, adsorption processes using activated carbons are the most widely used (Pezoti et al., 2015).

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Activated carbons (ACs) are materials used as efficient adsorbents in removal of a large variety of pollutants. In recent years, several researches have been carried out aiming to obtain new ACs from the renewable sources, as agro-industrial wastes, and new synthesis processes (Liu et al., 2016), which have been applied in adsorption studies of organic compounds (Acosta et al., 2016) and heavy metals (Karmacharya et al., 2016). ACs can be prepared from processes involving physical and/or chemical activating agents. Physical activation processes use CO₂, and water steam as activating agents, while chemical activation processes use chemical reagents. The chemical activation methods offer attractive characteristics compared to physical activation methods, such as simplicity, use of lower temperatures, shorter activation times, higher yields and development of porous structures on the materials (Li et al., 2010).

The development of ACs with fibrous structures shows advantages compared to other carbonaceous materials. Activated carbon fibers (ACFs) are amorphous carbonaceous materials that have high surface area and adsorption capacity values, functionalized surfaces, fast adsorption kinetics and uniform pores (Li et al., 2015). Thus, their preparation, characterization and application have been widely investigated in the recent years. Among the precursors used for ACFs preparations; synthetic fibers as polyacrylonitrile and viscose are widely used (Yusof et al., 2016). However, in order to use renewable sources, the literature reports the use of several ACFs precursors such as cotton fibers (Li et al., 2015), hemp (Vukčević et al., 2015), bamboo (Zhao et al., 2015), wood (Huang and Zhao, 2016) and seaweed (Ncibi et al., 2014).

In this work, we propose the preparation and characterization of new ACFs obtained from the pineapple leaf fibers, using H₃PO₄ as activating agent, and its application for removal of CFN from the aqueous solution. The pineapple (*Ananas comosus*) is a monocot plant, herbaceous, and perennial, originating in the Americas and belonging to *Bromeliaceae* family, and has been cultivated in Asia, Africa, and America (Chan et al., 2016). Pineapple fruit is consumed naturally or from processed products, highlighting the pineapple juice. After harvesting the fruit, pineapple leaves become a residue, which most often is burned to eliminate fungi and other parasites, composted or just piled to rot. The chemical activation with H₃PO₄ can provide ACFs with well-developed porosity from a wide variety of precursors. In addition, it has low environmental and toxicological constraints, and it can be used at lower activation temperatures than other chemical activating agents (Xu et al., 2014).

2. Materials and methods

2.1. Chemicals

Phosphoric acid (H₃PO₄, 85%), caffeine (CFN, ≤ 99%) and KBr (FT-IR grade) were purchased from Sigma-Aldrich. All other chemicals had analytical grade. CFN is a water-soluble weak base (K_s > 10,000 mg L⁻¹), it has pK_a of 8.30 and molecular weight of 194.19 g mol⁻¹ (Barbas et al., 2000). The chemical equilibrium between the CFN protonated and deprotonated forms, as well as the respective molecular structures dimensions are shown in Fig. 1S (Supplementary Information section).

2.2. Raw material

Pineapple plant leaves (*Ananas comosus*) were collected in the region of Maringá city, Paraná State, Brazil. The leaves were brought to laboratory, washed with tap water followed by deionized water for removal of residues, and then subjected to a scraping process to removal of mucilage and obtaining of the pineapple leaf fibers (PLFs). The PLFs were dried in oven at 65 °C by 24 h and cut into pieces with ca. 2.0 cm. The proximate analysis was carried out in triplicate according to standard methodology ASTM-D1762-1984 (ASTM, 1984).

2.3. Preparation of ACFs

ACFs were prepared from the slow pyrolysis process (low heating rate) at impregnation ratio of 1:1 (H₃PO₄:PLFs, v:m). Amount of 4.00 g of PLFs was placed to contact with 4.0 mL of H₃PO₄ (87%) into a stainless-steel reactor. The mixture was kept in oven at 65 °C for 24 h, and then placed in a muffle furnace with heating program of 2 h at 300 °C and 1 h at 500 °C, under N₂ flow of 100 mL min⁻¹ and heating rate of 5 °C min⁻¹. After the pyrolysis procedure, the material was firstly washed with NaOH solution (1.0 mol L⁻¹), and then distilled water up to the pH ≈ 7.0. The obtained material was dried at 100 °C for 24 h and properly stored for further analyses. Carbonized fibers (CFs) were prepared from the same procedure, however, without H₃PO₄. The materials' yields were calculated from Eq. (1):

$$Yield = \frac{W_c}{W_o} \times 100 \quad (1)$$

where W_c is the final mass and W_o is the initial mass of the material.

2.4. Characterization

The N₂ adsorption/desorption isotherms at 77 K for ACFs and CFs were obtained using a QuantaChrome, Nova 1200e equipment. The BET surface area (S_{BET}) values were calculated from the linear fit of Brunauer-Emmett-Teller (BET) equation to the relative pressure range (p/p°) of 0.05–0.20. The total pore volume (V_t) was defined as the maximum amount of N₂ adsorbed at relative pressure (p/p°) of 0.99, while the micropore volume (V_p) was determined from the α -plot method. The pore size distribution and the mesopore volume (V_m) were obtained from Barret, Joyner and Halenda (BJH) method (Barrett et al., 1951; Thommes et al., 2015). The pore diameter (D_p) was calculated from the relation $4V_t/S_{BET}$.

Surface groups of the materials were analyzed using the Fourier transform infrared spectroscopy (FT-IR). The samples were prepared as pellets of KBr and the spectra recorded with resolution of 4 cm⁻¹ and acquisition rate of 32 scan min⁻¹ in a range of 4000–400 cm⁻¹, using a Shimadzu IRTracer-100. The contents of acidic functional groups and lactones (total acidity) on ACFs were determined by the method described by Boehm (1994), and the pH at the point of zero charge (pH_{pzc}) was determined by method reported by Noh and Schwarz (1990).

The morphological features of precursor, CFs and ACFs were evaluated from the scanning electron microscopy (SEM), using a SuperScan SS-550 Shimadzu microscopy. Thermal stability of the materials was investigated from the thermogravimetric analyses (TGA), using a thermal analyzer Netzsch® PG/2/G Luxx under N₂ flow of 100 mL min⁻¹ and heating rate of 10 °C min⁻¹ from the room temperature up to 800 °C. The crystallinity of materials was evaluated by X-ray diffraction (XRD) patterns were recorded using a Shimadzu XR-7000 diffractometer, operating with a Cu K α ($\lambda = 1.540598 \text{ \AA}$) radiation source in a 2 θ range of 2–80° with step of 0.02°. Raman spectra were recorded with a Brüker dispersive micro Raman at wavelength (λ) of 532 nm and power of 20 mW, using a resolution of 9–15 cm⁻¹, slit of 25 × 1000 μm in an acquisition rate of 10 scans min⁻¹ and integration time of 5 s. Spectra were registered in the range of 2500–500 cm⁻¹.

2.5. Batch adsorption studies

Adsorption studies were performed using 25.0 mL of CFN solutions and 25.0 mg of ACFs, which were placed into polypropylene tubes and shaken in a thermo-shaker incubator at 200 rpm. The remaining CFN concentrations were determined (after removal of ACFs by vacuum filtration with Millipore membrane –0.45 μm) from a calibration curve, using an Agilent Cary 60 spectrophotometer at maximum wavelength (λ_{max}) of 273 nm. All studies were carried out in triplicate.

The pH influence on the CFN adsorption onto ACFs was investigated from 500 mg L⁻¹ concentration solutions, which had its pH values

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