Review

Comparison of the adsorption of lead by activated carbons from three lignocellulosic precursors

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ABSTRACT

Three activated carbons samples produced from Guava seeds, Tropical almond shells and Dindé stones were prepared by physical activation. The activated carbons have surface areas of around 1000 m^2 g^{-1} and high micropore volumes of around 0.40 cm^3 g^{-1}. They were studied for the removal of lead from water in batch mode. Sorption studies were performed at different temperatures, initial pH, initial concentrations and adsorbent doses. Maximum adsorption occurred at pH 6 for an adsorbent dose of 0.5 g L^{-1}. The sorption is favorable until an initial lead concentration of 90 mg L^{-1} for the activated carbons from Almond and Guava and only 25 mg L^{-1} for that of Dindé. The most favorable temperature is 30 °C for the activated carbons from Dindé and Almond with, 40 °C being favored by the one from Guava. The kinetic data were modelled with, the results showing that the Bangham model best describes the kinetics of the Almond and Dindé activated carbons and the Elovich model that of activated carbon from Guava seeds. Sorption equilibrium studies were conducted in a concentration range of lead from 0 to 230 mg L^{-1} and the isotherms were also modelled. The Khan equation gives the best fit for the sorption equilibrium data for the activated carbon from Almond, the Langmuir−Freundlich equation for the one derived from Dindé and the Redlich-Peterson for the activated Guava seeds carbon. Finally, the thermokinetic parameters were evaluated. With a maximum amount of lead adsorbed as high as 50 (Dindé), 96 (Guava) and 112 mg g^{-1} (Almond), these three activated carbons can be considered as efficient adsorbents for the remediation of lead from water.

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1. Introduction

High concentrations of toxic heavy metals have been observed in river sediments [1], agricultural soil [2] and acidic leachate [3] in French Guyana, in French West Indies as well as in many other regions in the world [4,5]. Such contamination has generally been caused by mining [2] and landfills [4].

Numerous studies have been conducted to eliminate toxic heavy metals from aqueous solutions. Precipitation by controlling the pH of the solution [6,7] and ion exchange [8,9] are widely used for reducing the level of contamination. Adsorption is another attractive option for heavy metal removal. Activated carbons [10–14], polymers [15,16], metal oxides [17,18] and other low-cost adsorbents, such as agricultural byproducts [19,20], have been used as adsorbents.

One of the advantages of the activated carbons is the existence of large surface areas and large porous volumes to adsorb high quantity of pollutants. Another advantage is their low cost when the activated carbon is prepared from waste materials, at the same time limiting waste stocks and transforming wastes into more valuable products.

This is the case for Guava seeds (*Psidium guajava*), Dindé stones (*Acrocomia karukerana*) and Tropical almond shells (*Terminalia catappa*) which come from agro-alimentary industries, the fruits being used to prepare juice from Guava and oil from Dindé and Tropical almond.

In this study, these agricultural byproducts, Guava seeds, Tropical almond shells and Dindé stones, are each transformed into activated carbon useful for the remediation of lead from water. The activated carbons are prepared by physical activation (carbonization plus oxidation with gas at high temperature in one or two

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separate steps). The purposes of this work are multiple. First, to study the synthesis of the activated carbons by physical activation with carbon dioxide and water vapor. Second, to evaluate the adsorption potential of the three different activated carbon sources for lead sorption, taking into account the physicochemical characteristics of the activated carbon and the operating conditions (temperature, lead concentration, pH, adsorbent dose). Third, to suggest a sorption mechanism. Fourth, the kinetics, the equilibrium and the thermodynamic aspects of the sorption process are also explored.

2. Experimental methods

2.1. Reagents

The 69.4% nitric acid solution (HNO$_3$) and the hydroxide sodium pastilles (NaOH) used to fix the pH and the lead nitrate (Pb(NO$_3$)$_2$) which is the lead ions source are analytical reagent (AR) grade chemical products from Prolabo Company. All solutions are prepared with deionized water.

2.2. The activated carbon samples

Three types of physically activated carbons are prepared from Guava seeds, Tropical almond shells and Dindé stones and are characterized according to the following procedures.

2.2.1. The lignocellulosic precursors

The lignocellulosic precursors are ground in an aluminum mill and sieved. The particles in the size range 0.4–1 mm are retained for experimentation. The botanical composition of the precursors is determined using the standard analysis for extractives, lignin, holocellulose, moisture and ash as described by Ouensanga et al. [21].

The textural characterization of the precursor is achieved by density measurements obtained by weighing the bulk sample with or without a liquid (mercury or methanol) at ambient temperature and atmospheric pressure. The total pore volume of the sample (V$_T$) is estimated from the density values by the expression:

$$V_T = \frac{1}{\rho_{Hg}} - \frac{1}{\rho_{CH_3OH}} \tag{1}$$

ρ_{Hg} being the precursor density calculated through mercury and ρ_{CH3OH}, the precursor density through methanol.

In addition, a scanning electron microscope (Hitachi S-2500) is used to observe the texture of the precursors.

2.2.2. Preparation of the activated carbons

The preparation of the activated carbons is carried out in two steps, a carbonization followed by a physical activation.

2.2.2.1. Carbonization step.
The operating conditions selected for the preparation of the chars are 800 °C during 2 h with a heating rate of 10 °C min^{-1} under a flow of nitrogen of 60 mL min^{-1}. 10 g of the precursor is introduced in an alumina sample holder which is placed in the reactor. The latter is made of a cylindrical quartz tube crossing an electrical furnace with a temperature recording of ±2 °C. The char yield is respectively 28% for Almond shells and Guava seeds, 32% for Dindé stones. The resulting char is stored and subsequently activated.

The elemental analysis of the three chars is realized at the Analysis Laboratory of CNRS Vernaison, France. The proximate analysis is achieved with a thermogravimetric analyser using the following procedure. A sample of char is heated from room

temperature to 110 °C in a N$_2$ atmosphere until complete dehydration, followed by decomposition at 850 °C for seven minutes to determine the quantity of volatile matters. The atmosphere is then changed to be oxidizing. The sample is cooled to 800 °C and maintained at this temperature until its weight remains unchanged. The weight loss during this period is due to the reaction of the fixed carbon with oxygen and the remaining residue is ash.

In addition, a scanning electron microscope (Hitachi S-2500) is used to characterize the texture of the chars.

2.2.2.2. Physical activation step.
The oxidation is realized via a mixture of carbon dioxide and water vapor (80% CO$_2$, 20% H$_2$O) at 850 °C. 5 g of the char is put in the reactor previously described for carbonization and put in contact with the oxidizing flow for different times leading to the production of activated carbons with different levels of burn-off.

According to the development of porosity versus burn-off, visualized in Fig. 1, a maximum is reached for all three chars somewhere 40 and 50% burn-off. Therefore, a burn-off of 50% has been retained for the samples named respectively PAC A, PAC D and PAC G. PAC G is the physically activated carbon at burn off 50% from Guava seeds, PAC A from tropical Almond shells and PAC D from Dindé stones. The PACs are stored and used after for the sorption studies.

2.2.3. Characterization of the activated carbons

2.2.3.1. Texture of the activated carbons.
The texture of the activated carbons is characterized via adsorption of nitrogen at 77 K using a Micromeritics ASAP 2010 apparatus. About 0.30 g of sample is outgassed at 250 °C for 48 h, prior to the adsorption measurements.

The specific surface area (S$_{BET}$) is evaluated by applying the Brunauer, Emmett and Teller (BET) equation [22] to the linear part of the BET plot and taking account the average area occupied by a molecule of N$_2$ to be equal to 16.2 Å^2.

The micropore volume (Vmi) is estimated from the N$_2$ adsorption isotherm by applying the Dubinin–Radushkevich (DR) equation [23] to the linear part of the DR plot. The total pore volume is determined from the amount of nitrogen adsorbed at P/P° = 0.99. The mesopore volume (Vme) is calculated by subtracting the micropore volume from the total pore volume. The DFT pore size distribution is calculated by assuming a slit like geometry for the micropores [24].

In addition, a scanning electron microscope (Hitachi S-2500) is used to determine the surface textural characteristics of the
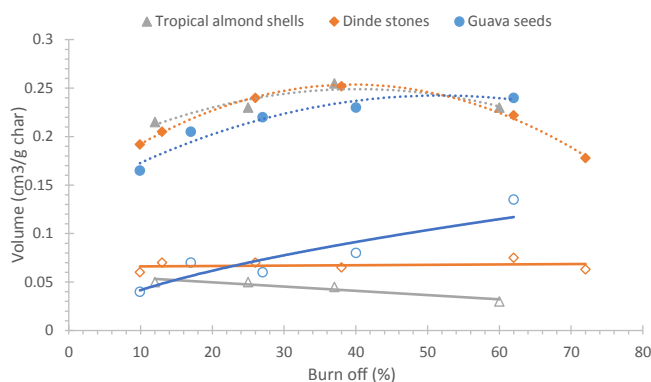

Fig. 1. Evolution of micropore volume (full legends) and mesopore volume (empty legends) per gram of starting char as a function of burn-off.