Adsorption of lead by chemically activated carbons from three lignocellulosic precursors

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A B S T R A C T

Guava seeds, Dindé stones and Tropical almond shells are chemically activated using sulfuric acid with an impregnation ratio of 1:1 then carbonized at 600 °C. The three activated carbons (CAC G, D and A) are characterized by TPD/MS, Boehm titration, DRIFT, SEM, N_2 and CO_2 adsorptions at 77 and 273 K respectively and later used for lead sorption. The experimental sorption data, kinetics and equilibrium, are adjusted with different models according to different theoretical foundations to interpret the sorption process. The kinetics is well described by the Elovich model showing the sorption is heterogeneous. The parameters α and β are calculated. The results show that the kinetics are positively influenced by the ultramicropore and mesopore volumes of the carbons. The equilibrium is well fitted by the Redlich Peterson model, compatible with heterogeneous adsorption sites. The parameters $K_{S,RP}$, Qmax and β are calculated. $K_{S,RP}$ is positively influenced by the sum of acid groups of the carbons. The optimum sorption conditions are 30 °C, initial pH 5–6, adsorbent dose 0.5 g L^{-1} and initial lead concentration 20 mg L^{-1} for CAC D and CAC G and 5 mg L^{-1} for CAC A. New suggestions are given to explain the influence of the operating conditions on the sorption results. The thermodynamics parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$ are calculated and show the sorption is favorable for the three carbons, it is exothermic and less random for the carbons from Almond and Dindé. A mechanism involving the OH, SH groups and the π electrons of the carbon is proposed to explain the sorption results. The activated carbons from Almond, Dindé and Guava adsorb maximum amounts of lead of 4.5, 7 and 11 mg g^{-1} respectively; they have the highest β Elovich parameter, $\Delta H°$ and $\Delta S°$ values from the literature.

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1. Introduction

Heavy metals especially cadmium, lead and mercury are found in freshwaters in Guyana, in the West Indies and in several other countries of the world. They can cause serious damage to human health: e.g. to the nervous system, the brain, the liver, the kidney and the reproductive system [1].

Many methods are available to remove heavy metal from water including chemical precipitation, ion exchange, electro flotation, membrane filtration and reverse osmosis but these techniques are generally expensive [2]. The work reported here deals with a low cost, ecofriendly and efficient technique to clean up water polluted by heavy metals: filtration via activated carbon.

Numerous adsorption studies have been conducted with activated carbons from shells of nuts, fruit stones and more generally from terrestrial or marine lignocellulosic residues which are very efficient at heavy metal removal [3–25].

In this study, the selected lignocellulosic precursors which will be transformed into activated carbons with a large porous surface to adsorb pollutants are tropical almond (*Terminalia Catappa*) shells, dindé (*Acrocomia karukerana*) stones and guava (*Psidium guajava)* seeds.

These precursors are chosen because they have high lignin and cellulose contents, respectively 40 wt% and 30 wt% [26], which make them suitable for carbonization [27]. Moreover, they are locally abundant, cheap and it is one way to recycle such waste materials.

Activated carbons can be prepared by physical or chemical activation. The first reported study about these precursors is about physical activation and a description of them can be found in Ref. [26].

This study uses chemical activation. Chemical activation involves soaking the precursor in a dehydrating agent (H_3PO_4, H_2SO_4, $ZnCl_2$) followed by a carbonization process at low temperature in a controlled atmosphere. Chemical activation has two advantages over the physical activation. First, a lower temperature to achieve the process, and second, a higher yield of activated carbon is obtained.

In this study, the activated carbons are prepared through chemical activation with sulfuric acid. Sulfur can form cross links in the carbonaceous matrix and may lead to a more rigid carbonaceous polymeric matrix which is efficient for the sorption.

Then, the activated carbons will be used for lead water treatment.

There are multiple aims of this research:

- To study the physical and the chemical characteristics of the three activated carbons
- To determine and model the kinetics and equilibrium of lead adsorption
- To determine the influences of the characteristics of the activated carbons and of the operating conditions on the adsorption results
- To calculate the thermodynamic parameters of adsorption such as the enthalpy and the entropy changes during adsorption
- And finally to propose a sorption mechanism.

2. Material and methods

2.1. Preparation and characterization of the activated carbons

2.1.1. Preparation of the chemically activated carbons

Almond shells, Dindé stones and Guava seeds are dried, crushed and sieved. The 0.4–1.0 mm diameter fraction is retained for experimentation. Note that the lignocellulosic and the elemental compositions of the precursors are given in [26].

Production of activated carbons begins by soaking the same weight of precursor and sulfuric acid (H_2SO_4, 98%) leading to an impregnation ratio of 1:1 for 24 h, then carbonization at 600 °C in a nitrogen atmosphere for 1 h, heating rate 10 °C min^{-1}. After cooling, the activated carbons samples are repeatedly washed with deionized water until the pH remains constant, dried at 105 °C, characterized and used for the batch adsorption studies.

CAC A is the chemically activated carbon from Tropical almond shells, CAC D from Dindé stones and CAC G from Guava seeds.

The production yield of CAC A, CAC D and CAC G are respectively 47, 39 and 42 wt%.

2.1.2. Physical characterization

The texture of the three activated carbons are characterized via adsorption of nitrogen at 77 K and carbon dioxide at 273 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 [28] to the initial linear part of the nitrogen BET plot.

The Dubinin–Radushkevich volumes (V_{DR}) are estimated from the N_2 and CO_2 adsorption isotherm by applying the Dubinin–Radushkevich (DR) equation [29] to the linear part of the DR plot.

The total pore volume (V_T) is determined from the amount of nitrogen adsorbed at $P/P° = 0.99$ and from the amount of carbon dioxide at $P/P° = 0.03$.

The density functional theory (DFT) pore size distribution is calculated by assuming a slit like geometry for the micropores [30].

The activated carbons surfaces are also observed by scanning electronic microscopy (SEM).

2.1.3. Chemical characterization

Chemically activated carbons surfaces are characterized by pH PZC using the Drift method [31]. The determination of acid and basic surface groups is realized by the Boehm method [32].

TPD/MS analysis is also conducted to more precisely determinate the surface functionalities of the activated carbon samples.

2.2. Preparation of the lead (II) ions solutions

A stock solution of lead (II) ions is prepared by dissolving an accurate mass of lead nitrate in deionized water. Other concentrations prepared from the stock solution by dilution vary between 10 and 50 mg L^{-1} and the pH of the working solutions is adjusted to the desired value with 1 M HNO_3 or 1 M KOH. Fresh solutions are used for each experiment.

The lead ion concentrations used in this study have approximately the same values found in natural waters. Note that the hydro soluble lead exists under the form Pb^{2+}, $Pb(HCO_3)^+$, $Pb(OH)^+$, $Pb(OH)_3^-$, $Pb(CO_3)_2^{2-}$ in function of the acidity of the water.

2.3. Batch adsorption studies

All batch experiments are conducted with adsorbent in Erlenmeyer flasks sealed with glass stoppers to avoid evaporation. Flasks are stirred using a magnetic stirrer at 400 rpm.

Note that the stirring is stopped before each removal and that the total volume removed does not exceed 10% of the initial volume of the lead ion solution.

2.3.1. Kinetics studies

Lead (II) ion solution (1 L) at an initial concentration of 50 mg L^{-1}, at initial pH 5 and at 30 °C is put in contact with 1 g of activated carbon (to obtain an adsorbent dose D of 1 g L^{-1}).

5 mL of solution is removed from the flask at regular intervals, filtered and the concentration of the residual lead (II) ion concentration (C_t) is measured using an atomic absorption spectrometer (VARIAN AA 240 FS) at $\lambda = 261.4$ nm. Note that the spectrometer measures only the absorption of the hydro soluble forms of lead.

The amount of lead adsorbed Q is calculated by the difference between the initial (C_0) and the instantaneous lead (II) ion concentration (C_t):

$$Q(mg.g^{-1}) = \frac{C_0 - C_t}{D} \tag{1}$$

The pH of each residual lead ion solution is measured with a Mettler Toledo FG2 pH meter.

2.3.2. Isotherm studies

50 mL of lead (II) ion solution at initial concentrations varying from 10 to 50 mg L^{-1}, at a fixed initial pH varying from 2 to 11, at the temperature T = 30 or 40 °C is put in contact with varying adsorbent doses of activated carbon (50 mg of activated carbon for an adsorbent dose D of 1 g L^{-1}, 100 mg for D equal to 2 g L^{-1}).

5 mL of solution is removed from the flask after 72 h, filtered and the concentration of the remaining lead in solution C_{eq} is measured by the same atomic absorption spectrometer.

The amount of lead adsorbed Q_{eq} is calculated from the difference between the initial (C_0) and the equilibrium lead concentration (C_{eq}):

$$Q_{eq}(mg.g^{-1}) = \frac{C_0 - C_{eq}}{D} \tag{2}$$