Chemical Engineering Journal 160 (2010) 549–555

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Thermodynamic aspects of the Pb adsorption using Brazilian sawdust samples: Removal of metal ions from battery industry wastewater

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ARTICLE INFO

Article history:
Received 16 October 2009
Received in revised form 25 March 2010
Accepted 26 March 2010

Keywords:
Lead
Wastewater
Calorimetry
Sawdust

ABSTRACT

Brazilian sawdust samples (*Caryocar* spp.; *Manilkara* spp.; and *Tabebuia* spp.) have been used for Pb(II) ions adsorption from water at 25 °C. The series of adsorption isotherms were adjusted to a modified Langmuir equation from data obtained by suspending the sawdust with $Pb(NO_3)_2$ solutions, which gave the maximum number of moles adsorbed as 89.10 ± 8.28; 145.04 ± 12.43 and 95.31 ± 8.28 mg g^{-1} for *Caryocar* spp.; *Manilkara* spp.; and *Tabebuia* spp., respectively. Thermodynamic data of interactions were studied by the calorimetric titration of Pb(II) in aqueous solution. Gibbs free energies were negative for all systems and the adsorption interactions presented the following exothermic enthalpic values: -1.99 ± 0.11; -3.20 ± 0.21 and -2.27 ± 0.11 kJ mol^{-1} for *Caryocar* spp.; *Manilkara* spp.; and *Tabebuia* spp., respectively. All liquid/solid interface adsorptions were entalpically and entropically driven. These sawdust samples were applied to remove Pb(II) from wastewater of a battery industry of Brasilia, DF, Brazil, which presented a Pb(II) concentration of 2.66 mg L^{-1}. The Pb(II) concentration in this wastewater was reduced to 2.49; 0.45 and 0.47 mg L^{-1} by application of *Caryocar* spp.; *Manilkara* spp.; and *Tabebuia* spp., respectively.

1. Introduction

The exponential growth of industrial activities and the increase of the use of many chemicals in industries have increased the pollution in the environment, mainly, in aquatic ecosystem [1–3]. The contamination of natural waters with toxic metals has become one of the major concerns of environmental researchers in recent years due to water importance to environment and mankind [4–6]. Thus, the presence of inorganic contaminants such as arsenic, cadmium, chromium, lead and mercury represents a big problem to the environment because they are not biodegradable and cause many diseases and disorders by accumulation in living organisms [7–9]. Among these toxic metal ions, lead must be highlighted, due to the Pb(II) is very toxic, causing many health problems to human such as: renal disturbances, hepatitis, encephalopathy, anaemia, lung inefficiency, bone lesions, hypertension, as well as, cancer [7,8,10].

Industries of pigments, mining, lead smelters, glass, and mainly, batteries have generated high levels of lead in waters [11,12]. In this way, the treatments used to remove toxic metals from industrial effluents based on exchange resins, chemical precipitation, electroflotation are expensive [7,8,13]. Thus, the application of low-cost materials, as byproducts of furniture industries, to remove contaminants from water is one way to develop a low expensive treatment of hazardous wastes [6,14–16].

In order to evaluate the interaction energy between contaminant and adsorbent, calorimetric studies have been extensively applied [17–20]. In 1784, Lavoisier and Laplace developed an ice calorimeter in order to determine the calorific capacity of materials, heat of reaction, ~~of~~ metabolic heat by applying the formula for the latent heat of melting water obtained by this ice calorimeter, once there were not accurate thermometers, thermistors or thermopiles to determine small energetic changes [21,22]. Since the development of technology of calorimeters, small energy values have been determined, and nowadays, it is possible to identify and quantify many phenomena of the distinct processes in colloidal systems in solid/liquid interfaces such as: energy distribution of the surface, adhesion energy, enthalpy of dilution, aggregation/micellization

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doi:10.1016/j.cej.2010.03.066

enthalpy, as well as, interaction between contaminant adsorbate molecules and the adsorbent [23]. Indeed, the calorimetric data is an important tool to understand the nature of the interactions between contaminant-adsorbent.

In this context, the adsorption of Pb(II) by Brazilian sawdust samples (*Caryocar* spp.; *Manilkara* spp.; and *Tabebuia* spp.) was followed. An understanding of the thermochemical characteristics of the adsorption interaction was developed by the determination of the calorimetric adsorption data at the solid/liquid interface, and these low-cost materials were applied to remove Pb(II) ions from battery industry wastewater.

2. Experimental

2.1. Chemicals

Brazilian sawdust samples of Piquiá (*Caryocar* spp.), Maçaranduba (*Manilkara* spp.) and Ipê (*Tabebuia* spp.) were obtained from Rancho da Cabocla Sawmill Ltda in Brazilian Santarém city. Sawdust adsorbents were grained and sieved by a range of sieves and only the particles smaller than 2.5 mm were used, as according to ASTM Method D4749 [17].

$Pb(NO_3)_2$, HCl, H_2SO_4, NaOH, benzene, ethanol, chloroform from Vetec and Folin-Denis reagent, vanillin from Aldrich were used without purification.

The water streams were collected in a battery industry effluent located in Distrito Federal, Brazil. Wastewater samples were collected into glass bottles, and the samples were stored in a refrigerator at 4 °C.

2.2. Characterization of sawdust samples

2.2.1. Extracts for lignin determination

33 g of sawdust samples were sequentially extracted in a soxhlet apparatus with benzene, benzene:ethanol (2:1), chloroform, and water. The isolated extracts were dried in an oven at 70 °C for 12 h and the residual air-dried wood powder. This powder was separated in order to determine the lignin content [18,19].

2.2.2. Extracts for total phenol, proanthocyanidin and tanin determinations

50 g of sawdust samples were submitted to an extraction with methanol:water (80:20) in a beaker at room temperature with stirring for 24 h. The mixture was filtered and the methanol was evaporated under reduced pressure at 40 °C. The remaining aqueous extract was divided in four fractions, freeze-dried for its conservation and separated in order to determine the total phenols, proanthocyanidins and tannins contents [18,19].

2.2.3. Proanthocyanidin contents

Proanthocyanidin determination was carried out by the vanillin method [18,19]. 1 mL of the aqueous extract was mixed with 2 mL of a freshly prepared vanillin solution (1 g/100 mL of 70% H_2SO_4) and maintained at 20 °C for 15 min. The absorption was measured at 500 nm. Calibration was performed with catechin aqueous solutions (2–40 $\mu g\,mL^{-1}$).

2.2.4. Lignin content

Lignin content of sawdust samples was determined as according to Björkmann technique. 100 g of dried sawdust samples were extracted in a soxhlet apparatus with ketone–water (9:1) and the organic solvent was evaporated under reduced pressure at 70 °C. After that, the aqueous mixture was acidified with diluted HCl until pH 2 was reached. The precipitated lignin was filtered and washed with a small amount of water. The lignin was dried at 70 °C for 12 h [18,19].

2.2.5. Total phenol contents

The total phenol content was determined by the Folin-Ciocalteu method. 2.5 mL of Folin-Ciocalteu reagent and 2 mL of aqueous solution of sodium carbonate (75 $g\,L^{-1}$) were added to 0.5 mL of the aqueous extract, and the mixture was kept at 50 °C for 5 min. After cooling, absorbance was measured at 760 nm. Aqueous solution of gallic acid (2–40 μg) was used as standard [18,19].

2.2.6. Tannin content

0.25 mL of aqueous extract was solubilized in 100 mL of aqueous solution with 5 mL Folin-Ciocalteau reagent, and 10 mL of aqueous solution of Na_2CO_3 7.5%. The tannin contends was determined using a UV–vis spectrophotomer at 760 nm [18,19].

2.2.7. Surface area

Nitrogen adsorption–desorption data were taken from an instrument Quantachrome NOVA 2200 gas sorption analyzer at 77 K. Surface area was calculated by the Brunauer–Emmett–Teller (BET) method, and pore size distribution was derived from the adsorption branches by using the Barrett–Joyner–Halenda (BJH) method.

2.3. Adsorption studies

The adsorption process was followed batchwise in an aqueous solution of $Pb(NO_3)_2$ with controlled pH 5 at 298 ± 1 K for 12 h. For this process, a series of samples containing about 25.0 mg of sawdust were suspended in 50.0 mL of aqueous $Pb(NO_3)_2$ solutions of different concentrations, varying from zero to 5.0 $mmol\,L^{-1}$. The best pH value was determined by using 50.0 mg of sawdust suspended in 50.0 mL of different aqueous $Pb(NO_3)_2$ solutions, which pH values varied from 1 to 6 and they were controlled by Clark/Lubs buffers [20]. The time required to reach the adsorption equilibria was determined by suspension of 25.0 mg of sawdusts in 50.0 mL of aqueous $Pb(NO_3)_2$ 5.0 $mmol\,L^{-1}$. At appropriate time intervals, the supernatant from each flask was collected and Pb(II) concentration was determined.

The effect of pH was determined by using 50.0 mg of sawdust suspended in 50.0 mL of different aqueous $Pb(NO_3)_2$ solutions, which pH values varied from 1 to 6 and they were controlled by Clark/Lubs buffers [20].

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The amount of metal ion adsorbed was determined from the difference in metal ion concentration measured by atomic adsorption spectrometry using a Buck model A-200 instrument (Buck Scientific, East Norwalk, CT, USA) in the aqueous sample before and after treatment with sawdust. All experiments were carried out in triplicate.

2.4. Calorimetric analysis

The adsorption of Pb(II) ions by Brazilian sawdust samples was followed calorimetrically by titration using an Adiabatic Solution Calorimeter Parr 6755 (Parr Instrument Company, Moline, IL, USA). In a typical experiment, 0.50 g of the material was suspended in 50.0 mL of water, equilibrated at 298.15 ± 0.02 K (thermostatically controlled), and titrated with aqueous solution of $Pb(NO_3)_2$