chemical engineering research and design xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Chemical Engineering Research and Design

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

Adsorption of Cd(II), Hg(II) and Zn(II) from aqueous solution using mesoporous activated carbon produced from *Bambusa vulgaris striata*

P.G. González [a,*], *Y.B. Pliego-Cuervo* [b]

[a] *Centro de Investigación en Micro y Nanotecnología, Universidad Veracruzana, Calzada Ruiz Cortínes No. 455, 94294 Boca del Río, Veracruz, Mexico*
[b] *División de Estudios de Posgrado e Investigación, IT de Orizaba, Oriente 9 No. 854, 94320 Orizaba, Veracruz, Mexico*

ABSTRACT

Mesoporous activated carbon (surface area of 608 m^2/g) has achieved high efficiency in removal of cadmium, mercury and zinc ions from water solution. The proposed low-cost adsorbent was physically activated with water steam from the bamboo species *Bambusa vulgaris striata*. The batch studies suggested an activated carbon dose of 0.6 g/L, solution pH of 9 and an equilibrium time of 16 h in static conditions. The pseudo-second order equations represented the adsorption kinetics with high correlation. Fitting of the experimental results to the Langmuir, Freundlich, Redlich–Peterson and Toth isotherm models showed an almost homogeneous surface coverage and presence of physical adsorption. The highest adsorption capacities, calculated from the Langmuir model, are 239.45, 248.05 and 254.39 mg/g of cadmium, mercury and zinc, respectively.

Keywords: Heavy metals; Adsorption capacity; Activated carbon; Isotherm models

1. Introduction

On the search of novel, low-cost and ecofriendly materials to remove pollutants from air, soil and water, can be found numerous alternatives. In this sense, there is a continuous work related to adsorption of several heavy metals on zeolites, membranes, polymers, resins, clays among others (Ali et al., 2012; Pintor et al., 2012; Gupta and Bhattacharyya, 2011). However, adsorption on activated carbon (AC) is still intensively studied as a center of many contributions and it is one of the most used and versatile techniques (Bhatnagar et al., 2013; Rivera-Utrilla et al., 2011; Dias et al., 2007).

AC materials are well-known as efficient adsorbents because of their surface and chemical properties (Jordá-Beneyto et al., 2008; Tamai et al., 2002). These characteristics could be controlled by the nature of the raw carbon source and the used activation method (Ahmedna et al., 2000). Therefore, different precursors are used to produce AC, with a special interest in those with high-carbon content, a low amount of inorganic compounds and a relative low-price (Rafatullaha et al., 2010; Demirbas, 2009). From here, the use of industrial or farm wastes as raw materials is an attractive alternative to prepare AC with potential applications (Ferro-García et al., 1988; Ahmedna et al., 2000; Demirbas, 2009). One of the advantages of this new generation of low-cost carbon precursors lies in the possibility to get benefits from waste materials. At the same time, this contributes to decrease costs of waste disposal and the negative impact on the environment.

From the environmental and health perspective, the precise removal of heavy-metal ions is an important issue. This group of toxic metals is commonly present in waste effluents from the mining, tanneries, textile mill products, electronics, electroplating and petrochemical industries (Chuah et al., 2005). Accumulation of heavy-metal ions in the

* *Corresponding author*. Tel.: +52 22913030866; fax: +52 22913030866.
E-mail addresses: pegonzalez@uv.mx, pegonzal@quim.ucm.es (P.G. González).
Received 5 November 2013; Received in revised form 4 February 2014; Accepted 11 February 2014
http://dx.doi.org/10.1016/j.cherd.2014.02.013

environmental (mainly soil and water) and later, on human tissue is due to their non-biodegradability and long half-life (Murugesan et al., 2006). Mercury and cadmium are the most toxic transition metals. Mercury affects the nervous and renal systems inducing numbness of the lips and members. The disease progression is reflected in the attack of the central nervous system, causing loss of sight, taste, hearing, speech and finally death (Ismaiel et al., 2013). Cadmium is classified as a human carcinogen and a teratogen agent impacting lungs, kidneys, liver and the reproductive organs (Boparai et al., 2011). Zinc is essential for life, but in high concentrations can be harmful for human health. Symptoms of intoxication by zinc include irritability, muscular stiffness, loss of appetite and nausea (Lalhruaitluanga et al., 2011).

Bamboos are a group of woody perennial plants in the grass family *Poaceae*, subfamily *Bambusoideae* (Krzesinska et al., 2006). Most of the bamboo species grow in the tropical regions of Africa, Asia and Latin America. Despite bamboos have notable properties such as stretchiness, hardness, low-cost and fast growing rate, their principal use has been limited to commercial handcrafts and construction materials (Lugt et al., 2006). In the literature only exists a few studies about the characteristics and amount of biomass produced yearly by some bamboo species. Specifically, the *Bambusa* family species from Asia have shown high production of useful amounts of biomass (more than 83 ton/ha) (Shanmughavel et al., 2001). Therefore, selection of bamboo as raw material yields in their abundance and availability, making them attractive renewable sources of biomass.

The aim of the present study was to identify the adsorption capacity of the metal ions Cd(II), Hg(II) and Zn(II) on mesoporous AC, containing high amount of carbonyl and carboxylic acidic groups, produced from *Bambusa vulgaris striata*. By using series of batch experiments was possible to obtain the best adsorption conditions (as a result of the adsorbent dose, pH and contact time) of the metal ions on the AC. Besides, fitting the experimental results to empirical models allowed understanding the nature of the adsorption process of these ions on the adsorbent. Recently, the use of the *B. vulgaris striata* species as a chemical AC precursor for electrochemical capacitors has been described (González-García et al., 2013). However, and to the best of our knowledge, earlier literature has not reported alternative uses for this material in environmental actions, providing an alternative for its potential use.

2. Experimental

2.1. Adsorbent

AC physically produced from the bamboo specie *B. vulgaris striata* has been use as adsorbent in the present study. The activation agent was water steam (25 cm^3/min), particle size 0.25 mm, activation time 2 h and a temperature of 650 °C. These experimental conditions were selected in the basis of previous studies (Boehm, 1990; Toles et al., 1999; González and Pliego-Cuervo, 2013) which described that formation of surface oxygenated acidic groups (SOAG), mainly as carbonyl and carboxylic groups is promoted by water steam treatments at relative short activation times.

2.1.1. Physicochemical characteristics

Election of the AC for this work lies in its physicochemical characteristics: apparent density (0.32 g/mL), moisture (31.32%), point of zero charge (9.91), total SOAG content (1.25 meq/g) and adsorption capacity (502 mg of iodine/g of AC). This last feature is close to the minimum value of the AC available commercially. A recent manuscript presents a detailed description about the synthesis and micro-textural characteristics of a group of sixteen AC, including the present one (González and Pliego-Cuervo, 2013). All of them produced from the bamboo species *B. vulgaris striata* and *Guadua angustifolia*.

2.1.2. Textural properties

The textural characterization of the AC previously described was using a Surface Area and Porosity Analyzer ASAP2020 (Micromeritics). The specific surface area (S_{BET}) was calculated according to BET theory (Gregg and Sing, 1982) in the relative pressure range of 0.05–0.25 to avoid over or underestimate the S_{BET} value. The total pore volume was determinate at the relative pressure $p/p_0 = 0.99$. The conventional comparison α_s plots based on the N_2 adsorption for a non-porous carbon reference (*Carbonpack F*) also provides significant information. The analysis of the N_2 isotherm plots by this empirical technique allowed to calculate the external surface area (S_e) of porous carbons from the slope of the linear section of the isotherm with $\alpha_s > 1.5$ (Suárez-García et al., 2002). On the other hand, the micropore volume (V_{mi}) was obtained from the next relationship:

$$V_{mi} = w_{mi} c_f \quad (1)$$

where w_{mi} is the amount adsorbed of nitrogen (g/cm^3) estimated from the intersection of the line adjusted to the section of the isotherm where $1.0 < \alpha_s < 1.5$, c_f is a conversion factor between the volume of gas and liquid adsorbate. For N_2 at 77 K, $c_f = 0.0015468$ (Kruk et al., 1997). Finally, the Barrett, Joyner and Halenda (BJH) method yields the pore size distribution (PSD).

2.2. Batch mode adsorption studies

All the chemicals used in this study were of analytical reagent grade. Deionized double distilled water was used for the experimental procedure. Metallic ions, Cd(II), Hg(II) and Zn(II), were obtained in solution from their respective nitrates. Adsorption studies were carried out by batch method in static conditions at 25 °C during 48 h. The adsorbent was placed in contact with 100 mL of metal solutions (V) with initial concentration (C_0) of 10 mg/L. After time elapsed, the respective batch suspension was filtered. On this final suspension, the equilibrium concentration (C_e) for each metallic ion was measured according to the American Society Testing and Materials (ASTM) methods: 3500 Cd-D, 3500 Hg-D and 3500 Zn-F.

For the estimation of the adsorbent dose (*m*), AC doses of 0.2, 0.4, 0.6, 0.8 and 1.0 g were used. The effect of the pH was studied by adjusting the pH solution at 3, 5, 7, 9 and 11 with NaOH 0.1 N solution. An optimal AC dose was used in these experiments.

2.3. Adsorption kinetics

The experimental adsorption kinetic studies were done measuring the residual metallic ion concentration after 4, 8, 12, 16 20 and 24 h. Optimum dose of AC and pH solutions were used for these determinations. The initial concentration was set up