Journal of Hazardous Materials 167 (2009) 260–267

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

The role of surface chemistry and solution pH on the removal of Pb^{2+} and Cd^{2+} ions via effective adsorbents from low-cost biomass

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ARTICLE INFO

Article history:
Received 16 July 2008
Received in revised form
30 November 2008
Accepted 23 December 2008
Available online 31 December 2008

Keywords:
Activated carbon
Surface modification
Solution pH
FTIR
Heavy metals removal

ABSTRACT

A deep understanding of adsorption of Pb^{2+} and Cd^{2+} ions from their aqueous solutions on activated carbons and their HNO_3-oxidized forms has been attempted. These activated carbons were obtained from date pits using different activation methods. Adsorption isotherms of Pb^{2+} and Cd^{2+} ions were determined from solutions at pH 3 and 5.9. The results revealed that all obtained isotherms exhibited the model fitting according to Langmuir equation. The oxidized samples prone, slightly, to the high affinity isotherm type. The results revealed also that the investigated carbons removed appreciable amounts of lead and cadmium ions which increased by increasing pH of solutions from 3 to 5.9. The adsorption capacity of the investigated carbons also increased by HNO_3 acid surface treatment. The results were discussed in light of a possible chemical modification by nitric acid resulting in the creation of a large number of surface functional oxygen species. This interpretation was confirmed by FTIR investigation. The solution-pH and the surface chemistry of the carbons were found to play a decisive role in the uptake of these heavy metal ions from aqueous solutions rather than the carbon texture characteristics.

1. Introduction

Today, the removal of heavy metal contaminants is one of the most important environmental issues to be solved. In the last years, the importance of heavy metals pollution control has encouraged a major research effect to develop effective means to identify and remove these toxic pollutants from drinking water and wastewater. The presence of heavy metals in the environment is of major concern because of their threat to human life and the environment. The current regulatory trend is for heavy metal discharge limits approaching those of drinking water standards [1]. For effluents with high metal concentrations, chemical precipitation processes (e.g. hydroxide, sulphide, carbonate) are the oldest and most frequently used due to its low cost. However, many metal bearing wastes contain substances, such as complexing agents, that decrease the effectiveness of precipitation processes leading to relatively high metal concentrations in the effluent. Thus, additional treatment processes, down-line from the precipitation process, may be required to “polish” the effluent prior to discharge. These tertiary processes may be the primary metal removal process from waste streams having low concentrations of metal ions. Examples of such processes involving separation procedures are ion exchange, reverse osmosis cementation, electrochemical, membranes, solvent extraction and adsorption. Ion exchange and reverse osmosis, while effective in producing and effluent low in metal ions, have high operation, and maintenance costs are subject to fouling [2].

Treatment with activated carbon (AC) has been reported to be efficient for removal of organic and inorganic pollutants from aqueous solutions [3,4]. Its application, in filters for removal of heavy metals (e.g. Hg) proved a competitive process in removal of trace amounts [5,6]. Adsorption on PAC indicated that the process was highly efficient in removing several metal ions from wastewater with an efficiency exceeding 80% [7]. Since then the adsorption by AC has become an established water treatment method for the removal of heavy metals, and hence received considerable attention [1,2,8–18]. These studies covered the removal of several metals including, essentially, Pb^{2+}, Hg^{2+}, Ca^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}, Cr^{3+}, and many others such as rare earths and gold [19]. In particular, lead and cadmium occupy a prominent position as many investigators mentioned their treatment with activated carbons prepared from commercial products, agricultural wastes or from coal origin [1,2,5,9–11,14,16,18–20]. This is attributed to their specific toxicity effects, as there, with Hg^{2+}, has been classified as priority pollutants by the US Environmental Protection Agency (EPA) [2].

Agricultural waste products are considered as a convenient source for preparation of activated carbons because of their continual availability, low cost, and feasibility for deriving wide spectra of activity. The adsorption characteristics of activated carbons are generally governed by the source of raw material and the preparation procedures used during carbonization and activation. Another

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doi:10.1016/j.jhazmat.2008.12.118

important factor is the surface chemistry of the carbons, particularly in case of metal ions removal [21].

The objective of the present study was to investigate the efficiency of removing lead and cadmium ions from aqueous solutions using activated carbon derived from a novel agricultural by-product; namely date pits. Several factors affecting this process are considered which include the solution-pH, conditions of preparation, texture characteristics, and surface modification through the treatment with nitric acid.

2. Experimental

2.1. Adsorbents

A series of activated carbons, obtained by various activation procedures, have been investigated [22,23]. One group of carbons was prepared by impregnation with phosphoric acid (30, 50, 70 vol%) followed by carbonization at 300, 500, or 700 °C for 3 h, then thoroughly washed with distilled water and finally dried at 110 °C. These carbons are denoted by the letters CP followed by two digits; the first indicating heat-treatment temperature 3, 5, or 7 and the second indicating acid concentration; 3, 5 or 7 respectively. Thus, e.g. CP-55 means a carbon activated by H_3PO_4 of 50 vol% and heat treated at 500 °C. The second group of carbons were prepared by the traditional steam activation, via carbonization at 500 °C for 3 h, followed by gasification by steam/N_2 at 850 °C up to various burn-off values. These carbons are denoted by the letters CS followed by the degree of burn-off (12–73%). Two more carbon samples were obtained by the one-step steam pyrolysis, at 600 or 700 °C, developed recently by Gergova et al. [24,25]. These are denoted by S-600 and S-700, respectively. A last carbon sample was prepared by impregnating the raw material with KOH followed by carbonization at 700 °C for 3 h, as recently suggested by Laine and Calafat [26]; this is denoted by K-700.

Portions of the activated carbons obtained under different activation conditions were subjected to oxidation by HNO_3 to introduce oxygen surface complexes [17]. The procedure was as follows: 50 cm^3 of concentrated nitric acid was added to 5 g of activated carbon, and the suspension was heated on a hot plate until dryness. The residue was washed with distilled water until no nitrates were present, and dried overnight at 110 °C.

2.2. Adsorbates

Pb(II) and Cd(II) metal ions were studied, the salts used were lead acetate for Pb(II) and cadmium nitrate for Cd(II). A stock solution of each metal salt was prepared (1000 mg/l) by dissolving the required amount of metal salt in its acidified double distilled water (in 1% HNO_3 or acetic acid solution) to prevent hydrolysis formation. All the chemicals or reagents used were of AR grade. The stock solutions of Pb(II) and Cd(II), were diluted with distilled water to obtain standard solutions.

2.3. Methodology of the equilibrium isotherms

Batch mode sorption studies of Pb(II) and Cd(II) from aqueous solutions were carried out to obtain the equilibrium isotherms at 25 °C. For determining the adsorption isotherms, 100 ml of metal solution of varying concentrations, ranged between 25 and 250 mg/l, was treated with 100 mg of adsorbent and agitated immediately for 24 h. This period of time was determined on the basis of our preliminary studies which was sufficient for the equilibrium uptake of these metal ions. Two series of experiments were carried out for each metal ions at two initial pH of 3 and 5.9. The pH values were adjusted by adding a controlled amount of 0.1 M nitric acid for Cd(II) or 0.1 M acetic acid for Pb(II) solutions, where the adsorption is significant but below the pH at which the metal hydroxide precipitation occurs. It is known that the metal hydroxide species begin to form at about pH 6 for lead and at about pH 8 for cadmium, for this reason the chosen-pHs here were below these limits. After equilibrium period, the solution was filtered. The residual metal concentrations for each metal in their test solutions were measured by using a Perkin-Elmer model 2380 Atomic Absorption Spectrometer. The metal concentration retained in the sorbent phase q_e (mg/g) was calculated by using the equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of the metal ion in solution (mg/l), V is the solution volume (liters) and W is dry weight of the sorbent mass (g).

3. Results and discussion

3.1. General consideration

The adsorption capacities Q_o (mg/g) for all investigated adsorbents towards every metal ions were calculated using the following the linear portion of the Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{1}{Q_o} C_e \quad (2)$$

where C_e is the equilibrium metal ion concentration (mg/l or ppm), q_e the amount of lead or cadmium ions adsorbed at equilibrium (mg/g) and Q_o (mg/g) and b (l/mg) are Langmuir constants related to adsorption capacity and energy of adsorption, respectively.

An interesting relationship is also plotted to demonstrate the removal capacity (%R) for the various prepared carbons as function of initial metal ions, Pb^{2+} or Cd^{2+}, concentrations. It is defined as the ratio of difference in metal concentration before and after adsorption ($C_0 - C_e$) to the initial concentration of metal ions.

$$\%R = \frac{C_0 - C_e}{C_0} \times 100 \quad (3)$$

Such relationship is useful to predict the performance or the efficiency of each carbon in treatment of wastewaters with variable loadings of these heavy metals, Pb^{2+} or Cd^{2+} ions.

3.2. Uptake of Pb^{2+} ions by activated carbons

Fig. 1 depicts the adsorption isotherms of Pb^{2+} by some investigated carbons in both forms oxidized and non-oxidized, in aqueous solutions at pH 3 and 5.9. All isotherms exhibit the L-type, Langmuir, as classified by Giles [27], despite a slight tendency to a high affinity isotherm, H-type, was shown by the oxidized carbons. It is clearly shown from Fig. 1 that the isotherms of the oxidized carbons attained the plateau or the monolayer coverage more faster than the non-oxidized forms. This finding indicates that the oxidized carbons are more efficient in adsorption of Pb^{2+} than the non-oxidized ones. Such behaviour could be ascribed to an effective formation of abundance of oxygen functional groups on the oxidized carbon surface. These functional groups could act as acidic active sites that increased progressively the sequestration of Pb^{2+} from aqueous solutions. The monolayer capacity, Q_o (mg/g), was evaluated from the linear Langmuir plots (Table 1). Since, in aqueous solution, the Pb^{2+} should be hydrated, a hydration number was suggested to be 4–7.5 [28]. The diameter of Pb^{2+}_{aq} then might be equal to 8.02 nm whereas the diameter of a water molecule is 0.276 nm. Therefore, with the exception of the ultra-micropores (less than 0.8 nm in diameter), all the surfaces areas corresponding to super-micropores, meso- and macropores would be effective and