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ScienceDirect
Bioresource Technology 98 (2007) 2787–2791
BIORESOURCE TECHNOLOGY

Removal characteristics of metal ions using degreased coffee beans: Adsorption equilibrium of cadmium(II)

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Received 23 January 2006; accepted 8 February 2006
Available online 2 April 2007

Abstract

The feasibility of using coffee beans after being dripped and degreased (DCB) as an adsorbent for base metals such as copper(II), zinc(II), lead(II), iron(III) and cadmium(II) were examined. The compositions of the DCB were characterized by Fourier transform infrared spectroscopy, scanning electronic micrograph and fluorescent X-ray. It was found that DCB contain sulfur and calcium from the analysis using fluorescent X-ray. The plant cell wall in DCB has the porous structure from the scanning electron microscopy (SEM) analysis, and the specific surface area was determined to be 1.2 m^2/g using the specific surface area analyzer. Batch adsorption experiments on DCB were carried out at various pHs in order to elucidate the selectivity of metal ions. All metals were adsorbed at low pH region (3.0–5.0). Of particular interest was the adsorption characteristics of cadmium(II) on DCB. The adsorption isotherm for cadmium(II) at pH 8 fitted with a Langmuir equation to yield an adsorption equilibrium constant of 55.2 mmol dm^{-3} and an adsorption capacity of 5.98×10^{-2} mmol g^{-1}. The desorption of cadmium(II) was easily achieved over 90% by a single batchwise treatment with an aqueous solution of hydrochloric acid or nitric acid at more than 0.01 mol dm^{-3}. These results suggested that DCB behaves as a cation exchanger.

Keywords: Degreased coffee beans; Heavy metals; Cadmium(II); Adsorption; Desorption

1. Introduction

Removal technology of heavy metal ions by biosorption is appeared more promising technology than the conventional methods for removing metal ions in the viewpoint of environmental protection. Considerable attention has been paid on the recovery and removal of heavy metal ions from aqueous systems by using various biosubstances or natural products (Volesky, 1990; Nakajima, 2002; Stephen and Fergus, 1987). The authors have studied the adsorption of heavy metals from aqueous systems by using biosorbents such as chitosan and activated carbon prepared from bamboo (Baba et al., 1999, 2002; Ohe et al., 2003). In recent years, the concentrations of cadmium and lead as a drinking water quality standard were established to be less than 0.01 mg dm^{-3} in Japan. The standard of lead(II) was reduced from 0.05 mg dm^{-3} to 0.01 mg dm^{-3} by The Ministry of Environment Japan in 1993. The various methods have been explored in order to achieve this standard (Takeshita et al., 2003; Vazquez et al., 2002; Trivette et al., 2001). In particular, removal of trace amounts of heavy metals can be achieved by means of selective adsorption processes. This technique, which has been extensively utilized in the water treatment, is one of the most promising process for the removal of heavy metals from drinking water, underground water and waste water (Xuan et al., 2002; Babic et al., 2002; Johanna et al., 2002).

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doi:10.1016/j.biortech.2006.02.040

Although a portion of coffee residues is used as compost and animal feed, most of them are burned as solid wastes. (Christopher et al., 2000). We are now focussing our attention on the possibilities of the discarded coffee beans as a new adsorbent. Degreased coffee beans (DCB) were prepared by dripping and degreasing coffee beans in water and ethanol as a heavy metal adsorbents. The adsorption of cadmium(II), copper(II), zinc(II), iron(III) and lead(II) on DCB at different pHs were studied. Furthermore, the adsorption isotherm of cadmium(II) on DCB, and desorption of adsorbed cadmium(II) were examined at 303 K.

2. Experimental

2.1. Preparation of degreased coffee beans (DCB) as an adsorbent

Commercial coffee beans purchased from Key Coffee Co., Tokyo, Japan were purified to remove the undesired contaminant prior to use them as adsorbents. The milled coffee beans were washed five times by boiling water (0.1 dm^3), followed by soxhlet extraction by ethanol for an exhaustive extraction of oily substance from coffee beans, for which the solid was packed into a filter paper thimble and kept in a soxhlet extractor for 24 h. After extraction, it was dried in vacuo and sieved to obtain fine grains of 500–840 μm in size.

2.2. Adsorption procedure

The metal ion concentration was prepared to approximately 5.0×10^{-2}–18.0×10^{-1} mmol dm^{-3} by using each standard sample solution for each. All experiments on the adsorption equilibria were performed by a batchwise method at 303 K (Dong et al., 2003; Pagnanelli et al., 2003; Mathialagan and Viraraghavan, 2003). The pH was adjusted either by adding a small amount of nitric acid or 25% ammonia solution. Equilibrium adsorption experiments were performed by shaking 0.1 g of DCB and 10 cm^3 of the metal ion solution in the sample tube in a shaker (120 strokes per minute) at 303 K for 24 h. After equilibrium was reached, DCB was separated by filtration, and then the equilibrium concentration of the metal ions were determined by a Hitachi Model Z-8000 Tokyo, Japan polarized zeeman atomic adsorption spectrophotometer. The amount of adsorbed metal ions were calculated from the concentration change in the aqueous solution before and after equilibrium by taking account of the volume of solution and the weight of the adsorbent. Here, the distribution ratio ($=D$ [$cm^3\ g^{-1}$]) was defined as the ratio of the amount of metal ion adsorbed (mol g^{-1}) to the equilibrium metal concentration (mol cm^{-3}). The equilibrium pH was measured by using a TOA electronics, Tokyo, Japan, Model HM-30G pH meter. All results shown here in agreed the mean value obtained from three times repeated adsorption experiment that remained within variation range of 3%.

3. Results and discussion

3.1. Characterization of DCB

The chemical component of DCB were evaluated mainly by Fourier transform infrared spectrophotometer (SHIMADZU, FT-IR-8200, Tokyo, Japan). For comparison, the coffee beans after and before degreasing process (CB). In the IR spectra, the characteristic peaks appeared at approximately 1745 cm^{-1} due to the resulting carboxyl linkage derived from xanthine derivatives such as caffeine. Since its absorption was not seen in DCB, it is likely that coffee ingredients, such as caffeine, were removed by degreasing process. The spectrum of DCB showed a broad band at 1070–1030 cm^{-1} assigned to ν(S=O). In order to check existence of sulfur, DCB was analyzed using fluorescent X-ray, JEOL, JSX-3201, Tokyo, Japan. The analysis supported the existence of sulfur atom in DCB. The other atom observed by fluorescent X-ray was found to be calcium from the ash content (Martin et al., 1998). The adsorption experiment of hydrochloric acid was carried out in order to determine the nitrogen content. The concentration of hydrochloric acid was changed over the concentration range of 1.0×10^{-3}–1.0×10^{-1} mol dm^{-3}. The equilibrium concentration of the hydrochloric acid was measured by the neutralization titration by a potentiometer, Kyoto Electronics, AT-200N, Kyoto, Japan. It was found that hydrochloric acid was not adsorbed on DCB, suggesting the absence of amine functional groups in DCB. However, DCB was found to contain sulfur and calcium on the cellulose skeleton.

The SEM of DCB is shown in Fig. 1. The micropores in DCB were formed during the soxhlet extraction using

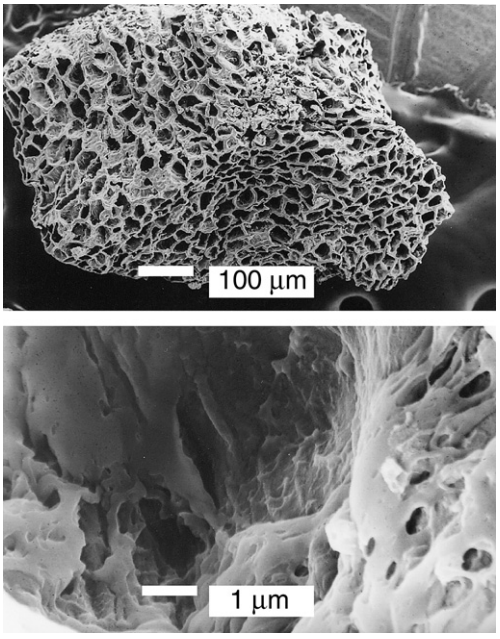

Fig. 1. Scanning electron micrograph of DCB. Accelerating voltage: 5 kV, magnification: ×50 and 5000.