Removal of heavy metal ions from solutions by coniferous barks

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Summary The abilities of 15 coniferous barks for removing toxic heavy metal ions were investigated. The barks considerably varied in the adsorption ability to each metal ion. Of the barks tested, high adsorption ability for heavy metal ions was found in *Picea abies* (Norway spruce). Equilibrium experiments using *P. jezoensis* (Yezo spruce) bark showed that the adsorption of Cd$^{2+}$ was greatly affected by the pH of solution and the initial Cd$^{2+}$ concentration in solution. The adsorption of Cd$^{2+}$ by *P. jezoensis* bark followed Freundlich isotherm in the concentration range 10-330 mg Cd$^{2+}$/L. The continuous column experiments using *P. jezoensis* bark indicated that the packing had retained 10.1-14.2 mg Cd$^{2+}$/g adsorbent until the column broke through.

Introduction

In recent years, the removal of toxic heavy metal ions from waste water has been desired for prevention of possible hazards in our environment. Heavy metal ions can be removed from water by several methods, including basic precipitation, ion exchange, and so on. Basic precipitation is currently the most inexpensive method, but it introduces undesirable waste sludge in large quantities. Ion exchange is efficient in removing heavy metal ions from solution, but synthetic ion exchange resins are still expensive for this object.

It has been reported that certain lignocellulosic wastes such as nut wastes (Friedman *et al.* 1972; Waiss *et al.* 1973; Randall *et al.* 1975, 1978; Henderson *et al.* 1977), tree leaves (Kimura *et al.* 1986; Aoyama *et al.* 1991; Watanabe and Kishi 1991; Saito *et al.* 1992), barks (Masri *et al.* 1974; Randall *et al.* 1974; Henderson *et al.* 1977; Fujii *et al.* 1988; Aoyama *et al.* 1993) and barley straw (Larsen and Schierup 1981) effectively adsorb heavy metal ions from aqueous solutions, indicating the potential utility of these materials to remove heavy metal ions from industrial effluents. Among these, barks are especially promising because of being available in large quantities from local sawmills.

In this paper, the adsorption abilities of coniferous barks for common toxic heavy metal ions were examined. The factors affecting removal of heavy metal ion from solution are also investigated using *Picea jezoensis* (Yezo spruce) bark.

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Materials and methods

Materials

The barks of *Abies sachalinensis* (Japanese fir) and *Picea glehnii* (Saghalin spruce) were collected from Asahikawa district forest. The other bark samples were obtained from the experimental forest of Hokkaido Forestry Research Institute, Bibai. Each fresh bark was air-dried and ground in a Wiley mill to pass through a 1 mm screen. A fraction of the ground bark (42–80 mesh) was washed thoroughly with deionized water, dried overnight at 45 °C and used for adsorption experiments. Activated carbons were obtained from Wako Pure Chemical Industries, Ltd.

Extraction

Ground *P. jezoensis* bark (42–80 mesh) was extracted with cold-water, hot-water, 1% NaOH aqueous solution and ethanol-benzene (1 : 2, v/v) mixture, separately, using the Japanese Industrial Standard methods (JIS P8004-1959, JIS P8005-1959, JIS P8006-1959, JIS P8010-1961). The extracted residues were subsequently air-dried.

Equilibrium experiments

The abilities of coniferous barks to adsorb heavy metal ions were determined in batchwise conditions using 1 mM solutions of Cd(NO₃)₂, Cu(NO₃)₂ and Zn(NO₃)₂, separately. The pH of each solution was adjusted to the desired value with dilute HNO₃ or dilute NaOH solution. The test solution (100 mL) was added to the adsorbent (0.5 g), and the suspension was shaken at 30 °C for 24 h. The adsorbent was then filtered off and residual heavy metal ions in the filtrate were determined by the atomic absorption spectrometry with a Hitachi Z-6000 instrument. The amount of heavy metal ion captured by the adsorbent was calculated from the difference between the initial and final concentrations of the metal ion in solution. Experiments were duplicated and the results averaged.

Column experiments

Ground bark of *P. jezoensis* was soaked into water for 1 h and the resulting slurry poured into a glass column (15 × 250 mm) fitted with a porous plug and a stopcock. After the adsorbent had settled, a wad of glass wool was placed on the top of the bed, and the liquid level run down to the top of the bed. The bed was fed with 1000 mL of 1 mM Cd(NO₃)₂ solution which was adjusted to pH 5 with dilute nitric acid. Flow of the test solution through the column was controlled by the stopcock at the bottom of the column. The amount of Cd²⁺ in the column effluent was determined in the same manner described for the determination of heavy metal ions in the equilibrium experiments.

Results and discussion

The abilities of coniferous barks to adsorb heavy metal ions were determined in batchwise conditions using 1 mM solutions of Cd(NO₃)₂, Cu(NO₃)₂ and Zn(NO₃)₂, separately. The bark adsorbents were equilibrated by shaking with the solutions at 30 °C for 24 h, and the decrease in the concentration of metal ion was determined by the flame atomic absorption spectrometry. For comparison, commercial activated carbons (powder and granular) were also examined.

The amounts of heavy metal ions adsorbed by coniferous barks are summarized in Table 1. It is apparent that barks considerably varied in the adsorption