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ORIGINAL ARTICLE

Efficacy of physically pretreated *Mangifera indica* biomass for Cu^{2+} and Zn^{2+} sequestration

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Abstract To develop a strategy for the eradication of Cu^{2+} and Zn^{2+} from contaminated waters, the waste biomass of *Mangifera indica* was pretreated physically (autoclaved, boiled and heated) for assessing the uptake capacity of native and pretreated biomass for Cu^{2+} and Zn^{2+} biosorption on batch scale, concentrating on pH, pretreatment, biosorbent dose, metal concentration, contact time and temperature as operational parameters. To measure the goodness-of-fit error functions as sum of square error (SSE), chi-square (χ^2) and residual root mean square error (RMSE) were used. Best results were obtained at pH 5 (80.65 mg/g) and 6 (94.25 mg/g) for Cu^{2+} and Zn^{2+}, respectively, with autoclaved leaves. Sorption capacity of biomasses was found to be decreased with increase in biosorbent dose and temperature while it increased with increase in metal ion concentration and with time. Freundlich isotherm was found favorable to describe sorption mechanism, whereas pseudo-second-order kinetic model was best employed to describe sorption rate.

1. Introduction

A very serious problem being faced by the public these days is the anthropogenic emission of dissolved metals into the aquatic environment. These metals are non-biodegradable and have the potential to be bioaccumulated by a range of organisms causing permanent negative ecological effects on both plants and animals (Al-Qodah, 2006). Techniques presently in vogue for the removal of heavy metals from contaminated waters include chemical precipitation, chemical oxidation or reduction, ion exchange, filtration, reverse osmosis and evaporation recovery (Hanif et al., 2007). These processes may be ineffective or highly expensive especially when the metals in solution are in the range of 1–100 mg/L (Volesky, 1997; Kratochvil and Volesky, 1998). With increasing environmental attentiveness, there is a growing trend of searching alternative technologies. Hence, biosorption emerged as the best alternative being environment-friendly and cost effective.

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Biosorption can be defined as the ability of the biological material to accumulate heavy metals through metabolically mediated or physiochemical pathways of uptake (Nadeem et al., 2008). Many chemical reactions are involved in the process of biosorption like ion exchange, complexation, chelation and adsorption by physical forces. Furthermore, numerous chemically active groups are responsible for biosorption viz carboxyl, hydroxyl, carbonyl, amine, imine, amide, sulfhydryl, thioether and sulfonate (Zafar et al., 2007). The use of various parts of plants as sorbents to sorb heavy metals from aqueous streams is reported in the literature and these include sunflower stalk (Sun and Shi, 1998), wheat bran (Dupond and Guillon, 2003), horseradish tree (Bhatti et al., 2007) and *Cicer arietinum* (Nadeem et al., 2009). Moreover, uptake capacity of biomass can be manipulated by physico-chemical modification of biomass. For example, mitigation of Cd^{2+} by *Sargassum muticum* biomass after physical treatment was considerably high (Lodeiro et al., 2004).

Copper is widely used in electroplating industries and its excess is usually known to deposit in brain, skin, liver, pancreas and myocardium (Nuhoglu, 2002) becoming dangerous to health. Industrial effluents from electroplating, photographic paper, fertilizers, pigments and mining industries contain Zn^{2+}, which causes respiratory incapacitation (increased breathing rate, volume and frequency of ventilation), coughing and decreased oxygen uptake efficiency. Zinc (Zn^{2+}) also damages aquatic life affecting gill membranes (Bhatti et al., 2007). Permissible limits of Cu^{2+} (Sheng-lian et al., 2006) and Zn^{2+} (World Health Organization, 1996; Conrad and Hens, 2007) in drinking water are 1.3 and 3 mg/L, respectively.

In the present study, different plant parts such as waste leaves, kernels, bark and seeds of the mango tree were used to investigate the potential of physically pretreated *Mangifera indica* biomass for the removal of Cu^{2+} and Zn^{2+}. Although mango is an evergreen tree, large quantities of old leaves are shed during vegetative flushing. The fallen leaves become mulch under the tree. The leaves contain a good amount of mangiferin (xanthone), benzophenones and glucoside. The bark possesses 16–20% tannin and gallo tannins. It yields a yellow dye. Kernels contain tannins, minerals and crude fiber and the seeds contain hypoxanthine and mangiferin. The phenolic, carboxylic and hydroxyl groups of these organic compounds may be basically responsible for sequestration of metal ions (Barreto et al., 2008).

2. Materials and methods

2.1. Reagents

All the chemical reagents used in the present investigation were of analytical grade which were purchased from Fluka Chemicals. The chemicals used in this study include HCl, NaOH, HNO_3, $ZnSO_4{\cdot}7H_2O$, $CuNO_3{\cdot}5H_2O$, for stock solution (1000 mg/L) of each metal ion, 4.42 g of $ZnSO_4{\cdot}7H_2O$ and 3.392 g of $CuNO_3{\cdot}5H_2O$ were dissolved in distilled water in separate beakers and quantitatively diluted to 1000 mL using distilled water and the volume was measured by a volumetric flask. Glassware was washed with 10% (v/v) HNO_3 and then rinsed with distilled water.

2.2. Biomass preparation

Waste leaves, kernels, bark and seeds of *M. indica* were collected from the Botanical Garden of the University of Agriculture, Faisalabad, Pakistan. Samples were extensively washed with distilled water to remove particulate material from their surface and then oven-dried at 60 °C for 72 h. Dried biomass was cut and ground using a food processor (Moulinex, France) and then sieved through a sieve (OCT-Digital 4527-01). The sieved material was stored in air-tight plastic containers for further experimentation.

2.3. Pretreatments of biomass

First, the biomass was dried at 60 °C for 12 h in an incubator. Thirty grams of each biomass sample were treated in three different ways (boiling, autoclaving and heating). In boiling, biomass was taken in 500 mL of distilled water and then boiled for 15 min. Biomass was autoclaved for 15 min at 121 °C and 15 psi. In heating, biomass was heated with Bunsen burner in a beaker at low heat for 10–15 min. Then the biomass was dried fully and sieved again.

2.4. Determination of the Cu^{2+} and Zn^{2+} contents in the solutions

Perkin-Elmer A Analyst 300 atomic absorption spectrophotometer equipped with an air-acetylene burner and controlled by Intel personal computer was used to determine concentrations of Cu^{2+} and Zn^{2+} in aqueous solutions before and after the equilibrium has established. The hollow cathode lamp was operated at analytical wavelength of 324.5 nm for Cu^{2+} and 213.9 nm for Zn^{2+} and slit as 0.2 nm for Zn^{2+} and 0.7 for Cu^{2+}.

2.5. Batch biosorption studies

In all experiments, fixed volume (100 mL) of Cu^{2+} and Zn^{2+} was thoroughly mixed with biosorbent of 0.25 mm size at 120 rpm and 30 °C for 24 h. Different conditions of pH (1–5) for Cu^{2+} and pH (1–6) for Zn^{2+}, biosorbent dose (0.1, 0.2, 0.3, 0.4 and 0.5 g), initial metal concentration (50, 100, 200, 400 and 800 mg/L), contact time (15, 30, 60, 120, 180, 240 and 360 min) and temperature (30, 40, 50, 60 and 70 °C) were evaluated during the study. The pH of the medium was adjusted with 0.1 N solutions of HCl and NaOH. The flasks were placed on a rotating shaker (PA 250/25, H) with constant shaking. The flasks were removed from the shaker after specified time and the solutions were filtered through a filter paper (Whatman No. 40, ashless). Preliminary experiments (pH and biosorbent dose) were performed using an initial concentration of 100 mg/L of each of Cu^{2+} and Zn^{2+} for screening studies.

2.6. Metal uptake

The Cu^{2+} and Zn^{2+} uptakes were calculated by the simple concentration difference method using the mass balance equation:

$$q = \frac{V(C_i - C_e)}{M}$$