Removal and recovery of heavy metals from aqueous solution using *Ulmus carpinifolia* and *Fraxinus excelsior* tree leaves

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Abstract

Ulmus carpinifolia and *Fraxinus excelsior* tree leaves, which are in great supply in Iran, were evaluated for removal of Pb(II), Cd(II) and Cu(II) from aqueous solution. Maximum biosorption capacities for *U. carpinifolia* and *F. excelsior* were measured as 201.1, 172.0 mg/g for Pb(II), 80.0, 67.2 mg/g for Cd(II) and 69.5, 33.1 mg/g for Cu(II), respectively. For both sorbents the most effective pH range was found to be 2–5 for Pb(II), 3–5 for Cd(II) and 4–5 for Cu(II). Metal ion biosorption increased as the ratio of metal solution to the biomass quantity decreased. Conversely, biosorption/g biosorbent decreased as the quantity of biomass increased. The biosorption of metal ions increased as the initial metal concentration increased. Biosorption capacities of metal ions were in the following order: Pb(II) > Cd(II) > Cu(II). The equilibrium data for Pb(II) and Cu(II) best fit the Langmuir adsorption isotherm model. Kinetic studies showed that the biosorption rates could be described by a second-order expression. Both the sorbents could be regenerated using 0.2 M HCl during repeated biosorption–desorption cycles with no loss in the efficiency of the Cu(II) removal observed. Biosorption of Pb(II), Cd(II) and Cu(II) was investigated in the presence of Na, K, Mg and Ca ions. The results from these studies show a novel way of using *U. carpinifolia* and *F. excelsior* tree leaves to remove Pb(II), Cd(II) and Cu(II) from metal-polluted waters.
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1. Introduction

Heavy metals are not biodegradable and tend to accumulate in biological systems, posing health hazards if their concentrations exceed allowable limits [1]. Industries, such as metal plating, mining, painting, car manufacturing, smelters and metal refineries are major sources of heavy metal pollution [2–4]. Traditional methods such as ion-exchange, chemical precipitation, ultrafiltration and chemical deposition do not seem to be economically feasible because of relative high costs, particularly when used for the removal of heavy metals at low concentrations (<100 mg/l) [5]. Furthermore, most of these methods generate toxic sludge [6], the disposal of which is an additional burden on the techno-economic feasibility of treatment procedures. Therefore, there is a need to find alternative methods which are environmentally friendly, effective and economic. Biological methods to adsorb metal ions may provide the answer. Successful metal biosorption has been reported using a variety of biological materials including micro-algae and seaweed, bacteria, fungi and crop residues [7–9], pine bark and needles [10], modified chitosan [11], petiolar felt-sheath of palm [12], papaya wood [13], loofa sponge and plant-immobilized biomass [14,15].

The objective of this study was to investigate the potential of *Ulmus carpinifolia* and *Fraxinus excelsior* tree leaves to treat wastewaters contaminated with heavy metals. The *U. carpinifolia* and *F. excelsior* tree leaves are in great supply, inexpensive and easily found around Arak, a city in the centre of Iran. There are no special commercial uses for them and because they are not a food source for livestock there is no risk of livestock poisoning. These attributes provided the incentive for investigating these two tree leaves as potential novel natural biosorbents.

2. Materials and methods

2.1. Biosorbent materials

The *U. carpinifolia* and *F. excelsior* tree leaves were gathered from twigs into clean plastic bags, washed with ion-free distilled

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water and laid flat on a clean table to dry. The dried leaves were ground and sieved to 40–50 mesh, then stored in plastic bags ready for use.

2.2. Metal ion solutions

The stock solutions of Pb(II), Cd(II) and Cu(II) were prepared by dissolving appropriate quantities of $Pb(NO_3)_2$, $Cd(NO_3)_2$ and $Cu(NO_3)_2$ salts in 5% HNO_3. All the chemicals used were AR grade and ion-free distilled water was used throughout. The solutions were adjusted to pH 5, or as otherwise stated, with 0.1 M HCl or 0.1 M NaOH. Fresh dilutions were made for each study.

2.3. Metal analysis

The concentration of each metal ion remaining in solution after biosorption was determined using a flame atomic absorption spectrophotometer (PerkinElmer 2380). Unless indicated, the data shown are the mean of three separate experiments. Two different controls were also performed. The control without sorbents showed whether metal ions were adsorbed onto the walls of the flask. The control without metal ions (ion-free distilled water instead of metal solution) was used to estimate any leaching from sorbents during the study period. All experiments were performed in triplicate.

Analysis of variance (ANOVA) and consequently Duncan's multiple range test ($p = 0.05$) [16] on the data were carried out to find out whether there are statistically significant differences between observed values and the expected ones.

2.4. FT-IR studies

FT-IR spectra of raw (before metal treatment) and treated (after metal biosorption) samples of solid tree leaves were obtained using a FT-IR spectrophotometer (Shimadzu IR Prestige, Japan). The mixture of dry tree leaves (about 0.1 g) with KBr (0.5 g) was grounded into fine particles and pressed into a tablet from. The FT-IR spectrum was then recorded.

2.5. Shake flask biosorption

Batch biosorption experiments were carried out in 250 ml Erlenmeyer flasks by transferring 100 ml of 50, 25 and 15.5 mg/l Pb(II), Cd(II) and Cu(II) solutions, respectively (to maintain similar molar concentrations for all the three metal ions) and 1 g (10 g/l) 40–50 mesh tree leaves. The mixtures were shaken on an orbital shaker at 200 rpm in tightly stoppered flasks at $25 \pm 5\,^{\circ}C$ for 60 min. The suspensions were filtered through Whatman filter paper (No. 42) and the concentration of metal ions in the filtrate was measured, from which the amount of metal ion biosorbed per unit mass of biosorbent (mg metal/g dry biosorbent) was determined. The time dependency of batch experiments was examined by varying the contact time of sorbents from 5 to 150 min. The influence of pH on metal ion biosorption was determined by equilibrating the suspensions in solutions of differing pH ranging from 1 to 6. For the adsorption

isotherm studies, the initial metal ion concentration was varied over the range of 5–5000 mg/l. The concentration of *Ulmus* and *Fraxinus* tree leaves was varied between 1 and 100 g/l to determine the ratio required for optimum biosorption. For the determination of any interference caused by the presence of other cations, monovalent Na and K, and divalent Mg and Ca (as the nitrate) were added to the Pb(II), Cd (II) and Cu(II) solutions ranging from 0 to 0.1 M.

2.6. Desorption and regeneration

The metal loaded *Ulmus* and *Fraxinus* leaves (1 g) were desorbed with 100 ml of 0.2 M HCl, which has been reported to be an efficient metal desorbent [17–19], for 60 min. The desorbed tree leaves were washed and the regenerated sorbents were used in three biosorption–desorption cycles to determine reusability of the leaves.

3. Results and discussion

3.1. Metal ion biosorption mechanism by plants

Various metal-binding mechanisms are thought to be involved in the biosorption process including ion exchange, surface adsorption, chemisorption and adsorption–complexation [20]. Plant cell walls, mainly consisting of polysaccharides, proteins and lipids, offer many functional groups such as carboxyl, carbonyl, hydroxyl and amino which can be involved in metal binding [21].

The FT-IR spectra before and after adsorption of metal ions by *Ulmus* and *Fraxinus* tree leaves in the range of 400–4000 cm^{-1} were taken to obtain information on the nature of possible cell–metal ions interactions and presented in Fig. 1. Since a high similarity between *Ulmus* and *Fraxinus* FT-IR spectra was observed and in order to save space, this study limits the demonstration to the *Fraxinus* spectrum.

The FT-IR spectroscopic analysis of metal-loaded biosorbent of *Fraxinus* tree leaf indicated intensity decrease and shifted strong asymmetrical stretching bands at 3321 (indicative of –OH and –NH groups) and 2927 cm^{-1} (indicative of C–H groups) when compared with that of unloaded biomass which showed the same absorption at 3338 and 2920 cm^{-1}, respectively. The similar band shift was observed for one of the double band of the carboxylate ion (at 1636 and 1431 cm^{-1}) moving from 1431 to 1390 cm^{-1}. These observations indicated the involvement of these functional groups in the biosorption process.

The order of affinity in metal ion removal by both sorbents may be explained by the Hard Soft Acid Base theory of Pearson (HSAB) [22]. This theory classifies different species as acids or bases arranged in a specific order of softness assuming that soft bases react preferentially with soft acids. The supposed active sites on the adsorbents, namely carboxylic and hydroxylic groups are soft bases that will react preferentially with soft acids (the metal ions in the solution). The softness order as acids of the investigated heavy metals is Pb(II) (3.58) > Cd(II) (3.04) > Cu(II) (2.89), in agreement with the affinity series observed from experimental tests [23].