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Kinetic and equilibrium studies of biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (*Amanita rubescens*) biomass

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ABSTRACT

The biosorption characteristics of Pb(II) and Cd(II) ions from aqueous solution using the macrofungus (*Amanita rubescens*) biomass were investigated as a function of pH, biomass dosage, contact time, and temperature. Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models were applied to describe the biosorption isotherm of the metal ions by *A. rubescens* biomass. Langmuir model fitted the equilibrium data better than the Freundlich isotherm. The maximum biosorption capacity of *A. rubescens* for Pb(II) and Cd(II) was found to be 38.4 and 27.3 mg/g, respectively, at optimum conditions of pH 5.0, contact time of 30 min, biomass dosage of 4 g/L, and temperature of 20 °C. The metal ions were desorbed from *A. rubescens* using both 1 M HCl and 1 M HNO_3. The recovery for both metal ions was found to be higher than 90%. The high stability of *A. rubescens* permitted ten times of adsorption–elution process along the studies without a decrease about 10% in recovery of both metal ions. The mean free energy values evaluated from the D–R model indicated that the biosorption of Pb(II) and Cd(II) onto *A. rubescens* biomass was taken place by chemical ion-exchange. The calculated thermodynamic parameters, ΔG°, ΔH° and ΔS° showed that the biosorption of Pb(II) and Cd(II) ions onto *A. rubescens* biomass was feasible, spontaneous and exothermic under examined conditions. Experimental data were also tested in terms of biosorption kinetics using pseudo-first-order and pseudo-second-order kinetic models. The results showed that the biosorption processes of both Pb(II) and Cd(II) followed well pseudo-second-order kinetics. Based on all results, It can be also concluded that it can be evaluated as an alternative biosorbent to treatment wastewater containing Pb(II) and Cd(II) ions, since *A. rubescens* is low-cost biomass and has a considerable high biosorption capacity.

1. Introduction

The presence of heavy metals contaminated in aqueous streams, arising from the discharge of untreated metal containing effluent into water bodies. They are non-degradable in the environment and can be harmful to a variety of living species. Besides the toxic and harmful effects to organisms living in water, heavy metals also accumulate throughout the food chain and may affect human beings [1]. For that reason, the removal of these metals from waters and wastewaters is important in terms of protection of public health and environment [2].

Heavy metals such as cadmium (Cd) and lead (Pb) often present in industrial wastewaters, are hazardous to the aquatic ecosystem and pose possible human health risk. High levels of Pb(II) can be traced to industrial discharges from variety of sources, such as batteries, paints, pigments and ammunition, petrol, cables, alloys and steels, plastics, the glass industry. The lead contamination is also due to effluents of vehicular traffic and the mixing of roadside runoffs. The presence of Pb(II) in drinkable water is known to cause various types of serious health problems [3]. Although the inorganic form of lead is a general metabolic poison and enzyme inhibitor, organic forms are even more poisonous [4,5]. On the other hand, cadmium is also a dangerous pollutant originating from metal plating, metallurgical alloying, mining, ceramics and other industrial operations [6]. Cadmium toxicity may be observed by a variety of syndromes and effects including renal dysfunction, hypertension, hepatic injury, lung damage and teratogenic effects [7].

The most widely used methods for removing heavy metals from wastewaters include ion-exchange, chemical precipitation, reverse osmosis, evaporation, membrane filtration, adsorption biological treatment [8]. Most of these methods suffer from some drawbacks, such as high capital and operational cost or the disposal of the residual metal sludge, and are not suitable for small-scale industries [9]. Biosorption plays an important role in the elimination of metal ions from aqueous solutions in water pollution control [10,11]. The main advantages of this technique are the reusability of biomaterial, low

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operating cost, improved selectivity for specific metals of interest, removal of heavy metals from effluent irrespective of toxicity, short operation time, and no production of secondary compounds which might be toxic [12]. Various biomasses have been used for removal of Pb(II) and Cd(II) ions from aqueous solution [13–16].

Macrofungi are edible fungi of commercial importance and their cultivation has emerged as a promising agro-based land-independent enterprise. More than 2000 species of macrofungi exist in nature but only about 22 species are extensively cultivated for commercial purposes [17]. The consumption of wild edible macrofungi is increasing, even in the developed world, due to a good content of proteins as well as a higher content of trace minerals [18]. Fungal biomass is better suitable for the removal of metals from wastewater than biomass because of their great tolerance towards heavy metals and other adverse conditions such as low pH, high cell wall binding capacity and high intracellular metal uptake capacity [19]. Several fungal biosorbents, *Penicillium* [20], *Rhizopus arrhizus* [21], *Rhizopus oryzae and Aspergillus oryzae* [22], and *Aspergillus niger* and *Mucor rouxii* [23,24] were studied as a potential biosorbent in heavy metals removal from aqueous solution. As far as the authors are aware, there is no investigation reported in the literature on the biosorption of Pb(II) and Cd(II) using the macrofungus, *A. rubescens*.

The objective of the present work is to investigate the biosorption potential of *A. rubescens* biomass in the removal of Pb(II) and Cd(II) ions from aqueous solution. Optimum biosorption conditions were determined as a function of pH, biomass dosage, contact time, and temperature. The Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models were used to describe equilibrium isotherms. Biosorption mechanisms of Pb(II) and Cd(II) ions onto *A. rubescens* biomass were also evaluated in terms of thermodynamics and kinetics.

2. Experimental procedures

2.1. Biomass preparation

The macrofungus, *A. rubescens* was collected from the East Black Sea region of Turkey. Samples were washed with deionized water and dried in an oven at 105 °C for 48 h. The dried biomass was ground and sieved through different sizes and 200–300 μm fraction. Dried samples were homogenized using an agate homogenizer and stored in pre-cleaned polyethylene bottles until biosorption experiments.

2.2. Reagents and equipments

All chemicals used in this work, were of analytical reagent grade and were used without further purification. Double deionized water (Milli-Q Millipore 18.2 MΩ cm^{-1} conductivity) was used for all dilutions. A pH meter (Sartorius pp-15, Germany) was employed for measuring pH values in the aqueous phase. A flame atomic absorption spectrometer (PerkinElmer AAnalyst 700, USA) with deuterium background corrector was used. All measurements were carried out in an air/acetylene flame. A 10 cm long slot-burner head, a lamp and an air-acetylene flame were used. The operating parameters for working elements were set as recommended by the manufacturer. Fourier Transform Infrared (FT-IR) spectra of dried unloaded biomass and Pb(II)-loaded biomass and Cd(II)-loaded biomass prepared as KBr discs were recorded at 400–4000 cm^{-1} wavenumber range using a FT-IR (JASCO-430, Japan) spectrometer.

2.3. Batch biosorption procedure

Biosorption experiments were optimized out at the desired pH value, contact time and biomass dosage level using the necessary biomass in a 250 mL stoppered conical flask containing 25 mL of test solution. A stock Pb(II) solution of 1000 mg/L was prepared was prepared by dissolving 1.8307 g $Pb(CH_3COOO)_2{\cdot}3H_2O$ in a 1000 mL of deionized water. A stock Cd(II) solution of 1000 mg/L was prepared was prepared by dissolving 2.3709 g $Cd(CH_3COOO)_2{\cdot}3H_2O$ in a 1000 mL of deionized water. The chemicals ($Cd(CH_3COOO)_2{\cdot}3H_2O$ and $Pb(CH_3COOO)_2{\cdot}3H_2O$) used for this study was analytical grades and they were supplied by Riedel-de Häen (Germany). Sodium phosphate buffer (0.1 mol/L) was prepared by adding an appropriate amount of phosphoric acid to sodium dihydrogen phosphate solution to result in a solution of pH 2. Ammonium acetate buffers (0.1 mol/L) were prepared by adding an appropriate amount of acetic acid to ammonium acetate solutions to result in solutions of pH 4–6. Ammonium chloride buffer solutions (0.1 mol/L) were prepared by adding an appropriate amount of ammonia to ammonium chloride solutions to result in solutions of pH 8.

Necessary amount of the biomass was then added and contents in the flask were shaken for the desired contact time in an electrically thermostatic reciprocating shaker (Selecta multimatic-55, Spain) at 120 rpm. The experiments were repeated at 20, 30, 40, and 50 °C. The time required for reaching the equilibrium condition was estimated by drawing samples at regular intervals of time till equilibrium was reached. The contents of the flask were filtered through 0.25 μm filters (Double rings, China) and the filtrate was analyzed for metal concentration by using flame AAS. Each determination was repeated three times and the results given are the average values. Standard deviations and error bars are indicated wherever necessary.

The percent biosorption of metal ion was calculated as follows:

$$\text{Biosorption (\%)} = \frac{(C_i - C_f)}{C_i} \times 100 \tag{1}$$

where C_i and C_f are the initial and final metal ion concentrations, respectively. Biosorption experiments for the effect of pH were conducted by using a solution having 10 mg/L of Pb(II) and 10 mg/L of Cd(II) concentration with a optimum biomass dosage of 4 g/L. Throughout the study, the contact time was varied from 5 to 90 min, the pH from 2 to 8, the initial metal concentration from 10 to 400 mg/L, and the biosorbent dosage from 0.1 to 20 g/L.

2.4. Desorption procedure

A sample volume of 25 mL, containing 10 mg/L of Pb(II) and 10 mg/L of Cd(II) ions, was transferred into a beaker; 10 mL of buffer solution was added. After a fast shaking, 4 g/L of *A. rubescens* was added and the mixture was shaken again for 90 min at 100 rpm. The system was filtered with blue band filter paper. Then the filter and constituents were washed with distilled water. In order to elute the adsorbed analytes onto *A. rubescens*, 8–10 mL of 1 mol/L HNO_3 was used. The final volume was completed to 25.0 mL with 1 mol/L HNO_3. Analyte contents of the final solution were determined by flame atomic absorption spectrometry. The same procedure was applied to the blank solution. In order to use the *A. rubescens* for next experiment, *A. rubescens* was washed with excess of 1 mol/L HNO_3 and distilled water, sequentially.

3. Results and discussion

3.1. FT-IR analysis

The FT-IR spectroscopy method was used to obtain information on the nature of possible cell–metal ions interactions. The same procedure (drying at 105 °C at 48 h and followed by sieving) as biomass prepared for the FT-IR spectra of unloaded and metal ions-loaded biomass. The FT-IR spectra of unloaded and metal loaded