Journal of Hazardous Materials 171 (2009) 500–507

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Removal of mercury(II) from aqueous solution using moss (*Drepanocladus revolvens*) biomass: Equilibrium, thermodynamic and kinetic studies

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ARTICLE INFO

Article history:
Received 22 April 2009
Received in revised form 6 June 2009
Accepted 8 June 2009
Available online 16 June 2009

Keywords:
D. revolvens
Mercury ion
Removal
Isotherm
Kinetics

ABSTRACT

The equilibrium, thermodynamics and kinetics of the biosorption of Hg(II) onto moss (*Drepanocladus revolvens*) biomass from aqueous solution were investigated. Optimum experimental parameters were determined to be pH 5.5, contact time 60 min, biomass concentration 4 g L^{-1} of solution, and temperature 20 °C. From the Langmuir model the maximum biosorption capacity of the moss biomass was found to be 94.4 mg g^{-1}. The mean free energy value (10.2 kJ mol^{-1}) evaluated by using the Dubinin–Radushkevich (D–R) model indicated that the biosorption of mercury ions onto *D. revolvens* was taken place by chemical ion-exchange. The kinetic studies indicated that the biosorption process of mercury ions followed well pseudo-second-order model. The calculated thermodynamic parameters (ΔG°, ΔS°, ΔH°) showed the biosorption to be exothermic and spontaneous with decreased randomness at the solid–solution interface. The recovery of the Hg(II) from *D. revolvens* biomass was found to be 99% using 1 M HCl. It was concluded that the *D. revolvens* biomass can be used as biosorbent for the treatment of wastewaters containing Hg(II) ions.

1. Introduction

Heavy metals are released continuously from different sources, industrial, agricultural and domestic wastes into the environment, which create problem for human as well as aquatic organisms. The pollution of water resources due to the indiscriminate disposal of heavy metals has been causing worldwide concern for the last few decades. It is well known that some metals can have poisonous or harmful effects on many forms of life [1].

Mercury is one of the most toxic heavy metals released in the environment and readily accumulated by organisms [2,3]. Mercury has very high tendency for binding to proteins and it mainly affects the renal and nervous systems [4]. In humans, the initial symptoms include numbness of the lips and limbs. As the sickness progresses, permanent damage is done to the central nervous system, and the victim experiences visual constriction, loss of motor coordination, and, in the final stages prior to death, loss of memory, speech, hearing, and taste. In addition, mercury is easily absorbed through skin, respiratory, and astrointestinal tissues [5]. Natural inputs of mercury to the environment are related to weathering of mercuriferous areas, the degassing from surface water and from the earth's crust through volcanic eruptions, naturally caused forest fires, and biogenic emissions [6]. In addition, this heavy metal is also released to the environment from anthropogenic activities that include agriculture, battery production, fossil fuel burning, mining and metallurgical processes, paint and chloralkali industries, and wood pulping [7]. The European Union considers mercury as a priority and hazardous pollutant and defines a maximum permissible concentration of total mercury as low as 1 μg L^{-1} for drinking water and 5 μg L^{-1} for wastewater discharge [8]. In view of the toxicity and in order to meet regulatory safe discharge standards, it is essential to remove heavy metals from wastewaters/effluents before it is released into the environment [9]. A number of technologies have been developed over the years to remove toxic metal ions from water. Conventional methods for the removal of heavy metals include ion-exchange, chemical precipitation, preconcentration, reverse osmosis, evaporation, membrane filtration, adsorption and biosorption [10]. These processes are expensive, and also have other shortcomings, such as incomplete removal of metals, limited tolerance to pH change, moderate or no metal selectivity, very high or low working levels of heavy metals, and production of toxic sludge or other waste products that also need disposal [11]. Hence, environmental and public health engineers have been searching for an inexpensive and efficient technology for the treatment of metal-containing wastes. The use of biosorption to remove heavy metals is one of such technology that has received considerable attention in the past two decades [12]. This method plays an important role in the elimination of heavy metal ions from aqueous solutions in water pollution control [13]. The main advantages of this technique are the reusability of biomaterial, low operating cost, improved

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doi:10.1016/j.jhazmat.2009.06.023

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 [14]. Various biomasses have been used for the removal of Hg(II) ions from aqueous solution [15,16].

Mosses are cryptogamic organisms which occur in almost all terrestrial ecosystems and by virtue of their ability to tolerate long periods of drought may even colonize areas with extreme environmental conditions [17]. They have been used for more than 20 years as biomonitors for the determination of atmospheric heavy metal deposition because of their high cation exchange capacity [18,19]. Different kinds of mosses have also been used for removing different heavy metals from aqueous solution [20–23]. *D. revolvens* is marked by its long, tapered leaves, which are strongly curled around to the extent of almost forming a circle. The leaves are orientated to one side of the stem. It is a robust plant and is usually tinged with orange, crimson or purple, mixed with yellowish-green. This moss species is a natural and readily available and considered as low-cost biomass.

In this study, the biosorption potential of the *D. revolvens* biomass to remove Hg(II) from aqueous solution was investigated using batch method. 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. The biosorption mechanisms of Hg(II) onto *D. revolvens* biomass were also evaluated in terms of thermodynamics and kinetics.

2. Experimental

2.1. Biomass preparation

The moss biomass (*D. revolvens*) sample was collected from the East Black Sea coast of Turkey. Samples were washed with deionized water and inactivated by heating in an oven at 70 °C for 48 h. The inactivated dried moss biomass was ground and sieved through different sizes and 180–300 μm fraction was used in all experiments.

2.2. Reagents and equipments

Analytical reagent grade chemicals were used in this study supplied from Sigma (St. Loius, MO, USA). Double deionized water (Milli-Q Millipore 18.2 MΩ cm^{-1} conductivity) was used for all dilutions. A pH meter, Sartorius pp-15 Model glass-electrode was employed for the measurement of pH values in the aqueous phase. Phosphate buffer solution ($H_2PO_4^-/H_3PO_4$) were prepared by mixing of appropriate volumes of 1 mol L^{-1} sodium dihydrogen phosphate and phosphoric acid solutions at pH 2. Acetate buffer solutions (CH_3COO^-/CH_3COOH) were prepared by mixing of appropriate volumes of 1 mol L^{-1} acetic acid and 1 mol L^{-1} sodium acetate solutions at pH 4. Phosphate buffer solutions ($H_2PO_4^-/HPO_4^{2-}$) were prepared by mixing of appropriate volumes of 1 mol L^{-1} sodium dihydrogen phosphate and 1 mol L^{-1} sodium hydrogen phosphate at pH 5 and 6. Ammonium buffer solutions were prepared by mixing of appropriate amounts of 1 mol L^{-1} ammonia and 1 mol L^{-1} ammonium chloride solutions at pH 8.

Perkin Elmer Analyst 700 (Norwalk, CT, USA) model AAS equipped with MHS 15 CVAAS system was used for mercury determination. A hallow cathode lamp operating at 6 mA was used and a spectral bandwidth of 0.7 nm was selected to isolate the 253.7 nm mercury line. $NaBH_4$ (1.5%, w/v) in NaOH (0.5%, w/v) was used as reducing agent. The analytical measurement was based on peak height. Reading time and argon flow rate were selected as 10 s and 50 mL min^{-1}, respectively. Fourier transform infrared (FT-IR) spectra of dried unloaded biomass and Hg(II)-loaded biomass were recorded using a FT-IR spectrometer (JASCO-430, Japan).

2.3. Batch biosorption procedure

A 1000 mg L^{-1} stock solution of Hg(II) was prepared by $HgCl_2$ (E. Merck, Darmstadt, Germany). Biosorption experiments were conducted using the solutions having 10 mg L^{-1} of Hg(II) with the optimum biomass concentration, 4 g L^{-1}.

The solutions (25 mL) including the biomass were shaken for the desired contact time in an electrically thermostatic reciprocating shaker (Selecta multimatic-55, Spain) at 120 rpm. The batch studies were performed at different experimental conditions, such as initial metal concentration (10–400 mg L^{-1}), contact time (5–120 min), pH (2–8), biomass concentration (0.4–16 g L^{-1}), and temperature (20–50 °C). The equilibrium time 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). The metal concentration of filtrate was analyzed using CVAAS. Each determination was replicated three times and the mean results were considered in the analysis. The percent biosorption of the metal ion was calculated as follows:

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

where C_i and C_f are the initial and final metal ion concentrations, respectively.

2.4. Desorption procedure

The desorption studies of Hg(II) from the biosorbent were carried out by using 1 M HNO_3 (10 mL) and 1 M HCl (10 mL). After determination of metal contents of the final solutions, the biosorbent was washed with excess of the acid solution and distilled water in order to reuse for next experiment. Consecutive sorption–desorption cycles were repeated ten times to establish the reusability of the biosorbent for Hg(II) removal from aqueous solution.

3. Results and discussion

3.1. FT-IR analysis

The FT-IR spectroscopy method was used to obtain information on the nature of possible biosorbent–metal ions interactions. Fig. 1 shows the FT-IR spectra of unloaded and Hg(II)-loaded biomass samples. The FT-IR spectra of the moss biomass indicate the pres-

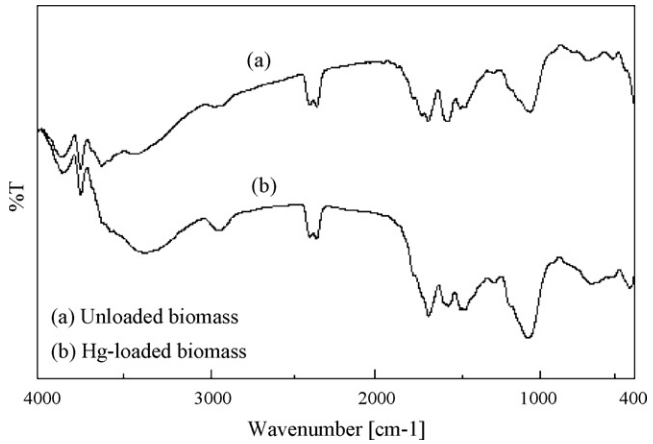

Fig. 1. FT-IR spectrum of unloaded and Hg(II)-loaded biomass.