

Removal of heavy metals by biosorption using freshwater alga *Spirogyra hyalina*

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Abstract

The use of biosorbents for heavy metal removal has revealed enormous potential of algae for biosorption. The dried biomass of *Spirogyra hyalina* was used as biosorbent for removal of cadmium (Cd), mercury (Hg), lead (Pb), arsenic (As) and cobalt (Co) from aqueous solutions at different initial concentrations of the heavy metals and contact time of the biomass. The results showed that highest amount of Cd, Hg and As was adsorbed when the initial heavy metal concentration was 40 mg l⁻¹ whereas Pb and Co exhibited greatest removal at 80 mg l⁻¹. The value of Freundlich model constant (1/n) for different metals ranged from 0.342 to 0.693 and the values of Langmuir separation factor values (R_L) varied between 0.114 and 0.719 that indicated favorable biosorption by the biomass. The order of metal uptake for the dried biomass was found to be Hg>Pb>Cd>As>Co. The finding of the study revealed that dried biomass of *S. hyalina* has much potential as a biosorbent for the sorption of Cd, Hg, Pb, As and Co.

Key words

Biosorption, Heavy metals, Isotherms, *Spirogyra hyalina*

Introduction

Biosorption is a term that describes the removal of heavy metals by the passive binding to non-living biomass from an aqueous solution (Davis *et al.*, 2003). The process has gained importance due to its advantages over conventional separation techniques such as chemical precipitation, ion exchange, reverse osmosis, membrane filtration and activated carbon adsorption. These advantages are the reusability of biomaterial, low operating cost, improved selectivity for specific metals of interest, short operation time and no production of secondary compounds which might be toxic (Spinti *et al.*, 1995; Srinath *et al.*, 2002). Metal removal by biosorption can be considered a relatively new technology, which can successfully be employed as a refining treatment in shallow bodies of water (1-5 m) having metal concentrations (1-20 mg l⁻¹) (Roy *et al.*, 1992; Nirmal Kumar *et al.*, 2006). The use of biosorbents of biological origin have emerged in the last decade as one of the most promising alternatives to traditional heavy metal management strategies. Of late, the attention has shifted to non-living dry alga biomass and other microorganisms for metal removal. The algae have many features that make them ideal candidates for the selective removal and concentration of heavy metals, which include high

tolerance to heavy metals, ability to grow both autotrophically and heterotrophically, large surface area/volume ratios, phototaxy, phytochelatin expression and potential for genetic manipulation (Suresh and Ravishankar, 2004).

Several researchers have reported the removal of heavy metal through algae, marine algae, bacteria, yeast and higher plants in immobilized as well as in free state. Ahuja *et al.* (1999) studied the sorption and desorption of Co by cyanobacteria such as *Oscillatoria angustissima*. Mostafa *et al.* (2005) studied the growth and metal removal efficiency of *Nostoc muscorum* and *Anabaena subcylindrica* in sewage and industrial wastewater effluents. *Spirulina platensis* (Solisio *et al.*, 2006) also showed considerable potential of adsorption. Biosorption of Pb(II), Ni(II) and Cr(VI) ions onto inactive *Saccharomyces cerevisiae* was investigated as function of initial pH, initial metal ion concentration and temperature by Ozer and Ozer (2003). The sorption of Hg and Pb from mono-metal and bi-metal solution using dried *Aspergillus niger* biomass was studied by Nirmal Kumar *et al.* (2010). Yan and Viraraghavan (2001) selected *Mucor rouxii* biomass immobilized in a polysulfone matrix and the biosorption column prepared was able to remove metal ions such

as Pb, Cd, Ni and Zn not only from single-component metal solutions but also from multi-component metal solutions. Further, green algal species such as *Chlorella vulgaris*, *Scenedesmus quadricauda* (Awasthi and Rai, 2004) and *Chlorella homosphaera* (Costa and Selma, 1990) have also been studied apart from marine algae (Nirmal Kumar *et al.*, 2009) for their biosorption capacities. The present work focused on the investigation of the capability of dried biomass of *Spirogyra hyalina* to remove heavy metal from aqueous solution at different initial concentrations of the heavy metals and at different exposure period (time) of dry biomass.

Materials and Methods

Preparation of biosorbent: The filamentous alga *Spirogyra hyalina* was obtained from fresh water Pariej Community Reservoir, Anand district, Gujarat, India, located at 22°33' N latitude and 72°38' E longitude in December, 2008. The alga was washed twice with tap water and thereafter with double distilled water thoroughly to eliminate adhering foreign particles like sand and debris. The washed biomass was first air dried for 24 hrs and then in an oven at 80°C to constant weight. The dried biomass was then ground in an analytical mill and then sieved through a 2 mm mesh size sieve and stored in polyethylene bottles.

Experimental procedure: Batch equilibrium experiments were performed at room temperature in 250 ml Erlenmeyer glass flasks containing aqueous solution of Cd, Hg, Pb, As and Co of known concentrations, *i.e.* 20, 40, 60 and 80 mg l⁻¹, prepared using analytical grade cadmium nitrate [Cd (NO₃)₂], mercuric chloride (HgCl₂), lead nitrate [Pb (NO₃)₂], arsenic trioxide (As₂ O₃) and cobalt chloride (CoCl₂). An accurately weighed 250 mg portion of biomass was added to each flask and the mixtures were agitated on a rotary shaker at 180 rpm for different time intervals, 30, 60, 90 and 120 min. Controls for each concentration without addition of heavy metals were also maintained. After the respective agitation period, the solutions were separated from the biomass by filtration and subjected to further analysis. All the biosorption experiments were conducted in triplicates to substantiate the results. The data shown are the mean values of three replicate determinations.

Instrumentation: Heavy metal content in all the filtrates was quantified using Inductively Coupled Plasma-optical emission spectroscopy (ICP-OES; Perkin Elmer Optima-3300 RL). The amount of metal sorbed at equilibrium, q (mg g⁻¹), which represents the heavy metal uptake was calculated from the difference in metal concentration in the aqueous phase before and after adsorption according to Basha *et al.* (2006).

Adsorption isotherms: Adsorption from aqueous solutions at equilibrium is usually correlated by Freundlich and Langmuir isotherm (Freundlich, 1907).

$$q = K Ceq^{1/n}$$

In this model, K (l g⁻¹) and $1/n$ are the constants to be determined from the data. For a good adsorbent, $0.2 < 1/n < 0.8$ and

a smaller value of $1/n$ indicates better adsorption and formation of rather strong bond between the adsorbate and adsorbent. Langmuir equation (Langmuir, 1916, 1917) is expressed as:

$$q = q_{max} bCeq / 1 + bCeq$$

Where q_{max} (mg g⁻¹) is the amount of adsorption corresponding to complete monolayer coverage, *i.e.*, the maximum adsorption capacity and b (l mg⁻¹) is the Langmuir constant.

Results and Discussion

Sorption and removal of heavy metals by algal biosorbents largely depend on the initial concentration of metals in the solution. Metal sorption initially increases with increase in metal concentration in the solution, and then becomes saturated after a certain concentration of metal (Mehta and Gaur, 2001). The metal uptake by the biomass for different heavy metals is shown in Fig. 1. Cadmium exhibited lowest metal uptake at 20 mg l⁻¹ ($q=2.192$) in 30 min and highest at 40 mg l⁻¹ ($q=9.832$) with contact time of 90 min. The minimum metal uptake for Hg was recorded at 20 mg l⁻¹ *i.e.* $q=5.396$ with contact time of 30 min which shooted to 39.212 (q) at 40 mg l⁻¹ in 120 min. For Pb, the metal uptake increased with increasing initial concentration of the metal, with least uptake at 20 mg l⁻¹ ($q=5.495$) at 30 mins contact time and highest at 80 mg l⁻¹ ($q=15.471$) at 120 min. Metal uptake for As was lowest at 20 mg l⁻¹ ($q=1.416$) in contact time of 30 min and exhibited peak at 40 mg l⁻¹ ($q=8.719$) in 120 min. The minimum Co uptake was observed at 20 mg l⁻¹, ($q=2.628$) in 30 mins whereas the maximum was at 80 mg l⁻¹ ($q=7.856$) in 120 min. The order of metal uptake for the dried biomass was found to be Hg>Pb>Cd>As>Co.

As evident from the above results, for all the metals studied, the least metal uptake was recorded at 20 mg l⁻¹ while initial concentration for highest uptake varied in different metals. Among all the metals studied, Cd, Hg and As recorded decrease in the metal uptake at higher concentrations after attaining the maximum values. This appears to be due to the increase in the number of ions competing for the available binding sites in the biomass and also due to the lack of binding sites for the complexation of these ions at higher concentration levels. At lower concentrations, all metal ions present in the solution would interact with the binding sites and thus facilitate maximum adsorption. At higher concentrations, more ions are left unabsorbed in solution due to saturation of binding sites (Ahalya *et al.*, 2005). Also, contact time for minimum uptake was found to be 30 min for all the metals. However, contact time for maximum uptake also differed for different metals.

The metal uptake capacity of the biomass was evaluated using Freundlich and Langmuir isotherms. The Langmuir isotherm (Langmuir, 1916, 1917) represents the equilibrium distribution of metal ions between the solid and liquid phases. The correlation coefficient for the different metals ranged from 0.126 to 0.980. q_{max} and b were determined from the slope and intercept of the plot. Highest q_{max} value was observed for Hg (35.714 mg g⁻¹). The

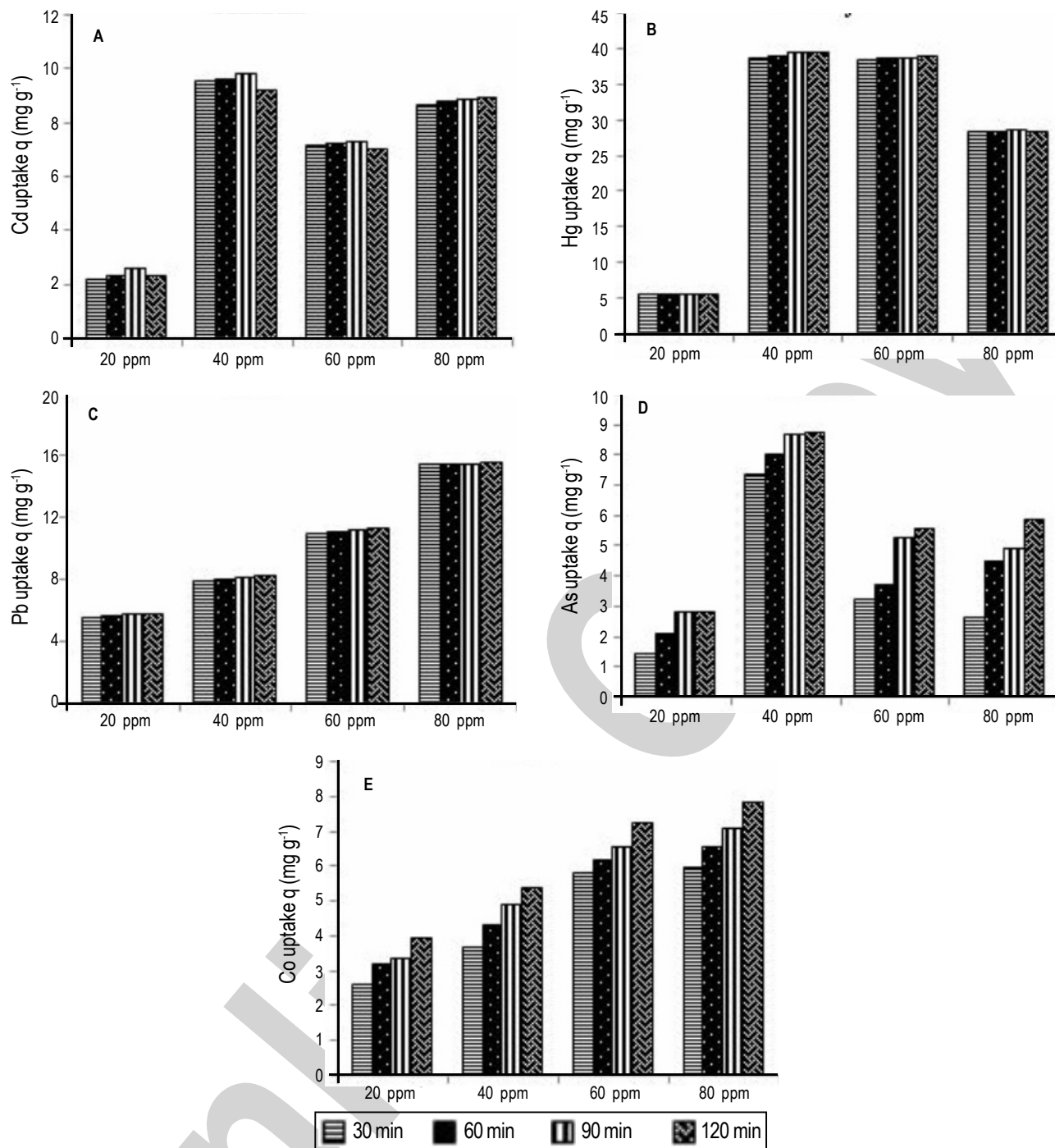


Fig. 1: Heavy metal uptake of (A) cadmium, (B) mercury (C) lead, (D) arsenic and (E) cobalt by dried biomass of *S. hyalina*

separation factor values (R_L) indicated (Table 1) that metal sorption onto the biomass was favorable (Hall *et al.*, 1966).

The linearised form of Freundlich adsorption isotherm was used to evaluate the sorption data. The values of $1/n$ ranged between 0.342 and 0.693 which indicates good adsorption (Table 1). According to Kadirvelu and Namasivayam (2000), n values between 1 and 10 represent beneficial adsorption. The

magnitude of K and n shows easy separation of heavy metal ion from wastewater and high adsorption capacity (Ahalya *et al.*, 2005). The value of n , which is related to the distribution of bonded ions on the sorbent surface, was found to be greater than unity indicating that adsorption is favorable. Tien (2002) found that the magnitude of K and n showed easy uptake of surface area and dry weight of algal cells. It was found to be the main factor influencing metal sorption and indicates favorable

Table - 1: Isotherm constants for cadmium (Cd), mercury (Hg), lead (Pb), arsenic (As) and cobalt (Co) biosorption on biomass of *S. hyalina*

Isotherm constants	Cd	Hg	Pb	As	Co
Freundlich					
1/n	0.693	0.565	0.664	0.342	0.588
R ²	0.981	0.354	0.976	0.087	0.658
Langmuir					
q _{max} (mg g ⁻¹)	18.181	35.714	31.250	4.808	12.821
b (l mg ⁻¹)	0.061	0.139	0.096	0.124	0.063
R _L	0.719-0.348	0.358-0.114	0.473-0.229	0.255-0.100	0.588-0.354
R ²	0.927	0.736	0.880	0.391	0.461

adsorption. For Cd, Pb and Co Freundlich model fitted satisfactorily as depicted by high values of correlation coefficients R².

Lower costs and higher efficiency at low metal concentrations make biotechnological processes very attractive in comparison with physico-chemical methods for heavy metal removal (Gadd and White, 1993). Biosorption using biomass derived from fresh water algae, marine seaweeds and fungi has recently attracted growing interest of researchers. Many potential binding sites occur in algal cell walls and alginate matrices (Saitoh *et al.*, 2001; Tam *et al.*, 1998). Algal cell surface has several kinds of functional groups with varying affinity for an ionic species. Low and high affinity functional groups are involved in sorption of metal ions at high and low concentrations of metal ions, respectively (Mehta and Gaur, 2001). Cell wall of green algae contains heteropolysaccharides, which offer carboxyl and sulfate groups for sequestration of heavy metal ions. The test alga was found to record high uptake values for Hg, Pb and Cd. Algal cells have revealed considerable potential in removal of heavy metal from aqueous solutions in previous studies. Alpana *et al.* (2007) observed 97% removal of Pb²⁺ by *Pithophora odeogonia* and 89% removal by *Spirogyra neglecta* in 30 min from a solution containing 5 mg l⁻¹ initial concentration of Pb²⁺ by a biomass concentration of 1 g l⁻¹. Rezaee *et al.* (2006) achieved 90% adsorption of Hg by *Spirogyra* species within 15 min and equilibrium reached at 30 min. Mendoza-Cozatl *et al.* (2006) recorded efficient Cd²⁺ removal by *Euglena gracilis* (80%) however, it was found to be less efficient for Pb with less than 15% removal. In the present study also similar findings were observed. *S. hyalina* recorded 89% removal of Hg and 83% removal for Pb. Further, higher removal of 133.3 mg Cu (II) g⁻¹ of dry weight of biomass of *Spirogyra* species was observed in 120 min contact period with an algal dose of 20 g l⁻¹ by Gupta *et al.* (2006). The results of the study indicated that the metal uptake was concentration-independent phenomena for Cd, Hg and As whereas for Pb and Co an increase in initial metal concentration resulted in higher metal uptake. Similar results were obtained by Ahuja *et al.* (1999) where, increase in cobalt concentration resulted in the increased uptake of Co²⁺. Thus, the result is typical for biosorption of metals involving no energy-mediated reactions, where metal removed from the solution is due to purely physico/chemical interactions between the biomass and metal in solution.

The study revealed that *S. hyalina* has much potential as a biosorbent for the removal of Cd, Hg, Pb, As and Co in aqueous solutions. Thus, this abundantly and cheaply available fresh water alga can be used for the development of efficient biosorbent materials for heavy metal removal.

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