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PJBS

ISSN 1028-8880

**Pakistan
Journal of Biological Sciences**

ANSI*net*

Asian Network for Scientific Information
308 Lasani Town, Sargodha Road, Faisalabad - Pakistan

Kinetics Modeling of Lead (II) and Cadmium (II) Biosorption from Aqueous Solutions by Brown Algae *Sargassum* sp. Biomass

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Abstract: Biosorption kinetics of lead (II) and cadmium (II) from aqueous solutions by *Sargassum* sp. biomass were studied. Kinetic experiments were done in three initial concentrations of Pb^{2+} and Cd^{2+} and fixed initial ratio of adsorbate to biosorbent in single component batch system. The heavy metals uptake was found to be rapid for all concentrations and reached to 88-96% of equilibrium capacity of biosorption in 15 min. Monitoring of pH in the kinetic experiments presented the simultaneous release of H^+ with the uptake of Pb^{2+} and Cd^{2+} , therefore ion exchange was confirmed to be one of the biosorption mechanisms. The experimental data were analyzed using four sorption kinetic models; the pseudo first-order (Lagergren), pseudo second-order, saturation (mixed-order) and second-order rate equations. The pseudo second-order and saturation rate equations described the biosorption kinetics of Pb^{2+} and Cd^{2+} with high correlation coefficient ($R^2 > 0.99$) and better than the other equations. Kinetic analysis presented a direct relationship between initial Pb^{2+} and Cd^{2+} concentrations and the rate of biosorption. The maximum uptake capacities of *Sargassum* sp. biomass for Pb^{2+} and Cd^{2+} were obtained 1.07 and 0.79 $mM g^{-1}$, respectively.

Key words: Biosorption, *Sargassum*, lead(II), cadmium(II), kinetic

INTRODUCTION

Aqueous heavy metals pollution represents an important environmental problem due to their toxic effects and accumulation throughout the food chain. Among heavy metals, lead and cadmium have high priority for removal from aqueous environments^[1-5].

The conventional technologies used to remove heavy metals from wastewater include, mainly, chemical precipitation, ion exchange, adsorption, membrane processes and evaporation^[6-8]. These methods have been found to be limited, since they often involve high capital and operational costs and may also be associated with the generation of secondary wastes which present disposal problems^[5,8]. Therefore, there is an urgent need for development of innovative but low cost processes, where metal ions can be removed economically. The search for new treatment technologies has focused attention on biosorption^[9-12].

Biosorption, the uptake of heavy metals by non-living biomass, can reduce capital costs by 20%, operational costs by 36% and total treatment costs by

28%, compared with the conventional methods^[13]. A number of different metal binding mechanisms have been postulated to be active in biosorption such as ion exchange, complexation, coordination, chelation, physical adsorption and microprecipitation^[5]. The biosorption technology can utilize naturally abundant biomass such as seaweeds and of these *Sargassum* has been identified for its high sorption capacity. *Sargassum* contains high amounts of alginate, well locked within its cellular structures, with abundant carboxylic groups capable of capturing metal ions present in solution. It is especially the guluronic acid in alginate that offers these functional groups for biosorption^[14-16].

Biosorption kinetics of heavy metals using various biosorbents have been studied. Loukidou *et al.*^[13] investigated the kinetic of chromium (VI) biosorption by *Aeromonas caviae* and the pseudo second-order rate equation was found in the best fitness with the experimental data. Kinetic data of cadmium (II) biosorption by chitin presented high correlation with the pseudo second-order rate equation^[17]. Biosorption of cobalt by *Ascophyllum nodosum* was very rapid and reached to

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equilibrium in 10 min^[18]. Zhang *et al.*^[19] observed that lead (II) biosorption on non-living *Rhizopus nigricans* reached equilibrium in 2 h and the biosorption rate was fast in the first 20 min. Cadmium (II) biosorption on *Aspergillus oryzae* reached equilibrium in 1h with 90% of biosorption taking place in the initial 10 min^[20].

The objective of this research was to study the biosorption kinetics of Pb²⁺ and Cd²⁺ by *Sargassum* sp. biomass. In order to analyze the experimental data of biosorption kinetics, the pseudo first-order, pseudo second-order, saturation and second-order rate equations were used.

MATERIALS AND METHODS

Preparation of biosorbent: The biosorbent used in experiments was brown algae, *Sargassum* sp. The biomass was harvested from Oman Sea on the coast of Chabahar, Iran. The biomass was washed with tap water and de-ionized water to remove sand and other impurities. The biomass sun-dried and then dried in an oven at 70°C. Dried biomass was ground in a laboratory blender. After this, the biomass was sieved to select particle between 0.2-0.3 mm for use. The biomass was subsequently loaded with H⁺ in a solution of 0.1 M L⁻¹ HCl (biomass concentration of 50 g L⁻¹) for 30 min under slow stirring. Later the biomass was washed with de-ionized water to remove excess H⁺. Finally the biosorbent again dried at 70°C for 24 h.

Kinetic experiments: Kinetic experiments were done in three initial concentrations of Pb²⁺ and Cd²⁺ and fixed initial ratio of adsorbate to biosorbent inside the single-component batch system with solutions volume of 1 L. Initial metal concentrations were 0.5, 1 and 5 mM L⁻¹ and initial ratio of a dsorbate to biosorbent was 2 mM g⁻¹, therefore 2.5, 0.5 and 0.25 g of the biosorbent were added to experiment vessels with initial metal concentrations of 5, 1 and 0.5 mM L⁻¹, respectively. Synthetic solutions of Pb²⁺ and Cd²⁺ were prepared using de-ionized water and nitrate salts of Pb(NO₃)₂ and Cd(NO₃)₂.4H₂O (Merck supplied).

The experiments were conducted at room temperature (20±°C). In all experiments, the mixture of solution and biosorbent was agitated in 200 rpm. Initial pH of solutions was adjusted with a pH meter (CAMLAB Ltd, Model CG842) to 5 by using 0.1-1 M L⁻¹ HCl and 0.1-1 M L⁻¹ NaOH and pH of the solutions was monitored continuously. The experiments were continued for 5 h and samples were drawn from the mixture at pre-determined time intervals for analysis.

Metal analysis: The biomass was removed by filtration through 0.45 µm membrane filters (mixed cellulose ester)

and filtrates were analyzed for residual metal concentration by a flame atomic absorption spectrophotometer (FAAS, Chem. Tech Analytical, Model ALPHA4).

Kinetics modeling: Kinetics of Pb²⁺ and Cd²⁺ biosorption were modeled by the pseudo first-order (Langergren), pseudo second-order, saturation (mised order) and second-order rate equations presented below as Eq. (1-4), respectively:

$$\ln \frac{(q_e - q_t)}{q_e} = -k_1 t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

$$\frac{1}{t} \ln \frac{C_0}{C_t} = -\frac{k_0}{K} - \frac{1}{K} \left(\frac{C_0 - C_t}{t} \right) \quad (3)$$

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \quad (4)$$

where, q_e and q_t are the amounts of metal ion sorbed (mM g⁻¹) at equilibrium and at any time, respectively; k₁ is the pseudo first-order rate constant of adsorption (min⁻¹); k₂ is the pseudo second-order rate constant of adsorption (g mM⁻¹ min⁻¹); C₀ and C_t are the concentrations of metal ion (mM L⁻¹) at t = 0 and at any time, respectively; k₀ (mM L⁻¹ min⁻¹) and K (mM L⁻¹) are saturation rate constants of adsorption and k is the second-order rate constant of adsorption (g mM⁻¹ min⁻¹)^[17,21,22].

RESULTS AND DISCUSSION

Kinetics study: The kinetic profiles of Pb²⁺ and Cd²⁺ biosorption by *Sargassum* sp. at various initial metal concentrations and fixed initial ratio of adsorbate to biosorbent (2 mM g⁻¹) are shown in Fig. 1. Pb²⁺ and Cd²⁺ uptake was relatively fast for all the concentrations studied. At the initial Pb²⁺ concentration of 5 mmol L⁻¹, the system reached to equilibrium within 30 min. In general, the heavy metals uptake reached to 88-96% equilibrium capacity of biosorption in 15 min. This rapid kinetics has significant practical importance as it will facilitate smaller reactor volumes ensuring efficiency and economy. Similar rapid metal uptake has been reported for the biosorption of Pb²⁺ using *Ecklonia radiata* wherein the system reached over 50-60% of the equilibrium uptake capacity in 10 min^[23]. The kinetic of chromium (III) biosorption by *Sargassum* sp. biomass was fast, reaching 60% of the total uptake capacity in 10 min^[24].

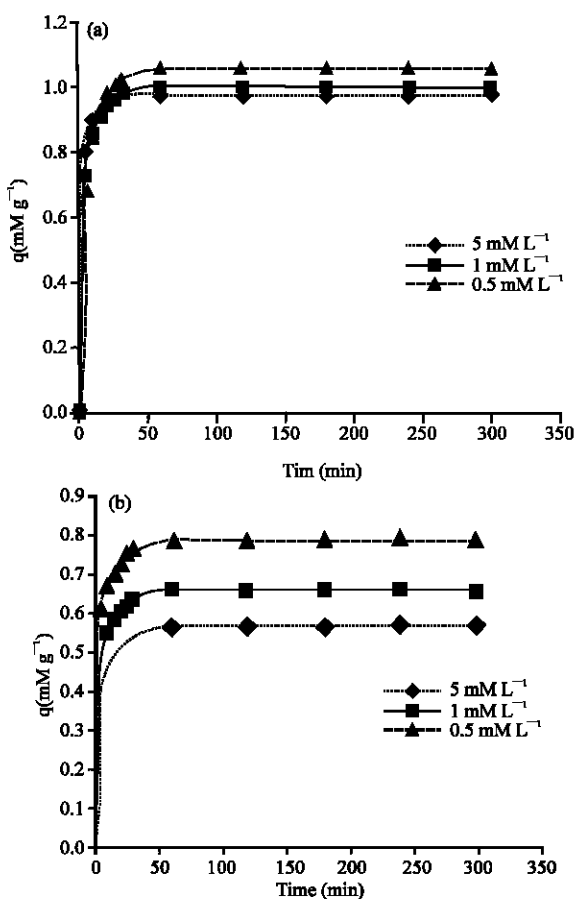


Fig. 1: Kinetic profiles of (a) Pb²⁺ and (b) Cd²⁺ biosorption by *Sargassum* sp.

The biosorption of lead (II) by *Durvillaea potatorum* was rather rapid and 90% of the total uptake occurred in 30 min^[25].

Equilibrium capacities of Pb²⁺ biosorption were obtained 0.98, 1.01 and 1.07 mM g⁻¹ at initial concentrations of 5, 1 and 0.5 mM L⁻¹, respectively (Table 1). In this manner equilibrium capacities of Cd²⁺ biosorption were obtained 0.57, 0.65 and 0.79 mM g⁻¹ at initial concentrations of 5, 1 and 0.5 mM L⁻¹, respectively (Table 1). As initial metals concentration increased, the equilibrium capacity of uptake decreased, thus the biosorption of Pb²⁺ and Cd²⁺ by *Sargassum* sp. biomass had higher efficiency in lower initial metal concentration.

Survey of pH variation: Monitoring of pH in the kinetic experiments presented the simultaneous release of H⁺ with the uptake of heavy metals, because pH of solutions was decreasing when the biosorption of Pb²⁺ and Cd²⁺ was being done. Initial pH of solutions was adjusted to 5 and

Table 1: Kinetic parameters of the pseudo first-order and pseudo second-order rate equations for the biosorption of Pb²⁺ and Cd²⁺ by *Sargassum* sp.

Metal ion	C ₀ (mM L ⁻¹)	Pseudo first-order model			Pseudo second-order model		
		q _e	k ₁	R ²	q _e	k ₂	R ²
Pb ²⁺	5	0.98	0.21	0.879	0.99	1.86	1.000
	1	1.01	0.14	0.839	1.01	0.83	1.000
	0.5	1.07	0.12	0.880	1.08	0.52	1.000
Cd ²⁺	5	0.57	0.11	0.377	0.57	1.07	1.000
	1	0.65	0.13	0.817	0.66	0.93	1.000
	0.5	0.79	0.12	0.464	0.79	0.87	1.000

C₀ = Initial concentration of metal ion, R = Correlation coefficient

Table 2: Kinetic parameters of the saturation and second-order rate equations for the biosorption of Pb²⁺ and Cd²⁺ by *Sargassum* sp.

Metal ion	C ₀ (mM L ⁻¹)	Saturation model			Second-order model		
		K	k ₀	R ²	q _e	k	R ²
Pb ²⁺	5	-3.88	0.0034	0.999	0.98	4.53	0.507
	1	-0.80	0.0010	0.998	1.01	2.43	0.782
	0.5	-0.40	0.0007	0.997	1.07	0.71	0.825
Cd ²⁺	5	-4.46	0.0011	1.000	0.57	0.98	0.962
	1	-0.88	0.0004	0.999	0.65	1.41	0.760
	0.5	-0.42	0.0002	1.000	0.79	0.91	0.860

C₀ = Initial concentration of metal ion; R = Correlation coefficient

final pH of solutions with initial Pb²⁺ concentrations of 5, 1 and 0.5 mM L⁻¹ were obtained 2.53, 3.25 and 3.47, respectively. Also final pH of solutions with initial Cd²⁺ concentrations of 5, 1 and 0.5 mM L⁻¹ were obtained 3.01, 3.51 and 3.75, respectively. This observation confirmed that ion exchange was one of the biosorption mechanisms. Diniz and Volesky^[16] observed that ion exchange was the main mechanism of lanthanum, europium and ytterbium biosorption by *Sargassum polycystum*. The biosorption of Zn²⁺ by *Oscillatoria angustissima* was an ion exchange phenomenon as a large amount of Mg²⁺ was released during Zn²⁺ uptake^[26]. Other studies with seaweed and fungal biomass have indicated ion exchange as the dominant mechanism of biosorption^[27-29].

Kinetics analysis: Figure 2 (a)-(d) and 3(a)-(d) show kinetics modeling of Pb²⁺ and Cd²⁺ biosorption by linear plots of the pseudo first-order, pseudo second-order, saturation and second-order rate equations (Eq. 1-4). Kinetic parameters of these equations for biosorption of Pb²⁺ and Cd²⁺ by *Sargassum* sp. biomass were shown in Table 1 and 2. The pseudo second-order and saturation rate equations described the biosorption kinetics of Pb²⁺ and Cd²⁺ with high correlation coefficient (R²>0.99) and better than the other equations. Kinetics analysis of Pb²⁺, Cd²⁺, Ni²⁺ and Zn²⁺ biosorption by *Mucor rouxii* represented that the pseudo second-order rate equation described the biosorption kinetics better than the Langergren model^[30].

The rate constants obtained from the pseudo second-order rate equation for Pb²⁺ biosorption are 1.86,

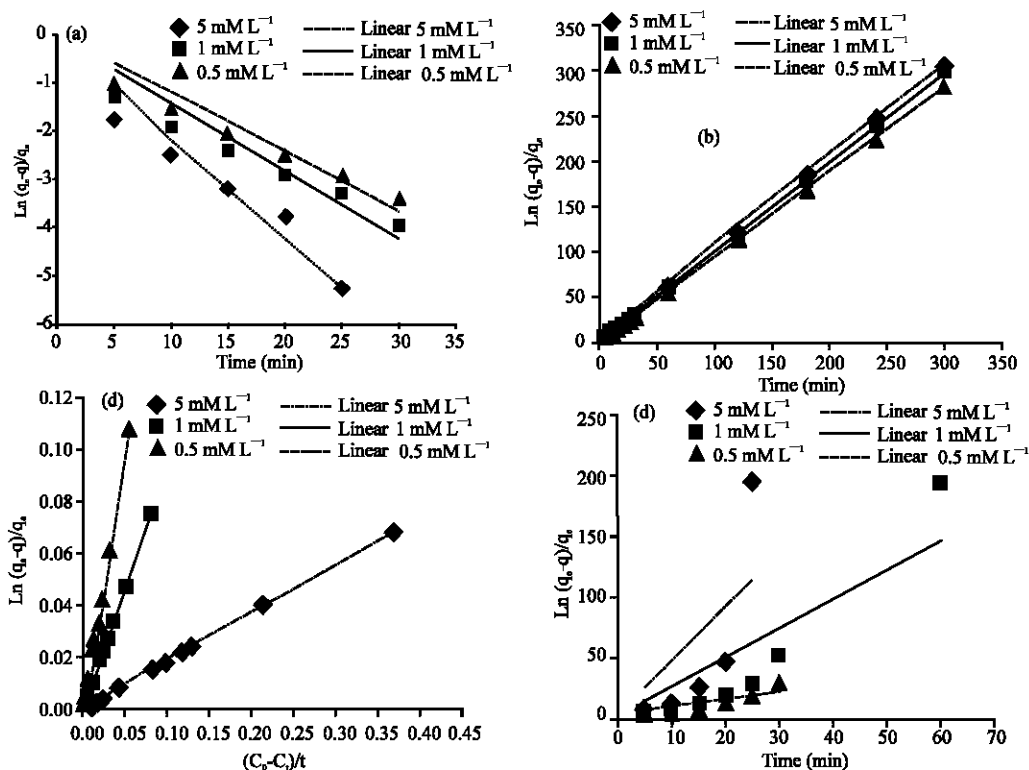


Fig. 2: Kinetics analysis of Pb^{2+} biosorption by linear plots of (a) pseudo first-order, (b) pseudo second-order, (c) saturation and (d) second-order rate equations

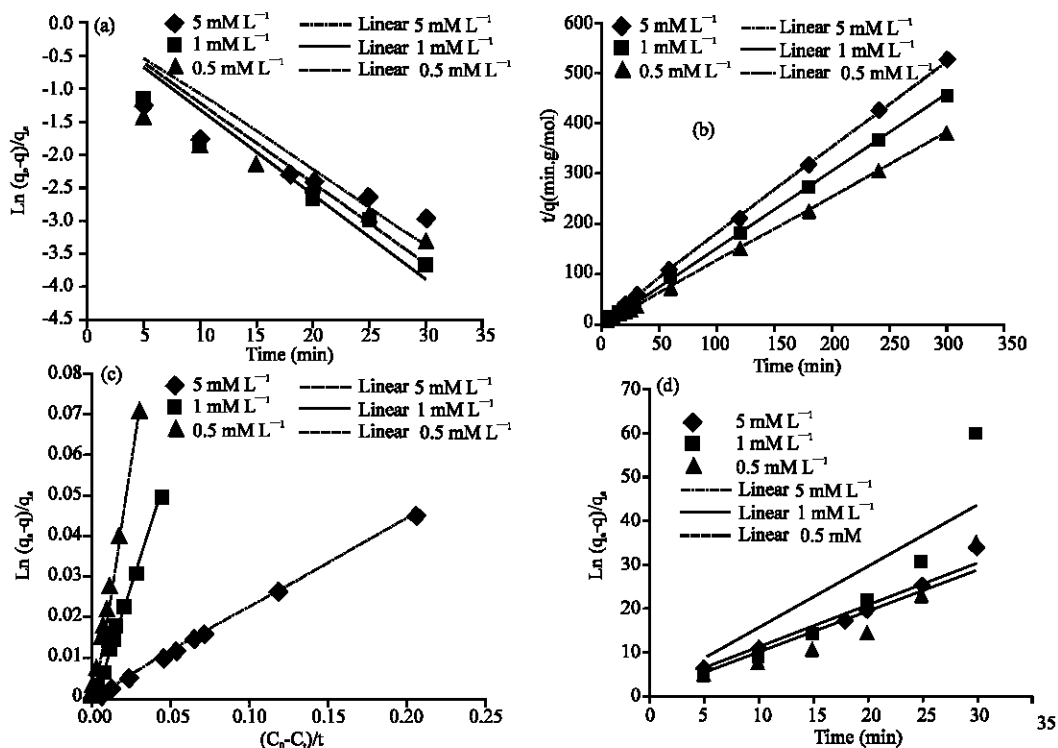


Fig. 3: Kinetics analysis of Cd^{2+} biosorption by linear plots of (a) pseudo first-order, (b) pseudo second-order, (c) saturation and (d) second-order rate equations

0.83 and 0.52 g mM⁻¹ min⁻¹ at initial Pb²⁺ concentrations of 5, 1 and 0.5 mM L⁻¹, respectively (Table 1). Also the rate constants of the saturation rate equation for Pb²⁺ biosorption are 0.0034, 0.0010 and 0.0007 mM L⁻¹ min⁻¹ at initial Pb²⁺ concentrations of 5, 1 and 0.5 mM L⁻¹, respectively (Table 2). The rate constants obtained from the pseudo second-order rate equation for Cd²⁺ biosorption are 1.07, 0.93 and 0.87 g mM⁻¹ min⁻¹ at initial Cd²⁺ concentrations of 5, 1 and 0.5 mM L⁻¹, respectively (Table 1). Also the rate constants of the saturation rate equation for Cd²⁺ biosorption are 0.0011, 0.0004 and 0.0002 mM L⁻¹ min⁻¹ at initial Cd²⁺ concentrations of 5, 1 and 0.5 mM L⁻¹, respectively (Table 2). An increase in initial Pb²⁺ and Cd²⁺ concentration led to an increase in the rate constant value, therefore there was a direct relationship between initial Pb²⁺ and Cd²⁺ concentration and the rate of biosorption by *Sargassum* sp. biomass. In other words, the biosorption of Pb²⁺ and Cd²⁺ by *Sargassum* sp. was faster in higher initial metal ion concentration.

Kinetic study was presented that Pb²⁺ and Cd²⁺ biosorption by *Sargassum* sp. biomass was relatively rapid, so that the heavy metals uptake reached to 88-96% equilibrium capacity of biosorption in 15 min. The biosorption of Pb²⁺ and Cd²⁺ had higher efficiency in lower initial metal concentrations. The maximum uptake capacities of the biosorbent for Pb²⁺ and Cd²⁺ were obtained 1.07 and 0.79 mM g⁻¹, respectively. Ion exchange was confirmed as one of the biosorption mechanisms. Kinetic analysis of Pb²⁺ and Cd²⁺ biosorption by *Sargassum* sp. biomass represented that the pseudo second-order and saturation rate equations described the biosorption kinetics better than the pseudo first-order and second-order rate equations. According to the pseudo second-order and saturation rate equations, the biosorption of Pb²⁺ and Cd²⁺ by *Sargassum* sp. was faster in higher initial metal ion concentration.

REFERENCES

- Rama, M.P., J.A. Alonso, C.H. López and E.T. Vaamonde, 2002. Cadmium removal by living cells of the marine microalga *Tetraselmis suecica*. *Biores. Technol.*, 84: 265-270.
- Kaewsarn, P., 2002. Biosorption of copper (II) from aqueous solutions by pre-treated biomass of marine algae *Padina* sp. *Chemosphere*, 47: 1081-1085.
- Kapoor, A., T. Viraraghavan and D.R. Cullimore, 1999. Removal of heavy metals using the fungus *Aspergillus niger*. *Biores. Technol.*, 70: 95-104.
- Sternberg, S.P.K., and R.W. Dorn, 2002. Cadmium removal using *Cladophora* in batch, semi-batch and flow reactors. *Biores. Technol.*, 8: 249-255.
- Volesky, B., 2001. Detoxification of metal-bearing effluents: biosorption for the next century. *Hydrometallurgy*, 59: 203-216.
- Aksu, Z., 2002. Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of nickel (II) ions onto *Chlorella vulgaris*. *Process Biochem.*, 38: 89-99.
- Eckenfelder, W.W.Jr., 2000. *Industrial Water Pollution Control*. 3rd Edn., McGraw-Hill, Boston, MA, pp: 138-142.
- Gupta, V.K., A.K. Shrivastava, and N. Jain, 2001. Biosorption of chromium (VI) from aqueous solutions by green algae *Spirogyra* species. *Water Res.*, 35: 4079-4085.
- Dönmez, G.Ç., Z. Aksu, A. Öztürk and T. Kutsal, 1999. A comparative study on heavy metal biosorption characteristic of some algae. *Process Biochem.*, 34: 885-892.
- Figueira, M.W., B. Volesky, V.S.T. Ciminelli and F.A. Roddick, 2000. Biosorption of metals in brown seaweed biomass. *Water Res.*, 34: 196-204.
- Hamdy, A.A., 2000. Biosorption of heavy metals by marine algae. *Current Microbiol.*, 41: 232-238.
- Jalali, R., H. Ghafourian, Y. Asef, S.J. Davarpanah and S. Sepehr, 2002. Removal and recovery of lead using nonliving biomass of marine algae. *J. Hazardous Materials*, B92: 253-262.
- Loukidou, M.X., A.I. Zouboulis, T.D. Karapantsios and K.A. Matis, 2004. Equilibrium and kinetic modeling of chromium (VI) biosorption by *Aeromonas caviae*. *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 242: 93-104.
- Davis, T.A., B. Volesky and R.H.S.F. Vieira, 2000. *Sargassum* seaweed as biosorbent for heavy metals. *Water Res.*, 34: 4270-4278.
- Davis, T.A., B. Volesky and A. Mucci, 2003. A review of the biochemistry of heavy metal biosorption by brown algae. *Water Res.*, 37: 4311-4330.
- Diniz, V. and B. Volesky, 2005. Biosorption of La, Eu and Yb using *Sargassum* biomass. *Water Res.*, 39: 239-247.
- Benguella, B. and H. Benaissa, 2002. Cadmium removal from aqueous solutions by chitin: Kinetic and equilibrium studies. *Water Res.*, 36: 2463-2474.
- Kuyucak, N. and B. Volesky, 1989. Accumulation of cobalt by marine algae. *Biotechnol. Bioeng.*, 33: 809-814.
- Zhang, L., L. Zhao, Y. Yu and C. Chen, 1998. Removal of lead from aqueous solution by non-living *Rhizopus nigricans*. *Water Res.*, 32: 1437-1444.

20. Kiff, R.J., and D.R. Little, 1986. Biosorption of Heavy Metals by Immobilized Fungal Biomass. In: Immobilization of Ions by Biosorption, Hunt, E.H., (Ed.), Ellis Horwood, Chichester, UK., pp: 219.
21. Azizian, S., 2004. Kinetic models of sorption: A theoretical analysis. *J. Coll. Interface Sci.*, 276: 47-52.
22. Metcalf and Eddy, Inc., 2003. Wastewater Engineering: Treatment and Reuse. 4th Edn., McGraw-Hill, New York, pp: 260-265.
23. Matheikal, J.T. and Q. Yu, 1996. Biosorption of lead from aqueous solutions by marine algae *Ecklonia radiata*. *Water Sci. Technol.*, 34: 1-7.
24. Cossich, E.S., C.R.G. Tavares and T.M.K. Ravagnani, 2002. Biosorption of chromium (III) by *Sargassum* sp. biomass. *Elect. J. Biotechnol.*, 5: 133-140.
25. Matheikal, J.T. and Q. Yu, 1999. Biosorption of lead (II) and copper (II) from aqueous solutions by pre-treated biomass of Australian marine algae. *Biores. Technol.*, 69: 223-229.
26. Ahuja, P., R. Gupta and R.K. Saxena, 1999. Zn²⁺ biosorption by *Oscillatoria angustissima*. *Process Biochem.*, 34: 77-85.
27. Crist, D.R., R.H. Crist, J.R. Martin and J. Watson, 1993. Ion Exchange System in Proton-metal Reactions with Algal Cell Walls. In: Metals-Microorganisms Relationships and Applications, Bauda, P., (Ed.), FEMS symposium abstracts, Metz, France, May 5-7, Societe Francaise de Microbiologie, Paris, France, pp: 13.
28. Fourest, E. and J.C. Roux, 1992. Heavy metal biosorption by fungal mycelial by-products: Mechanism and influence of pH. *Applied Microbiol. Biotechnol.*, 37: 399-403.
29. Schiewer, S. and B. Volesky, 1996. Modeling of multi-metal ion exchange in biosorption. *Environ. Sci. Technol.*, 30: 2921-2927.
30. Yan, G. and T. Viraraghavan, 2003. Heavy metal removal from aqueous solution by fungus *Mucor rouxii*. *Water Res.*, 37: 4486-4496.