

Biosorption of Cadmium by Waste Shell Dust of Fresh Water Mussel *Lamellidens marginalis*: Implications for Metal Bioremediation

Asif Hossain,^{†,§} Satya Ranjan Bhattacharyya,[‡] and Gautam Aditya^{*,†,§}

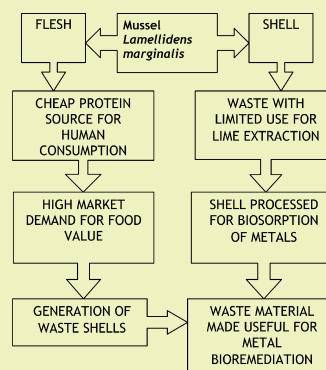
[†]Ecology Laboratory, Department of Zoology, The University of Burdwan, Golapbag, Burdwan 713104, India

[‡]Saha Institute of Nuclear Physics, 1/AF Bidhan Nagar, Kolkata 700 064, India

[§]Department of Zoology, University of Calcutta, 35 Ballygunge Circular Road, Kolkata 700019, India

ABSTRACT: The ability of the shell dust of freshwater mussel *Lamellidens marginalis* (MSD) to remove cadmium from the aquatic system was evaluated. The results indicate that MSD, a waste biomaterial, bears the potential to remove cadmium from contaminated water with a biosorption capacity of 18.18 mg g⁻¹ at pH 6. At equilibrium, the adsorption data fitted to Langmuir ($r^2 = 0.992$) significantly more than the Freundlich equation ($r^2 = 0.66$). Regression analysis suggests that the biosorption kinetics followed the pseudo-second-order model ($r^2 = 0.999$) better than the Lagergren model ($r^2 = 0.879$). The possible mechanism of biosorption appeared to be ion exchanges with Fe, Al, Si, In, Co, and Ca ions together with binding of different functional groups such as -OH, -C=O, -C=C, and -C-C, as revealed through FTIR and EDX analyses. Although low in comparison to cadmium, the MSD-adsorbed zinc ($q_{\max} = 10.64$ mg g⁻¹) and lead ($q_{\max} = 8.06$ mg g⁻¹) varied in amounts, depending upon the initial metal ion concentration and biomass of the adsorbent. These observations substantiate MSD as a low cost and environment friendly biosorbent for heavy metal ion bioremediation.

KEYWORDS: Biosorption, Cadmium, Mussel shell dust (MSD), Isotherm, Kinetics



INTRODUCTION

Heavy metal-induced pollution is a major concern for the sustainability of aquatic ecosystem functions. Accumulation of heavy metals at different trophic levels results in reduction of diversity and stability of the food webs that in turn contribute to the degradation of aquatic ecosystems. Because many of the aquatic resources are used by humans, potential health risks owing to dispersal and accumulation of heavy metals are highly possible. Empirical evidence supports that heavy metals can reach humans through food webs at a magnified level, affecting the physiological, behavioral, and biochemical processes.^{1,2} Thus, removal of heavy metals from the aquatic ecosystem is essential to reduce the ill-effects at population and ecosystem levels.³ Although metal removal methods based on ion exchange, chemical precipitation, coagulation, activated charcoal, electrochemical basis, and membrane technology alone or in combination have evolved in the recent past,⁴ the risks of generating secondary pollutants are associated with many of these methods. Alternatively, use of biological materials for metal removal has been promoted to minimize the cost with increased effectiveness.⁵ Application of biological materials available from natural sources reduces the possibilities of yielding unwanted chemicals without interfering with the ecosystem functions. This is substantiated through observations on the metal adsorption ability of different microorganisms,⁶ mushrooms,⁷ algae,^{8,9} and hydrophytes,¹⁰ many of which are hyper accumulators of metals.^{10,11} Application of aquatic animals in metal adsorption is also empirically tested as evident from studies on crab and acra shell biomass,^{12–14} calcined shells,¹⁵ and marine^{4,16–18} and freshwater bivalves.¹⁹

Successful metal removal strategies require selection of the appropriate form and variety of biological materials based on ecosystem specific requirements. Uncontrolled application of living specimens for metal removal can result in biological invasion and hinder ecosystem functions. In many instances, the use of the biological species in metal removal is constrained because of their value as food and other economic products.^{5,16} Although the ability of metal removal might be high in these biological resources, their potential as aquaculture resources limits their application in metal bioremediation.^{5,16,19} Animal body parts that are treated as wastes provide an alternative way of using biological materials for metal removal. This is evident from the use of egg shells and crab shells for metal adsorption and subsequent removal from ecosystems.^{12–14} Earlier studies have demonstrated cadmium uptake by living snails and mussels, including *Lamellidens marginalis* (Lamarck, 1819, Bivalvia: Unionidae), when exposed to cadmium for long-term period.^{5,19} However, the economic value of *L. marginalis* as a cheap source of protein limits the application of living individuals for metal filtration or bioadsorption. Instead, use of dead shell dust for this purpose appears to be a better substitute. In view of this proposition, an assessment of the metal removal capacity was made using the shell dusts of the fresh water mussels *L. marginalis* (MSD) using cadmium as a model metal. The biosorption capacity of MSD was also tested against lead and zinc to justify the generalized nature of the

Received: January 4, 2014

Revised: November 5, 2014

Published: November 17, 2014

metal removal capacity. In West Bengal, India, *L. marginalis* is common in wetlands and is harvested for human consumption of soft tissue, which is a cheap source of minerals and protein. Earlier studies on living *L. marginalis* have demonstrated metal removal capacity *in situ*, justifying their use in metal bioremediation. The results of the study are expected to highlight the potential use of the mussel shell in metal removal from freshwater and enable comparisons with similar products of biological origin.

MATERIALS AND METHODS

Preparation of Material. Freshwater mussels (*Lamellidens marginalis*) are common aquaculture products sold in local fish

Table 1. Elemental Profile of MSD before and after Treatment with Cadmium Metal as Obtained from EDX Study

before treatment			after treatment		
elements	weight %	atom %	elements	weight %	atom %
carbon	22.62	35.98	carbon	19.91	32.24
oxygen	36.75	43.88	oxygen	39.26	47.73
aluminum	2.59	1.83	aluminum	1.21	0.87
silicon	6.31	4.29	silicon	3.63	2.52
calcium	23.11	11.02	calcium	32.1	15.58
iron	4.36	1.49	iron	2.21	0.77
phosphorus	1.73	1.07	cadmium	1.68	0.29
cobalt	0.16	0.05			
indium	2.37	0.39			
total	100	100	100	100	

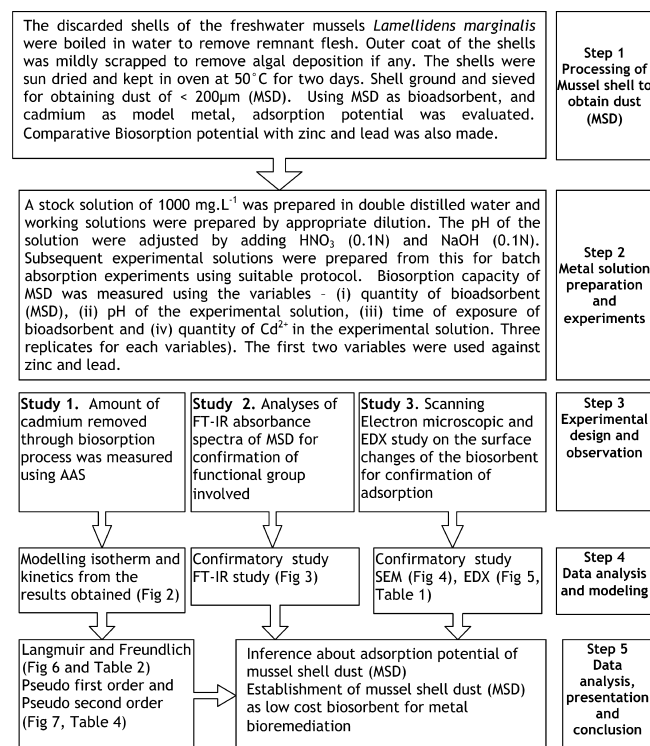


Figure 1. Outline of the study (steps 1–5) to assess the adsorption potential of shell dust of the freshwater mussel *Lamellidens marginalis* (MSD).

markets of Burdwan, India. Following extraction of the muscular portion of the body mass, the shells of the mussels are discarded as

waste. The intact discarded shells of the mussels were collected from the fish markets. Remaining tissues (remains of anterior and posterior adductor muscles) attached to the shells were cleared by boiling water and subsequent washing in distilled water. The shells were then sundried for 2 days and kept in an oven at 50 °C for the next 2 days for complete drying.

The shells were pulverized in mortars and pestles to fine granules. The granules were then sieved through 500 µm and consequently through 200 µm net. Granules of two different sizes were now produced: 500–200 µm and ≥200 µm. Initially, the larger-sized granules adsorbed a lesser amount of cadmium and thus were not studied further. The ash content of the dust was 72.30%, and the water content capacity was 1785.6 mg g⁻¹. Elemental composition of the MSD obtained from the energy-dispersive X-ray spectroscopy (EDX) study is given in Table 1.

Preparation of Metal Solution. In order to prepare metal solutions, chloride salts of cadmium, zinc, and lead were considered. For each metal, a separate stock solution of 1000 mg L⁻¹ was prepared in double distilled water, and the subsequent working solutions were prepared by appropriate dilution. The pH of the solutions was adjusted to the required levels using 0.1(N) HNO₃ and NaOH. The inorganic chemicals used in the present experiments were purchased from Merck India, Ltd.

Experimental Procedure. The outline of the experimental procedure followed in the present study is shown in Figure 1. The batch sorption experiments were done in a 250 mL Erlenmeyer flask that contained 100 mL of solution of the particular cadmium ion concentration at the required pH and relevant amount of mussel shell dust (MSD). The flasks were sealed with wax paper and shaken in a shaking incubator (Lab Companion, SI-300R, India) at a required temperature at 150 rpm for the required time. After shaking for a particular time, the solution of the flasks were centrifuged at 2000 rpm and then filtered through Whatman no. 41 filter paper (GE Healthcare U.K., Ltd.). Estimation of the metal concentration of the filtrates was done by atomic absorption spectroscopy (GBC Avanta 1.3, India). The influence of the pH of the solution for biosorption equilibrium was studied, following adjustment of the working solution to a pH range of 2 to 7. The effect of contact times between the solution and the MSD were monitored for an 80 min time period, with observations at every 10 min time interval. For equilibrium studies, seven levels of the metal ion concentrations were considered ranging between 25 and 1000 mg L⁻¹, while for the optimum biosorption study, the MSD biomass was varied at five levels between 200 and 1000 mg.

The following equation was used to estimate the amount of cadmium ion adsorbed on the MSD.²⁰

$$q_e = v/m(c_o - c_e)$$

where, q_e = amount of metal adsorbed, v = volume of solution, m = mass of adsorbent, c_o = initial concentration of the solution, and c_e = equilibrium concentration of the solution.

Analyses of FT-IR Absorbance Spectra of MSD. The IR spectra of protonated or Cd²⁺-loaded MSD were recorded by FT-IR spectroscopy (PerkinElmer FTIR, Model RX1, U.S.A.). Samples of 100 mg of KBr discs containing 1% of the final ground powder of each test were prepared prior to 24 h of experimental data recording.

SEM and EDX Analyses. Raw and metal-adsorbed MSD were dried and prepared for scanning electron microscopic studies. The samples were attached by the stubs with cello tape and gold plated in a sputter coater before use in the SEM. An electron acceleration potential of 20 kV was applied for the microscopic observations. SEM photographs were taken in a HITACHI S530 scanning electron microscope at the required magnification.

For EDX analyses, the samples were studied by a field emission gun-based scanning electron microscope with energy-dispersive X-ray analysis (SEM/EDX) (Quanta model by FEI Co., The Netherlands) for morphological data as well as for the presence of elemental information on the samples. EDX spectra were taken from the area corresponding to the SEM image shown in the inset. The SEM studies were done at 30 kV in the low vacuum mode. EDX spectra were taken

in the “region mode” with bombardment of energetic electrons for a duration of 100 s.

Comparative Study with Lead and Zinc. In order to assess the biosorption capacity of MSD for other metals, equilibrium studies using lead and zinc were carried out separately, following the similar protocol of cadmium. In this study, seven levels of metal ion concentrations were considered ranging between 25 and 1000 mg/L, and for the optimum biosorption study, the MSD biomass was varied at five levels between 200 and 1000 mg. The metal removal ability was observed at pH 6 and 60 min of exposure time. Three replicates were considered for each metal concentration and MSD biomass.

Equilibrium Modeling. In order to comment on the maximum cadmium ion biosorption potential by the MSD, adsorption equilibriums were estimated. For the equilibrium study, the experiments were performed at different initial cadmium ion concentration (25–1000 mg/g). Langmuir and Freundlich adsorption models were used in describing the equilibrium between adsorbed cadmium ions on the MSD (q_e) and in solution (c_e) at a particular temperature. The parameters of the Langmuir equation²¹ were determined from a linear form of the following equation

$$c_e/q_e = (c_e/a) + 1/b$$

where a = maximum amount of metal ions/unit mass of adsorbent to form a monolayer, and b = equilibrium constant. The linear plot of c_e/q_e against c_e indicates the applicability of the Langmuir modeling in the experiment.

The Freundlich equation²² stated below was also used to estimate the kinetic modeling

$$q_e = k_f c_e^{1/n}$$

where, k_f and $1/n$ are the Freundlich constants indicating the adsorption capacity and intensity, respectively. The linear plot of $\log q_e$ against $\log c_e$ indicates the applicability of the Freundlich modeling in the experiment.

Kinetic Modeling. The pseudo-first-order model in adsorption was proposed by Lagergren. It describes that the rate of adsorption is proportional to the number of unoccupied binding sites of the biosorbent. This model works well in the region where the biosorption process occurs quickly.²³ The Lagergren equation²⁴ or pseudo-first-order reaction is mathematically expressed as

$$dq/dt = k_1(q_e - q_t)$$

where q_e = amount of adsorbed metal ion on biosorbent at equilibrium, q_t = amount of adsorbed metal ion on biosorbent at time “ t ”, and k_1 = Lagergren constant.

Integrating the above equation and transforming to log scale-

$$\log(q_e - q_t) = \log q_e - k_1(t/2.303)$$

The linear plot of $\log(q_e - q_t)$ against time indicates whether this kinetic model is applicable for biosorption process. Because the pseudo-first-order model for prediction of biosorption may not be suitable for a long period of the adsorption process,²⁵ as an alternative, compatibility with the pseudo-second-order equation was judged using the following equation²⁵

$$q_t = q_e((q_e k_2 t)/(1 + q_e k_2 t))$$

where q_e = amount of adsorbed metal ion on biosorbent at equilibrium, q_t = amount of adsorbed metal ion on biosorbent at time “ t ”, and k_2 = second order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$). A linear plot of t/q against t will allow justifying the compatibility of the biosorption of MSD with the above equation.

RESULTS AND DISCUSSION

Effect of pH of Solution. The biosorption procedure was maintained over the experimental range of pH 2–7. The sorption procedure was influenced by the pH of the medium in two ways: metal solubility and total charge of the functional

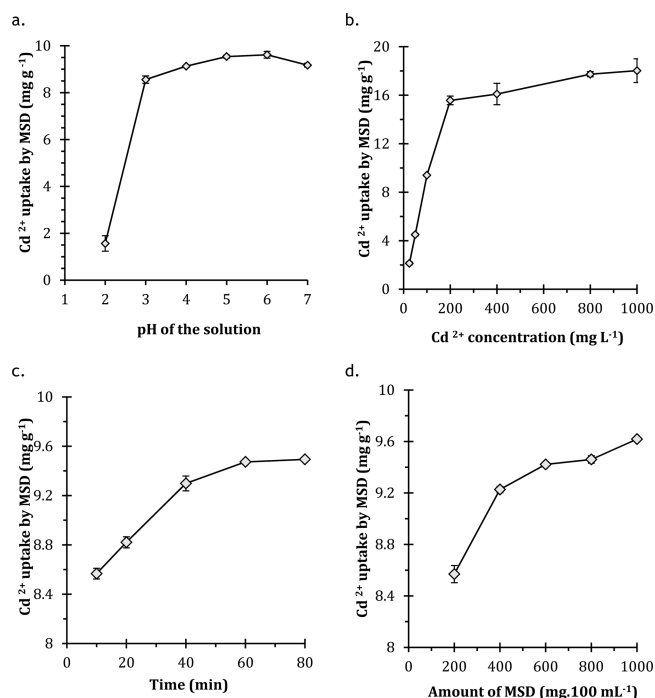


Figure 2. (a) Effect of pH of the solution on biosorption of cadmium on MSD at 30 °C, initial cadmium ion concentration of 100 mg L⁻¹, contact time of 60 min, and biosorbent dose of 1 g of 100 mL⁻¹ solution. (b) Effect of initial cadmium ion concentration of solution on biosorption on MSD at 30 °C, pH 6, contact time of 60 min, and biosorbent dose of 1 g of 100 mL⁻¹ solution. (c) Effect of time on biosorption of cadmium on MSD at 30 °C, pH 6, initial cadmium ion concentration of 100 mg/L, and biosorbent dose of 1 g of 100 mL⁻¹ solution. (d) Effect of biosorbent dose on biosorption of cadmium on MSD at 30 °C, pH 6, initial cadmium ion concentration of 100 mg L⁻¹, and contact time of 60 min.

groups of the biosorbent. The optimum pH, at which the procedure shows the highest adsorption for the biosorbent, was estimated. At high pH, that is, at an alkaline condition, precipitation of the metal takes place, while at low pH, metal sorption capacity decreases owing to high protonation. The experiment was carried out using 100 mL of solution having 100 mg L⁻¹ Cd²⁺ and 100 mg of the MSD at 30 °C in reference to varying pHs of the solution. The pH-dependent adsorption of the metal ion by MSD is shown in Figure 2a, which reflects that the metal sorption was negligible at pH 2 and increased with an increase in pH of the solution until the highest adsorption at pH 6. The metal sorption declined with a further increase in the pH of the solution (Figure 2a).

Effect of Initial Metal Ion Concentration. An increase in cadmium metal adsorption was observed with a corresponding increase in initial cadmium ion concentration. Seven different Cd²⁺ ion concentrations were used in the study, ranging between 25 and 1000 mg L⁻¹. At an initial concentration of 25 mg L⁻¹, the lowest adsorption was observed, while the highest adsorption was observed at 800 mg L⁻¹ concentration. Metal adsorption did not increase with a further increase in Cd²⁺ ion concentration in the solution (Figure 2b).

Influence of Biosorbent dose. The cadmium biosorption potential of the MSD increased with an increase in the available amount of MSD used in treating the metal solution. The increase in amount of biosorbent augmented the availability of free binding sites or exchanging group to adsorb the metal ion

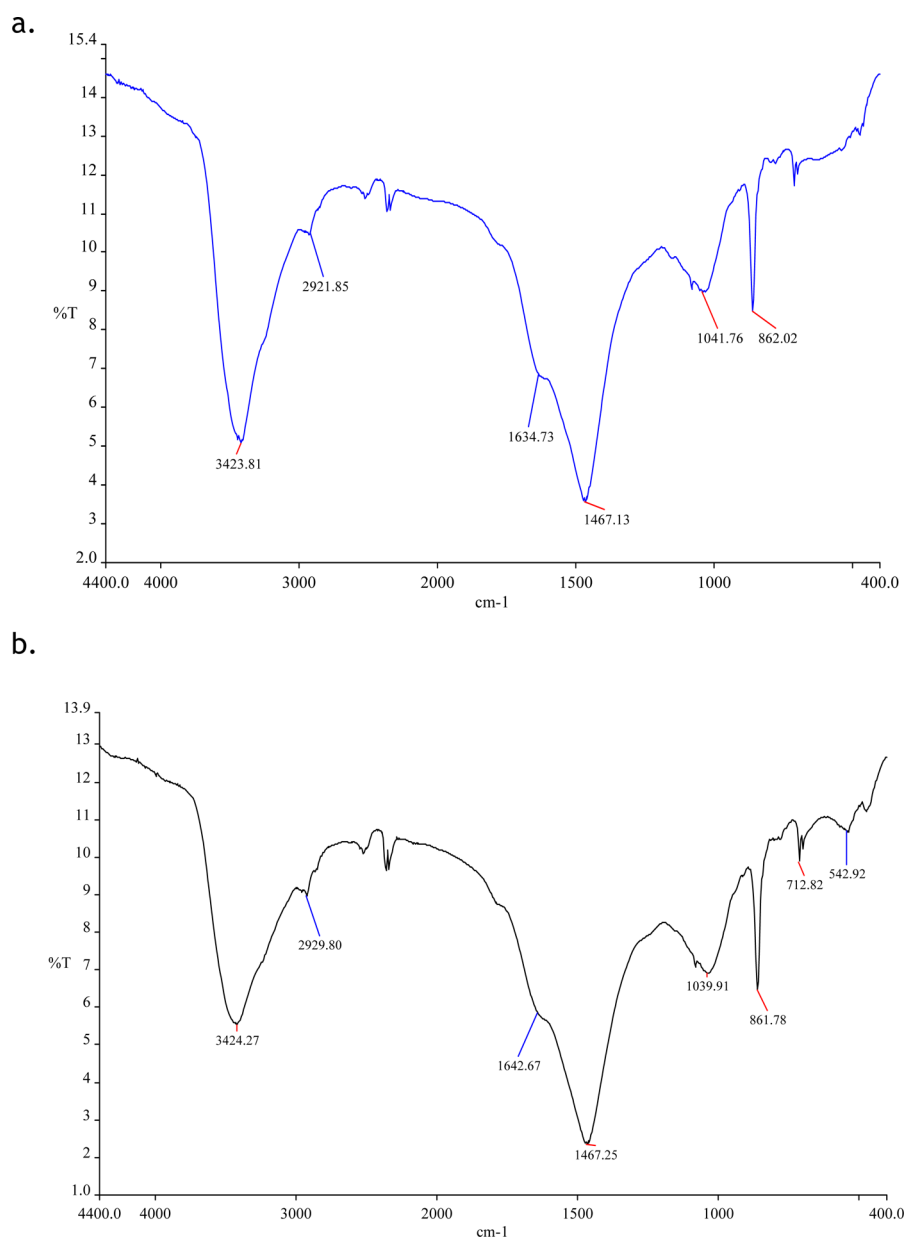


Figure 3. FTIR absorbance spectra of mussel shell dust (MSD) (a) before and (b) after biosorption of cadmium.

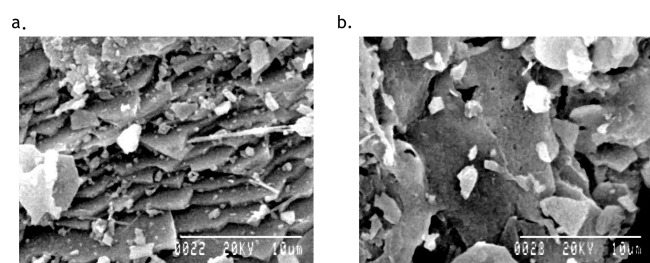


Figure 4. Scanning electron micrograph (SEM) of mussel shell dust (a) before and (b) after the biosorption of cadmium (magnification at 4000 \times).

from the solution. Thus, at 100 mg L⁻¹ metal ion concentration, the increase in the MSD amount resulted in increased metal ion adsorption up to the limit of 1000 mg L⁻¹ (of MSD), as used in the experiment (Figure 2c).

Effect of Contact Time. The sorption potentials of the MSD over time were monitored from 10 to 20, 40, 60, and 80 min by using 100 mL of 100 mg L⁻¹ Cd²⁺ at pH 6 (Figure 2d). In the initial time period, metal adsorption was less with more free binding sites being available. With an increase in the time period of interaction, the free sites became gradually saturated with metal resulting in increased adsorption. At the 10 min time interval, the lowest adsorption was noted that increased with time to saturate at 60 min, beyond which the metal uptake remained almost the same (Figure 2d). The variation in uptake of the cadmium ions with time were used in fitting the kinetic models.

FT-IR Study. In order to study the mechanism of cadmium removal and the main functional groups responsible for Cd²⁺ binding, FTIR spectroscopy of the MSD was performed. The IR spectra of protonated and cadmium-loaded MSD are shown in Figure 3a and b, respectively. The peak at 3424 cm⁻¹ indicates the presence of hydroxyl (-OH) groups. The strong

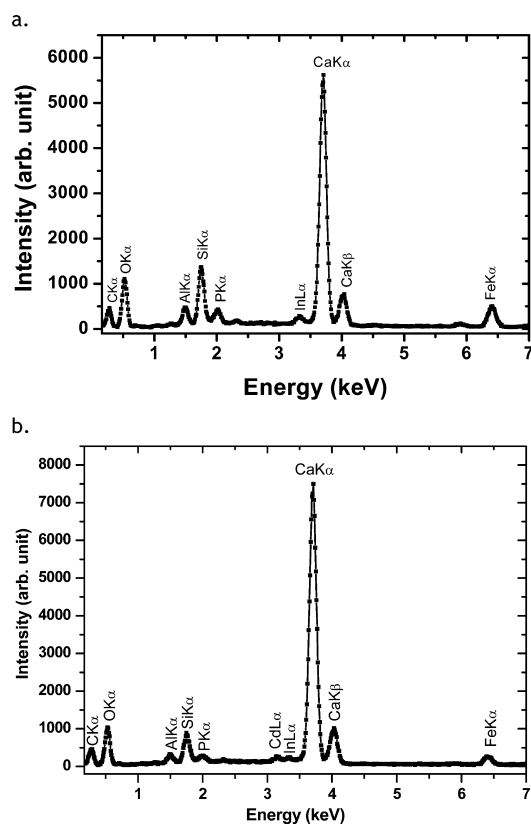


Figure 5. EDX spectra of the mussel shell dust (MSD) (a) before and (b) after cadmium biosorption.

band at 2921 cm^{-1} is due to the C–H stretching frequency, and the peak at 1634 cm^{-1} is due to the C=O stretching mode of the primary and secondary amides.²⁶ The weak band at 1462 cm^{-1} is attributed to the aromatic C=C, and the strong band at 1041 cm^{-1} is due to the C–O stretching of the alcoholic groups,²⁷ which is possibly linked to the degradation of the glycosylated proteins of the shell matrix.²⁸ The FTIR of metal-loaded MSD shows that a distinct shift of some bands and a change in intensity indicate the ion exchange behavior of MSD.

Scanning Electron Micrograph (SEM) and EDX Analyses. The surface structure of the free and cadmium-loaded MSD was analyzed under scanning electron microscope. The scanning electron micrographs of the dried MSD before and after the Cd^{2+} treatment at $4000\times$ magnification are shown in Figure 4a and b, respectively, reflecting irregular morphological structure of the particles and lamellar stratified surface of the MSD before adsorption. The SEM image of the MSD post-exposure to Cd^{2+} is characterized by a spongy layer indicating that surface precipitation occurred during the sorption.¹⁷ Cadmium sorption by a CaCO_3 compound generally follows surface precipitation because of similar ionic radii^{29,30} of the divalent calcium and cadmium.

The structure of the dust provides a large surface area for interaction with the cadmium ion of the solution. The elemental profile of the shell dust before and after the treatment of the cadmium solution was estimated using EDX analysis. The prominent peaks in the EDX spectra correspond to C K α , O K α , Al K α , Si K α , P K α , Ca K α , Ca K β , Fe K α , etc. in the untreated MSD and in addition a Cd L α peak in treated MSD (Figure 5a,b). Both the treated and untreated MSD showed strong peaks corresponding to calcium. The elemental

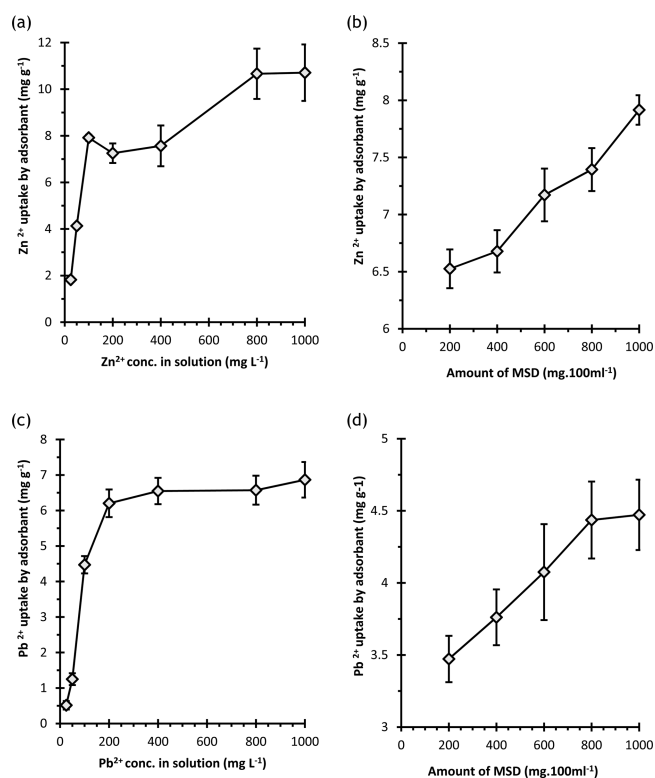


Figure 6. Biosorption of the metals zinc and lead. Effect of (a) initial zinc ion and (c) lead ion concentration of solution on biosorption on MSD at $30\text{ }^\circ\text{C}$, pH 6, contact time of 60 min, and biosorbent dose of 1 g of 100 mL^{-1} solution. Effect of biosorbent dose on biosorption of (b) zinc and (d) lead on MSD at $30\text{ }^\circ\text{C}$, pH 6, initial metal ion concentration of 100 mg L^{-1} , and contact time of 60 min.

profile of the treated MSD on EDX shows 1.68% of cadmium on weight basis that strongly suggests the adsorption of the heavy metal to the MSD (Table 1).

Comparative Study with Zinc and Lead. The adsorption of zinc and lead by MSD increased as a function of metal ion concentration. Similar to cadmium, the lowest adsorption was observed at 25 mg L^{-1} of metal ion concentration, while highest adsorption was observed at 800 mg L^{-1} concentration for zinc (Figure 6a) and at 1000 mg L^{-1} concentration for lead (Figure 6c). The biosorption potential of the MSD for both zinc and lead increased with an increase in the available amount of MSD (Figure 6b,d). Thus, at 100 mg L^{-1} metal ion concentration, an increase in metal adsorption was observed with a corresponding increase in the MSD amount up to the limit of 1000 mg L^{-1} for zinc and 800 mg L^{-1} for lead. Although the adsorption pattern seems to be lower than cadmium, nonetheless the result substantiates MSD as a potent biosorbent of a wide range of metals.

Adsorption Isotherm. The biosorption isotherm is important in wastewater treatment as it implies an estimation of the biosorption capacity of the adsorbent. The linear representations of the Langmuir and Freundlich isotherms of cadmium, zinc, and lead adsorption at $30\text{ }^\circ\text{C}$ are shown in Table 2. For all the metals, the values of the coefficient of determination are higher in the Langmuir equation compared to the Freundlich equation (Table 2), indicating that the Langmuir model is more suitable for describing the biosorption equilibrium of metals on the mussel shell dust. The q_{max} value for cadmium (18.18 mg g^{-1}) was higher than both zinc ($q_{\text{max}} =$

Table 2. Coefficients of Langmuir and Freundlich Isotherm Models for Cadmium, Zinc, and Lead Biosorption by MSD

linear equations and Langmuir constants	cadmium	zinc	lead
equation	$y = 0.055x + 0.933$	$y = 0.094x + 3.929$	$y = 0.124x + 18.80$
R^2	0.992	0.934	0.887
q_{\max} (mg g ⁻¹)	18.18	10.64	8.06
b (L mg ⁻¹)	0.06	0.02	0.01
equation	$y = 0.317x + 0.410$	$y = 0.248x + 0.722$	$y = 0.576x - 1.651$
R^2	0.660	0.647	0.667
n	3.16	4.03	1.74
k_F	1.51	2.06	0.19

Table 3. Comparative Data of Biosorption Capacities for Cadmium by Different Biosorbents

adsorbent	q_{\max}^a (mg g ⁻¹)	ref
olive waste	6.55	27
raw corn stalk	3.39	31
brewer's yeast	10.17	32
corn cob	4.73	33
rice straw	13.9	34
wheat bran	15.71	35
castor seed hull	6.98	36
walnut tree sawdust	5.76	37
bamboo charcoal	12.08	38
chitosan/bentonite	12.05	39
coconut copra meal	4.99	40
mussel shell dust (MSD)	18.18	Present study

^a q_{\max} : maximum metal uptake capacity.

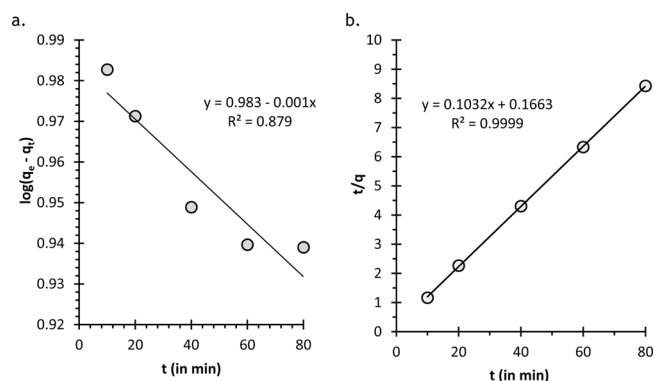


Figure 7. (a) Pseudo-first-order plot for biosorption of cadmium on MSD (pH 6, temperature 30 °C, biosorbent = 1 g, and cadmium ion concentration = 100 mg g⁻¹). (b) Pseudo-second-order plot for biosorption of cadmium on MSD (pH 6, temperature 30 °C, biosorbent = 1 g, and cadmium ion concentration = 100 mg/g).

10.64 mg g⁻¹) and lead ($q_{\max} = 8.06$ mg g⁻¹) (Table 2). The equilibrium models of cadmium biosorption support that under optimum conditions (pH 6, biosorbent dose of 1 g, Cd²⁺ concentration of 100 mg L⁻¹, and 60 min time period) 18.18 mg g⁻¹ is the maximum biosorption capacity of MSD. Maximum cadmium biosorption capacities of similar low cost

biosorbents are shown in Table 3. Although the materials of plant origin (Table 3) like rice husk, rice straw, and alike⁴¹ show the ability to adsorb metals, the potential risk of leaching of lignin, tannin, and other metabolites may cause unwanted interference with the food chain. In contrast, MSD is mainly composed of calcium carbonate, degradation of which, if any, will not yield unwanted compounds to the ecosystem. Artificially prepared composite materials^{12,42} are also useful for metal removal but are relatively less cost effective than MSD.

Biosorption Kinetics. The kinetic model is necessary for determination of the optimal condition of the biosorption process. For the evaluation of differences in the sorption process, the kinetics of metal uptake were described by the pseudo-first-order and pseudo-second-order models.²⁵ The linear plots obtained from the pseudo-first-order and pseudo-second-order models at 100 mg L⁻¹ initial Cd²⁺ concentrations, pH 6, and at 30 °C temperature are shown in Figure 7a and b, respectively. For the pseudo-first-order model, although the correlation coefficient ($r = -0.937$) was satisfactory (Figure 7a, Table 4), the calculated metal uptake (9.6 mg g⁻¹) and coefficient of determination ($r^2 = 0.879$) remained lower than the values obtained from the pseudo-second-order model (Figure 7b, Table 4). The higher correlation coefficient ($r = +0.999$) and coefficient of determination ($r^2 = 0.999$) and the calculated metal adsorption (9.8 mg g⁻¹) supported the compatibility of the biosorption process with the pseudo-second-order model.

CONCLUSION

The present work indicates that at pH 6, the maximum biosorption capacity (q_{\max}) of MSD is 18.18 mg g⁻¹ for cadmium, followed by 10.64 mg g⁻¹ for zinc and 8.64 mg g⁻¹ for lead. The elemental profile obtained through SEM-EDX analyses for cadmium revealed a clear peak of cadmium biosorption on MSD with exchange of Fe, Al, In, Si, and Ca ions. The main functional groups responsible for chelation were OH, C=O, C=C, and C-C, as supported by FTIR analysis. The cadmium biosorption process followed both pseudo-first-order ($r^2 = 0.879$) and pseudo-second-order ($r^2 = 0.999$) kinetics. The results indicate that MSD can be considered a low-cost and environment friendly biosorbent for metal bioremediation, especially for cadmium (Figure 8), opening a

Table 4. Comparison of Rate Constants and Equilibrium Metal Uptake for Cadmium Binding by MSD at pH 6 and Initial Metal Ion Concentration of 100 mg L⁻¹

metal	$q_{e \text{ exp}}$ (mg g ⁻¹)	first-order model			second-order model		
		k_1 (min ⁻¹)	$q_{e \text{ cal}}$ (mg g ⁻¹)	R^2	k_2 (g mg ⁻¹ min ⁻¹)	$q_{e \text{ cal}}$ (mg g ⁻¹)	R^2
cadmium	18.18	0.001	9.61	0.879	0.58	9.8	0.999

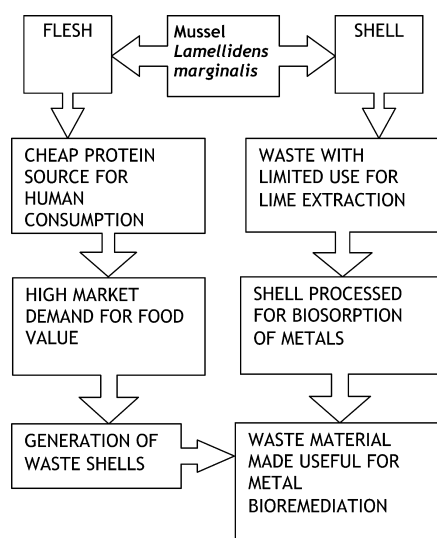


Figure 8. Economic value and uses of the freshwater mussel *Lamellidens marginalis*. The flesh is consumed as food, and its market demand generates shell as waste product with limited use in indigenous lime production. The processed shell (mussel shell dust, MSD), comprising mainly calcium carbonate, exhibits high potential for metal adsorption and therefore can be used for metal bioremediation. In the present study, cadmium metal adsorption by MSD has been demonstrated, justifying the use of waste shell dust in metal bioremediation.

new dimension of the economic value of the freshwater mussel *Lamellidens marginalis*, apart from being a cheap protein source.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +91-3422656566. Fax: +91-342-253045. E-mail: gautamaditya2001@gmail.com.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are grateful to the anonymous reviewers for their critical evaluation and suggestions that enhanced the manuscript to its present form. We express our gratitude and regards to Prof. David Allen for his kind cooperation and encouragement in revising the earlier version of the manuscript. We are thankful to the respective heads of the Department of Zoology, Department of Chemistry, and Department of Environmental Science, The University of Burdwan, Burdwan, India, for the facilities provided including DST-FIST. We acknowledge the instrumental facilities provided by SINP, Kolkata, India, and Department of Zoology, University of Calcutta, Kolkata, India. A.H. thankfully acknowledges the financial assistance provided by the Council of Scientific and Industrial Research (CSIR), New Delhi, India (Sanction 20-12/2009(ii)EU-IV, dated May 31, 2010).

REFERENCES

- (1) Bernard, A. Cadmium and its adverse effects on human health. *Indian J. Med. Res.* **2008**, *128*, 557–564.
- (2) Johri, N.; Jacquillet, G.; Unwin, R. Heavy metal poisoning: The effects of cadmium on the kidney. *Biometals* **2010**, *23*, 783–792.
- (3) Burger, J. Assessment and management of risk to wildlife from cadmium. *Sci. Total Environ.* **2008**, *389*, 37–45.

(4) Liu, Y.; Sun, C.; Xu, J.; Li, Y. The use of raw and acid pretreated bivalve mollusk to remove metals from aqueous solutions. *J. Hazard. Mater.* **2009**, *168*, 156–162.

(5) Gifford, S.; Dunstan, R. H.; O'Connor, W.; Koller, C. E.; MacFarlane, G. R. Aquatic zooremediation: Deploying animals to remediate contaminated aquatic environment. *Trends Biotechnol.* **2006**, *25*, 60–65.

(6) Hetzer, A.; Daughney, C. J.; Morgan, H. W. Cadmium Ion biosorption by the thermophilic bacteria *Geobacillus stearothermophilus* and *G. thermocatenulatus*. *Appl. Environ. Microbiol.* **2006**, *72*, 4020–4027.

(7) Vimala, R.; Das, N. Biosorption of cadmium(II) and lead(II) from aqueous solution by using mushrooms: a comparative study. *J. Hazard. Mater.* **2009**, *168*, 376–382.

(8) Gupta, V. K.; Rastogi, A. Biosorption of lead from aqueous solutions by green algae *Spirogyra* species: Kinetics and equilibrium studies. *J. Hazard. Mater.* **2008**, *152*, 407–414.

(9) Gupta, V. K.; Rastogi, A.; Nayak, A. Biosorption of nickel onto treated alga (*Oedogonium hatei*): Application of isotherm and kinetic models. *J. Colloid Interface Sci.* **2010**, *342*, 533–539.

(10) Sinha, R. K.; Herat, S.; Tandon, P. K. Phytoremediation: Role of Plants in Contaminated Site Management. In *Environmental Bioremediation Technologies*; Singh, N., Tripathi, R. D., Eds.; Springer, New York, 2007; pp 315–330.

(11) Krämer, U. Metal hyperaccumulation in plants. *Annu. Rev. Plant Biol.* **2010**, *61*, 517–534.

(12) Kamari, A.; Ngah, W. S. W. Isotherm, kinetic and thermodynamic studies of lead and copper uptake by H₂SO₄ modified chitosan. *Colloids Surf., B* **2009**, *73*, 257–266.

(13) Vijayaraghavan, K.; Palanivelu, K.; Velan, M. Biosorption of copper(II) and cobalt(II) from aqueous solutions by crab shell particles. *Bioresour. Technol.* **2006**, *97*, 1411–1419.

(14) Dahiya, S.; Tripathi, R. M.; Hegde, A. G. Biosorption of lead and copper from aqueous solutions by pre-treated crab and arca shell biomass. *Bioresour. Technol.* **2008**, *99*, 179–187.

(15) Pena-Rodriguez, S.; Fernandez-Calvino, D.; Novoa-Munoz, J. C.; Nunez-Delgado, A.; Fernandez-Sanjurjo, M. J.; Alvarez-Rodriguez, A. Kinetics of Hg (II) adsorption and desorption in calcined mussel shells. *J. Hazard. Mater.* **2010**, *180*, 622–627.

(16) Gifford, S.; Dunstan, R. H.; O'Connor, W.; Macfarlane, G. R. Quantification of in situ nutrient and heavy metal remediation by a small pearl oyster (*Pinctada imbricata*) farm at Port Stephens. *Australia. Mar. Pollut. Bull.* **2005**, *50*, 417–422.

(17) Du, Y.; Lian, F.; Zhu, L. Biosorption of divalent Pb, Cd, Zn on aragonite and calcite mollusk shells. *Environ. Pollut.* **2011**, *159*, 1763–1768.

(18) Du, Y.; Zhu, L.; Shan, G. Removal of Cd²⁺ from contaminated water by nano sized aragonite mollusk shell and the competition of coexisting metal ions. *J. Colloid Interface Sci.* **2012**, *367*, 378–382.

(19) Jana, B. B.; Das, S. Potential of freshwater mussel (*Lamellidens marginalis*) for cadmium clearance in a model system. *Ecol. Eng.* **1997**, *8*, 179–193.

(20) Sharma, M.; Kaushik, A.; Kaushik, C. P. Biosorption of reactive dye by waste biomass of *Nostoc lincia*. *Ecol. Eng.* **2011**, *37*, 1589–1594.

(21) Langmuir, I. The adsorption of gases on plane surface of glass, mica and platinum. *J. Am. Chem. Soc.* **1918**, *40*, 1361–1403.

(22) Freundlich, H. M. F. Über die adsorption in losungen. *Z. Phys. Chem.* **1906**, *57A*, 385–470.

(23) Witek-Krowiak, A.; Szafran, R. G.; Modelski, S. Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent. *Desalination* **2011**, *265*, 126–134.

(24) Lagergren, S.; Sven, K. Zur theorie der sogenannten adsorption gelöster stoffe. *Vetenskapsakad. Handl.* **1898**, *24*, 1–39.

(25) Ho, Y. S.; McKay, G. Pseudo-second order model for sorption process. *Process Biochem.* **1999**, *34*, 451–465.

(26) Reddy, H. K. D.; Seshiah, K.; Reddy, A. V. R.; Rao, M. M.; Wang, M. C. Biosorption of Pb²⁺ from aqueous solutions by *Moringa oleifera* bark: Equilibrium and kinetic studies. *Hazard. Mater.* **2010**, *174*, 831–838.

- (27) Blazquez, G.; Martin-Lara, M. A.; Tenorio, G.; Calero, M. Batch biosorption of lead (II) from aqueous solutions by olive tree pruning waste: equilibrium, kinetics and thermodynamic study. *Chem. Eng. J.* **2011**, *168*, 170–177.
- (28) De Paula, S. M.; Silveira, M. Studies on molluscan shells: Contributions from microscopic and analytical methods. *Micron* **2009**, *40*, 669–690.
- (29) Prieto, M.; Cubillas, P.; Fernandez-Gonzalez, A. Uptake of dissolved Cd by biogenic and abiogenic aragonite: a comparison with sorption onto calcite. *Geochim. Cosmochim. Acta* **2003**, *67*, 3859–3869.
- (30) Perez-Garrido, C.; Fernandez-Diaz, L.; Pina, C. M.; Prieto, M. In situ AFM observations of the interaction between calcite surfaces and Cd-bearing aqueous solutions. *Surf. Sci.* **2007**, *601*, 5499–5509.
- (31) Azouaou, N.; Sadaoui, Z.; Mokaddem, H. Removal of cadmium from aqueous solution by adsorption on vegetable wastes. *J. Appl. Sci.* **2008**, *8*, 4638–4643.
- (32) Cui, L.; Wu, G.; Jeong, T. Adsorption performance of nickel and cadmium ions onto brewer's yeast. *Can. J. Chem. Eng.* **2010**, *88*, 109–115.
- (33) Ramos, R. L.; Jacome, L. A. B.; Rodriguez, I. A. Adsorption of cadmium (II) from aqueous solution on natural and oxidized corncob. *Sep. Purif. Technol.* **2005**, *45*, 41–49.
- (34) Ding, Y.; Jing, D.; Gong, H.; Zhou, L.; Yang, X. Biosorption of aquatic cadmium (II) by unmodified rice straw. *Bioresour. Technol.* **2012**, *114*, 20–25.
- (35) Nouri, L.; Ghodbane, I.; Hamdaoui, O.; Chiha, M. Batch sorption dynamics and equilibrium for the removal of cadmium ions from aqueous phase using wheat bran. *J. Hazard. Mater.* **2007**, *149*, 115–125.
- (36) Sen, T. K.; Mohammad, M.; Maitra, S.; Dutta, B. K. Removal of Cadmium from aqueous solution using castor seed hull: A kinetic and equilibrium study. *Clean Soil Air Water* **2010**, *38*, 850–858.
- (37) Yasemin, B.; Zek, T. Removal of heavy metals from aqueous solution by sawdust adsorption. *J. Environ. Sci.* **2007**, *19*, 160–166.
- (38) Wang, F. Y.; Wang, H.; Ma, J. W. Adsorption of cadmium (II) ions from aqueous solution by a new low-cost adsorbent—Bamboo charcoal adsorption of cadmium (II) ions from aqueous solution by a new low-cost adsorbent—Bamboo charcoal. *J. Hazard. Mater.* **2010**, *177*, 300–306.
- (39) Arvand, M.; Pakseresht, M. A. Cadmium adsorption on modified chitosancoated bentonite: batch experimental studies. *J. Chem. Technol. Biotechnol.* **2012**, *88*, 572–578.
- (40) Ho, Y. S.; Ofomaja, A. E. Biosorption thermodynamics of cadmium on coconut copra meal as biosorbent. *BioChem. Eng. J.* **2006**, *30*, 117–123.
- (41) Gupta, V. K.; Jain, R.; Varshney, S. Removal of Reactofix golden yellow 3 RFN from aqueous solution using wheat husk—An agricultural waste. *J. Hazard. Mater.* **2007**, *142*, 443–448.
- (42) Saleh, T. A.; Gupta, V. K. Column with CNT/magnesium oxide composite for lead (II) removal from water. *Environ. Sci. Pollut. Res.* **2012**, *19*, 1224–1228.