Kinetic and Thermodynamic Studies on Biosorption of Zinc by Mango (*Mangifera indica*) Peel Powder from Metal Bearing Aqueous Solution

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Abstract

The ability of mango peel, a natural biosorbent, to remove zinc(II) ions from aqueous solution by the process of biosorption was investigated in the present study. The experiments were carried out by both batch and shake methods at temperature range of 25-45°C. The influence of initial zinc ion concentrations, initial biosorbent doses and contact times were evaluated for both unripe and ripe mango peel. Zinc ion removal increased significantly as the initial metal ion concentration increased from 0.5 mg/L to 5 mg/L. However, biosorption of zinc was more in batch processes in comparison to shake processes for both types of biosorbents. The equilibrium process was best described by the Langmuir isotherm model, with a maximum biosorption capacity of 3.23 mg/g biomass at 45°C. The biosorption was relatively quick (approx. 10 min). Biosorption kinetics followed a pseudo-first order model. The results indicated that mango peel was effective as a biosorbent for removing zinc ions from aqueous solution. Thus, it could be applied as a low cost material with potential biosorptive capacity in wastewater treatments for remediation of heavy metal contamination.

Keywords: Biosorption, zinc, mango peel, Langmuir, kinetics, thermodynamics.

Introduction

Heavy metals are natural components of the earth's crust which neither could be degraded nor destroyed (Duffus, 2002). In traces, these heavy metals are essential for living systems, including humans (Anwar *et al.*, 2009). Natural processes like volcanic activity and weathering of rocks release heavy metals continuously into the aquatic environment (Bansal *et al.*, 2009). However, almost all human activities have potential contribution to migration of heavy metals into non-contaminated areas as dust or leachates through the soil and spreading of heavy metals containing sewage sludge are examples of events contributing towards contamination of the ecosystems (Gaur and Adholeya, 2004). The enhanced concentration of heavy metals thus poses a significant threat to the environment and public health because of their toxicity, accumulation in the food chain and persistence in nature (Ashraf *et al.*, 2010). The toxicity of heavy metals to aquatic organisms has been a subject of interest to biologist for many years (Annadurai *et al.*, 2002). Toxic metals such as Cd, Zn, Cr, Pb, Mn and Cu find their ways to the surface waters from metal plating industries, nickel batteries, pigments and as stabilizers of alloys (Low and Lee, 1991). Over a few decades, several chemical methods have been devised for the treatment and removal of heavy metals. The commonly used procedures for removing metal ions from aqueous streams include chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction (Bhattacharyya *et al.*, 2002).

However, the disadvantages like incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require careful disposal has made these methods comparatively cost prohibitive for removing heavy metals from aqueous effluents (Ahalya *et al.*, 2003). Moreover, these processes are inapposite when the metal concentrations range between 1-100 mg/L (Basumajumdar *et al.*, 2004). Recent studies have shown that heavy metals can be removed using plant materials such an palm pressed fibers and coconut husk, water fern *Azolla filiculoidis*, peat moss, duck weed *Wolffia globosa*, lignocellulosic substrate extracted from wheat bran, *Rhizopus nigricans*, cork and yohimbe bark wastes and leaves of indigenous biomaterials, *Tridax procumbens*. Apart from the plant based materials, chemical modification of various adsorbents like phenol formaldehyde cationic matrices, polyethylonamide modified wood, sulphur containing modified silica gels and commercial activated charcoals also employed (Oboh *et al.*, 2009). Agricultural waste or by-products have been investigated for biosorption both in batch and continuous systems. Chemical treatment of such biomass and/or by-products could also improve their sorption ability (Sirilamduan *et al.*, 2011). The by-products from edible substances like banana peels would be excellent choice as biosorbent for metal removal from metal loaded waters as they are cheap sources to be utilized commercially (Abbasi *et al.*, 2013).

The goal of the present study is to decipher the ability of mango peels to remove zinc from solutions containing the metal ions. Zinc is a toxic metal at higher concentrations that is considered as secondary raw materials of batteries, which can be mixed with surface waters from the battery industry effluents (Ferella *et al.*, 2006). On the other hand, mango peels are usually discarded from the common households and have no as such commercial value. That is the reason for the choice of this material as biosorbent, probably for the first time in literature. The kinetic and thermodynamic parameters were studied both in batch processes and on shaking.

Materials and methods
Preparation of adsorbent: Fresh mango (*Mangifera indica*) peels were obtained from households of Burdwan district, West Bengal. These were washed with distilled water, followed by rinsing with deionized water and dried in an oven at 70°C for 48 to 72 h until a constant weight. The dried biomaterials were ground using domestic mixer and stored in airtight plastic bottles for further use as biosorbent without any chemical or physical treatment. Peels of both unripe and ripe mango were used in the present study and designated UMP and RMP respectively for the rest of the work.

Preparation of metal bearing solutions: A stock solution of zinc was prepared in deionized distilled water with analytical grade zinc (II) sulphate salt (Merck, India). All working solutions of varying concentrations were obtained by diluting the stock solution with distilled water. The pH of the solutions was adjusted to a pH of 4.5 to prevent hydrolysis. For the preparation of stock solutions with concentrations 100 mg/L of the metal, 439.6 mg $ZnSO_4.7H_2O$ was dissolved in 1000 mL water.

Time dependent biosorption study: The time-dependent batch and shake experiments were performed using a procedure reported previously with minor modifications (Ashraf *et al.*, 2011). The time intervals chosen for the time dependence studies were 5, 10, 20, 30, 60, 90 and 120 min. Metal concentrations of the treatment solutions were chosen to be 0.5, 2.5 and 5 mg/L. Speed of orbital shaker was kept at 200 rpm for the shake experiment. Temperature was set at 32 ± 2°C. This procedure was repeated in quadruplicate for the two biosorbents.

Dose dependent biosorption study: The biosorbent dose dependent batch and shake experiments were performed using a procedure reported previously with minor modifications (Ashraf *et al.*, 2011). The sorption of metals at biosorbent concentrations of 0.5 and 1 g were used. Time was already optimized and speed of orbital shaker was set at 200 rpm for the shake experiment. Metal concentrations of the treatment solutions were chosen to be 0.5, 2.5 and 5 mg/L. Temperature was set at 32 ± 2°C. This procedure was repeated in quadruplicate for the two biosorbents.

Temperature dependent biosorption study: Temperature dependent batch and shake experiments were performed using a procedure reported previously with some minor modifications (Hossain *et al.*, 2012). The temperatures chosen for the study were 25±2, 32±2, 37±2 and 45±2°C. Metal concentrations of the treatment solutions were chosen to be 0.5, 2.5 and 5 mg/L. Speed of orbital shaker was kept at 200 rpm for the shake experiment. This procedure was repeated in quadruplicate for the two biosorbents.

Estimation of zinc: Zinc was estimated with Zincon using formation of Zn^{2+}–Zincon complex following a published procedure with some modification (Sabel *et al.*, 2010). The treated solutions were mixed with borate buffer (50 mM, pH 9.0) containing urea (8 M) and Zincon (40 µM) solution. Following incubation at 22 ± 2°C for 5 min, the absorbance at 615 nm was recorded in a Systronics UV-Vis spectrophotometer (model–2202).

Statistical analysis: All the experiments were performed in quadruplicate and data were presented as mean of the four experimental values. The analyses were done with the software 'SPSS Statistics 17.0' (SPSS Inc. USA).

Results and discussion
Biosorption kinetics: In the present study, biosorption capacity to zinc was determined as a function against time to obtain the optimum contact time for the biosorption of UMP and RMP to the metal ions. Figure 1 and 2, respectively, shows the results of the biosorption equilibrium of zinc ions on UMP and RMP with time. It can be seen from the figures that the biosorption process is very fast and reaches equilibrium at about 10 min. Therefore, a total of 120 min of contact time was chosen as the biosorption time for the experimental test to ensure that equilibrium to be achieved. Adsorption is a multi-step process involving transport of the solute molecules from the aqueous phase to the surface of the solid particles followed by diffusion into the interior of the pores. In order to study the controlling mechanisms of the adsorption process, Lagergren's pseudo-first-order and Ho's pseudo-second order kinetic models were used to test the experimental data (Bahrami *et al.*, 2012). It was observed that the present data did not fit well to the equation for pseudo-second order kinetics (R^2= 0.914) was obtained and the theoretical value of q_e does not agree well with the experimental value, indicating that the biosorption does not conform to the pseudo-second order kinetics. We assume that the biosorption follow psudo-first order kinetics although the logarithmic graph could not be plotted with this data.

Biosorption isotherms: The amount of zinc absorbed at different equilibrium metal concentrations is given in Table 1. The results indicated that both peel powders were equi-active in removal of zinc ions from solutions.

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Table 1. Amounts of zinc absorbed (mg/g biomass) by mango peel powder at 32°C
at different equilibrium metal concentrations.

Process	Sample	Biosorbent dose (g/L)	Equilibrium metal concentration (mg/L)		
			0.5	2.5	5
Batch	UMP	0.5	0.31±0.07	1.44±0.16	2.71±0.12
		1.0	0.31±0.09	1.43±0.11	2.64±0.16
	RMP	0.5	0.29±0.05	1.07±0.15	2.24±0.15
		1.0	0.29±0.08	1.03±0.11	1.86±0.08
Shake	UMP	0.5	0.28±0.05	1.25±0.12	2.08±0.12
		1.0	0.23±0.07	1.04±0.14	1.87±0.15
	RMP	0.5	0.26±0.08	1.20±0.13	2.20±0.15
		1.0	0.22±0.06	1.15±0.11	1.93±0.10

Results are expressed as mean±SD of four values.

Fig. 1. Effect of contact time on zinc biosorption by UMP with adsorbent doses 0.5 g/L (a) and 1 g/L (b) [metal conc = 0.5, 2.5 and 5 mg/L; pH = 4.5; stirring speed = 200 rpm; temp = 32°C; (B) and (S) denotes batch and shake processes respectively].
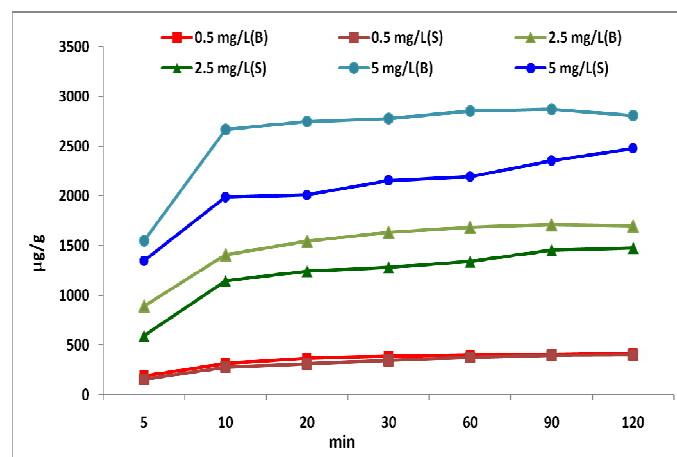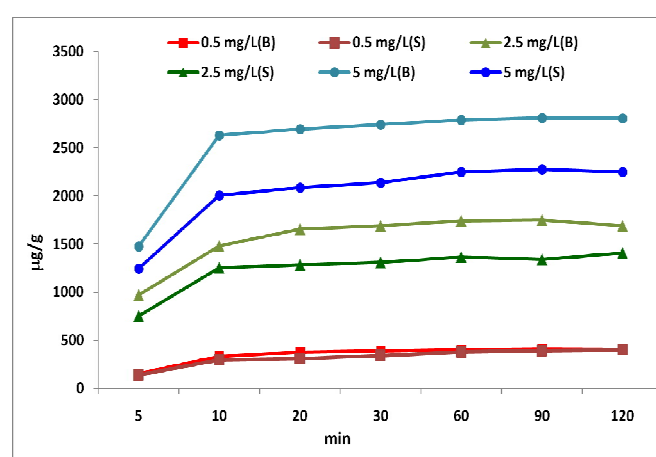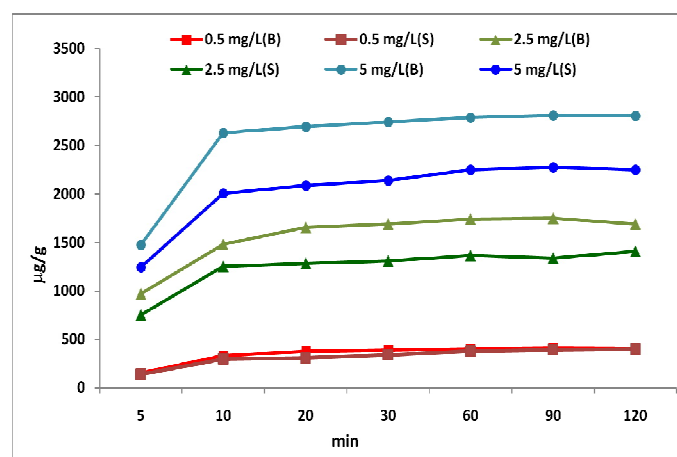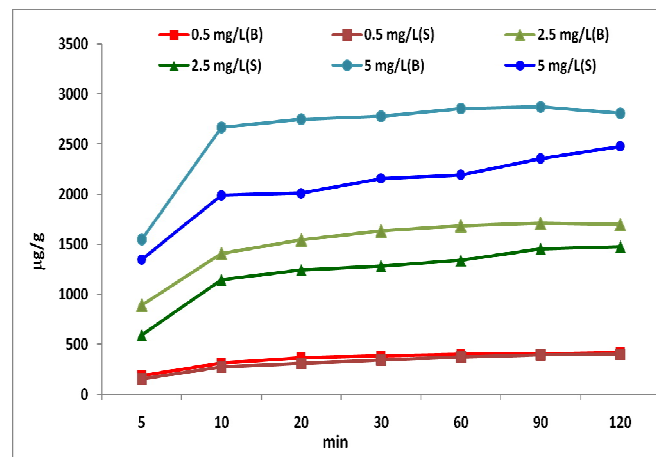
Fig. 2. Effect of contact time on zinc biosorption by RMP with adsorbent doses 0.5 g/L (a) and 1 g/L (b) [metal conc = 0.5, 2.5 and 5 mg/L; pH = 4.5; stirring speed = 200 rpm; temp = 32°C; (B) and (S) denotes batch and shake processes respectively].

However, efficiency of metal removal was greater in the batch process, probably due to very less mechanical stress in the process where the chance of losing metal ions from the surface is negligible. It can also be seen that the removal capacity decreased with increasing biosorbent dose. This might be due to less exposure of the surface for efficient adsorption at higher biosorbent dose, where there was a possibility of aggregation and clumping of the sorbents.

An adsorption isotherm depicts the fraction of sorbate molecules or ions that are partitioned between liquid and solid phases at equilibrium. Adsorption of zinc by UMP and RMP was described using two adsorption isotherms–Langmuir and Freundlich models. Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. Once a site is filled, no further sorption can take place at that site.

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Table 2. Regression coefficients of mango peel powder for zinc biosorption at 32°C at different equilibrium metal concentrations.

Process	Sample	Biosorbent dose (g/L)	Regression coefficient (R^2)	
			Langmuir	Freundlich
Batch	UMP	0.5	0.997	0.941
		1.0	0.998	0.944
	RMP	0.5	0.919	0.934
		1.0	0.930	0.937
Shake	UMP	0.5	0.982	0.924
		1.0	0.995	0.940
	RMP	0.5	0.951	0.939
		1.0	0.944	0.913

As such, the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved (Bahrami *et al.*, 2012). The amount of zinc adsorbed (q_e) at equilibrium metal concentrations of C$_e$ can be defined by the Langmuir equation as (Feng *et al.*, 2009):

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m}$$

Where, q_m is the maximum monolayer adsorption capacity of the biosorbent, and *b* is the Langmuir constant. The plot of C$_e$/q_e versus C$_e$ should be a straight line with slope of 1/q_m and intercept of 1/($q_m b$) when the biosorption follows the Langmuir equation. On the other hand, Freundlich isotherm is applicable to both monolayer (chemisorption) and multilayer adsorption (physisorption) and is based on the assumption that the adsorbate adsorbs onto the heterogeneous surface of an adsorbent (Yang, 1998). The amount of zinc adsorbed (q_e) at equilibrium metal concentrations of C$_e$ can be defined by the Freundlich equation as (Feng *et al.*, 2009):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

Where, K$_F$ and 1/*n* are Freundlich isotherm constants related to biosorption capacity and intensity of biosorption, respectively. The plot of log q_e versus log C$_e$ should be a straight line with slope of 1/*n* and intercept of log K$_F$ if the biosorption follows Freundlich model. The regression coefficients for Langmuir and Freundlich models are listed in Table 2. It was observed that the equilibrium data for UMP agreed well with the Langmuir model, exemplifying that the biosorption of zinc on the surface was a monolayer biosorption. However, for RMP, the regression coefficients were less for both the models indicating non-linearity in both the systems. This might be due to difference in the chemical character of the surface functional groups present in RMP.

Biosorption thermodynamics: In order to describe thermodynamic behavior of the biosorption of zinc ions on UMP and RMP from metal bearing aqueous solutions, changes in Gibb's free energy (ΔG^o) as the thermodynamic parameter were calculated according to the following equation (Feng *et al.*, 2009):

$$ΔG^o = - RT \ln K_D$$

Where, *R* is the gas constant, *R* = 8.314 J mol^{-1} K^{-1}; *T* is the thermodynamic temperature (in K) and K$_D$ is the distribution coefficient. Again, K$_D$ can be calculated by the following relation:

$$K_D = \frac{q_e}{C_e}$$

Where q_e is the biosorption capacity at equilibrium and C$_e$ is the equilibrium metal ion concentration in the metal bearing solution. It has been observed that changes in ΔG^o were calculated to be −371.64, −1166.45, −2319.61 and −4018.66 KJ mol^{-1} for zinc biosorption at temperatures 25, 32, 37 and 45°C for UMP dose of 0.5 g and metal concentrations of 0.5 mg/L. The ΔG^o values became −322.08, −735.37, −1314.44 and −3542.76 KJ mol^{-1} for RMP. The negative ΔG^o values indicated thermodynamically favorable and spontaneous nature of the zinc biosorption by the mango peels. However, at higher initial metal concentrations, the ΔG^o values were calculated to be positive, which indicated that the process would not be spontaneous at higher metal ion concentrations. Also increase in negative ΔG^o values with increasing temperature indicated that the process would be feasible at higher temperatures. The data also indicated that UMP was better than RMP regarding ability of biosorption of zinc from metal bearing solutions.

Conclusion
The present study lent credence to the fact that a waste material like mango peel, in powdery form, could be a potential candidate for removal of zinc ions from metal bearing solution containing zinc at concentration ranges of 0.5 mg/L to 5 mg/L. The biosorbent has high metal removing capacity, which ranged up to 3 mg/g biomass at a metal concentration of 5 mg/L. Biosorption kinetic is found to fit best in the equation for pseudo-first order kinetics. The biosorption equilibrium data fit well to the Langmuir isotherm for unripe mango peel. The maximum biosorption capacity is found to be 3.23 mg/g biomass at 45°C. Batch processes were found to be more effective than the shake processes. The thermodynamic calculation indicates the feasibility, exothermic and spontaneous nature of the biosorption of Zn(II) ions at temperature range of 25-45°C.

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