Kinetic and Thermodynamic studies for Cadmium (II) biosorption from aqueous solutions using *sea urchin test*

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Abstract: Since biosorption is a low cost and effective method for treating metal-bearing wastewaters, understanding the process kinetics is important for design purposes. In the present study, the performance of the *sea urchin test* for removing cadmium from synthetic metal bearing aqueous solutions has been evaluated. Pseudo-first-order, pseudo-second-order, were fitted to the experimental data and the results showed that the data well fitted to the pseudo second order rate equation (R^2 = 0.99) and the estimated metal uptake is approximately equal to the experimental value. Intraparticle diffusion model and Boyd models are used to evaluate the rate controlling mechanism. Thermodynamic parameters such as standard Gibbs free energy (ΔG^0), standard enthalpy (ΔH^0) and standard entropy (ΔS^0) were evaluated. The result showed that bio sorption of cadmium (II) ions onto *sea urchin test* was spontaneous and exothermic nature.

Key Wards: Biosorption, Cadmium (II), *sea urchin test*, kinetics, thermodynamics.

1. Introduction

Because of the Industrial Revolution, the processing of natural resources increased which ultimately lead to accumulation of heavy metals in the aqueous environment. Today, two hundred and fifty years later, in the Metal Removal Age, we are all too aware of the risks inherent to the uncontrolled dissemination of heavy metals in the environment. The metals that are of greatest concern are those that, by either their presence or their accumulation, can have a toxic or an inhibitory effect on living beings [1]. If directly discharged into the sewage system, they may seriously damage the operation of sewage processes, as well as make the biological sludge unsuitable for application to agricultural land

Cadmium is the one of the most common toxic metals found in industrial effluents. The toxic effects of cadmium in human were first reported in Japan in the 1950s where the municipal sewage sludge was used as a fertilizer to the rice crop [2].Cadmium enters into water bodies through discharge of waste effluents from various industries like, metal plating industries, industries of Cd–Ni batteries, phosphate fertilizer, mining, pigments, stabilizers and alloys [3]. Exposures to Cadmium causes sever health effects viz. renal dysfunction, liver damage, bone degradation and hypertension in human [4]. Cadmium is a potent neuro toxic metal and permissible limit for cadmium in drinking water is 0.003 mg/L [5]. Due to this cadmium has been included in red list of priority pollutants by Department of Environment, UK [6] and in List I (the ''black list") of Directive 76/464/EEC [7]. USEPA has also classified cadmium as group B1 carcinogen [8]. So, removal of this metal from water and wastewater is the concern of the day.

There are several methods such as chemical precipitation, chemical oxidation or reduction, filtration, electrochemical treatment, application of membrane technology, evaporation recovery, solvent extraction and

ion-exchange processes, have been traditionally employed for heavy metal removal from industrial wastewater. However, these techniques are ineffective and expensive, especially when the metal ions are at low concentrations (around 1–100 mg/l) [9]. Therefore there is a need for the development of economical, effective and zero sludge methods for removal of cadmium from wastewater and potable water.

In the last few years, biosorption has been shown to be an economically feasible alternative method for removing trace metal from wastewater and water supplies. Biosorption is the removal of materials (compounds, metal ions, etc.) by inactive, non-living biomass (materials of biological origin) due to ''high attractive forces'' present between the two [10]. Living as well as dead (metabolically inactive) biological materials have been sought to remove metal ions. It was found that various functional groups present on the surface of the cell wall offer certain forces of attractions to adsorb the metal ions on to the surface of the biosorbent. Different plant-and-microorganism-derived materials[11] have been used for metal removal, such as sawdust [12] and other plant residue [13,14], yeast [15,16], inactivated bacteria [17], fungus [18], algae [19],fresh water algae [20] and aquatic plants and seaweed [21,22]. Volesky has shared his views about the biosorption process in his recent review [23], he stated that currently biosorption of metals' is only the 'tip of the ice-berg' and in future, it must focus on utilization for purification and recovery of high valued products.

Literature search on biosorption using non living species suggests the following advantages over other traditional metal removal techniques. The materials can be found easily as wastes or by-products and at almost no cost, no need of growth media, independent of physiological constraints of living cells, process is very rapid because non-living material behaves as an ion exchange resin, metal loading is very high, no aseptic conditions required, process is reversible and metal can be desorbed easily thus recycling of the materials is quite possible [24].

Biosorption using living specimens [25-27] and their derivatives may cause biological invasion or secondary pollution thereby hindering the ecosystem functions and also increase the cost of the overall wastewater treatment process. However earlier studies suggest that unlike other approaches, calcium carbonate derivatives may be a potential cost-effective biosorbent for removal of heavy metals [28, 29]. Shells of the *sea urchins* can be considered as a cheap source of calcium carbonate. The sea urchins are found across the ocean floors worldwide, and sea urchin tests amass as waste at seashore. Thus *sea urchins test* can be considered as biosorbent. To asses this hypotheses the present study aimed at evaluation of metal biosorbent capacity of the shell dust of the *sea urchins* using cadmium as a model metal.

The present work aimed on the investigation of the kinetics and thermodynamic parameters of the biosorption of Cd(II) ions from aqueous solution using sea urchin test as biomass. Experimental parameters affecting the biosorption process such as pH, contact time, biomass dosage and temperature were studied but the results were not discussed in this paper. The kinetics experiment data is analyzed using Pseudo-first-order, pseudo-second-order, intraparticle diffusion model, Boyd models and Elovich equation. The biosorption mechanism was also studied in terms of thermodynamics.

2. Materials and Methods

2.1. Preparation of biosorbent

Purple *sea urchins* are collected from the nearby beach area and cleaned well with fresh water. The spines and the flesh were removed and each test is broken into two halves and dried to about a day in the sunlight. The remaining flesh and organic matter if any adhered to the test surface was also removed. The test pieces are again cleaned with tap water first thoroughly and again with distilled water in order to neutralize the traces of salinity if any in the laboratory. These test pieces were allowed to dry in open air at room temperature and powdered using ball mill. The test powder is graded by using BSS sieve set to get the required average size for using as an adsorbent.

2.2. Chemicals

A stock solution of Cadmium of 1000 mg L^{-1} was prepared in double distilled water and working solutions were prepared by appropriate dilution. The pH of the solution was adjusted by adding HNO_3 (0.1 N) and NaOH (0.1 N). All the inorganic chemicals that have been used in these experiments were purchased from Merck India Ltd., India. All the experiments were repeated four times and the average values have been reported. Also, blank experiments were conducted to ensure that no biosorption was taking place on the walls of the apparatus used.

2.3. Experimental procedure

The batch biosorption experiments were performed in 250 mL Erlenmeyer's flask that contained 30 mL solution of a particular cadmium ion concentration at required pH and relevant amount of *sea urchin test* powder. The flasks were sealed with wax paper and shaken in a shaking incubator (Lab Companion, SI-300R, India) at 150 rpm with appropriate time and temperature. After shaking for a particular time period, the solution of the flasks was filtered using Whatman 42 filter paper (Sigma–Aldrich, UK) for estimation of metal concentration by atomic absorption spectroscopy (GBC Avanta Ver 1.32, Australia). The effect of contact times between solution and the *sea urchin test* powder were monitored by varying it from 10 to 80 min at optimum pH the same data is used for kinetic analysis. For thermodynamic studies equilibrium experiments were conducted at different temperature like 20, 30, 40, 50⁰C. The amount of Cadmium ions adsorbed on the *sea urchin test* was estimated following the equation.

$$q_e = (C_0 - C_f) X \frac{V}{M} \qquad (1)$$

where q_e = amount of metal adsorbed (mg g^{-1}), v = volume of solution (mL), M = mass of adsorbent in (g), C_o = initial concentration of the solution (mg L^{-1}) and C_f = equilibrium concentration of the solution (mg L^{-1}).

3. Results and discussion

3.1. Kinetic modelling

3.1.1 The Pseudo First-Order Lagergren Equation

The pseudo-first order model in adsorption was proposed by Lagergren. It describes 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. Lagergren equation [30] or pseudo-first order reaction is mathematically expressed as

$$\frac{dq}{dt} = k_1(q_e - q_t) \qquad (2)$$

where q_e is the amount of metal ion adsorbed on biosorbent at equilibrium (mg g^{-1}), q_t the amount of metal ion adsorbed on biosorbent at time 't' (mg g^{-1}) and k_l is Lagergren constant (min^{-1}). Integrating the above equation and transforming to log scale

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (3)$$

Linear plot of log(q_e – q_t) against time indicates whether this kinetic model is applicable or not for biosorption process.

3.1.2 The Pseudo-Second Order Equation

The pseudo-second order equation in this case as described by Ho [31] is

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

or

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{t}{q_e}\right) \qquad (4)$$

Where q_e = amount of adsorbed metal ion on biosorbent at equilibrium (mg g^{-1}), q_t = amount of adsorbed metal ion (mg g^{-1}) on biosorbent at time't', k_2 = second order rate constant (g mg^{-1} min^{-1}). A linear plot of t/q vs. t indicates whether this model of biosorption is applicable for this case or not.

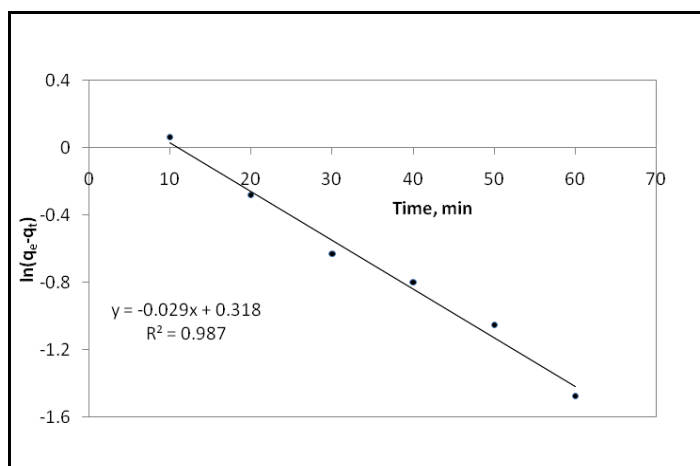**Fig. 1: pseudo first order biosorption of Cd(II) by** *sea urchin test* **for 20 mg/L of metal and 0.1 g/ 30 ml of biomass concentrations.**
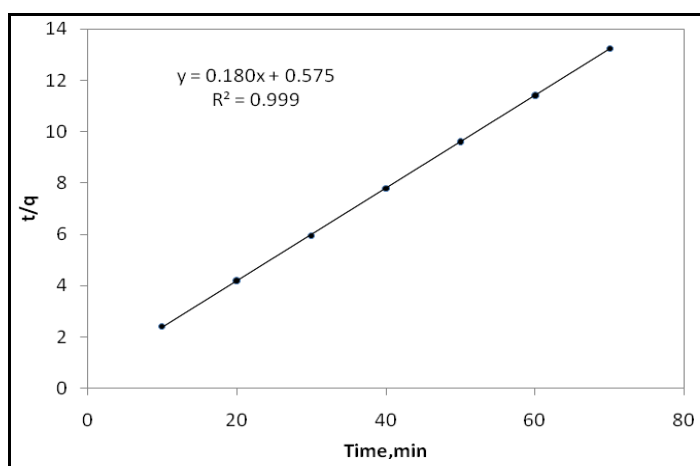

Fig. 2: pseudo second order biosorption of Cd(II) by *sea urchin test* **for 20 mg/L of metal and 0.1 g/ 30 ml of biomass concentrations**.

Table.1: Adsorption rate constants, q_e **estimated and coefficient of correlation associated to the Lagergren pseudo-first and second-order adsorption for the** *Sea urchin test* **biomass**

Metal	$q_{e\ exp}$ (mgg^{-1})	Pseudo first order model			Pseudo second order model		
		$k_1(min^{-1})$	$q_{e\ cal}$ (mgg^{-1})	R^2	$k_1(min^{-1})$	$q_{e\ cal}$ (mgg^{-1})	R^2
Cadmium	5.287	0.029	1.246	0.987	0.05634	5.55	0.999

The results of kinetic parameters are shown in Table 1. The validity of each model was checked by the fitness of the straight lines (R^2 values). The q_e (cal) values calculated from pseudo-first-order kinetic model differed significantly from the experimental values. However, in the pseudo-second-order kinetic model the calculated q_e (cal) is very close to q_e (exp). Further, the values of correlation coefficients (R^2) of pseudo-first-order model were less than pseudo- second-order model indicating that the pseudo-second order is better obeyed than the pseudo-first-order model.
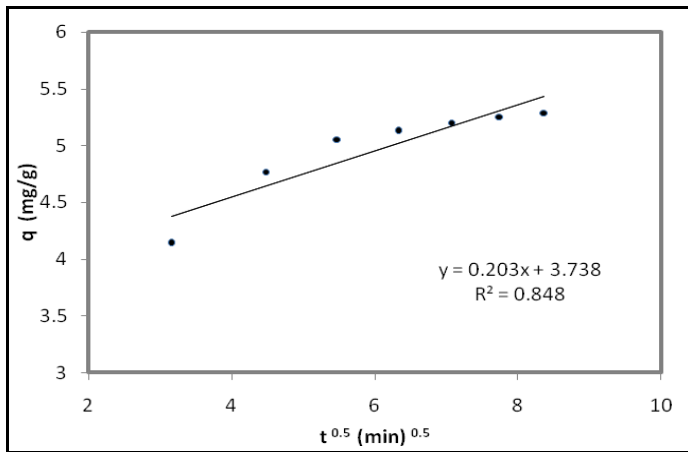
3.1.3 Intra-particle diffusion model

Fig. 3: Intra particle diffusion model for biosorption of Cd(II) by *sea urchin test* for 20 mg/L of metal and 0.1 g/ 30 ml of biomass concentrations.

The intra-particle diffusion model is used to investigate the diffusion controlled adsorption system. The probability of the intra-particle diffusion was explored by using the following equation [32]:

$$q_t = k_{id}t^{1/2} + C \qquad (5)$$

where q_t (mg g⁻1) is the adsorption capacity at any time t (min), k_{id} is the intraparticle diffusion rate constant (mg g⁻1 min1/2), C is the value of intercept which gives an idea about the boundary layer thickness, i.e., the larger intercept; the greater is the boundary effect. The plot of q_t vs. the squareroot of time obtained for the adsorption of Cd(II) onto *sea urchin test* is shown in fig. 3. The intraparticle rate constant k_{id} is 0.203(mg g⁻1 min1/2) and intercept C is 3.738. The plot is not linear over the whole time range, indicating that more than one step is involved in the adsorption of metal ions. If the intra-particle diffusion is the only rate-controlling step then the plot should pass through the origin, else the boundary layer diffusion affects the adsorption to some degree. The linear curve is deviated from the origin or near saturation because of the differences in the mass transfer rate in the initial and final stages of adsorption. The plot is not passing through origin indicating that the intra particle diffusion is not the only rate determining factor.
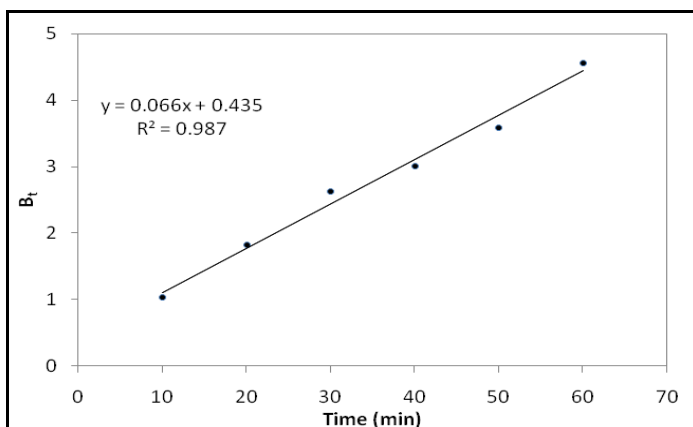
3.1.4 Boyd model

Fig. 4: Boyd model for biosorption of Cd(II) by *sea urchin test* for 20 mg/L of metal and 0.1 g/ 30 ml of biomass concentrations.

Boyd model is applied to check whether sorption proceeds via film diffusion or intraparticle diffusion mechanism. The model can be expressed in the following form [33]:

$$F = \left(1 - \frac{6}{\pi^2}\right)exp(-B_t) \qquad (6)$$

where F= q_t/q_e; q_e is the amount of metal ions adsorbed at equilibrium (mg g^{-1}), q_t represents the amount of ions adsorbed at any time t (min) and B_t is a mathematical function of F. Eq. (12) can be rearranged by taking the natural logarithm to obtain the equation:

$$B_t = -0.4977 - \ln(1 - F) \qquad (7)$$

The plot of B_t vs. t is shown in fig. 4, which is linear with the correlation coefficient (R^2) is 0.987. The results suggest that the adsorption process is controlled by film diffusion.

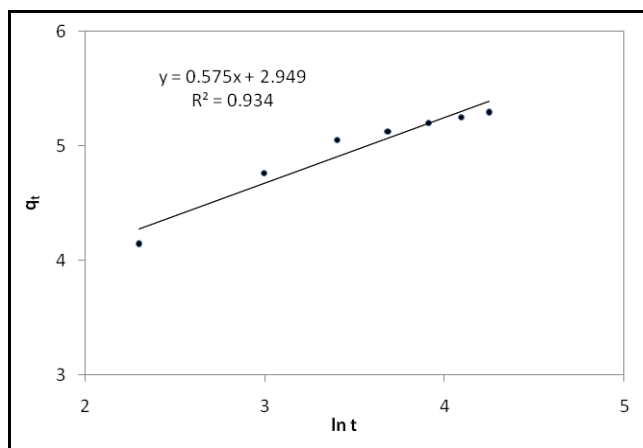### 3.1.5 The Elovich Rate Equation

Fig. 5: Elovich model for biosorption of Cd(II) by *sea urchin test* for 20 mg/L of metal and 0.1 g/ 30 ml of biomass concentrations.

The Elovich equation has been applied satisfactorily to some chemisorption processes. The Elovich equation can be written in the following form [34]:

$$q_t = \left(\frac{1}{b}\right)\ln(ab) + \frac{1}{b}\ln t \qquad (8)$$

where a (mg g^{-1} min^{-1}) is the initial sorption rate and b (g mg^{-1}) is the desorption constant related to the extent of surface coverage and activation energy for chemisorption. The parameters (1/b) and (1/b) ln(ab) can be obtained from the slope and intercept of the linear plot of q_t vs. lnt (fig.5). The plot is linear with good correlation coefficient (R^2) of 0.934. This suggests that the sorption process follows the pseudo-second-order kinetic model based on the assumption that the rate determining step may be chemisorption, involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate.
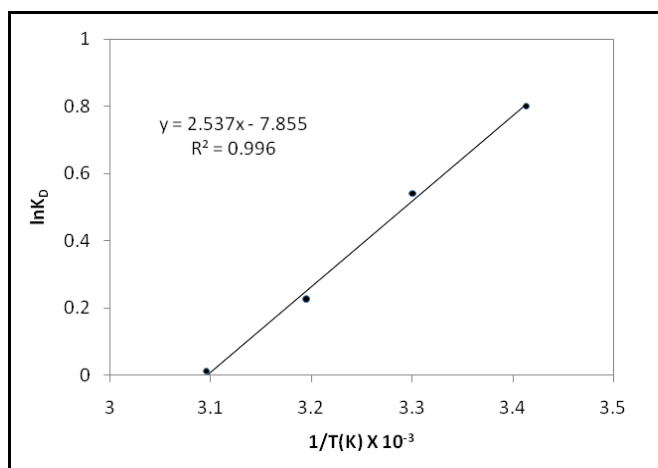

Fig. 6: Plot of ln(K_D) vs. 1/T for the estimation of thermodynamic parameters for biosorption of Cd(II) onto *sea urchin test* biomass.

**Table.2: Thermodynamic parameters for the biosorption of cadmium on *Sea urchin test*
biomass at different temperatures**

T(^{0}C)	ΔG^0(kJ/mol)	ΔH^0(kJ/mol)	ΔS^0(kJ/mol K)	R^2
20	-1.94849			
30	-1.35853	-21.0926	-65.306	0.996
40	-0.58649			
50	-0.02988			

3.2. Biosorption thermodynamics

In the environmental engineering practice, thermodynamic parameters including standard enthalpy change (ΔH), standard entropy change (ΔS) and standard free energy change (ΔG) should be considered in order to determine if the biosorption will occur spontaneously. Thus, (ΔH) and (ΔS) were obtained from the Van't Hoff equation:

$$\ln(K_D) = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{9}$$

Where, ΔS^0 and ΔH^0 were calculated from the slope and intercept of linear plot of log Kc versus 1/T. Equilibrium constant (K_D) [35] is calculated from the following relationship:

$$K_D = \frac{q_e}{C_e} \tag{10}$$

where, q_e and C_e are the equilibrium concentrations of metal (mg/L) on adsorbent and in solution, respectively. The very useful relationship between standard free energy change and equilibrium constant is given by the following equation:

$$\Delta G^o = -RT \ln K_D \tag{11}$$

Where, T (K) is the absolute temperature, R (8.3145 J/mol K) gas constant, ΔG^o is the standard free energy change. The values of ΔS^0 and ΔH^0 were calculated from the slope and intercept of linear plot of log Kc versus 1/T shown in fig.6. The decrease in ΔG^o values with increase in temperature shows a decrease in feasibility of biosorption at higher temperatures. The enthalpy of biosorption (ΔH^o) as shown in Table.2 was found to be −21.0926 kJ/mol. The negative ΔH^o is indicator of exothermic nature of the biosorption and also its magnitude gives information on the type of biosorption, which can be either physical or chemical. The enthalpy value (−21.0926 kJ/mol) indicated that the biosorption process of Cd(II) ions onto *sea urchin test* biomass proceeded chemically because it falls into the 20.9–418.4 kJ/mol(Deng et al., 2007). The ΔS^0 parameter was found to be −65.306 J/mol K for Cd(II) biosorption. The negative ΔS^0 value suggests a decrease in the randomness at the solid/solution interface during the biosorption process.

4. Conclusions

This study focused on the kinetics of the biosorption of Cd(II) ions onto *sea urchin* biomass from aqueous solution and thermodynamic parameters. Kinetic examination of the equilibrium data showed that the biosorption of Cd(II) ions onto *sea urchin* followed well the pseudo-second-order kinetic model. From the Boyed model analysis it can be concluded that the film diffusion is the rate controlling step and from the Elovich equation, sorption of Cd(II) ions onto the surface of *sea urchin test* is by chemisorptions. The thermodynamic calculations indicated the feasibility, exothermic and spontaneous nature of the biosorption process at 293–333^0 K. Based on results, it can be concluded that the *sea urchin* is an effective and alternative biomass for the removal of Cd(II) ions from aqueous solution because of its considerable biosorption capacity, being of natural, renewable and thus cost-effective biomass.

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