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Research Article

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Biosorption of cadmium (II) from aqueous solutions using *sea urchin test* as biosorbent

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ABSTRACT

Biosorption of cadmium (II) ions from aqueous solution onto sea urchin test was investigated in a batch system. Equilibrium, kinetic and thermodynamic studies were conducted by considering the effects of pH, contact time, initial cadmium (II) concentration, biomass loading and temperature. Results showed that the uptake of cadmium (II) ions increased with the increase of pH and biomass loading and decreased with increase of initial cadmium (II) concentration and temperature. Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models were used to analyze the equilibrium data. Langmuir isotherm model described the experimental data well followed by Dubinin–Radushkevich and Freundlich isotherm models. The maximum biosorption capacity (q_{max}) is 11.904mg/g at the optimum biosorption conditions.

Key words: Biosorption, Cadmium (II), *sea urchin test*, isotherm, Langmuir, Freundlich

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INTRODUCTION

Pollution of the aquatic environment by the presence of heavy metals is an issue of great concern. Industrial waste water often contains considerable amount of heavy metals and organic pollutants that should jeopardize the aquatic environment and public health if discharged without proper treatment. The removal of these metal ions from drinking water is a real challenge due to their trace quantities, formation of complexes with natural organic matter and toxic even at very low concentrations [1]. Pragmatic evidences propose that the metals like cadmium, chromium, copper, zinc, mercury, lead and alike, enters into the water bodies through discharge of several industrial wastes.

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

Considerable research has been carried out in developing cost-effective heavy metal removal techniques. Physicochemical 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.

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], and aquatic plants and seaweed [20,21]. Volesky has shared his views about the biosorption process in his recent review [22], 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.

Research in biosorption using non living species suggests the following advantages over other conventional metal removal techniques. The materials can be found easily as wastes or by-products and at almost no cost, no need of costly 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 [23].

Application of living specimens [24-26] and their derivatives for removal of heavy metals may cause biological invasion or secondary pollution thereby hindering the ecosystem functions. Microorganism-based and other biomasses often need to be cultured and/or tediously processed before application as biosorbent of metal ions [11]. This would 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 [27, 28]. 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 potential of the *sea urchin test* biomass for removal of Cd(II) ions from aqueous solution. Experimental parameters affecting the biosorption process such as pH, contact time, biomass dosage and temperature were studied. The equilibrium biosorption data were evaluated by Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models. The biosorption mechanism was also studied in terms of kinetics and thermodynamics.

EXPERIMENTAL SECTION

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 influence of pH of the solution on biosorption equilibrium was studied after changing the pH of the solution in a range of 2–7. 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. For equilibrium studies five different metal ion concentrations between 20 and 100 mg $L^{-}1$ were used, while, for optimum biosorption study, the *sea urchin test* biomass was varied between 0.1 and 0.5 mg. The amount of Cadmium ions adsorbed on the *sea urchin test* was estimated following the equation [9].

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

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}).

RESULTS AND DISCUSSION

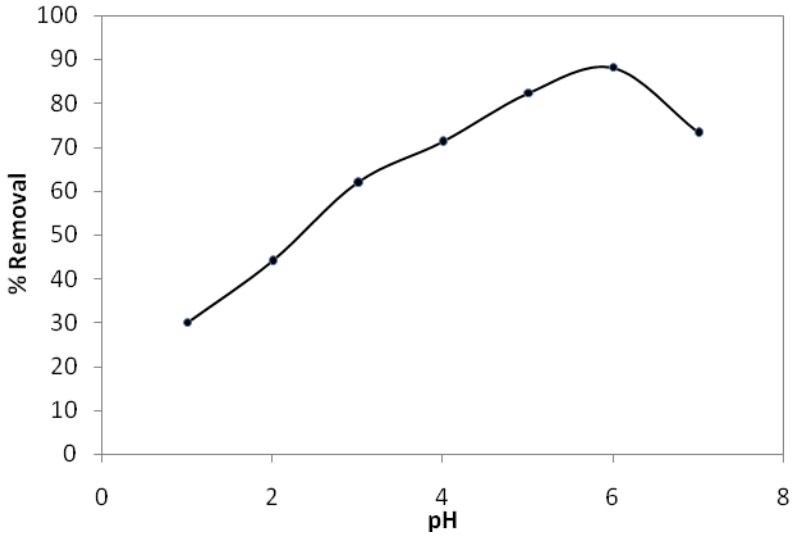

Fig. 1: Effect of pH on Cd(II) removal by *sea urchin test* for 20mg/L. metal and 0.1 g/30 mL. of adsorbent concentrations

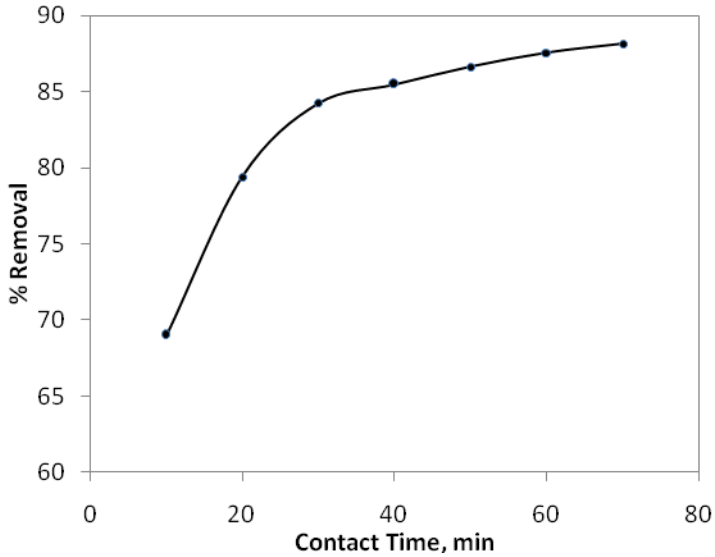

Fig. 2: Effect of contact time on removal of Cd(II) by *sea urchin test* for 20mg/L of metal concentration and 0.1g/30mL of adsorbent concentration at pH of 6

4.1. Effect of pH of the solution

Biosorption will be affected by the pH of the medium in two ways – metal solubility and total charge of the functional groups of the biosorbent. The biosorption procedure was maintained over a range of pH 2–7. The experiments were carried out using 30 mL solution of 20mg L^{-1} Cd^{2+} and 100 mg of the *sea urchin test* at 25^0C in

reference to varying pH of the solution. The optimum pH, at which the metal removal is highest for the biosorbent was estimated. At high pH precipitation of the metal was observed. At low pH, possibly due to high protonation, metal sorption capacity decreased. As shown in the fig. 1 the pH dependent adsorption of the metal ion by *sea urchin test* indicated that the metal sorption was negligible at pH 2, which increased with increase in pH. At pH 6, highest adsorption was observed that declined with further increase in pH of the solution.

4.2. Effect of contact time

The sorption potential of the *sea urchin test* over time were monitored from 10 min to 20, 40, 60, 80 min by using 30 mL of 20 mg L^{-1} Cd^{2+} at pH 6 (fig. 2). At the beginning, metal adsorption was less due to more binding sites remained free when treated for the short period of time and increased rapidly as the treatment time increases. It showed lowest adsorption of 66.89% when treated for 10 min and increased over time to saturate value of 88.12% at 60 min and after that the uptake remained almost same. The variation in uptake of the cadmium ions with time were used in fitting the kinetic models.

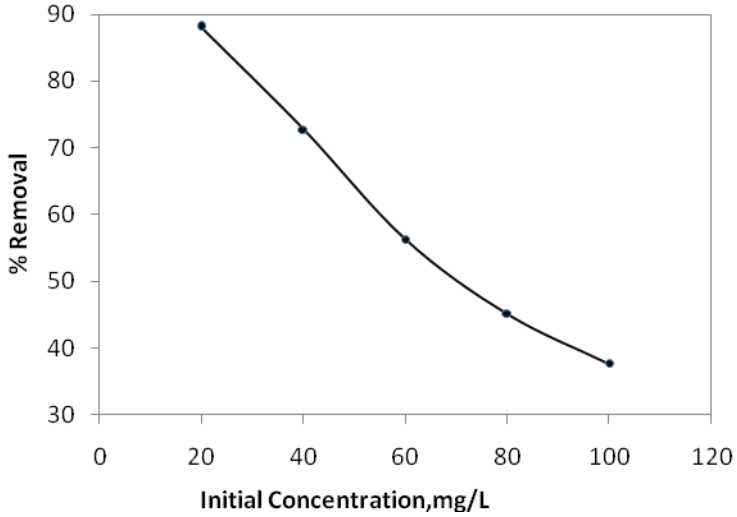

Fig. 3: Effect of metal ion concentration on removal of Cd(II) by *sea urchin test* at 0.1 g/30mL of adsorbent concentration, pH 6 and contact time 80 min

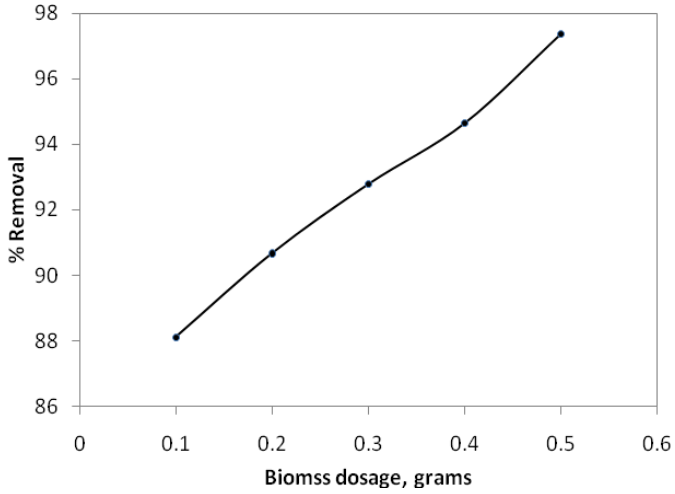

Fig. 4: Effect of *sea urchin test* dosage on removal of Cd(II) for 20mg/L of metal solution concentration at pH 6 and 80 min of contact time

4.3. Effect of initial metal ion concentration

Initial metal ion concentration sturdily influences the metal uptake in the biosorption of aqueous solutions. Metals ions are adsorbed on active sites of the surface of the adsorbent while with the increase of metal ion concentration all active sites are saturated and the vacant sites are filled. In the present study, the effect of initial Cd^{2+}concentration on sorption examined by varying it from 20 to 100mg L^{-1} at an initial pH value of 6 while maintaining the *sea urchin test* amount of 0.1 g L^{-1}. This data is further utilized for developing adsorption isotherms models for fitment from which the efficiency of the adsorbent can be calculated. The results were presented in fig.3. It shows that with

an increase in the Cd^{2+}concentration from 20 to 100mg L^{-1}, the percentage removal decreases from 88.12% to 37.69%. The decrease in the percentage removal of Cd^{2+}can be explained with the fact that all the adsorbents had a limited number of active sites, which would have become saturated above a certain concentration

4.4. Influence of the biosorbent dose

The cadmium biosorption potential of the *sea urchin test* augmented over its increase in amount in the treatment solution. The more the amount of biosorbent is present, the more the free binding sites or exchanging groups are available to adsorb the metal ion from the solution. For the 20 mg L^{-1} metal ion concentration the increase in biosorbent amount, resulted in increased metal ion adsorption and above a certain dose it remained same or slightly higher due to comparatively higher number of free sites and lesser number of metal ions (fig. 4).

4.5. Equilibrium studies and isotherm modelling

The biosorption isotherm models described the biosorption data at equilibrium and showed the correlation between the mass of solute adsorbed per unit mass of sorbent at equilibrium.In this study, three important sorption isotherm models were selected to fit experimental data, which are namely Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models. Langmuir isotherm models the mono layer on sorption surface. This model supposes that the sorption process takes place at a specific sorption surface. The attraction between molecules decreases as getting further from the sorption surface.

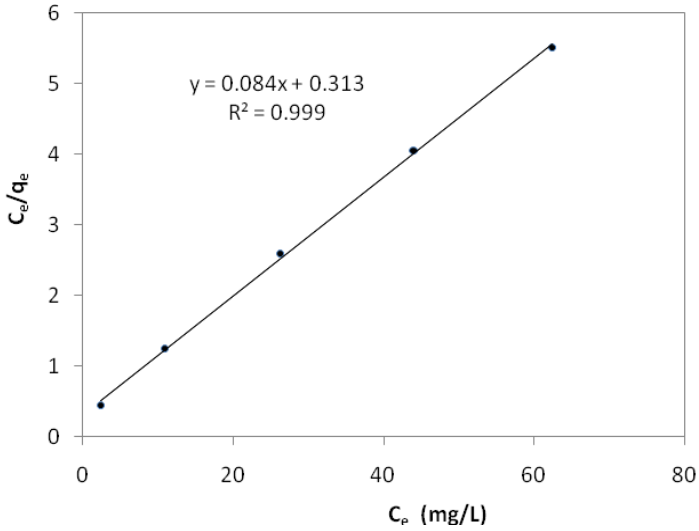

Fig. 5: Langmuir adsorption isotherm for Cd(II) at 0.1 g/ 30 ml of biomass concentration at pH 6 and contact time of 80 min

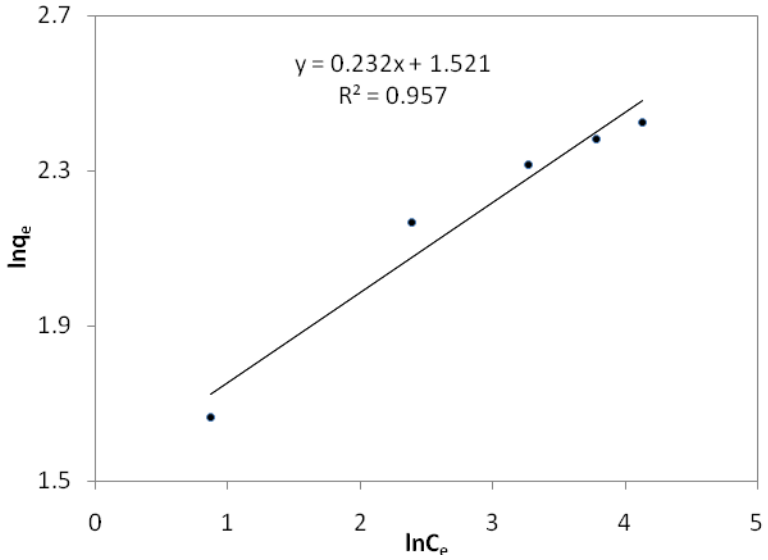

Fig. 6: Freundlich adsorption isotherm for Cd(II) at 0.1 g/ 30 ml of biomass concentration at pH 6 and contact time of 80 min

Langmuir isotherm can be defined according to the following equation [29].

$$\frac{C_e}{q_e} = \frac{1}{K_L\, q_{max}} + \frac{C_e}{q_{max}} \qquad (2)$$

where q_e is the equilibrium metal ion concentration on the adsorbent (mg/g), C_e is the equilibrium metal ion concentration in the solution (mg/L), q_m is the monolayer biosorption capacity of the adsorbent (mg/g), and K_L is the Langmuir biosorption constant (L/mg) relating the free energy of biosorption. fig. 5 indicates the linear relationship between the amount (mg) of Cd(II) ions adsorbed per unit mass (g) of *sea urchin test* against the concentration of Cd(II) ions remaining in solution (mg/L). The correlation coefficient (R^2) were found to be 0.999 for Cd(II) biosorption. The high R^2 values indicated that the equilibrium data well fitted to the Langmuir model. In other words, the sorption of metal ions onto *sea urchin test* was taken place at the functional groups/binding sites on the surface of the biomass which is regarded as monolayer biosorption. The K_L value was found as 0.268 L/mg for Cd(II) ion. The maximum biosorption capacity (q_m) was found to be 11.904 mg/g for Cd(II) ion(Table.1).

Freundlich isotherm is used for modeling the adsorption on heterogeneous surfaces. This isotherm can be explained as follows [30]:

$$ln q_e = ln K_f + \frac{1}{n} ln C_e \qquad (3)$$

where K_F is a constant relating the biosorption capacity and $1/n$ is an empirical parameter relating the biosorption intensity, which varies with the heterogeneity of the material. fig. 6 shows the Freundlich isotherms obtained for the biosorption of Cd(II) ions onto *sea urchin test* biomass using Eq. (3). From Table.1 the values of K_F and $1/n$ were found to be 2.869 and 0.232, respectively. The $1/n$ value was between 0 and 1, indicating that the biosorption of Cd(II) onto *sea urchin test* biomass was favourable at studied conditions. However, compared to the R^2 values, 0.957 with that obtained from the Langmuir model, it can be noted that the Langmuir isotherm model is better fitted the equilibrium data.

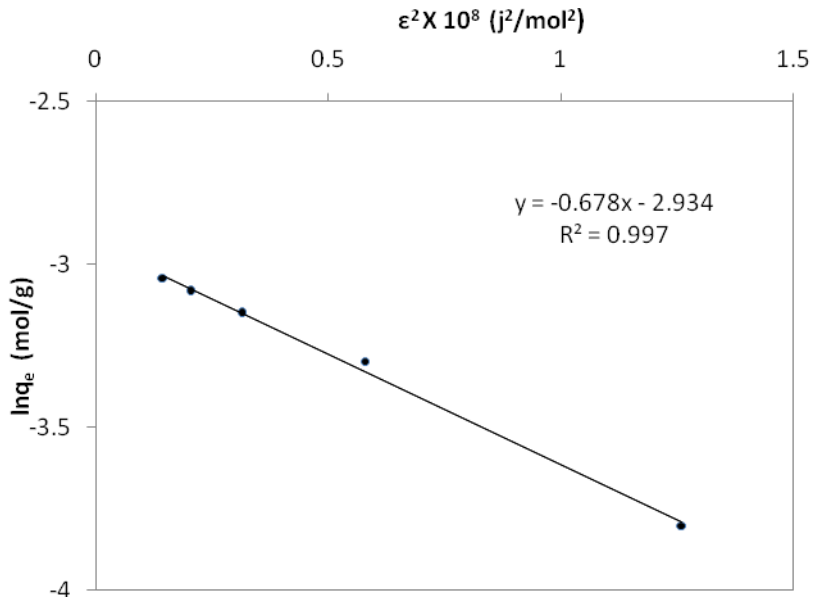

Fig. 7: Dubinin– Radushkevich isotherm adsorption isotherm for Cd(II) at 0.1 g/ 30 ml of biomass concentration at pH 6 and contact time of 80 min

The equilibrium data were also applied to the D–R isotherm model to determine the nature of biosorption process as physical or chemical. The linear form of the D–R isotherm equation [31]:

$$ln q_e = ln X_m - \beta \varepsilon^2 \qquad (4)$$

where q_e is the amount of metal ions adsorbed on per unit weight of biomass (mol/L), q_m is the maximum biosorption capacity (mol/g), β is the activity coefficient related to mean biosorption energy (mol^2/J^2) and ε is the Polanyi potential ($\varepsilon = RTln\left(1+\frac{1}{C_e}\right)$).

The D–R isotherm model well fitted the equilibrium data since the R^2 value was found to 0.997 (fig.7). From the intercept of the plot, the q_m value was found to be 13.08×10^{-2} mg/g. The mean biosorption energy (E, kJ/mol) is as follows

$$E = \frac{1}{\sqrt{-2\beta}} \qquad (5)$$

The mean free energy of biosorption gives information about biosorption mechanism, physical or chemical. If E value is between 8 and 16 kJ/mol, the biosorption process follows chemically and if E < 8 kJ/mol, the biosorption process is of a physically [32]. The mean biosorption energy was calculated as 8.58 kJ/mol for the biosorption of Cd(II) ions. These results indicated that the biosorption process Cd(II) onto *sea urchin test* may be carried out chemically via involving valence forces through sharing or exchange of electrons between sorbent and sorbate[33].

Table .1: Langmuir, Freundlich and D-R isotherm constants for the biosorption of cadmium on*Sea urchin test* biomass

Metal	Langmuir isotherm model			Freundlich isotherm model			D–R isotherm model		
	q_{max} (mgg^{-1})	K_L ($L\ mg^{-1}$)	R^2	1/n	K_f	R^2	q_{max} (mgg^{-1})	β	E kJ/mol
Cadmium	11.904	0.268	0.99	0.232	2.869	0.957	$13.08x10^{-2}$	$0.678x10^{-8}$	8.587

CONCLUSION

This study focused on the biosorption of Cd(II) ions onto *sea urchin* biomass from aqueous solution. The operating parameters, pH of solution, contact time, biomass dosage, and temperature, were effective on the biosorption efficiency of Cd(II). Biosorption equilibrium was better described by the Langmuir isotherm model than the Freundlich model. The monolayer biosorption capacity of *sea urchin* for Cd(II) was found to be 11.904 mg/g ions. From the D–R model, the mean energy was determined as 8.58 kJ/mol, indicating that the biosorption of Cd(II) onto *sea urchin* biomass may be carried out chemically. 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. The thermodynamic calculations indicated the feasibility, exothermic and spontaneous nature of the biosorption process at $293–333^0$ K. Based on all results, it can be also 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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