Biosorption of Cu(II) onto the Adsorbent Prepared from Sea Urchin Test: Equilibrium and Thermodynamic Studies

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ABSTRACT

The potential of biomass prepared from shells of sea urchin to adsorb copper from aqueous solutions was studied. The extent of biosorption of Cu(II) ions was found to be dependent on the solution pH, biosorbent dose, initial cadmium ions concentration and contact time. These four independent process variables were optimized using traditional one variable at a time technique. Equilibrium biosorption data was analyzed using Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models. Equilibrium dynamics were well described by Langmuir isotherm. The results indicated that sea urchin bears the competence to remove copper from aqueous medium having maximum capacity of 12.5 mg g^{-1} at favorable process conditions. The mean adsorption energies evaluated using the D–R model indicated that the sorption of Cu(II) onto sea urchin mainly takes place by chemisorption. Thermodynamic energy functions such as ΔG^0, ΔH^0 and ΔS^0 were evaluated and these parameters reveled that biosorption of copper ions onto sea urchin was spontaneous and exothermic in nature. These remarks substantiate sea urchin as an economical and naturally available biosorbent for copper removal from polluted wastewater.

Keywords: Biosorption; Copper; Sea urchin; Isotherm; Thermodynamics

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INTORDUCTION

To provide amenities and facilities to unceasing global population, rapid industrialization is inevitable. Enhanced industrial and social development activities have contributed to environmental pollution by discharging hazards heavy metals into ecosystem [1]. Water pollution became global challenge of today because of indiscriminate discharge of industrial, agricultural and domestic waste effluents into the environment. The major contributors to such sever pollution are the effluents from heavy manufacturing industries like fertilizer, bulk chemicals and pharmaceutical industries, plastic and paint, mining and metallurgical processing, paper and pulp, petrochemical and battery manufacturing industries [2]. Reducing heavy metals concentration in the aquatic environment to acceptable limits using economical and eco-friendly technologies becomes more and more urgent Copper is one of the essential micronutrients for all living cells, but it is harmful to the ecological system at high concentrations [3-7]. Copper is used extensively in various industrial applications and house hold purposes like air conditioning tubing systems, electrical winding, plumbing, electronic chips, metal coating and gear wheel because of its unique physical and chemical characteristics of high electrical and thermal conductivities, corrosion resistivity. Many industries like fertilizer and pesticide industry, wood pulping and paper mills, printed circuit board production, tanning industry, electrical appliances manufacturing units and ore and metal smelting industry are sources of copper effluents [8-10]. Therefore, reducing concentration levels of copper in wastewater to acceptable limits is essential before discharging

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into the environment. Several physico-chemical techniques are available to treat heavy metal contaminated water like chemical or electrostatic precipitation, ultra filtration, chemical reduction and oxidation, ion-exchange filtration, solvent extraction, etc. [9]. But it was found that all these techniques had some economical and technical limitations like ineffective at low concentrations, requires costly reagents and filter membranes, production of secondary sludge which needs further treatment, etc. [8-11].Extensive research has been carried out over the last two to three decades on biosorption as a potential method for removal of hazardous elements from heavy metal contaminated waste water, especially at very low concentration (1-100 ppm) [12-14]. Biosorption is defined as adsorption of materials onto the surface of biosorbent prepared from inactive or non living biomass through various mechanisms [15]. Different kinds of biological material belonging to three major types i.e., sludge from industry and household, agricultural waste and plant residues and dead microbial mass are tested by several researchers [16-18]. Brewery waste biomass, brown and green algae, saw dust, rice straw, and activated carbon derived from various plant waste, shell powder of almond, pistachio, hazelnut and walnut [19-24] are few examples of biosorbents used by investigators.However recent literature revealed that biomass derived from calcium carbonate sources has shown better performance in removal of metal ions from waste effluents [26,27]. Sea urchin shells are good source of calcium carbonate; moreover they are found across the ocean floors worldwide and amass as waste at seashore. Thus sea urchins were considered as biosorbent. The present study was carried out to assess biosorption capacity of sea urchins for removal of Cu (II) ions form synthetic metal ion solutions.

MATERIALS AND METHODS

Preparation of biomass
The sea urchins shells collected from nearby beach were first washed with tap water. Then spines and flesh were peeled off and broke down into two halves. After drying for more than one day in the sunlight the leftover organic matter was also removed from surface. Later shell pieces were again washed thoroughly with tap water and distilled water to neutralize sea salinity. Air dried test pieces were pulverized using ball mill and graded to obtain fine powder as an adsorbent.

Preparation of Cu(II) stock solution
Synthetic aqueous solution of Cu (II) was prepared by dissolving appropriate amount of copper sulphate salt in distilled water. Stock solution of concentration 1000 ppm was prepared and working solutions were prepared by appropriate dilution. HNO_3 (0.1 N) and NaOH (0.1 N) were used for adjusting the pH of the solution. All the analytical grade chemicals were purchased from Merck India Ltd.

Biosorption experiments (Batch mode)
Cu (II) removal capacity of sea urchin was investigated by varying pH, initial Cu (II) ions concentration, biomass dosage and, temperature, while keeping the volume of reaction mixture as 30ml. Mixing was carried out in orbital shaker at 120 rpm. Samples were collected and filtered using Whatma filter paper (No.1). Residual Cu (II) in solution was measured using Atomic Absorption Spectroscopy. Triplicate experiments were conducted and the mean values have been recorded. Blank experiments were also run to ensure biosorption.

Equilibrium modeling
Equilibrium studies are carried out to predict maximum Cu (II) removal by sea urchin. Experiments were designed and conducted by varying initial Cu (II) concentration in the range of 20–100 mg l^{-1} by fixing other parameters as constant. Langmuir, Freundlich and D–R isotherm models were used in establishing equilibrium relation between Cu (II) ions adsorbed onto the sea urchin (q_e) and residual Cu (II) ions in solution (c_e). Langmuir isotherm has been extensively used for dilute solutions in following linear form [28]:

$$\frac{c_e}{q_e} = (c_e / a) + 1 / ab \text{ ------------ (1)}$$

where, '*a*' is maximum metal uptake per unit mass of adsorbent to form complete monolayer and '*b*' represents the affinity of binding sites. The plot of (c_e/q_e) against (c_e) indicates the applicability of this model . Freundlich model [29] can be described by the equation given below:

$$q_e = k_f c_e^{1/n} \text{ -------------------- (2)}$$

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where, the value of k_f and n are indicators of adsorption capacity and intensity. The linear plot of log (q_e) against log (c_e) describes the fitness of the this model. D–R isotherm model is used to determine the nature of biosorption process as physical or chemical. The linear form of this model is expressed as [30]:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \text{ ------------------ (3)}$$

Where q_e and q_m are equilibrium and maximum metal uptake (mol/g) respectively, β is activity coefficient represents mean biosorption energy (mol^2/J^2) and ε is the Polanyi potential which is calculated from the following equation

$$\varepsilon = RT \ln\left(1 + \frac{1}{c_e}\right) \text{ ------------------- (4)}$$

The mean biosorption energy (*E*, kJ/mol) is calculated from Eq. (5)

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

Biosorption thermodynamics

In any field of engineering, thermodynamic analysis is carried out to assess the feasibility of the process. Especially in wastewater treatment to develop eco-friendly process this analysis is essential. Energy functions such as enthalpy change (ΔH^0), entropy change (ΔS^0) and free energy change (ΔG^0) are used to explore nature and feasibility of the process. Thus, (ΔH^0) and (ΔS^0) were obtained from slope and intercept of plot of Eq. (6):

$$\ln(K_D) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \text{ --------------------- (6)}$$

Whereas K_D is calculated from Eq. (7):

$$K_D = \frac{q_e}{c_e} \text{ ----------------------------------- (7)}$$

where, q_e and C_e are meta uptake and residual metal concentrations at equilibrium. [31]. Then free energy change is calculated from Eq. (8):

$$\Delta G^0 = -RT \ln(K_D) \text{ ----------------------- (8)}$$

Where, T (K) is temperature, R (8.3145 J/mol K) is gas constant, and ΔG^o is standard free energy change.

RESULT AND DISCUSSION

Effect of initial pH of solution

In biosorption initial metal solution pH plays important role by controlling degree of ionization of solution and surface charge of biosorbent. Its effect on biosorption of Cu (II) onto sea urchin was tested over the range of 1−7. Percentage of Cu (II) removal as a function of pH was shown in figure1. Metal adsorption was increased with pH and reached the highest point at 5, after this a drastic fall in metal removal was noticed. With increase in initial pH, concentration of H$^+$ and H$_3$O$^+$ ions decreases in solution and also cell wall ligands carries negative charge which promotes sorption of positively charged Cu (II) ions [24,25]. At alkali pH metal precipitation was noticed in the form of copper hydroxide resulting decrease in metal removal. The pH value of 5 has been considered as most favorable condition to carry on further experimental work.

Effect of contact time

The adsorption performance of sea urchin over time was examined up to 60 min in 30 ml of 20 mg l^{-1} copper solution by maintaining pH at 5 (Figure 2). It was noticed that in the early time period, metal removal rate was very rapid. Many researchers affirmed it availability of more binding sites at the beginning for adsorption. Around half of the metal was removed within first 10 min., after that it was sustained at lower rates and finally reached equilibrium at 55 min., when the total active surface of biomass was occupied by metal ions. Maximum copper removal at equilibrium was recorded as 89.17% within 55 min.
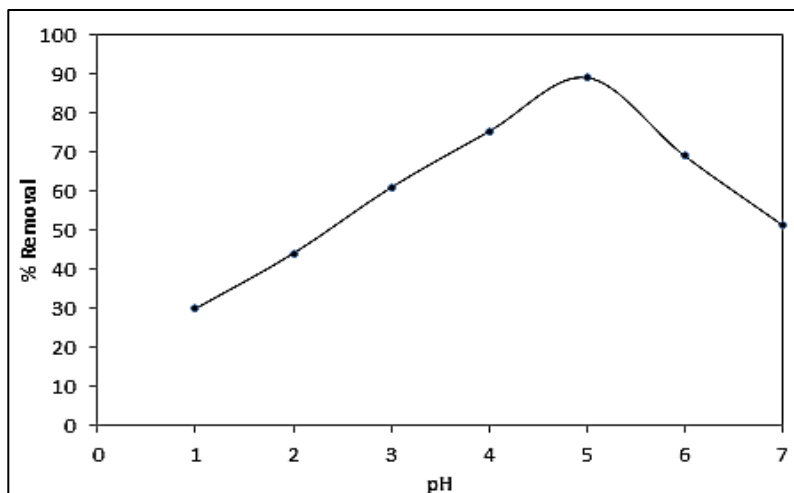
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Figure 1: Effect of pH on Cu(II) removal by *sea urchin test* **for 20mg/L. metal and 0.1 g/30 mL. of adsorbent concentrations**
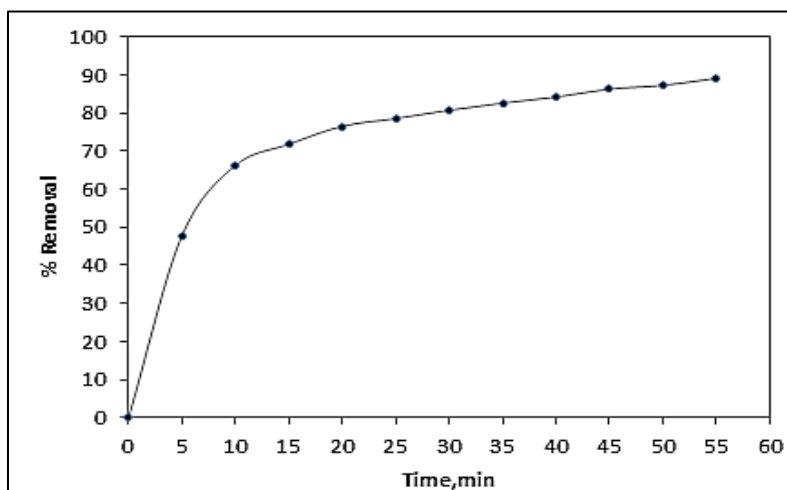

Figure 2: Effect of contact time on removal of Cu(II) by *sea urchin test* **for 20mg/L of metal concentration and 0.1g/30mL of adsorbent concentration at pH of 5**

Effect of initial cu (II) ions concentration

The effect of initial strength of Cu (II) ions on adsorption onto sea urchin was shown in figure 3. It was tested over a range of 20 to 100 mg l^{-1} with an interval of 20. From figure 3 it was noticed that sorption of Cu (II) decreased with an increase of initial Cu (II) ions strength. Maximum percentage of Cu (II) removal was noticed at 20 mg l^{-1} due to the availability of more surface area for metal binding and less number of metal ions available in the solution. While lowest adsorption was recorded at 100 mg l^{-1}, because of saturation of all active sites with available more number of metal ions. A similar trend was reported for copper removal using brown seaweed [32].

Effect of biosorbent dosage

Figure 4 depicts the effect of biomass dosage on removal of copper from the solution containing 20 mg/l copper with different amounts of biomass at equilibrium. Biosorption capacity of the sea urchin was increased from 88.12% to 95.18% with an increase of sea urchin dosage from 0.1 g to 0.5 g. This increase is obvious due to availability of more binding surface area. Similar results were reported for removal of copper using crab shell as biosorbent [33].

Adsorption isotherm

Equilibrium sorption capacity of an adsorbent can be theoretically estimated and nature of biosorption can be described from adsorption isotherms. Linear representation of Langmuir and Freundlich isotherms of copper adsorption were shown in Figs.5 and 6. Predicted and experimental metal uptake, adsorption constants and R^2 values for both models are presented in table 1. Langmuir model was more compatible to experimental results, indicating

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that it is more competent for determining the equilibrium copper biosorption capacity of sea urchin. Maximum capacity of sea urchin at favorable conditions of pH 5, sea urchin mass of 0.1 g, Cu (II) concentration of 20 mg l^{-1}, and 55 min time period was found to be 12.5 mg g^{-1}. Further equilibrium data was fitted to D-R isotherm as shown in figures 4-7. The mean free energy of biosorption estimated from isotherm was 8.573(Table 1) which confirmed the process as chemisorption. Although biomass derived from plant material adsorb heavy metal ions more effectively, sludge generated from lignin, tannin, and other materials may cause unwanted interference with environment [34]. In contrast, this calcium carbonate derived biomass will not permeate any toxic compounds to the environment.
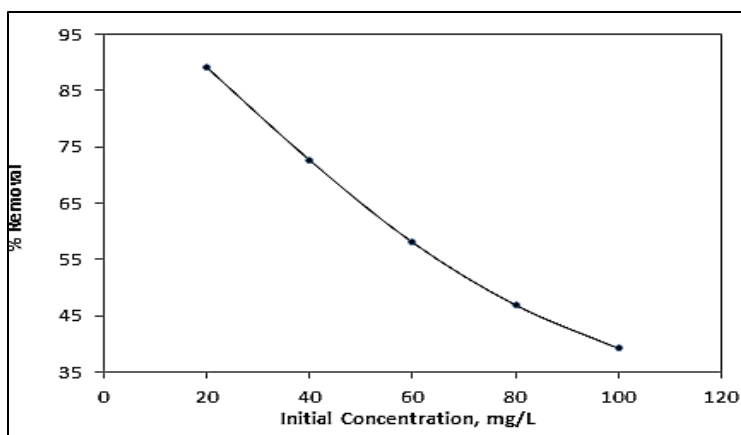

Figure 3: Effect of metal ion concentration on removal of Cu(II) by *sea urchin test* at 0.1 g/30mL of adsorbent concentration, pH 5 and contact time 55 min
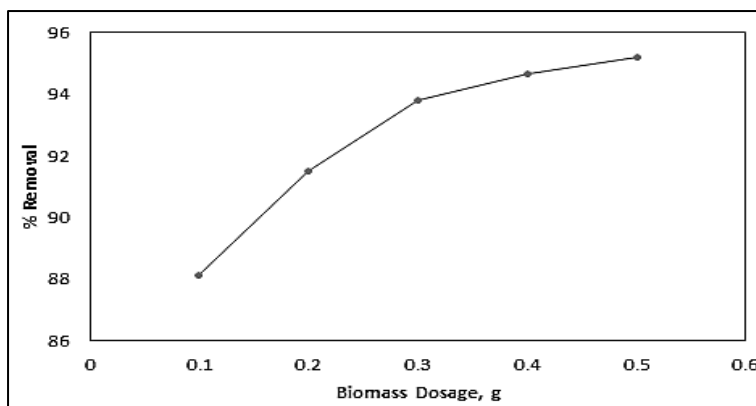

Figure 4: Effect of *sea urchin test* dosage on removal of Cd(II) for 20mg/L of metal solution concentration at pH 2 and 80 min of contact time
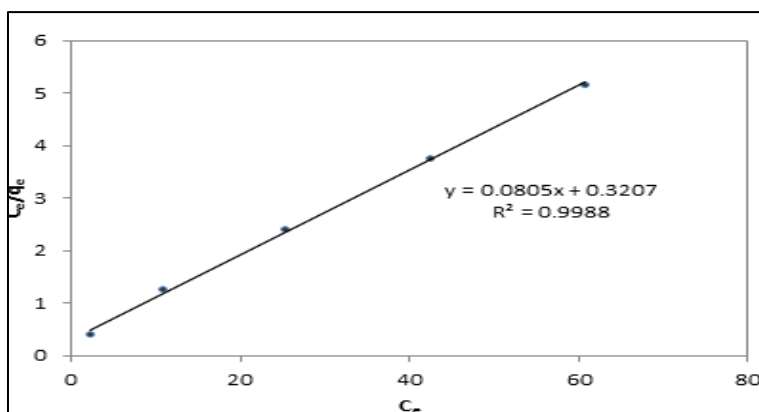

Figure 5: Langmuir adsorption isotherm for Cu(II) at 0.1 g/ 30 ml of biomass concentration at pH 5 and contact time of 55 min
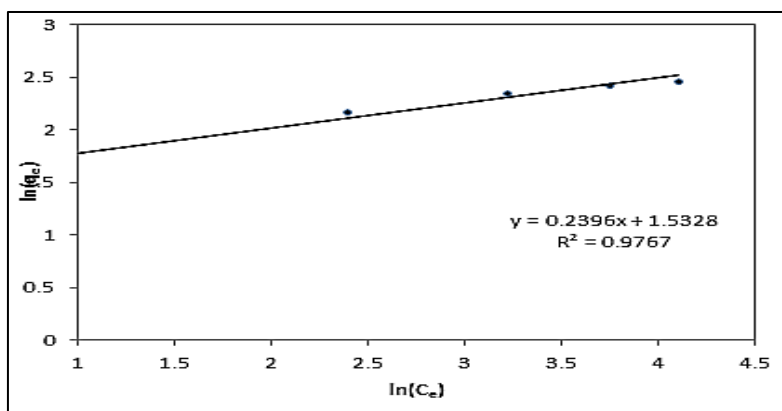
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Figure 6: Freundlich adsorption isotherm for Cu(II) at 0.1 g/ 30 ml of biomass concentration at pH 5 and contact time of 55 min
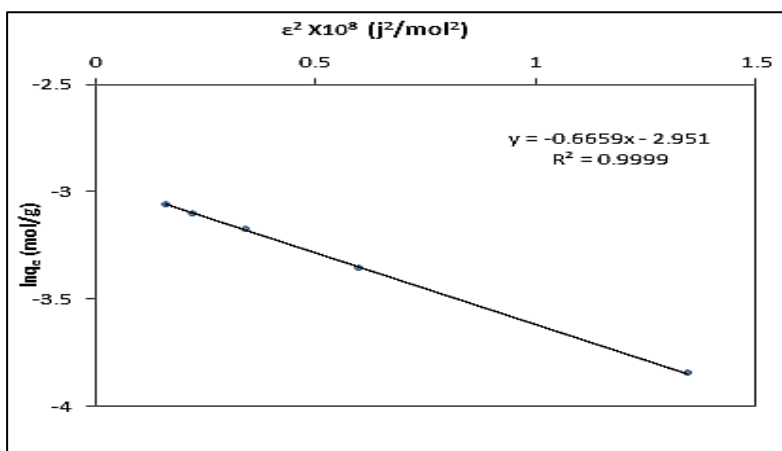

Figure 7: Dubinin– Radushkevich isotherm adsorption isotherm for Cu(II) at 0.1 g/ 30 ml of biomass concentration at pH 5 and contact time of 55 min

Table 1: Langmuir, Freundlich and D-R isotherm constants for the biosorption of Cu (II) onto 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
Copper	12.5	0.25	1	0.239	2.89	0.98	13.28	0.678x10^{-8}	8.573

Biosorption thermodynamics
The thermodynamic energy functions ΔS^0 and ΔH^0 were calculated from the linear plot of log K_D versus 1/T shown in figure 8 and ΔG^o was calculated from equilibrium constants (K_D). In this study the negative values of ΔG^o confirm the natural possibility of process with high preference of copper at low temperatures. The value of ΔH^o for biosorption of copper onto sea urchin was obtained as −21.0926 kJ/mol (Table 2). The negative value of ΔH^o reflects that the sorption process is exothermic; moreover its scale also gives valuable information of process whether it is a physical process or chemical reaction. The enthalpy change of the process (-21.0926 kJ/mol) indicated that the adsorption of Cu (II) ions onto sea urchin was chemical reaction between adsorbate and adsorbent. In addition the negative value of entropy changes also describes a decrease in the randomness at the solid/solution interface during the biosorption process. It further suggests the stability of both metal ions on the surface of sea urchin.
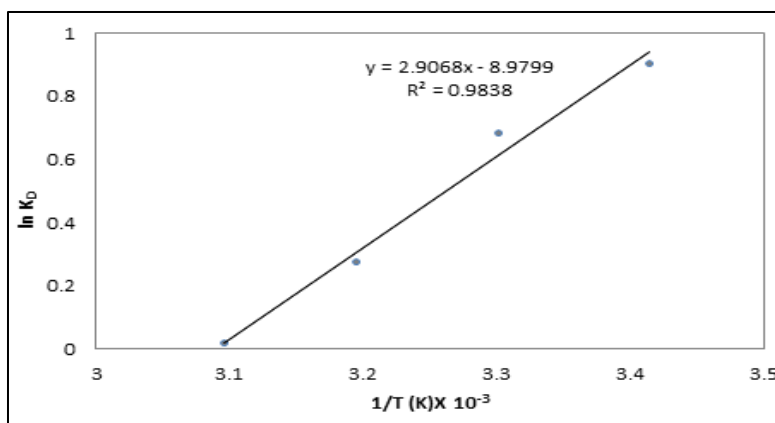
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Figure 8: Plot of ln(K_D) vs. 1/T for the estimation of thermodynamic parameters for biosorption of Cd(II) onto *sea urchin test* biomass

Table 2: Thermodynamic parameters for the biosorption of Cu (II) onto *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	-2.20276			
30	-1.72918	-24.16	-74.651	0.98
40	-0.71361			
50	-0.0436			

CONCLUSION

Biosorption potential of biomass prepared from sea urchin for the removal of copper from aqueous metal solutions was investigated. Batch mode experiments were conducted by varying one parameter at a time to find out effect of individual process parameter and it was found that the process is strongly affected by following independent factors i.e., initial copper concentration, biomass concentration and the pH of the solution. Sea urchin was found to be very competent in removing copper ions (89.17%) and also the maximum removal rate was achieved within 55 min of contact time at optimum pH of 5. The equilibrium data was well described by Langmuir model. The activation energy falls within the range considered for process when chemisorption predominates, which also accounts for the speed at which the operation occurs. Thermodynamic parameters (ΔH^0, ΔS^0 and ΔG^0) of the copper ions indicate that the process is exothermic and proceeds spontaneously for the sea urchin.

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