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Investigation of Cr(VI) Sorptiononto C.limonium:Equilibrium, Kinetic,Thermodynamic studies

Sumalatha B[1]*, Prasanna Kumar Y[2], King P[3]

[1]Department of Chemical Engineering, Vignan University, Vadlamudi,A.P, India
[2]Visakha Institute of Engineering & Technology, Visakhapatnam, A.P, India
[3]Department of Chemical Engineering, Andhra University College of Engineering, Visakhapatnam, A.P, India

Abstract : The present study was undertaken to evaluate the feasibility of citrus lemonium peel waste for the removal of Cr(VI) ions from aqueous solutions. Batch experiments were performed to study the biosorption of Cr(VI) on c.lemonium peel biosorbent. The maximum biosorption capacity of c.lemonium peel biosorbent for Cr(VI) removal was ca. 22mgg−1. Two simplified kinetic models viz. pseudo-first-order, pseudo-second-order models were tested to describe the biosorption process. Kinetic parameters, rate constants, equilibrium sorption capacities, and related correlation coefficients for kinetic models were determined. It was found that the present system of Cr(VI) biosorption on c.lemonium peel biosorbent could be described more favorably by the pseudo-second-order kinetic model. The biosorption process has been found to be exothermic. The results of the present study suggest that c.lemonium peel waste can be used beneficially in treating industrial effluents containing heavy metal ions.

Keywords : Biosorption,*Cr(VI)*, C.limonium, isotherm models, kinetic models, Thermodynamic studies.

Introduction

Heavy metal pollution is considered as one of the prime candidates for causing environmental problems. Chromium (VI) is one of the heavy metals having catastrophic health effect on human body which includes nasal irritation, skin ulceration, lung cancer and respiratory diseases like bronchial asthma. The toxicity of Cr (VI) imposes two major health hazards i.e. genotoxicity andcarcinogenicity mainly due to the interaction of chromate ionswith genetic material i.e. deoxy-ribose nucleic acid (DNA) and freeradical (e.g. thiyl, hydroxyl) formation respectively. Anthropogenic activitylike leachate from landfill disposal, fly ash disposal and domestic or industrial sewage have increased concentration of Cr (VI) inatmosphere. Cr (VI) has been used widely in a variety of industriessuch as photography, tannery, ceramic, glass industries, pigments,paints, fungicides chrome alloy and metallurgic industries.Wastewater generated from these industries has been found tocontain significant amount of chromium that exists in twooxidation states as Cr (III) and Cr (VI). The maximum permissiblelimit for hexavalent chromium in inland is 0.1 mg/L whereas forpotable water is 0.05 mg/L, respectively.There are severalmethods available for Cr removalwhich includechemical precipitation, ion exchange, reduction, electrochemicalprecipitation, solvent extraction, membrane separation, cementation, evaporation and foam formation.However, high energy andchemical requirement, incomplete removal, generation of toxicsludge are the limiting factors of these treatment procedures .

Many studies have been reported using different natural biosorbents like activated carbon from sugarcane bagasse, Nymphaearubra, dried water hyacinth roots, sulphuric acid treated cashew nut shell, modified corn stalk, Echorniacrassipes and activated carbon fromTamarind wood. Thereare four mechanisms of biosorption for Cr (VI) viz., anionicadsorption, adsorption coupled reduction, anionic and cationicadsorption and cationic adsorption[1].

One of the important agricultural wastes is peel of different fruits, which can serve as potential adsorbents for the removal of diverse types of pollutants especially metal ions. Different types of fruit peels have been investigated so far for wastewater treatment. The aim behind using fruit peels as biosorbents is that it will provide a two-fold advantage to environmental pollution. Firstly, the volume of wastes could be partly reduced and secondly, prepared biosorbent can treat toxic industrial effluents at a reasonably cost. The aim of this study was to examine the efficiency of citrus limonium peel waste as biosorbent for the removal of arsenic from aqueous solutions. Equilibrium and kinetic studies were performed to describe the biosorption process[2].

2. Experimental

2.1 Preparation of biosorbent

Citrus limonum was collected from juice shops and washed with de-ionised water several times to remove impurities. Then completely dried in sunlight for about 3-4 weeks. It was crushed into small pieces and was powdered using domestic mixer. The test powder was graded using BSS sieve set to get the required average size for using as biosorbent. In the present study the powdered materials in the range of 75-212 µm average particle size were then directly used as biosorbent without any pre-treatment. This biosorbent powder was stored in moisture free glass bottles.

2.2. Chemicals and metal solution

A stock solution of 1000 mg/l of Cr(VI) was acquired by dissolving potassium dichromate (Merck Company) in distilled water. The test solutions of various concentration 20,40,60,80,100 mg/l were prepared from the stock solution. The solution pH was balanced utilizing 0.1M HNO_3 and 0.1M NaOH toward the start of the trial and not controlled subsequently. The conical flasks (250 ml) were shaken at 180 rpm in a temperature controlled rotatory shaker.

2.3. Biosorption Experimental procedure

The batch biosorption experiments were performed at room temperature in 250 ml reagent bottles that contained 30 ml solution of a particular arsenic ion concentration at required pH and relevant amount of *.climonium peel* powder. The flasks were sealed with wax paper and shaken in a shaking incubator (Lab Companion, SI-300R, India) at 180 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 spectrophotometer(Shimadzu AA-6300). The influence of pH of the solution on biosorption equilibrium was studied after changing the pH of the solution in a range of 2–10. The effect of contact time between solution and *the c.limonium peel* powder were monitored by varying it from 0 to 60 min at optimum pH. For equilibrium studies five different metal ion concentrations between 20 and 100 mg/l were used, while, for optimum biosorption study, the *c.limonium peel* biomass was varied between 0.1 and 0.5g. The percent Cr(V) removal was calculated for each run by following expression[3]:

$$\%\text{Biosorption} = \frac{C_i - C_e}{C_i} \times 100 \qquad (1)$$

where C_i and C_e were the initial and final concentration of Cr(VI) in the solution in mg/L. The amount of chromium ions biosorbed on the *c. limonium peel* powder was estimated from the differences between metal quantity added to the biomass and metal content of the supernatant using the following equation.

$$q = (C_0 - C_e)\frac{V}{W} \qquad (2)$$

where q = amount of metal biosorbed (mg/g), v = volume of solution (ml), w = mass of biosorbent (g), C_o = initial concentration of the solution (mg/l) and C_e = equilibrium concentration of the solution (mg/l).

3. Results And Discussion

3.1. Effect of pH of the solution

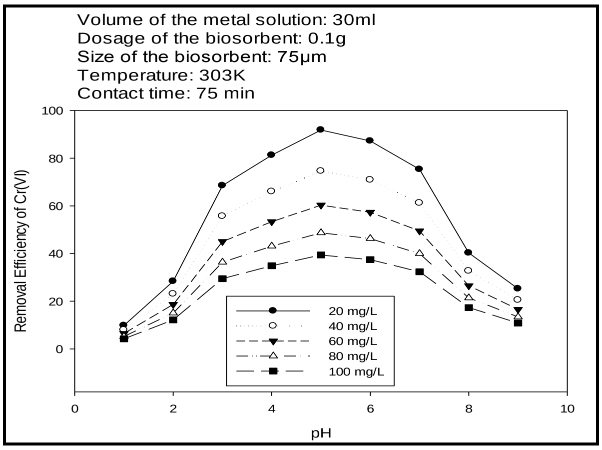

Fig1: Effect of pH on Cr(VI) removal by *c.limonium peel* for 20,40,60,80,100mg/l metal and 0.1g/30ml of biosorbent concentration.

The biosorption limit of the biosorbent and speciation of metals in the solution was pH dependent. The influence of pH was more on the solubility of metal ions and the concentration of the counter ions on the functional groups of the biosorbent cell walls. Fig.1 shows the effect of pH on the biosorption of Cr(VI) ions in aqueous solution. Maximum biosorption capacities was obtained at 5. At low pH value of 2, the biosorption capacity for the metal ions was observed to be moderate, due to the competition between hydrogen ions and chromium metal ions at the sorption sites. As the pH value increased, the availability of negatively charged cell surfaces will be more, allowing greater metal uptake. If the pH value is > 5, the formation of insoluble arsenic hydroxide precipates suppresses the contact of metal with the biosorbent[4].

Effect of contact time

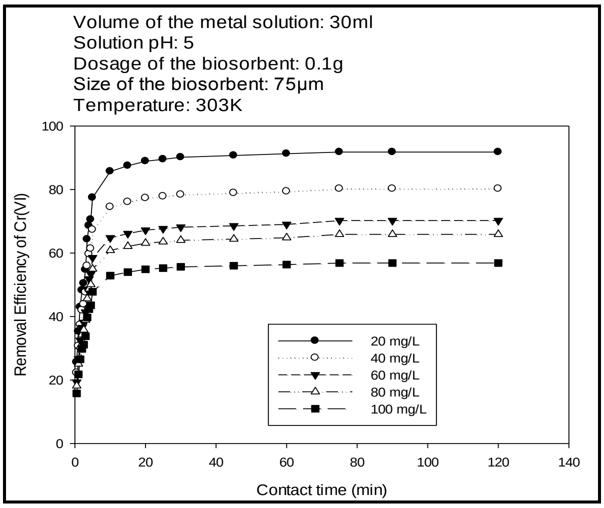

Fig2: Effect of contact time on Cr(VI) removal by *c.limonium peel.* for 0,40,60,80,100mg/l metal and 0.1g/30ml of biosorbent concentration.

The sorption potential of the c. *limonium peel*over time was observed from 0.5 min to 10,15, 20,25,30,35, 40, 45,50,55,60 min by using 30 ml of 20 mg/l Cr(VI) at pH 5 (Fig. 2). The experimental results showed that the biosorption of arsenic ions on to the *c. limonium peel* has the contact time of 75min was sufficient to achive equilibrium. Afetr 75 min there is no change in biosorption with an increase in contact time. Therefore at the end of 75 min, metal uptake and unbiosorbed Cr(VI) concentrations were taken as the equlibrium values(q_{eq}(mg),c_{eq}(mg)) resp.

Effect of initial metal ion concentration

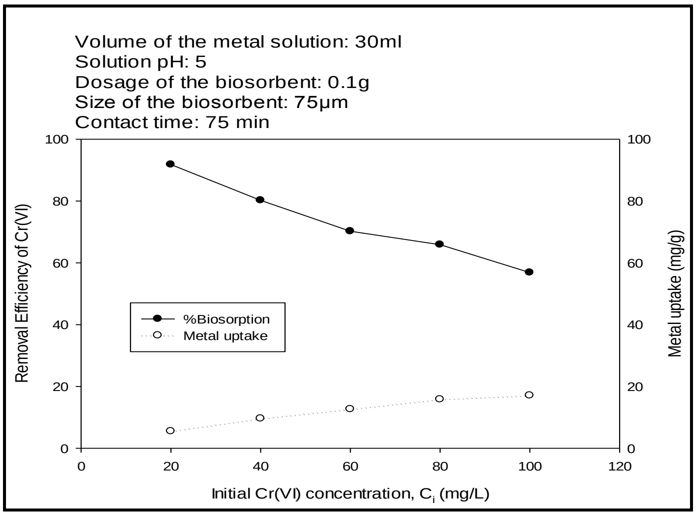

Fig3: Effect of metal ion concentration on Cr(VI) removal by *c.limonium peel.* of 0.1g/ 30ml of biosorbent concentration.

The experiments were taken out utilizing different concentrations of arsenic solution under the determined optimum pH values and contact time. The impact of arsenic concentration was examined in the range of 20–100 mg/L. The results are presented in Fig.3. The metal uptake increased and the percentage biosorption decreased with increased in metal ion concentration. It was observed that with the high concentration of metal ions there is a competition between metal ions to adsorb on the active sites of biosorbent because of having minimum binding sites available as compared to the metal ions. So there is a reduction in the biosorption efficiency with the increasing of metal ion concentration. As a result, the purification yield can be increased by diluting the waste waters containing high metal ion concentrations.

3.4 Effect of biosorbent dosage

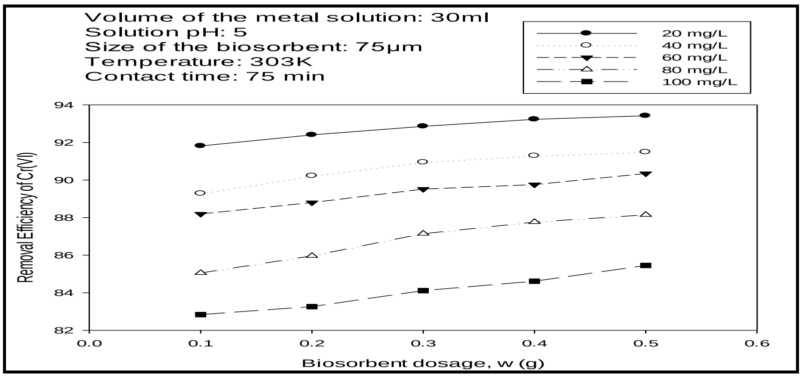

Fig4: Effect of biosorbent dosage on Cr(VI) removal by *c.limonium peel.* for 20, 40, 60, 80, 100mg/l metal and 0.1 to 0.5g/30ml of biosorbent concentration.

The sorption capacity of Cr(VI) onto *c. limonium peel* by varying biosorbent dosage from 0.1g to 0.5g is shown in Fig.4. From the results it was found that the biosorption of Cr(VI) increased with an increase in biosorbent dosage and is highly dependent on biosorbent concentration. Increase in biosorption by increase in biosorbent dosage was because of increase of ion exchange site ability, surface areas and the number of available biosorption sites. It was observed that as the biosorbent concentration increased % biosorption decreased

4. Biosorption Equilibrium

Freundlich, Langmuir, were used to describe the equilibrium between biosorbed ions on the biomass cell (q_e, q) and ions in the solution (C_e, q).

Freundlich Isotherm

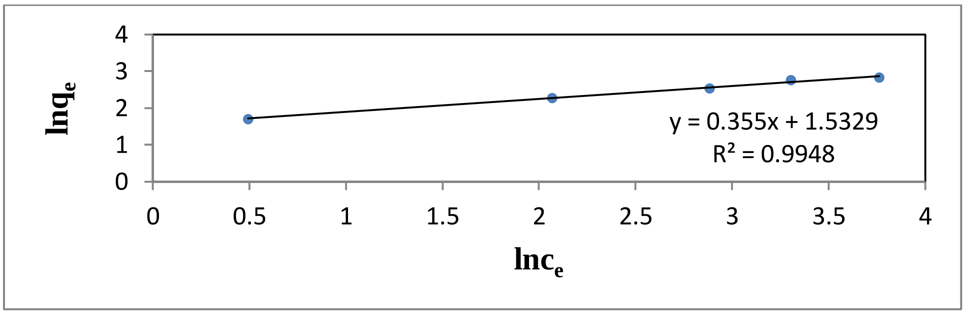

Fig5: Freundlich biosorption isotherm at 0.1g/30ml of biosorbent concentration

The empirical Freundlich equation is used for modeling the sorption on heterogeneous surface. Thelinearized Freundlich equation is represented as [6,7]

$$\ln q = \ln K_f + \frac{1}{n} \ln C_{eq} \qquad (3)$$

K_f is an indication of the biosorption capacity of the biosorbent; n indicates the effect of concentration on the biosorption capacity and represents the biosorption intensity.These values of n and K_f can be acquired from the slopes and the intercepts of the linear plots individually. The logarithmic plot of sorbed and equilibrium concentration gives a straight line with a coefficient of determination is 0.994 indicating that sorption data fitted well with the Freundlich model (Fig.5). The value of 1/n for Cr(VI) is 0.355 g/l and K_f value is 4.627 mg/g.**4.2**

Langmuir isotherm

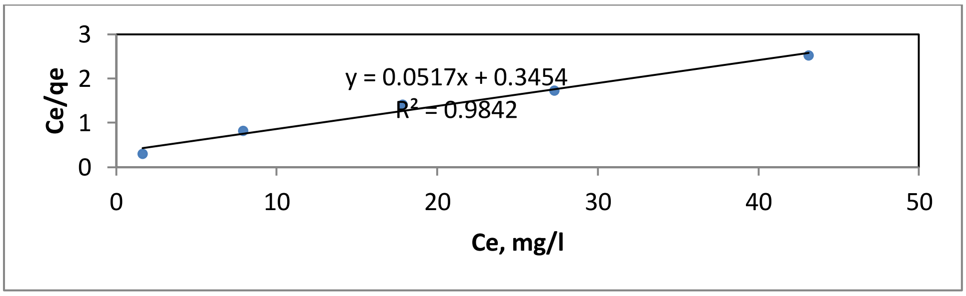

Fig. 6: Langmuir biosorption isotherm at 0.1g/30ml of biosorbent concentration.

Linear form of Langmuir isotherm equation is represented as[9]

$$\frac{C_e}{q_e} = \frac{1}{K_l q_{\max}} + \frac{C_e}{q_{\max}} \qquad (4)$$

These values q_{max} and K_l (where K_l, is the biosorption equilibrium constant) can be acquired from the slopes and the intercept of the linear plot. In Fig.6 C_e/q_e is plotted against C_e yielding a straight line with R^2

(0.984). The value of q_{max} (19.6 mg/g) was calculated from the slope of the linear plot, whereas the value of K_l (0.1478 L/mg) was derived from the intercept.

5.Kinetic Studies

The kinetics of the biosorption data was analyzed using two kinetic models, pseudo-first order and pseudo-second order. These models correlate solute uptake, which are important in predicting the reactor volume. These models are explained as follows.

5.1The Pseudo First-Order Equation

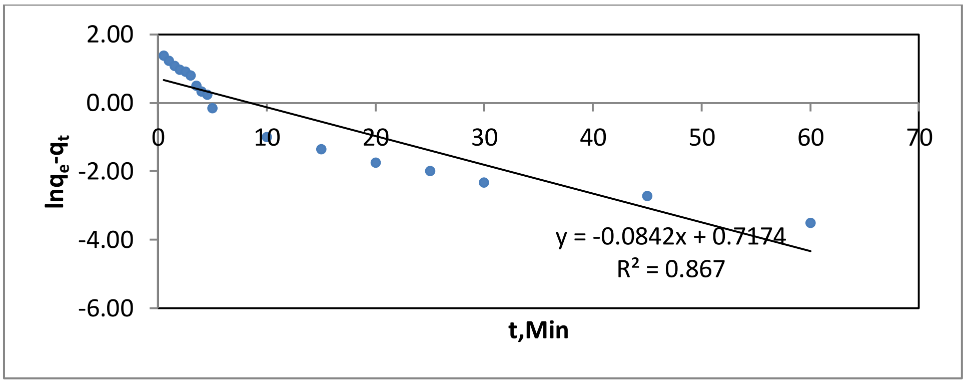

Fig. 7: pseudo first order for 20 mg/l of metal and 0.1 g/ 30 ml of biomass concentration.

The kinetics equation proposed by Lagergren[12] has been used to describe the biosorption of biosorbate from an aqueous solution. The pseudo first-order model is described by Eq.5

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \qquad (5)$$

where q_e is the amount of metal ion biosorbed on biosorbent at equilibrium (mg/g), q_t is the amount of metal ion biosorbed on biosorbent at time ‘t’ (mg/g) and k_l is Lagergren constant

(min^{-1}). Integrating the above equation and transforming to log scale.

Linear plot of $\ln(q_e - q_t)$ against time indicates whether this kinetic model is applicable or not for biosorption process. The results of kinetic parameters are shown in table1.

5.2The Pseudo Second-Order Equation

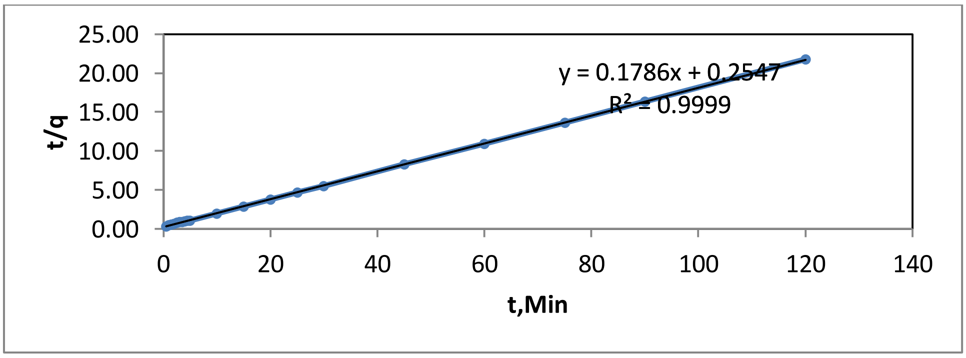

Fig. 8: pseudo second order for 20 mg/l of metal and 0.1 g/ 30 ml of biomass concentration.

The pseudo second-order kinetic model is given as[12]

$$\frac{t}{q_t} = \frac{1}{k_2 q^2{}_e} + \frac{1}{q_e} \qquad (6)$$

Where q_e = amount of adsorbed metal ion on biosorbent at equilibrium (mg/g), q_t = amount of adsorbed metal ion (mg/g) on biosorbent at time't', k_2 = second order rate constant (g/mg min). A linear plot of t/q vs t indicates whether this model of biosorption is applicable for this case or not.The values of constants of kinetic models obtained from the plots for biosorption of Cr(VI) onto c. limonium peel at 303^0K are shown in Table 1 .The data showed good agreement with the pseudo second-order kinetic model (R^2 = 0.999). However, the value of the determination coefficient (R^2) indicates the applicability of the pseudo second-order model for describing the experimental results to a higher degree of accuracy. In addition, Fig.8 and Table 1, show that the q values (q_e,cal) determined from the pseudo second-order model were closer to the experimental q values (q_e, exp) than those determined from the pseudo first-order model.

Table.1: Biosorption rate constants, q_e estimated and coefficient of correlation associated to the pseudo-first and second-order biosorption for the c. limonium peel biomass

Metal	$q_{e\,Exp}$ (mg/g)	Pseudo first order			Pseudo second order		
		$K_1(min^{-1})$	q_e cal(mg/g)	R^2	K_2	q_e cal(mg/g)	R^2
Chromium	5.51	0.084	2.048	0.867	0.124	5.617	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 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.

Thermodynamic Studies

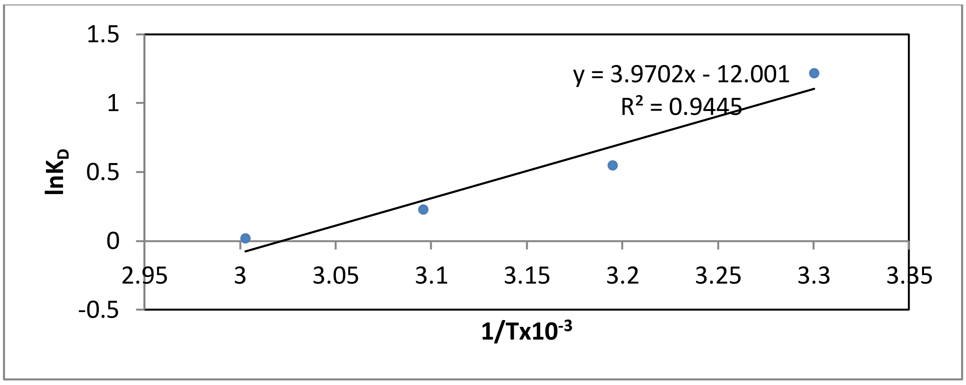

Fig.9 : Plot of $\ln(K_D)$ vs. 1/T for the estimation of thermodynamic parameters for biosorption of Cr(VI) onto c.limonium peel biomass.

In any field of engineering, thermodynamic analysis is carried out to assess the feasibility of the process. 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 the following equation[5,10].

$$\ln(K_D) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (7)$$

Whereas K_D is calculated from $K_D = \frac{q_e}{C_e}$

where, q_e and C_e are meta uptake and residual metal concentrations at equilibrium. Then free energy change is calculated from Eq

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

Where, T (K) is temperature, R (8.3145 J/mol K) is gas constant, and ΔG^o is standard free energy change.The thermodynamic energy functions ΔS^0 and ΔH^0 were calculated from the linear plot of log K_D versus 1/T shown in Fig9. 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 arsenic at low temperatures. The value of ΔH^o for biosorption of arsenic onto c.limonium peel was obtained as −33.006 kJ/mol. The negative value of ΔH^o reflects that the sorption process is exothermic and spontaneous.

Conclusion

The batch experiments were conducted with the biomass of *c. limonium peel* and it exhibited the potential of Cr(VI) removal from an aqueous solution. Optimum pH, contact time, initial metal ion concentration, dosage for biosorption in this study were 5,75 min, 20mg/l, 0.1g respectively. With an increase in the initial metal ion concentration percentage of biosorption decreased and metal ion uptake capacity increased. It was observed that percentage of biosorption increased and metal ion uptake capacity decreased by increase in the amount of biomass. The biosorption process followed the Freundlich isotherm model. Kinetic studies on the biosorption of Cr(VI) onto *c. limonium peel* revealed that experimental data were fitted with the pseudo second-order kinetic model and that film diffusion initially controls the sorption process. Thermodynamic parameters (ΔH^0, ΔS^0 and ΔG^0) of the Cr(VI) ions indicate that the process is exothermic and proceeds spontaneously for the c.limonium peel. Based on the experimental data it was notified that *c. limonium peel* is an appropriate biosorbent for the removal of chromium from an aqueous solution.

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