Int. J. Chem. Sci.: 13(2), 2015, 817-829
ISSN 0972-768X
www.sadgurupublications.com

STUDIES ON THE REMOVAL OF Ni (II) FROM AQUEOUS SOLUTION BY ACTIVATED CARBON DEVELOPED FROM COTTONSEED CAKE ACTIVATED WITH SULPHURIC ACID

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ABSTRACT

Activated carbon was prepared from cottonseed cake (CSCC) by chemical activation with sulphuric acid followed by bicarbonate addition, was applied for the adsorption of Ni (II) from aqueous solutions. Batch experiments were carried out to study the effect of various parameters such as contact time, pH and adsorbent dosage on Ni (II) along with, commercial activated carbon (CAC). Surface morphology and elemental analysis of CSCC and CAC before and after adsorption were characterized by SEM and EDX. Compared with CAC, the CSCC had a wider applicable range of pH from 3.0-8.0. Equilibrium data agreed well with Langmuir isotherm for CSCC and CAC, respectively. Based on the Langmuir isotherm the adsorption capacity was found to be 43.48 mg g^{-1} for CSCC, which was significantly 3.2 times greater than that of CAC (13.42 mg g^{-1}). The kinetic data followed pseudo-second order model and thermodynamic parameter shows that the process is spontaneous in nature.

Key words: Ni (II), Aqueous solution, Activated carbon, Cottonseed.

INTRODUCTION

The pollution of heavy metals has gained worldwide attention due to their toxicity, difficult degradation, and accumulation in the living organisms. Therefore, treatment of wastewater contaminated by heavy metals is an important environmental concern[1]. Among various heavy metals, Ni (II) is a common pollutant in different industrial effluents. Ni (II) is commonly found in wastewater effluents generated from industries involved in mineral processing, paint formulation, electroplating, porcelain enameling, copper sulfate

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manufacturing and steam-electric power plants[2]. The tolerance limit[3] of nickel in drinking water is 0.01 mg/L. Higher concentrations of nickel cause cancer of lungs, nose and bone. Dermatitis (nickel itch) is the most frequent effect of exposure to nickel, such as coins and costume jewelry. Acute Ni (II) poisoning causes dizziness, headache, nausea and vomiting, chest pain, dry cough and shortness of breath, rapid respiration, cyanosis, and extreme weakness and DNA damage[3].

Various technologies such as chemical precipitation, ion-exchange, chemical coagulation, adsorption, extraction, and membrane separation have been recently developed for heavy metal removal from aqueous systems[4]. Among these technologies, adsorption process offers optimum removal of heavy metals from aqueous solution in terms of initial cost, simple design, and easy operation[5]. Although a variety of materials can be employed in adsorption process, activated carbon is among the most widely used adsorbent. Activated carbon is considered to be universal adsorbent because of its inherent physical properties such as large surface area, porous structure, high adsorption capacity and large reactive surface[6].

Activated carbon derived from various agricultural waste products such as almond husk[7], coconut oilcake[3], tamarind nuts[8], palm shell[9], olive stone[10], and peanut shell[11] have been successfully applied towards nickel (II) removal. The aim of this study is to investigate the application of activated carbon prepared from cottonseed cake (CSCC) and its capacity for Ni (II) removal from aqueous solution has been investigated. The effect of various parameters like contact time, pH and adsorbent dosage has been studied. Various kinetics and isotherm models were tested with experimental data. Simultaneously the performance of CSCC was evaluated with commercial activated carbon (CAC) procured from market.

EXPERIMENTAL

Procedure for adsorbent preparation and activation

The cottonseed cake sample, which has been produced at a cottonseed oil factory, was used in this study. The oilcake was washed with water, dried in hot air-oven at 100-110°C for 24 hr. Then, it was treated with concentrated sulphuric acid in 1:2 weight ratios and kept in an air-oven at 150 ± 5°C for 24 hr. The carbonized material was washed with distilled water and soaked in 1% sodium bicarbonate for 24 hr to remove any free acid. The material was then washed with distilled water, dried and sieved to 20-50 ASTM mesh size for use in the experiments (CSCC). The commercially available activated carbon (CAC) (SD fine chemicals) was procured from the market and sieved to 20-50 ASTM mesh size and used for evaluation purposes. The characteristics of both carbons were tested as per ISI- 877[12] and given in Table 1.

Table 1: Characteristics of the carbon

Parameter	CSCC	CAC
Bulk density (g mL^{-1})	0.62	0.70
Moisture (%)	12.80	19.80
Ash (%)	11.80	9.00
Solubility in water (%)	2.20	0.58
Solubility in 0.25 M HCl (%)	14.56	2.28
pH	6.10	8.20
Decolorizing power (mg g^{-1})	2.50	1.60
Phenol number	78.00	40.00
Ion exchange capacity (m equiv g^{-1})	0.36	Nil
Surface area (m^2g^{-1})	92.00	85.00
Iron (%)	0.01	0.01

Preparation of solutions

A stock solution containing 100 mg L^{-1} of Ni (II) was prepared by dissolving 0.4479 g of AR $NiSO_4.6H_2O$ in 1000 mL of deionized water. Standard solutions of different concentrations as might be required were later prepared from the stock. The pH of the solution was adjusted using 0.1 N HCl or 0.1 N NaOH solutions.

Batch adsorption studies

The batch experiments were carried out in polythene bottles (300 mL capacity). 100 mL of the solution containing 10 mg L^{-1} of Ni (II) ions under investigation adjusted desired pH were taken in bottles and equilibrated for specific periods of time in a temperature-controlled shaker. At the end of equilibration period, the solutions were centrifuged and the Ni (II) concentrations were determined with an atomic absorption spectrophometer. Adsorption isotherm and kinetic studies were carried out with different initial concentrations of Ni (II) by the modified carbon dosage at constant level. Ni (II) removal (%) was calculated using the following equation:

$$\text{Removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \qquad \ldots(1)$$

The adsorption capacity of Ni (II) ions adsorbed per gram of adsorbent (mg g^{-1}) was calculated by –

$$q_e = \frac{C_0 - C_e}{M} \times V \qquad \ldots(2)$$

where C_0 and C_e are the initial and equilibrium Ni (II) concentrations (mg L^{-1}); V is the volume of the Ni (II) solution (L); M is the mass of the adsorbent used (g), respectively.

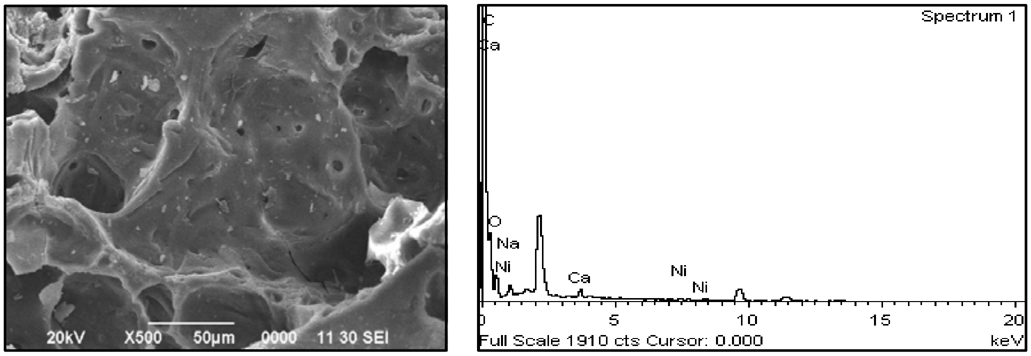
SEM-EDX analysis

A scanning electron microscope (JOEL JSM 6360) was used to visualize the surface morphology and structure of Ni (II) ion-loaded adsorbent. EDX was used to confirm the elements present in the adsorbent before and after adsorption of the metal ions.

RESULTS AND DISCUSSION

SEM-EDX analysis

The SEM image (Fig. 1) shows a highly porous morphology of adsorbent with pores of different sizes and shapes. The pores were prominent on the surface of sorbent before sorption. After the sorption of Ni (II) ions the pores were filled, as confirmed with an EDX analysis. The EDX spectra of the Ni (II) ion adsorbed on CSCC and CAC show peaks for the metal ions in addition to the other cations, confirming the adsorption of Ni (II) ions on the surface of the adsorbent (Fig. 1).



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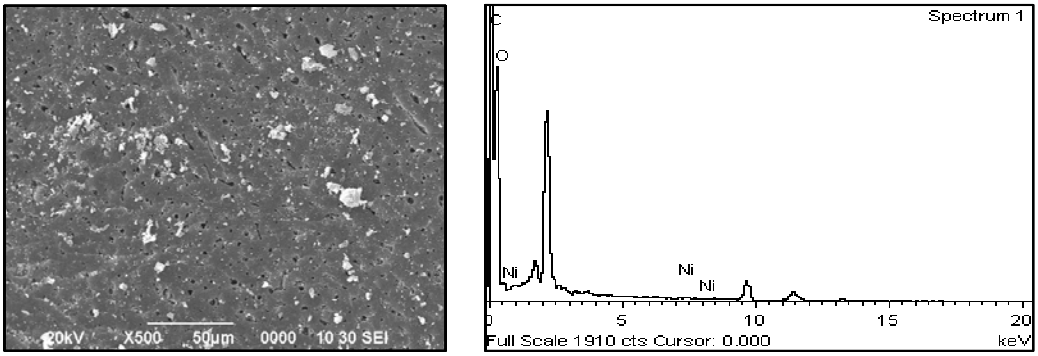

Fig. 1: SEM image of CSCC, CAC and EDX patterns for CSCC, CAC after Ni (II) adsorption

Effect of agitation time

From Fig. 2, it shows that the removal of Ni (II) ions increases with time and attains equilibrium in 5 h for both CSCC and CAC for an initial Ni (II) concentration of 10 mg L^{-1} and carbon dosage 100 mg/100 mL. In the case of CSCC and CAC 92 and 28% Ni (II) removal was achieved, respectively.

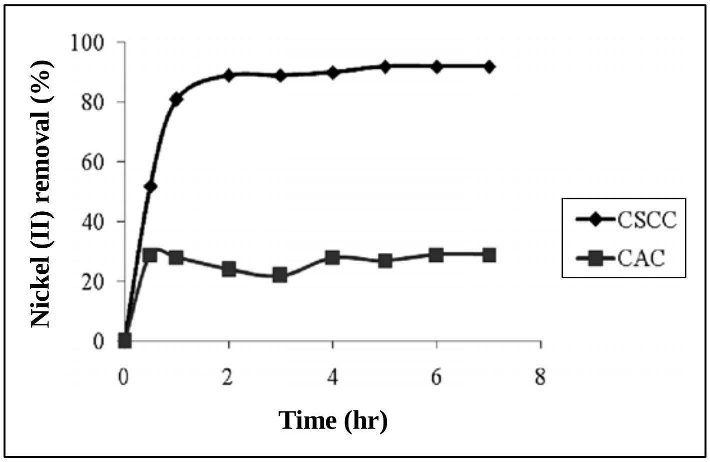

Fig. 2: Effect of agitation time on Ni (II) adsorption

Effect of pH

From Fig. 3, it could be observed that the adsorption increases with increase in pH and attains maximum removal of 92% over the pH range at 3.0-8.0 for CSCC and 33% at pH

6.5 for CAC. It could be noticed that CSCC is two times more effective in the removal of Ni (II) ions when compared with CAC under optimum pH conditions. Moreover CSCC has a wide range of pH when compared with CAC. The fact that at low pH the cations compete with the H^+ ions in the solution for active sites and therefore lower adsorption. The surface charge of the adsorbent is a strong function of the pH. Therefore, at high pH values surface of the adsorbent has a higher negative charge which result higher attraction of cations. At higher pH, Ni (II) ions precipitated as their hydroxides which decreased the rate of adsorption.

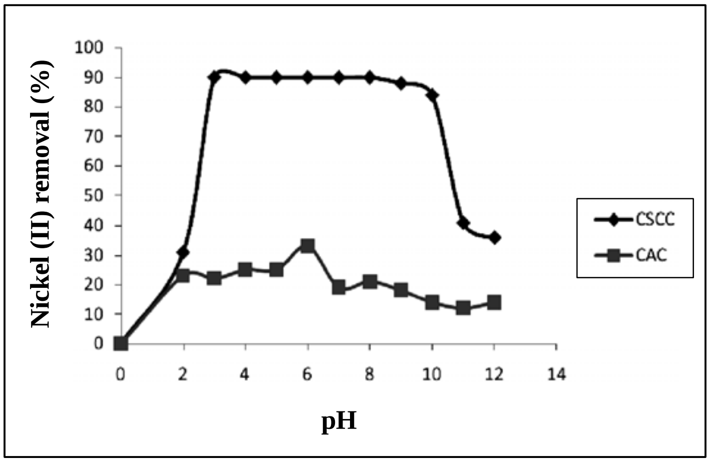

Fig. 3: Effect of pH on the adsorption of Ni (II)

Effects of carbon dosage

Fig. 4 shows the removal of Ni (II) as a function of carbon dosage by both CSCC and CAC. It is evident that 99% removal of Ni (II) from 100 mL solution containing 10 mg L^{-1} of Ni (II), a minimum carbon dosage of 300 mg of CSCC is required. However, for the same solution a maximum removal of only 44% was observed for CAC dosage of 500 mg/100 mL. This data clearly indicated that CSCC is nearly 1.7 times more effective than CAC. This may be due to the moderate ion-exchange capacity of CSCC as compared to CAC.

Adsorption isotherms

The purpose of the adsorption isotherms is to relate the adsorbate concentration in the bulk and the adsorbed amount at the interface. The simplest adsorption isotherm is based on the assumptions that every adsorption site is equivalent and that the ability of a particle to bind there is independent of whether or not adjacent sites are occupied. Langmuir and Freundlich isotherm are commonly used in batch adsorption studies.

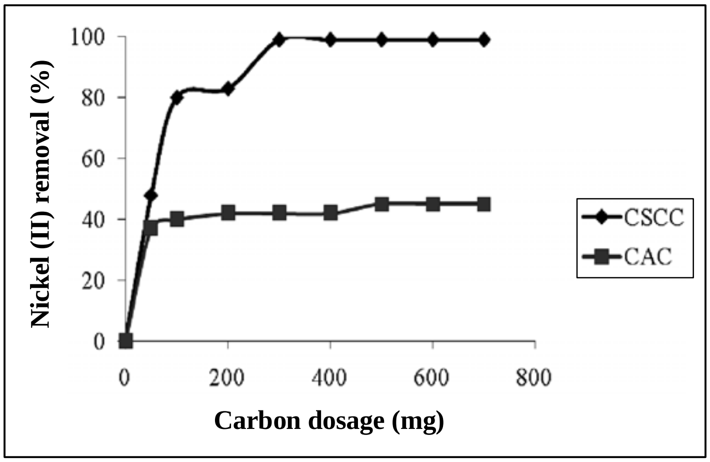

Fig. 4: Effect of carbon dosage on the Ni (II) adsorption

The Langmuir model[13] assumes that the uptake of metal ions occur on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions. The model takes the following form:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \quad \ldots(3)$$

Where, C_e is the equilibrium concentration (mg L^{-1}), q_e is the amount of nickel adsorbed per unit mass of the adsorbent (mg g^{-1}), and Q_0 and b are Langmuir constant related to adsorption capacity and energy of adsorption, respectively. Langmuir constants can be obtained from the plot of C_e/q_e versus C_e.

To determine whether the adsorption is favourable, a dimensionless constant separation factor or equilibrium parameter R_L is defined based on the following equation[14]:

$$R_L = \frac{1}{1 + bC_0} \quad \ldots(4)$$

The Freundlich[15] isotherm is derived by assuming a heterogeneous surface with a non uniform distribution of the heat of sorption. It can linearly be expressed as follows:

$$\log q_e = \log K_F + (1/n) \log C_e \quad \ldots(5)$$

where K_F (mg g^{-1}) and 1/n are the Freundlich constants related to sorption capacity and intensity, respectively. The values of 1/n less than 1 represent a favourable adsorption. The Freundlich constants can be obtained from the plot of log q_e versus log C_e.

The linearized Langmuir and Freundlich adsorption isotherms of Ni (II) ions obtained at 27 ± 2°C is given in Fig. 5 and 6. The isotherm constants and correlation coefficients (R^2) are summarized in Table 2. From Table 2, the CSCC and CAC are fit well into Langmuir model based on the R^2 value and the values of R_L are in between 0-1 indicating a favourable adsorption process. It could be concluded that the homogeneous distribution of active sites on the carbon adsorbent system is predominant. According to Langmuir isotherm, the monolayer saturation capacity (Q_o) of Ni (II) ion was found to be 43.48 mg g^{-1} for CSCC, which was about 3.2 times greater than that of CAC (13.42 mg g^{-1}).

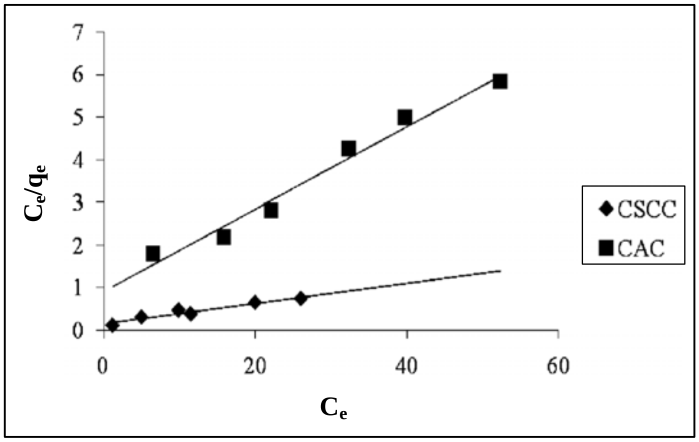

Fig. 5: Langmuir adsorption isotherm for adsorption of Ni (II)

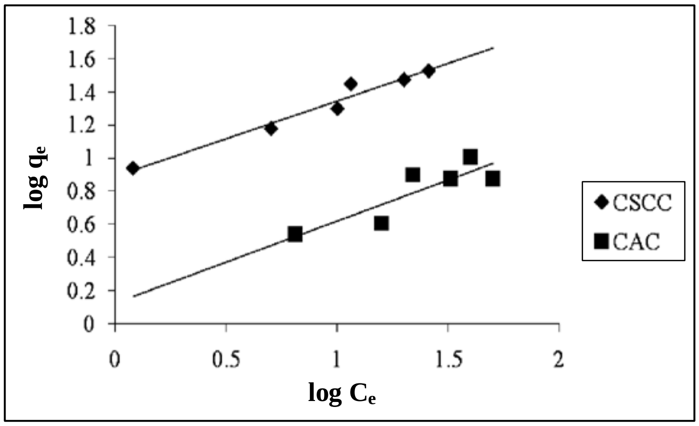

Fig. 6: Freundlich adsorption isotherm for adsorption of Ni (II)

Table 2: Isotherm parameters for Ni (II) adsorption onto CSCC and CAC

Adsorbent	Freundlich isotherm			Langmuir isotherm			
	K_F (mg g^{-1})	1/n	R^2	Q_0 (mg g^{-1})	b (L mg^{-1})	R^2	R_L
CSCC	7.80	0.454	0.899	43.48	0.173	0.937	0.37-0.09
CAC	1.34	0.497	0.762	13.42	0.937	0.976	0.10-0.02

Adsorption kinetics

In order to find out the mechanism of sorption, adsorption kinetics of the Ni^{2+} ions on the CSCC and CAC were studied using the pseudo-first order[16] and pseudo-second order[17] models.

The pseudo-first order reaction equation of Lagergren was widely used for the adsorption of liquid/solid system on the basis of solid capacity. Its linear form is generally expressed as follows

$$\text{Log}\,(q_e\text{-}q_t) = \log q_e - \frac{k_1}{2.303}\,t \quad \ldots(6)$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the adsorption amount at equilibrium and at time t (min), respectively. k_1 (min^{-1}) is the rate constant of the pseudo-first order adsorption process. The constants were determined experimentally by plotting of log (q_e-q_t) versus t and given in Table 3. The correlation coefficient (R^2) values are found to be lower than that of pseudo-second order kinetics and the theoretical values ($q_{e,\,cal}$) are far lower than those experimental data, $q_{e,exp}$ (Table 3), implying that the adsorption process does not follow fully the pseudo-first order adsorption rate expression.

The pseudo-second order model is based on the assumption that the adsorption follows second- order rate equations. The linear form can be written as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \ldots(7)$$

where k_2 (g $mg^{-1}min^{-1}$) is the rate constant of adsorption. By plotting a curve of t/q_t against t, q_e and k_2 can be evaluated. In order to compare quantitatively the applicability of kinetic models in fitting to data, the percentage relative deviation (P %) was calculated by the following expression:

$$\text{P (\%)} = 100/\text{N} \sum \left[\frac{q_{e(\exp)} - q_{e(theo)}}{q_{e(\exp)}} \right] \quad \ldots(8)$$

Where $q_{e(exp)}$ is the experimental value of q_e at any value of C_e, $q_{e(cal)}$ is the corresponding calculated value of q_e and N is the number of observations. It is found that the lower value of percentage deviation (P %), better is the fit. It is generally accepted that when P% value is less than 5, the fit is considered to be excellent[18].

The values of q_e, k_2, and R^2 are listed in Table 3. The R^2 values are also closer to unity (Table 3), confirming the applicability of the pseudo-second order equation. In addition, difference between the $q_{e,\ exp}$ and $q_{e,\ cal}$ is very little (Table 3), reinforcing the applicability of this model. Furthermore, the percent relative deviation (P %) is also found to be less than 5% in the case of pseudo-second order. This suggests that the rate-limiting step of this sorption system may be controlled by chemical sorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate. Therefore, the pseudo-second order constant k_2 is applied to calculate the film and pore diffusion coefficients.

Table 3: Pseudo-first order and pseudo-second order constants for Ni (II) adsorption onto CSCC and CAC

Adsorbent	**C_0 (mg L^{-1})**	**q_e (exp) (mg g^{-1})**	**Pseudo-first order**				**Pseudo-second order**			
			k_1 (min^{-1})	**q_e (cal) (mg g^{-1})**	**R^2**	**P (%)**	**k_2 (g mg^{-1} min^{-1})**	**q_e (cal) (mg g^{-1})**	**R^2**	**P (%)**
CSCC	3	2.50	0.007	2.93	0.925	17.20	0.005	2.40	0.964	4.00
	5	4.20	0.016	7.47	0.907	77.86	0.001	4.38	0.957	4.29
	7	6.50	0.005	2.33	0.981	64.15	0.005	6.80	1.000	4.62
	10	9.95	0.009	2.55	0.978	74.37	0.010	10.10	0.999	1.52
CAC	3	2.10	0.014	1.44	0.988	31.43	0.010	2.20	0.989	4.76
	5	2.90	0.016	3.13	0.882	8.04	0.007	3.00	0.974	3.45
	7	3.80	0.014	3.50	0.947	7.89	0.005	3.95	0.949	3.95
	10	5.40	0.018	4.18	0.980	22.59	0.005	5.20	0.997	3.70

In order to further assess the nature of the diffusion process responsible for the adsorption of Ni (II) on CSCC and CAC, attempts were made to calculate the pore and film diffusion coefficients for various concentrations of Ni(II) using the following the equation[19]:

$$D_p = 0.03\ r_o^2 / t_{1/2} \qquad \ldots(9)$$

where D_p is the pore diffusion coefficient ($cm^2\ s^{-1}$), r is the radius of the sorbent (cm), and $t_{1/2}$ is the half-life period (sec).

$$D_f = 0.23\ r_o\ d\ C^* / C\ t_{1/2} \qquad \ldots(10)$$

where D_f is the film diffusion coefficient ($cm^2\ s^{-1}$), d is the film thickness (cm), and C*/C is equilibrium loading of the sorbent. According to Michelsen[20] et al., if film diffusion to be the rate determining process in the adsorption of heavy metals on a sorbent, the values of film diffusion coefficient (D_f) should be between 10^{-6} and 10^{-8} $cm^2\ s^{-1}$. If pore diffusion D_p were to be rate determining process, its value should be in the range of 10^{-11}-10^{-13} $cm^2\ s^{-1}$. It is evident from the Table 4 that the removal of Ni (II) follows film diffusion process, since the coefficients values are closer to the range of 10^{-6}-10^{-8} $cm^2\ s^{-1}$.

Table 4: Diffusion co-efficient for the removal of Ni (II) by CSCC and CAC

Concentration of Ni (II) (mg $L^{-1)}$	Diffusion co-efficient ($cm^2\ s^{-1}$) CSCC		Diffusion co-efficient ($cm^2\ s^{-1}$) CAC	
	Pore diffusion (D_p)	Film diffusion (D_f)	Pore diffusion (D_p)	Film diffusion (D_f)
3	8.266×10^{-9}	1.829×10^{-8}	1.240×10^{-8}	2.314×10^{-8}
5	2.066×10^{-8}	4.628×10^{-8}	1.653×10^{-8}	2.557×10^{-8}
7	1.653×10^{-8}	4.100×10^{-8}	1.653×10^{-8}	2.381×10^{-8}
10	4.133×10^{-8}	6.613×10^{-8}	2.066×10^{-8}	2.975×10^{-8}

Thermodynamic parameter

To judge whether the adsorption process is spontaneous or non-spontaneous, the value of free energy of adsorption (ΔG^o) was calculated by the following equation,

$$\Delta G^o = - RT \ln b \qquad \ldots(11)$$

Where, R is the universal gas constant (8.314 J $mol^{-1}\ K^{-1}$), T is the absolute temperature (K) and b is the Langmuir constant. The value of ΔG^o is -4.376 and -0.160 KJ mol^{-1} for CSCC and CAC, respectively. The negative value of ΔG^o indicates the spontaneous nature of the adsorption.

CONCLUSION

The results of the present investigation show that the activated carbon prepared from cottonseed cake waste, generated from oil industries after extracting oil, is capable of removing Ni (II) effectively from aqueous solution. Equilibrium data agreed well with Langmuir isotherm for CSCC and CAC. The adsorption capacity of CSCC is found to be more and quantitative than CAC based upon its wider pH range for adsorption of Ni (II) and also on the carbon dosage. The adsorption of Ni (II) on both carbons follows pseudo-second order kinetics with film diffusion process and ion exchange process being the essential rate controlling step. Thermodynamic study shows that the adsorption is spontaneous and feasible. The results obtained in this study; show that CSCC is a good and effective adsorbent for the removal of heavy metals and could be used in water and wastewater treatment.

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Accepted : 31.01.2015