Thermodynamic, Kinetic, Batch Adsorption and Isotherm Models for the Adsorption of Nickel from an Artificial Solution Using Chloroxylon Swietenia Activated Carbon

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   Chloroxylon Swietenia tree bark was used as an eco-friendly bio-adsorbent in our research work. This work investigates the adsorption efficiency of nickel using a batch adsorption technique. *Chloroxylon swietenia,* commonly known as East Indian satinwood, is also known as Porasu in Tamil. *Chloroxylon swietenia* activated carbon (CSAC) was prepared from *Chloroxylon swietenia* tree bark as an adsorbent. Effective experimental parameters such as carbon dosage, effect of pH parameter, contact time, pseudo-first order kinetic model, and Elovich model were employed for the removal of nickel from an aqueous solution. The equilibrium data was calculated using adsorption isotherm models such as Langmuir and Freundlich. The percentage removal of nickel was calculated by thermodynamic parameters. Our results proved that the removal of nickel by CSAC was endothermic and spontaneous in nature. The adsorption of nickel on CSAC was determined by using the Fourier transform infrared spectroscopy technique.

Keywords: *Chloroxylon Swietenia* Activated Carbon (CSAC), Nickel(II) ions, Adsorption isotherm, Kinetic, contact time and sticking probability (S*)

INTRODUCTION

   Water is indispensable to human beings, plants, and animals. But recently, water has become easily polluted due to anthropogenic activities. The effluent contains many toxic metals such as Ni, Pb, Cd, *etc.* that are released into the environment from various chemical industries such as refinery oil plants, mining activities, electroplating, electro-less nickel plating, manufacturing of batteries, rubber industries, plastic industries, and textile industries [1,2]. These toxic metals are very harmful to aquatic living organisms and human beings [3]. They lead to health issues such as kidney and lung damage, and gastrointestinal disorders. Nickel is abundant on the Earth. It is mainly used in nickel plating, the manufacturing of steam electric power plants, and nickel-cadmium batteries. Nickel compounds are carcinogenic in nature. It affects the lung in the human body [4,5]. Nickel is a well-known toxic pollutant. The high concentration of nickel also causes anemia, diarrhea, headache, chest pain, vomiting, tightness in chest, shortness and rapid breathing problems, and hepatitis [6].

   Coagulation, ion exchange, precipitation, adsorption, electrochemical processes, solvent extraction, and flotation techniques were used to remove nickel ions from waste water [7-10]. Consequently, there is a need for adsorption of nickel ions in waste water [11,12]. In order to overcome this

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problem, we have employed activated carbon to remove the nickel from artificial solutions using adsorption techniques.

Our aim in this research work is to introduce the *Chloroxylon Swietenia* Activated Carbon (CSAC) as a bio-adsorbent synthesized from *Chloroxylon Swietenia* tree barks to remove the nickel ions in stock solution under different experimental methods such as carbon dosage, effect of initial pH, contact time, kinetic model, Langmuir adsorption isotherm, and Freundlich adsorption isotherm models.

MATERIALS

Adsorbate

In this work, GR grade reagents were used. The reagents were purchased from Madras Scientific Company, India. The Stock Solution (1000 ppm) has been prepared by Nickel(II) Nitrate hexa-hydrate and distilled water. This stock solution was once further diluted to the required concentrations before using.

Adsorbent

Chloroxylon Swietenia tree bark was collected from Komapuram village near Pudukkottai, South India (Fig. 1). Freshly collected tree bark was dehydrated and dried well and carbonised with a minimum amount of conc. H_2SO_4, which was maintained at 160 °C for 8 h and 30 min. Thereafter, the obtained activated carbon was thoroughly cleaned and dried at 120 °C for one hour. It was dipped in 5% $NaHCO_3$ and left for a day to remove any remaining acid [13]. Carbonized fabric was heated at 1100 °C for half a day in a muffle oven. Finally, the dried powder was sieved with the aid of a mesh.

EXPERIMENTAL METHODS

Batch Adsorption Experimental Method

A Batch adsorption experiment was conducted in Erlenmeyer 250 ml flasks by using 50 ml of Ni(II) ion solution of different initial concentrations. The experimental tests were done in the temperature range of 30, 40, 50 and 60 °C. The initial pH was used in the removal of nickel using CSAC and was determined at a pH of 3 to 9 with concentration solution of Ni ion. This method was carried

Fig. 1. Chloroxylon swietenia bark activated carbon.

out in a mechanical shaker with time intervals. The pH values of the initial Ni(II) ion solution (50 mg l^{-1}) were adjusted using a 0.1 molar solution of hydrochloric acid or sodium hydroxide solution. CSAC was mixed with Ni(II) ion solution and agitated for the sample until equilibrium was obtained. After the agitation, the Ni(II) ion solution was withdrawn at different time intervals, between 15 to 60 minutes, and centrifuged at 120 rpm for 10 min. The following equations were used for the elimination of Nickel ion percentage [14].

$$Percentage\ removal\ of\ Ni = \left[\frac{C_0 - C_t}{C_0}\right] \times 100 \qquad (1)$$

$$Q = \frac{C_i - C_t}{m} \times V \qquad (2)$$

Where C_i and C_t are the initial and liquid phase concentrations of Ni(II) at time 't' (mg l^{-1}), Q is the amount of nickel adsorption onto CSAC adsorbent at any time (mg g^{-1}), m is the mass of CSAC, and V is the volume of solution of Nickel.

RESULT WITH DISCUSSIONS

Contact time for Adsorption of Nickel

The agitation time for the removal of nickel ion on
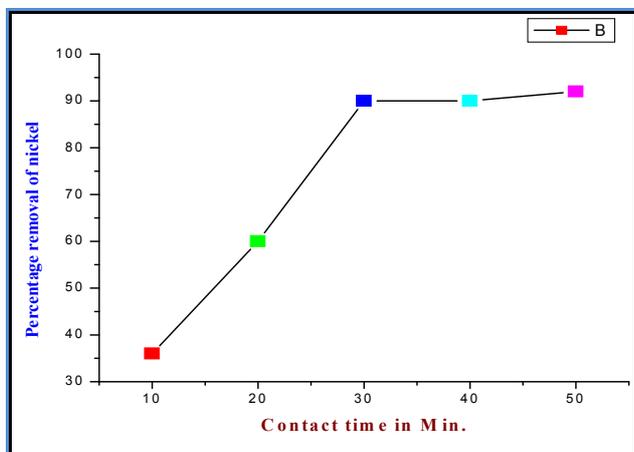
Fig. 2. Contact Time for Nickel Adsorption{[Nickel] = 20 mg l^{-1}; Temperature 30 °C; CSAC of Adsorbent dose = 0.025 g/50 ml}.

Fig. 3. Carbon dosages for the removal of nickel [Nickel] = 20 mg l^{-1}; Temperature 30 °C; Contact time 60 min}.

CSAC was studied with time intervals, which are shown in Fig. 2. The percentage of removal of nickel ion increased with an increase in agitation time; thereafter, it attains equilibrium at 30 min. The percentages of removal efficiency of nickel ions at 10 to 30 min as a removal percentage of Ni(II) adsorption, were 32, 58 and 90%, respectively. The graph was gradually increased until it reached the saturation point of Ni(II) ion on CSAC [15].

Carbon Dosage for Adsorption Studies of Nickel

The carbon dosages studied for the percentage removal of nickel ion ranged from 0.025-0.250 g. The Percentage removal of nickel ion increased as carbon doses increased. The extended adsorption was due to an increase in active sites on the surface of CSAC. In Fig. 3, the maximum removal of nickel ions was at 20 mg l^{-1}, and the adsorption dosage was 0.025 g/50 ml. Figure 3 also indicates that there is an increase in removal percentage as an adsorbent dosage increases to a certain point. Because of the availability of pore level in the surface area of CSAC, then it attains equilibrium due to the flow of adsorbate from liquid to the CSAC surface [16,17].

The Initial pH Parameter for Adsorption Studies

The initial pH solution was studied in the pH from 3 to 9. As shown in figure, the percentage removal of nickel ions

increased to 89% before gradually declining after pH 6.4. The least pH value was obviously specified that the CSAC adsorbent may become positively charged as a result of being covered by H_3O^+ ions and thus, the competitive effect of H_3O^+ ions, the electrostatic repulsion between the Ni ions, and the positively charged active adsorption sites on the surface of the CSAC led to a decrease in uptake of Ni ions. At larger pH values, the active sites of CSAC receive a negative charge, leading to an increase in nickel ion due to the electrostatic forces [18].

Isotherm Models

Adsorption isotherm model. Isotherm models were used to describe the relationship between the mass of substances that held onto the adsorbent [19]. The q_e value was calculated by the following formula.

$$q_e = \frac{(C_0 - C_t)}{W} \tag{3}$$

a) Freundlich isotherm for adsorption studies. Freundlich isotherm is an empirical formula, which is employed for the adsorption of solutes from solution onto solid surface. This expression is shown in Eq. (4).
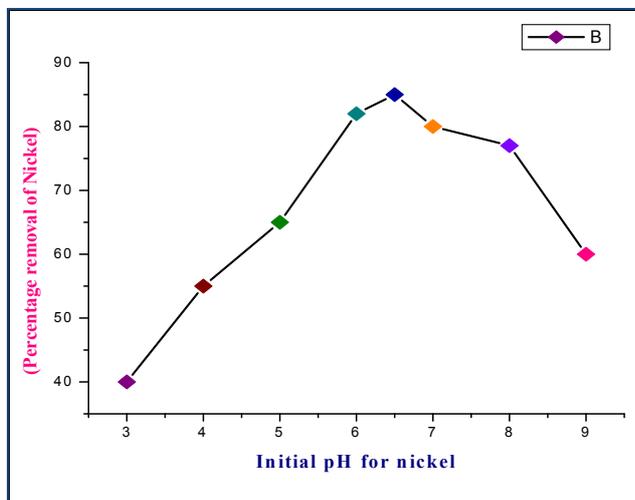
Fig. 4. Graph pH for the elimination of nickel {[Nickel] = 20 mg l^{-1}; Temperature 30 °C; Carbon dose = 0.025 g/50 ml^{-1}}.
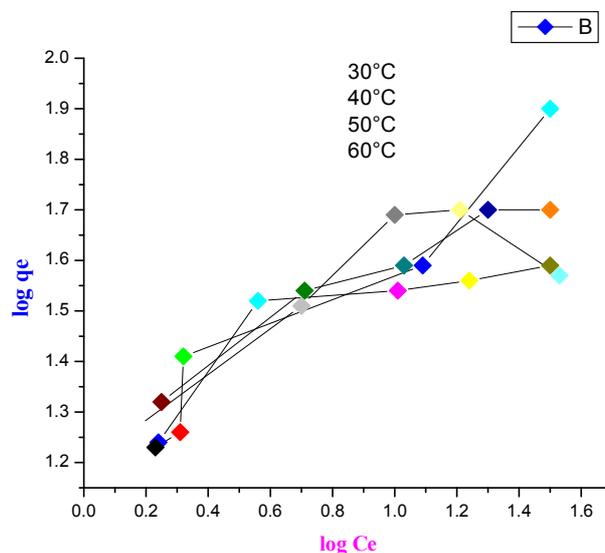
Fig. 5. Freundlich adsorption isotherms for nickel adsorption.

$$q_e = K_F C_e^{1/nF} \tag{4}$$

It can be linearized:

$$\ln q_e = \ln K_F + \frac{1}{nF} \ln C_e \tag{5}$$

Where q_e: quantity of nickel ion held at equilibrium (mg g^{-1})

C_e: concentration of nickel ion in the aqueous level at equilibrium (ppm)

K_F and 1/nf: Freundlich constants for adsorption capacity and adsorption intensity

The K_F– and 1/nF were calculated from the slope as well as intercept of the lnq$_e$ *vs*. lnC$_e$ plot and the values are shown in Tables 1 and 2. The values of K_F specified that CSAC had a high adsorption capacity for Ni(II) removal in stock solution [20]. The n$_F$ should have values in the range of 1 and 10 (*i.e.*, 1/n$_f$ < 1) to time to be determined as favourably adsorbed by CSAC, which is shown in Fig. 5.

b) Langmuir model for nickel adsorption. According to the Langmuir adsorption isotherm theory, the active surfaces have equivalent affinity for the adsorbate. The Mathematical form of the Langmuir adsorption expression is represented as

Table 1. Equilibrium Parameters for the Removal of Nickel onto CSAC

Ni	C$_e$ (mg l^{-1})				Q$_e$				Removal (%)			
	30 °C	40 °C	50 °C	60 °C	30 °C	40 °C	50 °C	60 °C	30 °C	40 °C	50 °C	60 °C
10	2.032	1.648	1.100	1.044	15.935	16.704	17.800	17.912	79.676	83.521	89.001	89.562
20	6.042	5.496	4.967	3.846	27.915	29.009	30.066	32.307	69.789	72.522	75.166	80.768
30	12.562	11.977	10.437	9.670	34.875	36.046	39.126	40.660	58.125	60.076	65.211	67.767
40	19.272	17.624	16.718	15.681	41.457	44.752	46.565	48.638	51.821	55.940	58.206	60.797
50	28.564	27.573	26.964	25.363	42.873	44.855	46.071	49.274	42.873	44.855	46.071	49.274

Table 2. Isotherm Models for the Removal of Nickel Ions on CSAC

Types of adsorption isotherm	Constant	Temperature (°C)			
		30	40	50	60
Freundlich	K_F (mg g^{-1}) (l m^{-1})$^{1/n}$	12.928	14.607	17.811	18.960
	n_F	2.618	2.742	3.152	3.075
	R^2	0.971	0.971	0.974	0.963
Langmuir	Q_m (mg g^{-1})	50.074	51.710	51.177	54.293
	K_L (l m^{-1})	0.213	0.251	0.373	0.404
	R^2	0.997	0.992	0.994	0.997

$$\frac{C_e}{q_e} = \frac{1}{q_m^{KL}} + \frac{C_e}{q_m} \qquad (6)$$

Here, q_e is the quantity of nickel held in adsorbate at equilibrium (mg g^{-1}), C_e is the concentration of nickel in the stock solution at equilibrium (ppm), q_m is the maximum nickel intake (mg g^{-1}), and K_L is the Langmuir constants related to adsorption capacity and the adsorption energy (mg g^{-1}). The linear plot of C_e/q_e *vs.* C_e was plotted to find the values of q_m and K_L, shown in Fig. 6, and the collected data was given in Table 2. The values of K_L decreased with an increase in temperature. The high values of K_L show the more adsorption affinity. The equilibrium parameter (R_L) is calculated by Eq. (7) [21,22].

$$R_L = \frac{1}{1 + KLC_0} \qquad (7)$$

Where C_0: - initial concentration of nickel ion
The R_L values for nickel ion removal were calculated from 30 °C to 60 °C temperatures and different concentrations. In Table 3, at all tested concentrations and temperatures, the values of R_L for Ni(II) removal on the CSAC were < 1 and > 0, which indicates that the adsorption was favorable.

Analytical Evidence

    FT-IR spectroscopy. The FT-IR spectra of fresh *Chloroxylon Swietenia* Activated Carbon before and after adsorption of nickel ions are shown in Fig. 7. This study determines the characteristic surface of the CSAC adsorbent, which is responsible for the adsorption of Ni(II)

Table 3. The R_L Values for the Removal of Nickel Iions onto CSAC

Ni	Temperature (°C)			
	30 °C	40 °C	50 °C	60 °C
10	0.1578	0.1374	0.0969	0.0902
20	0.0857	0.0738	0.0509	0.0472
30	0.0588	0.0504	0.0345	0.0320
40	0.0448	0.0383	0.0261	0.0242
50	0.0361	0.0309	0.0210	0.0194
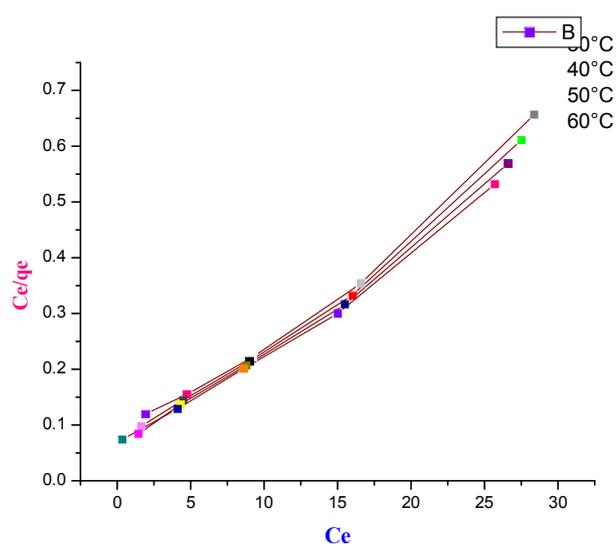
Fig. 6. Langmuir model for the elimination of Nickel.
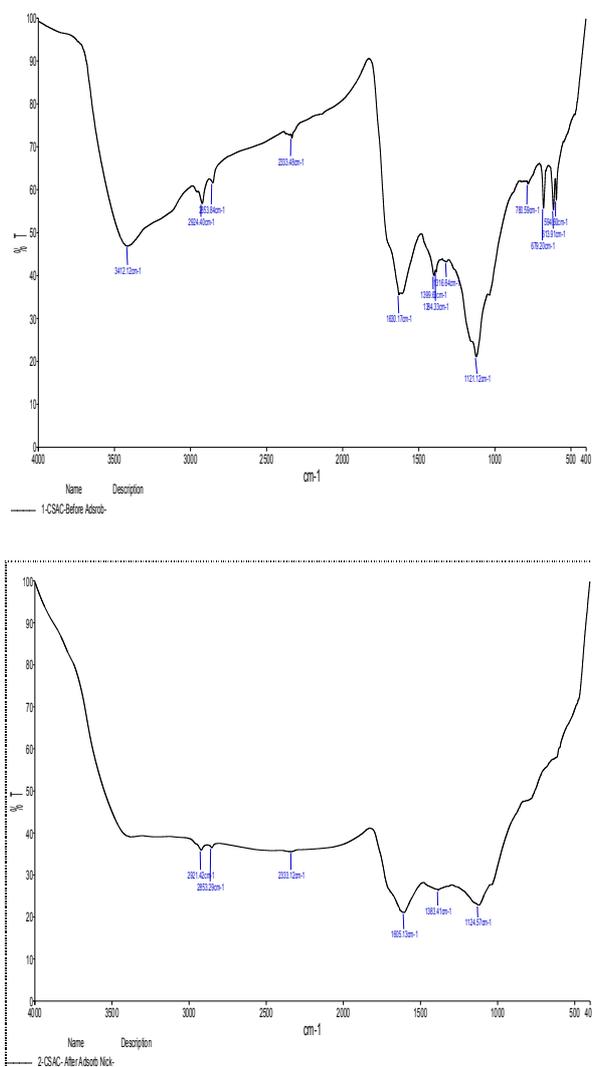
Fig. 7. FT-IR Spectra for before and after adsorption of nickel on CSAC.

ions. A slight reduction in stretching vibration adsorption bands was obtained. The stretching vibration band for hydroxyl group was found at 3412 cm^{-1}. It clearly shows that adsorption of nickel ions on CSAC adsorbent occurs by physical attraction forces, but not by the chemical forces [23,24].

Eeffect of Temperature

In this study, the nickel adsorption increased speedily from 303 k to 333 k; this is because an increase in

experimental temperature affects the adsorption and leads to an increase in surface coverage area of CSAC. It may also be the reason behind the increased infiltration of nickel into the inner micro pores at high temperature [20]. This indicates on endothermic adsorption process at controlled condition.

Kinetics for Adsorption

The mechanism of the removal of nickel with rate can be calculated using adsorption kinetics. Accumulation of metal on the surface of the adsorbent can be evaluated by the following mechanisms: A) Initial speed binding of Nickel on CSAC adsorbent; B) Two kinetic models have been employed to analyze the adsorption of metals.

First-order pseudo kinetic method was employed for determination of adsorption reaction rate. It was proposed by Lagergren in 1898. The plot of $\ln(q_e - q_t)$ has been linearly related with time t. Value of $\ln(q_e - q_t)$ *versus* time t must impart a linear correlation from the values of k_1 that is calculated from the slope [25].

Pseudo-first order for nonlinear form equation is given as

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{8}$$

Pseudo-first order for linear form equation is given as

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{9}$$

Where q_e and q_t refer to the amount of Ni(II) ion adsorbed (mg g^{-1}) at equilibrium and at any time, t (min), respectively and k_1 (1 min^{-1}) is the equilibrium rate constant for the pseudo-first order. Pseudo-second order for non-linear form equation is given as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{10}$$

Pseudo-second order for linear form equation is given as

$$\frac{t}{q_t} = \frac{1}{k^2 q_e^2} + (\frac{1}{q_e})t \tag{11}$$

The slope and intercept of the t/q_t *vs.* t plot were used to

Table 4. Adsorption Kinetics for the Removal of Ni(II) Ions on CSAC

Ni	Temperature (°C)	Second order kinetic (Pseudo)				Elovich kinetic model		
		q_e	k_2	R^2	H	α	β	R^2
10	30	24.4695	1.15E-03	0.9558	0.6858	1.4E+00	1.77E-01	0.9592
	40	21.3583	2.43E-03	0.9773	1.1092	2.6E+00	2.18E-01	0.9592
	50	19.9794	5.68E-03	0.9925	2.2679	1.5E+01	3.26E-01	0.9592
	60	19.9224	6.19E-03	0.9935	2.4585	2.0E+01	3.44E-01	0.9592
20	30	51.5329	3.31E-04	0.8236	0.8786	1.9E+00	9.12E-02	0.9058
	40	46.0919	5.33E-04	0.9104	1.1318	2.3E+00	9.54E-02	0.9288
	50	43.3668	7.94E-04	0.9654	1.4928	3.0E+00	1.00E-01	0.9601
	60	41.6346	1.16E-03	0.9658	2.0124	4.5E+00	1.10E-01	0.9431
30	30	52.9790	4.73E-04	0.7938	1.3276	2.8E+00	8.52E-02	0.8280
	40	51.7320	7.29E-04	0.9566	1.9508	4.0E+00	8.36E-02	0.9402
	50	59.0265	5.52E-04	0.9716	1.9235	3.8E+00	7.17E-02	0.9677
	60	52.1389	1.17E-03	0.9990	3.1890	6.6E+00	8.45E-02	0.9889
40	30	64.9919	4.96E-04	0.9728	2.0940	3.9E+00	6.20E-02	0.9734
	40	67.0329	5.23E-04	0.9929	2.3493	4.4E+00	6.08E-02	0.9905
	50	65.6576	6.56E-04	0.9927	2.8272	5.3E+00	6.23E-02	0.9820
	60	66.5664	7.19E-04	0.9953	3.1839	6.0E+00	6.23E-02	0.9835
50	30	122.7070	6.20E-05	0.4612	0.9339	2.3E+00	5.29E-02	0.8589
	40	109.8911	8.83E-05	0.5667	1.0663	2.5E+00	5.21E-02	0.8635
	50	87.0309	1.75E-04	0.6930	1.3274	2.9E+00	5.52E-02	0.8563
	60	93.1346	1.61E-04	0.6531	1.3951	3.1E+00	5.16E-02	0.8425

calculate the pseudo-second rate constant, k_2, in pseudo-second order kinetic model. The equilibrium rate constant values (k_2) were shown in Table 4. In Table 4, the value of R^2 (0.9905) is correlated to the pseudo-second order model exposed of Ni(II) adsorption [26].

Elovich model. The general Elovich equation is given by the following formula

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \tag{12}$$

Where α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is the desorption constant (g mg^{-1}). To simplify the Elovich equation of Chien and Clayton (1980), it is assumed that $\alpha\beta t \gg t$, and by applying boundary conditions qt = 0 at t = 0 and $q_t = q_t$ at t = t Eq. (13) becomes:

$$q_t = \frac{1}{\beta \ln(\alpha\beta)} + \frac{1}{\beta \ln t} \tag{13}$$

Since removal of nickel fits with the Elovich model, a plot of q_t vs. ln(t) should yield a linear relationship with the slope of (1/β) and an intercept of (1/β) ln (αβ). The values of α, β, and correlation coefficient (γ) are shown in Table 4. The data such as α, β, and γ were computed by the Elovich equation. It was specified that the values of α (initial adsorption rate) increased with temperature to the α values in pseudo-second order kinetics, which is due to increased active sites in CSAC.

Thermodynamical Studies

Thermodynamic constants were calculated to prove the adsorption nature of the present investigation. The values of ΔG, ΔH, and ΔS were determined to assess the possibility of spontaneous thermodynamics. The entropy change and enthalpy change were calculated from the Van't Hoff model [27].
From the plot values of ln$K$ as ordinate and 1/T as abscissa,

Table 5. Thermodynamic Quantities for the Removal of Nickel Ions on CSAC

Ni	$\Delta G°$				$\Delta H°$	$\Delta S°$	Ea	S*
	30 °C	40 °C	50 °C	60 °C				
10	-3441.550	-4223.533	-5614.746	-5951.023	23.725	89.727	2.023E+04	6.593E-05
20	-2109.143	-2525.574	-2974.087	-3972.875	16.081	59.674	1.212E+04	2.545E-03
30	-826.047	-1063.429	-1687.280	-2057.230	12.264	42.996	7.720E+03	1.989E-02
40	-183.565	-621.217	-889.533	-1214.810	10.010	33.766	5.642E+03	5.098E-02
50	-723.101	-537.486	-422.868	-80.415	6.876	20.235	3.163E+03	1.636E-01

we obtained the values of ΔH and ΔS using Eq. (15). We also obtained ΔG values from this equation.

$$K_t = \frac{C_{Ae}}{C_e} \quad (14)$$

$$\Delta G = \Delta H - T\Delta S \quad (15)$$

Where

ΔG: Free energy change (kJ mol^{-1}),
R: Universal gas constant (8.314J mol^{-1} K^{-1}),
K: Thermodynamic equilibrium constant,
T: Absolute temperature (K).

$$\Delta G = \Delta H - T\Delta S = -RT\ln K_c \quad (16)$$

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (17)$$

$$2.303\log\frac{q_e}{C_e} = \frac{\Delta S}{R} = \frac{\Delta H}{RT} \quad (18)$$

$$\log\frac{q_e}{C_e} = \frac{\Delta S}{R \times 2.303} - \frac{\Delta H}{RT \times 2.303} \quad (19)$$

The ΔS, ΔH, and ΔG values were obtained from the plot of log(q$_e$/C$_e$) *vs.* 1/T.
The enthalpy for physisorption was reported to be between 3.0 and 63.0 kJ mol^{-1} in liters. The ΔH values ranged from 1 to 8 kJ mol^{-1} are shown in Table 5, which indicate that the adsorption of Ni ion on CSAC was physisorption. The positive value of ΔH and the negative value of ΔG indicate that the adsorption of nickel onto CSAC was endothermic

and spontaneous in nature. The values of activation energy (E$_a$) and sticking probability (S*) were calculated from the slope and intercept of the plot of ln(1 - θ) *vs.* 1/T, which derived from the modified Arrhenius type equation and is related to surface coverage (θ) as given in the following equations.

$$\theta = (1 - \frac{C_e}{C_i}) \quad (20)$$

$$S^* = (1 - \theta_e)\frac{-E_a}{RT} \quad (21)$$

The S* value is dependent on the temperature of the system, which supports physical adsorption. The values are listed in Table 5. The $\Delta G°$ values were negative at all temperatures indicate that the reaction was spontaneous. The $\Delta G°$ values are shown in Table 5. Again, positive $\Delta H°$ values confirm that the adsorption was endothermic in nature. The positive value of $\Delta S°$ reflects the affinity of the adsorbent toward Ni(II) ion. The results are shown in Table 5, which indicate that the probability of the Ni(II) ion held on the surface of the adsorbent is very high as S* << 1; these values proved the possibility of physical adsorption.

CONCLUSIONS

This investigation was to evaluate whether CSAC could be employed as an alternative biosorbent for the adsorption of heavy metals in industrial effluents due to the high adsorption efficiency of nickel from stock solution. The adsorption of nickel ion using CSAC was affected by the effects of pH, temperature, contact time, and adsorbent

dose. The removal of nickel on CSAC was determined at 90% when 0.025 g of CSAC was agitated with a nickel solution of 20 mg l^{-1} for 30 min. The equilibrium data was fitted using isotherm models. According to pseudo-first order kinetics, the adsorption data was favorable. Analytical studies proved the characteristics of an adsorbent as well as the adsorption of Ni(II) ion onto CSAC. The negative values of $\Delta G°$ clearly indicated the spontaneity of nickel adsorption. The positive values of ΔS and the positive values of $\Delta H°$ indicated that they were endothermic in nature. The feasibility of nickel adsorption on activated carbon prepared from Chloroxylon Swietenia tree bark was proved by adsorption isotherm models, kinetic model, and thermodynamic studies.

ACKNOWLEDGMENTS

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