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Adsorption of Ni(II) from aqueous solution by activated carbons derived from tobacco stem

C. Narasimha Rao[a], K. Subbarayudu[a], Y. Vijaya[b], M. Venkata Subbaiah[c,*]

[a]*Deparment of Chemistry, Sri Venkateswara University, Tirupati 517502, AP, India*
[b]*Department of Chemistry, Vikrama Simhapuri University, Nellore 524003, AP, India*
[c]*Department of Chemical Engineering, Keimyung University, 2800 Dalgubeoldaero, Dalseo-Gu, Daegu 704-701, Republic of Korea*
Tel. +82 01068251981; email: mvsmunagapati@gmail.com

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ABSTRACT

Activated carbons from tobacco stem were identified as the most potent Ni(II) sorbent (Q_0 = 97.32 mg/g). The tested plant material adsorbed Ni(II) optimally at pH 5.3. The efficiency of the adsorbent was investigated using batch adsorption technique under different experimental conditions such as solution pH, initial metal ion concentration, and agitation time. The adsorption of Ni(II) followed pseudo-second-order kinetics. Adsorption isotherms were expressed by Langmuir and Freundlich models. Langmuir adsorption model fits the experimental data reasonably well than Freundlich model for the present study. The thermodynamic parameters such as standard Gibb's free energy change (ΔG°), standard enthalpy change (ΔH°), and standard entropy change (ΔS°) were evaluated. The thermodynamics of Ni(II) on activated carbons from tobacco stem indicates its spontaneous and endothermic nature. The results obtained show that activated carbons from tobacco stem, which has a very low economic value, may be used for the effective treatment of aqueous solutions contaminated with Ni(II).

Keywords: Biosorption; Activate carbons from tobacco stem; Isotherms; Kinetics; Thermodynamics

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1. Introduction

Of the most common toxic contaminants of industrial wastewaters, heavy metals are known to deleteriously affect all kinds of living organisms [1]. The rate at which effluents are discharged into the environment, especially water bodies is increasing as a result of urbanization. The presence of heavy metals in the environment is of major concern because of their bioaccumulating tendency, threat to human life, and the environment [2,3]. Ni(II) may be beneficial at trace amounts as an activator of some enzyme systems but the Ni(II) ion intake over the permissible limits results in different types of disease such as pulmonary fibrosis, lung cancer, renal edema, skin dermatitis, and gastrointestinal disorder such as nausea, vomiting, and diarrhea [4]. Hence, it is necessary to develop a low-cost, easily available material to remove Ni(II) from aqueous solutions. Removal of heavy metals from wastewater is an extremely significant step because of their destructive effects. Membrane separation [5] and adsorption [6] are the commonly employed methods

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*Corresponding author.

for the removal of heavy metals from aqueous solutions [7–11]. Removal of Ni(II) by adsorption using lignin [8], kaolin/poly (glycine) composites [9], bacteria [10], chelating sponge [11] were reported in the literature. Among biosorbent materials, activated carbons from agricultural wastes have proved to be both economic and eco-friendly as they are abundantly available, highly efficient in dilute effluents, and have high surface area-to-volume ratio. These provide a cost-effective solution for industrial wastewater management.

The tobacco tree of family Solanaceae is native to the Indian subcontinent. Unfortunately tobacco stems almost become waste after tobacco leaf reaped, which constitute a serious environmental problem and breaks the balance of ecological environment.

Hence, it is very significant to explore multipurpose utilization technologies to dispose waste tobacco stems. For this purpose, in the present study, adsorption of Ni(II) ions onto activated carbons derived from tobacco stems was investigated systematically with the variation in the parameters of pH, adsorbent dosage, agitation time, and the initial concentration of the adsorbate. The kinetics of Ni(II) adsorption system has been studied based on the assumption of pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. Langmuir and Freundlich isotherms were used to analyze the equilibrium data at different temperatures.

2. Materials and methods

2.1. Reagents and materials

Nickel Sulfate ($NiSO_4 \cdot 6H_2O$) was purchased from S.D. Fine Chemicals, Mumbai, India. Hydrochloric acid and Sodium hydroxide used for pH adjustment were procured from Merck, Germany. All glassware were cleaned with 20% nitric acid and repeatedly washed with triple distilled water then dried in oven for 1 h. All the reported values were average of the values obtained by repeating the experiment three times.

2.2. Preparation of biosorbent

The activated carbons were prepared by following standard procedures available in the literature [12]. Tobacco bark used in the present work was collected from adult trees (District Chittoor, Andhra Pradesh, India). The collected bark was washed with permuted water to remove dust particles and water soluble material, followed by repeated washing until the wash water contained no color. The washed materials were then completely dried in an oven at 80˚C for 24 h. The dried barks were then cut into small pieces, crushed, and sieved to eliminate fine particles (<0.5 mm). The obtained material was washed repeatedly with distilled water until the wash water contained no color and its electric conductivity and pH remain constant. The obtained material was then dried in an air circulating oven at 80˚C for 2 d and used for the preparation of activated carbons.

The material is impregnated with a boiling solution of 10% $ZnCl_2$ for 2 h and soaked in the same solution for 24 h. At the end of 24 h, the excess solution was decanted off and air dried. The materials were placed in muffle furnace, carbonized at 400˚C for 50 min. The dried material was powdered and activated in a muffle furnace kept at 800˚C for 50 min. The carbons obtained after activation were washed sufficiently with 4 N HCl. Then the material was washed with plenty of water to remove excess acid, dried, powdered, and preserved in glass bottles for use as adsorbents.

2.3. Characterizations of the adsorbent

Tobacco is an important crop with special economic value. The output of tobacco stem is almost equal to that of tobacco leaf. The wastes released due to industrial activities involved in tobacco generation constitute a serious environmental problem. Now a day’s tobacco stems almost became waste after tobacco leaf reaped and most of these were discarded as solid wastes. It produced the environmental contamination and air pollution. Hence, it is very essential to explore multipurpose utilization technologies to dispose tobacco stems. The approximate analysis of properties of activated carbons from tobacco stem is shown is Table 1.

Table 1
Characteristics of the adsorbent

Characteristics	Values
Moisture content (%)	11.8
Ash content (%)	13.89
Fixed carbon	73.1
Volatile matter (%)	14.40
Specific gravity, S	0.89
Conductivity, mS/cm	0.19
Porosity	50.56
Bulk density, D	0.44
Surface area, m^2/g	342
Matter soluble in water (%)	1.03
Matter soluble in acid (%)	1.59

2.4. Batch and equilibrium studies

All batch biosorption experiments were carried out in 125 mL stoppered Erlenmeyer flasks containing 100 mL of aqueous Ni(II) solution. The flasks were agitated at a constant speed of 160 rpm for 4 h in an incubator shake. The pH values of the solution were adjusted with dilute 0.1 N HCl or NaOH. The time required for reaching the equilibrium was estimated by drawing samples at regular time intervals. The biosorbent was separated by filtration and the metal content in the filtrate was determined by flame atomic absorption spectrometer. All the experiments were repeated three times and the average results were presented. The amount adsorbed per unit mass of adsorbent at equilibrium was obtained using the following equation:

$$q = \frac{(C_i - C_e)V}{M} \tag{1}$$

where q (mg/g) is the biosorption capacity of equilibrium, C_i and C_e are the initial and equilibrium concentrations (mg/L) of Ni(II), respectively, M (g) is the mass of biosorbent, and V (L) is the solution volume.

3 Results and discussion

3.1. Effect of agitation time and initial Ni(II) concentration

The rate of adsorption is important for designing batch adsorption experiments. Hence, the effect of agitation time on the adsorption of Ni(II) was investigated. The adsorption of Ni(II) ion increased until the agitation time reached 300 min. Further increase in agitation time did not enhance the adsorption process. So, the optimum agitation time was selected as 300 min for further experiments (Fig. 1).

To study the effect of initial concentration of Ni(II) ion on adsorption process, 100 mL of Ni(II) solution of different concentrations ranging from 50 to 150 mg/L was stirred with 2.0 g of adsorbent at 300 K for a contact period ranging from 20 to 300 min. As shown in Fig. 1 at any constant agitation time, the percentage removal of Ni(II) decreased as the initial concentration increased due to the saturation of binding sites. The metal removal capacity of the adsorbent was saturated and gradually decreased mainly due to binding of metal ions on all the available sites at certain metal concentration [13].

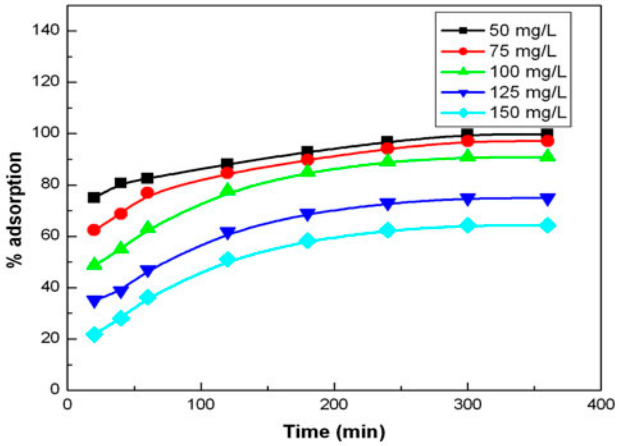

Fig. 1. Effect of agitation time on Ni(II) removal (adsorbent dosage: 2 g/100 ml; pH: 5.3; temperature: 298 K).

3.2. Effect of adsorbent concentration

It is evident from Fig. 2 that the percentage removal of Ni(II) at a concentration of 50 mg/L increases with increasing adsorbent concentration up to 2.0 g. Hence, an adsorbent dosage at 2.0 g was chosen for all experiments.

3.3. Effect of pH

The pH of the medium is an important parameter in the adsorption process of metal ions from aqueous solutions. In order to evaluate the influence of this parameter, experiments were carried out at different initial pH values. The pH ranges are chosen from 2 to 7 in order to avoid precipitation of metal hydroxides, which has been estimated to occur at pH > 7 as can be observed in speciation diagram previously reported [14]. Fig. 3 shows the effect of solution pH on the percentage adsorption of Ni(II) ions in the pH range of 2–7. From Fig. 3 it is evident that the extent of

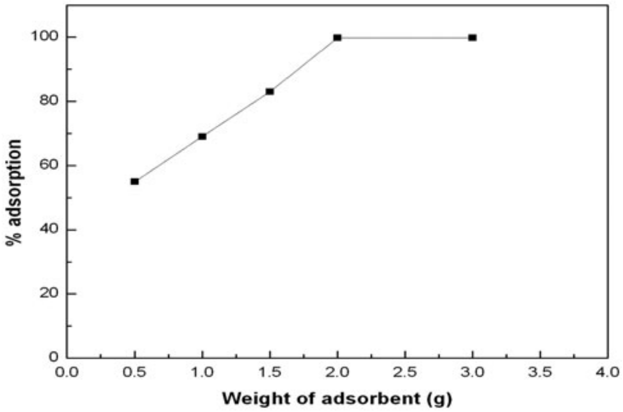

Fig. 2. Effect of adsorbent concentration on adsorption of Ni (II) (concentration: 50 mg/L; pH: 5.3; temperature: 298 K).

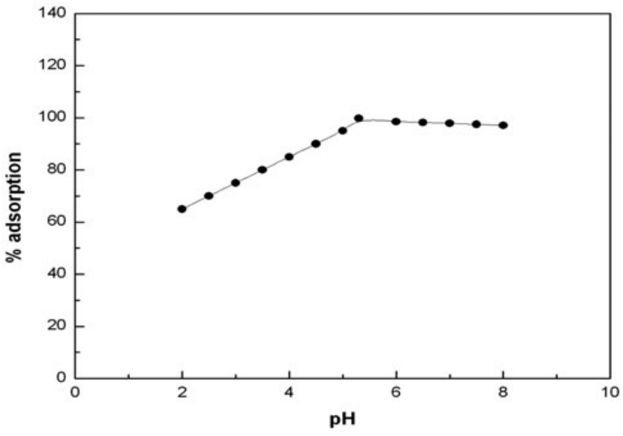

Fig. 3. Effect of pH on adsorption of Ni(II) (concentration: 50 mg/L; temperature: 298 K; adsorbent dose: 2.0 g/L).

adsorption increases with increase of pH up to 5.3 and then remained constant. The effect of pH of the medium on the extent of adsorption can be explained with the involvement of hydronium ions in the adsorption process. At low pH values the concentration of hydronium ions is more than that of metal ions hence these are bound to the adsorbent leaving the hydronium ions unbound. When pH value is increased the concentration of metal ions decreases and the metal ions are adsorbed on the adsorbent. When pH of the solution was further increased a decrease in adsorption of Ni(II) was observed due to the soluble hydroxide complex hence, all the experiments were carried out at pH 5.3.

3.4. Kinetic studies

The rate of adsorption depends upon the chemical reaction between functional groups present on the surface of adsorbent and metal ions. This chemical reaction involves in most cases, cation exchange reactions, formation of metal–organic complex, mass transport processes, diffusion across the liquid film surrounding the adsorbent particles, bulk transport in the liquid phase, or diffusion into micropores and macropores. The characteristics of adsorbent like the physicochemical nature of the surface, the physical form of the adsorbent particles, the availability of its surface to adsorbate molecules or ions, surface area, etc. determine the rate of adsorption.

To assess the uptake rate and contact time needed for the completion of adsorption reaction, kinetic experiments are performed. Kinetic studies are carried out in batch experiments using variable initial sorbate concentration, sorbent dose, particle size, agitation speed, pH values, and temperatures [15]. The pseudo-first-order and pseudo-second-order, and intraparticle diffusion models were examined. The pseudo-first-order rate equation is [16,17]:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \tag{2}$$

where q_e and q_t are the amounts of Ni(II) adsorbed on adsorbent (mg/g) at equilibrium and at t time, respectively, and K_1 is the rate constant of first-order adsorption (min^{-1}). The straight line plots of log $(q_e - q_t)$ against t (Fig. 4) were used to determine the rate constant (K_1) and correlation coefficient (R^2) values of the Ni(II) under different concentration range.

The pseudo-second-order rate equation is [18]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where K_2 is the rate constant of second-order adsorption (g/mg min). The straight line plots of t/qt against t (Fig. 5) have been tested to obtain rate parameters.

The intraparticle diffusion model is based on the theory proposed by Weber and Morris [19]. According to this theory,

$$q_t = K_{id} t^{0.5} + C \tag{4}$$

where q_t (mg/L) is the amount adsorbed at time t (min), K_{id} (mg/g min$^{-0.5}$) is the rate constant of intraparticle diffusion, and C is the value of intercept which gives an idea about the boundary layer thickness.

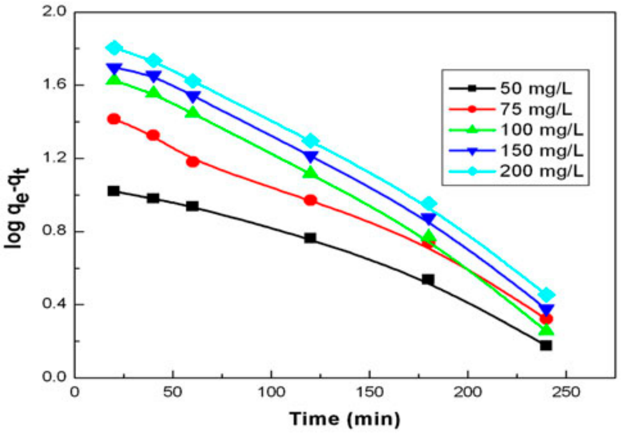

Fig. 4. Lagergren plots for the adsorption of Ni(II) by activated carbons from tobacco stem (pH: 5.3; adsorbent dosage: 2 g/L).

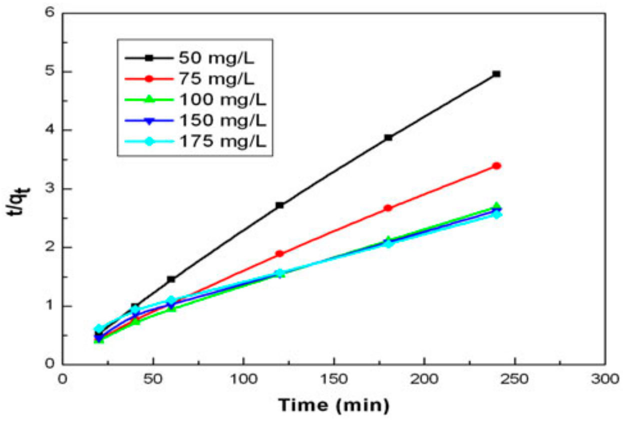

Fig. 5. Pseudo-second-order plots for the adsorption of Ni (II) by activated carbons from tobacco stem (pH: 5.3; adsorbent dosage: 2 g/L).

If the plot of q_t vs. $t^{0.5}$ gives a straight line, then the adsorption process is controlled by intraparticle diffusion only. Multi-linear plots indicate the influence of two or more steps on the adsorption process. In Fig. 6 the initial curved region corresponds to the external surface uptake, the second region relate the gradual uptake indicating intraparticle diffusion as the rate-limiting step, and final region indicates the equilibrium uptake.

From Table 2, it is evident that correlation coefficient values of pseudo-second-order model are higher than those of pseudo-first-order, and intraparticle diffusion models. Hence, it can be confirmed that adsorption of Ni(II) in the present study follows pseudo-second order kinetics.

3.5. Equilibrium studies

To compare different biomaterials under different operational conditions, and to design and optimize an operating procedure development of an equation by analyzing the equilibrium data is important [20]. The commonly used equations for describing adsorption equilibrium for water and wastewater treatment applications are Freundlich and Langmuir equations.

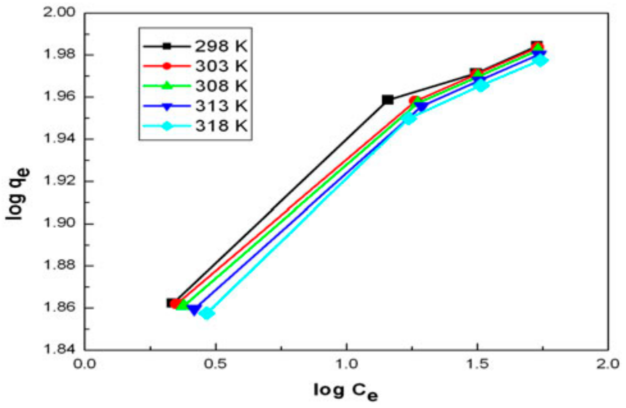

Fig. 6. Weber–Morris model for the adsorption of Ni(II) by activate carbons from tobacco stem (pH: 5.3; adsorbent dosage: 2 g/L).

The empirical Freundlich equation based on sorption on a heterogeneous surface is [21].

$$q_e = k_f (C_e)^{1/n} \tag{5}$$

where q_e is the amount adsorbed at equilibrium (mg/g), C_e the equilibrium concentration (mg/L), K_f and n are equilibrium constants indicative of adsorption capacity and adsorption intensity, respectively.

Eq. (5) can be linearized in logarithmic form as given below.

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \tag{6}$$

The plots of log C_e vs. log q_e at different temperatures are found to be linear (Fig. 7) which indicate the applicability of Freundlich model.

The assumptions from Langmuir equation are (a) A finite number of identical sites which are energetically uniform are present on the solid surface. (b) The amount adsorbed has no influence on the rate of adsorption i.e. there is no interaction between adsorbed species (c) when the surface reaches saturation a monolayer is formed.

Table 2
Kinetic parameters for adsorption of Ni(II) by activated carbons from tobacco stem

Ni(II) (mg/L)	Lagergren first order		Pseudo-second-order		Weber and Morris		
	K_1	R^2	K_2	R^2	K_{id}	C	R^2
75	0.0108	0.9928	0.0008	0.9991	2.0011	39.8442	0.9877
100	0.0141	0.9942	0.0003	0.9983	3.4748	35.1987	0.9826
125	0.0137	0.9938	0.0002	0.9951	4.2099	25.8027	0.9834
150	0.0139	0.9949	0.0001	0.9967	5.2422	12.3590	0.9827

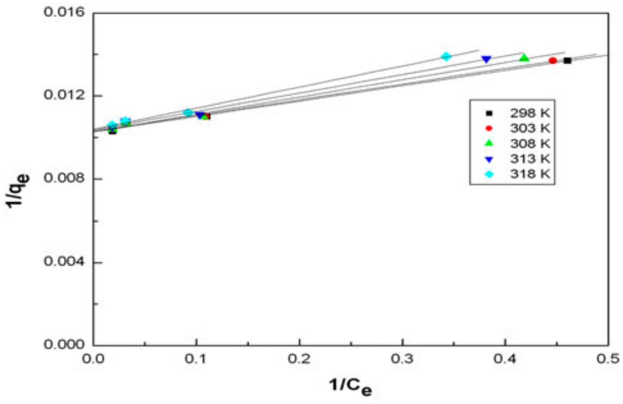

Fig. 7. Freundlich plots for the adsorption of Ni (II) by activated carbons from tobacco stem (pH: 5.3; adsorbent dosage: 2 g/L).

The Langmuir equation has the form [21]:

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^o} \tag{7}$$

where q_e is the amount adsorbed at equilibrium (mg/g), C_e the equilibrium concentration (mg/L). Q_0 and b are Langmuir constants indicating adsorption capacity and energy, respectively. By plotting (C_e/q_e) vs. C_e (Fig. 8), Q^0 and b can be determined.

From the correlation coefficient values (Table 3) of Langmuir and Freundlich models it is found that the adsorption of Ni(II) better fits to Langmuir model. From Langmuir isotherm, the values of Q_0 and b have been evaluated and the adsorption capacity of activated carbons from tobacco stem for Ni(II) uptake was compared with other adsorbents (Table 4). It is evident that the adsorption capacity of the adsorbent used in the present work is significantly higher than reported for other adsorbents in the literatures [22–25].

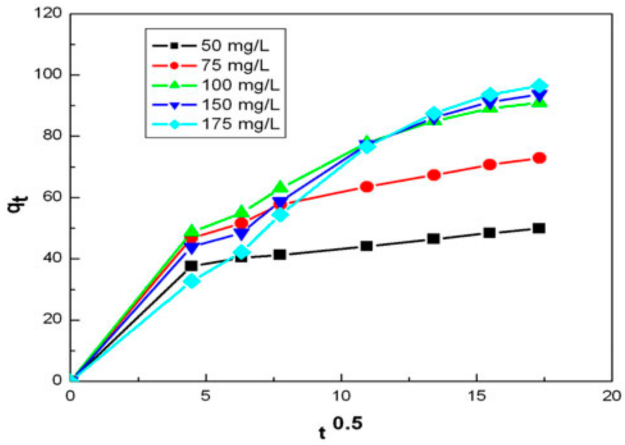

Fig. 8. Langmuir plots for the adsorption of Ni(II) by activated carbons from tobacco stem (pH: 5.3; adsorbent dosage: 2 g/L).

3.6. Thermodynamic studies

Temperature is a major factor influencing the adsorption. The effect of temperature was studied in the range of 298–318 K. The standard Gibbs free energy change (Δ*G*°), standard enthalpy change (Δ*H*°), and standard entropy change (Δ*S*°) for the adsorption process were obtained using the following equations.

$$\Delta G^0 = -RT \ln K_c \tag{8}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{9}$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{10}$$

where T is the temperature in Kelvin, R is the gas constant (8.314 kJ/mol), K_c is the equilibrium constant. The enthalpy change (ΔH°) and the entropy change (ΔS°) can be calculated from a plot of ln K_c verses $1/T$ (not shown) and the values are presented in Table 5. Values of standard free energy changes ΔG° are negative confirming that adsorption of Ni(II) on to activated carbons from tobacco stem is spontaneous and thermodynamically favorable. The more negative values of ΔG° indicate a higher driving force to the adsorption process. As the temperature increases the

Table 3
Langmuir and Freundlich isotherm parameters for the adsorption of Ni(II) on to activated carbons from tobacco stem

Metal ion	Temperature (K)	Langmuir				Freundlich			
		Q_0 (mg/g)	b (L/mg)	K_1	R^2	K_f (mg/g)	$1/n$	n	R^2
Ni(II)	298	97.32	1.389	135.192	0.9960	70.70	0.0838	11.9346	0.9343
	303	97.02	1.356	131.580	0.9969	70.46	0.0843	11.8630	0.9332
	308	97.32	1.226	119.329	0.9963	69.90	0.0854	11.706	0.9305
	313	96.54	1.156	111.566	0.9956	69.15	0.0869	11.502	0.9258
	318	96.15	1.030	99.010	0.9982	67.48	0.0912	10.968	0.9429

Table 4
Comparison of adsorption capacities of the adsorbents for the removal of Ni(II) with those other adsorbents

Metal	Adsorbent	Q_0 (mg/g)	Reference
Ni(II)	Kaolinite	1.669	[22]
	Eerbeek sludge	12.02	[23]
	Nedalco sludge	13.33	[23]
	Brown seaweed (Sargassum wightii)	18.58	[24]
	Waste Fe(III) / Cr(III) hydroxide	21.0	[25]
	Activated carbons from Tobacco stem	97.32	Present work

Table 5
Thermodynamic parameters for the adsorption of Ni (II) on to activated carbons from tobacco stem at different temperatures

Ni(II) (mg/L)	ΔG°					ΔS°	ΔH°
	298 K	303 K	308 K	313 K	318 K		
75	−0.7852	−0.7351	−0.5290	−0.3490	−0.0575	−0.0173	14.033
100	−0.8632	−0.6631	−0.4236	−0.3409	−0.1913	−0.0109	9.130
125	−1.2431	−1.0652	−0.8281	−0.6134	−0.1450	−0.0009	2.479
150	−1.8150	−1.2982	−0.7623	−0.4893	−0.1592	−0.0017	1.978

ΔG° value decrease indicating less driving force which results in lesser adsorption capacity at higher temperatures. The positive values of ΔH° indicate that the adsorption process is endothermic in nature. The negative values of ΔS° indicate the stability of adsorption process without any structural change at solid–liquid interface.

4. Conclusions

The current study emphasize on the ability of activated carbons from tobacco stem to adsorb Ni(II) from aqueous solutions. The adsorption was dependent on solution pH, initial metal ion concentration, adsorbent dosage, agitation time, and temperature. The maximum uptake capacity of the adsorbent used was found to be 97.32 mg/g. The experimental data was found to fit better with the pseudo-second-order model for entire temperature range. Biosorption equilibrium was better described by Langmuir isotherm model than by Freundlich isotherm model. The negative values of ΔS° show the stability of the sorption process. The values of ΔH° and ΔG° show the endothermic and spontaneous nature of adsorption process on the surface of activated carbons from tobacco stem. The study revealed that this adsorbent is inexpensive, easily available material, and effective in removing Ni (II) from aqueous solutions.

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