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NICKEL BIVALENT METAL ION ADSORPTION FROM AQUEOUS SOLUTION BY PREPARED ACTIVATED CARBON FROM *PERGULARIA DAEMIA*

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ABSTRACT

The activated carbon produced from *Pergularia daemia* stem was chemically activated using sulfuric acid and utilized as an adsorbent for the removal of nickel (II) from aqueous solution in the concentration range 10-50 mg/L. Adsorption experiments were carried out in a batch process and various experimental parameters such as effect of contact time, carbon dosage and pH on percentage removal have been studied. Adsorption results obtained, shows that the Ni (II) uptake being attained at pH 6.7. The equilibrium adsorption data was better fitted to the Langmuir's and Freundlich adsorption models. Kinetic modeling of the process of removal was carried out and the process of removal was found to follow a pseudo second order model, Elovich model and Intraparticle diffusion model the value of rate constant for adsorption process was calculated. The thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined and the negative values of ΔG° indicated that the process of removal was spontaneous at all values of temperatures. It was concluded that activated carbon produced from *Pergularia daemia* stem has an efficient adsorption capacity for removal of nickel bivalent mental ion.

Keywords: *Pergularia Daemia* Activated Carbon (PDAC), Nickel(II) ion, Adsorption isotherm, Kinetics, Equilibrium models, Thermodynamic parameters.

1. INTRODUCTION

Throughout the world, the pollution of water resources has increased due to the disposal of heavy metals. Removing heavy metals from water and wastewaters as a result of industrialization has turned out to be a serious problem. Discharging of metals into water resources is one of the most critical issues regarding pollution which may have negative effects on the quality of water supply [1-4]. Increasing concentrations of heavy metals in water resources have negative effects on the quality of water and have caused severe threats to the health of humankind, which are mainly related to their non-degradability and toxicity [5-7]. There are different heavy metals such as Cd, Cu, Zn, Ni, and Cr in surface. Nickel has a broad usage in industry due to its strong crystalline structure, corrosion resistance, and greenish blue color. It is one of the essential materials in electroplating industries, tanneries, paint and pigments, wood preservation, and alloy making processes. Human toxicity of Ni(II) includes skin irritation to lung cancer, as well as kidney, liver, and gastric damage [8,9].

In the present investigation the adsorption of Ni (II) ion on activated carbon prepared *Pergularia daemia* by carbonization with concentrated sulphuric acid was done. The kinetic and equilibrium adsorption data obtained were utilized to illustrate the sample systematized. The amounts and rates of adsorption of Ni (II) ion using above activated carbon from aqueous solution were then measured. The literature survey shows that no work has been done so for lift up the *Pergularia daemia* as an adsorbent.

2. EXPERIMENTAL

All the reagents used in the experiments were of analytical (AR) grade and were obtained from scientific equipment company Trichy. Stock solutions were prepared by dissolving 4.953 g of nickel nitrate ($Ni(NO_3)_2.6H_2O$) in 1000 ml of deionized water. All experimental solutions were prepared by diluting the stock solution to the required concentration.

2.1. Preparation of adsorbent

The natural plant material of *Pergularia daemia* used in the present investigations was collected from a nearby Poompuhar area [10, 11]. The stem was washed with distilled water several times to remove the dirt and dust and was subsequently dried in a hot air oven at 110°C. Afterward, carbonization of the stem was carried out by adding w/v ratio Conc. H_2SO_4 to get the primary carbon. The primary carbon was activated at >900°C for 6 hrs under optimized conditions to obtain the activated carbon.

2.2. Experimental Procedure of Batch Method

Batch experiments [12] were conducted to study the influence of important parameters like the pH, contact time, initial Ni (II) ion concentration, other ions and temperature on the removal of Ni (II) ion onto activated *Pergularia daemia* carbon. For Adsorption Isotherms, Ni (II) ion solution of different concentrations (10-50 mg/L) and at different temperatures (30-60°C) with known pH and known amount of adsorbent (0.025g/L) were agitated at 120 rpm until the equilibrium was reached then the solution was kept to settle down and the residual concentration of Ni (II) ion were analyzed by UV-Visible spectrophotometer at 460 nm. All the experiments were carried out at normal pH for removal of Ni (II) ion from aqueous solution. Effect of pH on Ni (II) ion removal was studied over a pH range of 3.0-9.0. The initial pH of the solution was adjusted by addition of dil. HCl or dil. NaOH. The effect of sorbent dosage on adsorption rate was investigated using the procedures described above, except that different dosages (10-250 mg/50ml) were used. The amount of adsorption at time t, q_t (mg/g), can be determined using the following formula.

$$q_t = V \times \frac{(C_0 - C_t)}{w} \tag{1}$$

Where, $q_{(t)}$ is the mass of adsorbed Ni (II) ion per unit mass of adsorbent (mg g^{-1}) (C_0) and (C_t) are the initial and actual concentration (g dm^{-3}) of Ni (II) ion at time, respectively V is the volume of the treated solution (ml), w is the mass of adsorbent (g). The removal percentage of Ni (II) ion can be calculated as following relationship

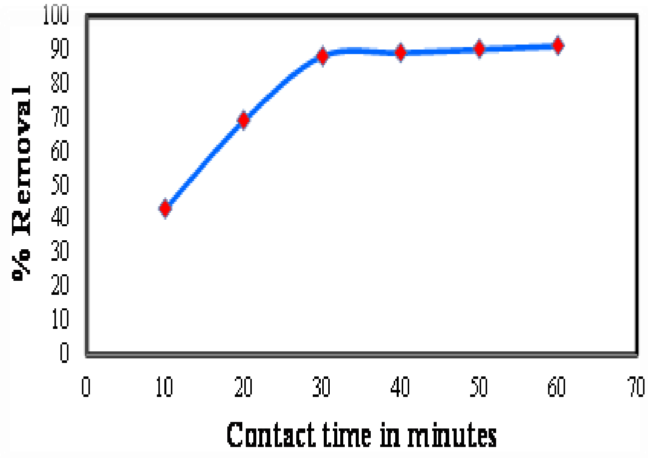
$$\% \text{ Removal} = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \tag{2}$$

Based on the adsorption kinetics experiments, the process time for the equilibrium adsorption experiments was chosen, long enough assuming that the considered sorbent/sorbate system is equilibrated.

3. RESULTS AND DISCUSSION

3.1. Contact time

In order to establish the equilibration time [13] for maximum uptake and to know the kinetics of the adsorption process, Ni (II) ion adsorption on APDC adsorbent was investigated as a function of contact time and the results were shown in fig. 1 and the equilibrium data are given in table 1. The figure shows that the uptake rate was initially rapid with maximum of the adsorption was complete within 30 min. Equilibrium was achieved within 50 min., therefore, an equilibration period of 60 min. was selected for all further experiments.



[Ni (II) ion]=10mg/L; Temperature 300C; Adsorbent dose= 0.025g/50mL.

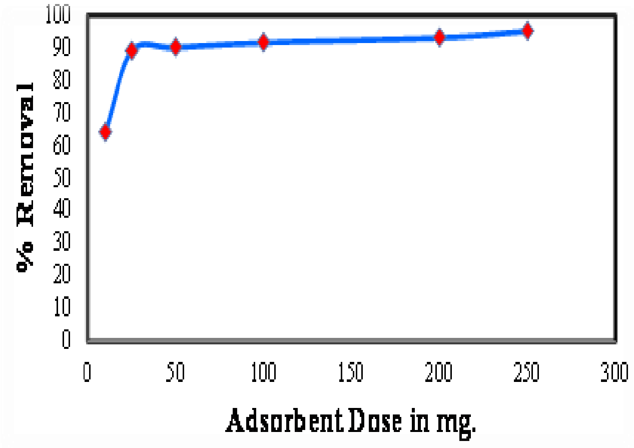
Fig. 1: Effect of Contact Time on the Removal of Ni (II) ion

Table 1: Equilibrium Parameters for The Adsorption Of Nickel (Ii) Ion Onto Apdc

C_0	Ce (Mg / L)				q_e (Mg / L)				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	1.92	1.56	1.04	0.99	16.16	16.89	17.92	18.03	80.81	84.44	89.61	90.14
20	6.74	5.19	4.69	3.63	26.51	29.62	30.62	32.73	66.28	74.05	76.55	81.84
30	11.86	11.31	9.86	9.13	36.27	37.38	40.29	41.74	60.45	62.30	67.15	69.56
40	18.20	16.64	15.79	14.81	43.60	46.71	48.42	50.38	54.50	58.39	60.53	62.98
50	33.10	31.23	30.65	30.18	33.81	37.55	38.70	39.65	33.81	37.55	38.70	39.65

3.2. Effect of adsorbent dosage

The adsorption of the Ni (II) ion on APDC was studied by varying the adsorbent dose [14] for 50 mg/L of Ni (II) ion concentration. The percentage of adsorption increased with increase in the APDC dose, which is attributed to increased carbon surface area and the availability of more adsorption sites. Hence, all studies were carried out with 0.025g of adsorbent/50 ml of the varying adsorbate solutions of 10, 25, 50, 100, 200 and 250 mg/L. The results obtained from this study are shown in fig. 2. The amount of Ni (II) ion adsorbed per gram reduced with increase in the dosage of APDC. This reveals that the direct and equilibrium capacities of Ni (II) ion are functions of the activated APDC dosage.

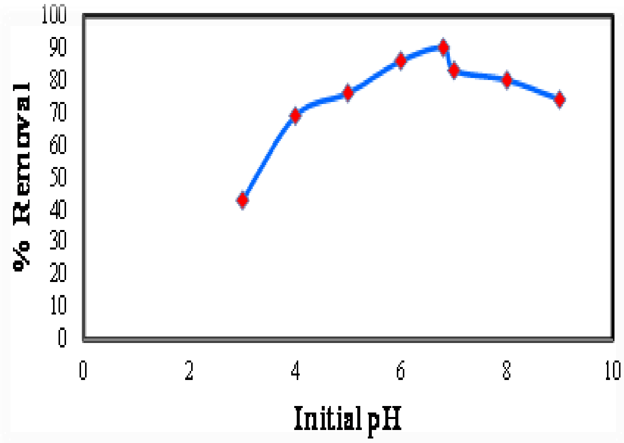


[Ni (II) ion] = 10mg/L; Temperature 300C; Contact Time 60 min.

Fig. 2: Effect of Adsorbent dose on the Removal of Ni (II) ion

3.3. Effect of Initial pH

Previous research [15] has shown that the adsorption of Ni (II) ion onto an adsorbent is highly pH dependent since, the functional groups, which are responsible for interaction between Ni (II) ion and adsorbent, can be protonated or deprotonated to produce different surface charges in solution at different pH values. Therefore the effects of initial solution pH were studied in the pH range of 3-9 for removal of Ni (II) ion from aqueous solution. The percentage removal increased around 39.65 % to 90.14 % whereas it decreased slowly after pH 6.8 that is pH_{zpc} (Zero point charge) as shown in fig.3. The pH_{zpc} of any adsorbent is a very important characteristic that determines the pH at which the surface has net electrical neutrality. It is well-known that for cationic Ni (II) ion adsorption, negatively charged groups on the adsorbent are necessary. At lower pH values ($pH < pH_{zpc}$), the surface charge of the surface of APDC may get positively charged as a result of being surrounded by H_3O^+ ions and thus the competitive effects of H_3O^+ ions as well as the electrostatic repulsion between the Ni (II) ion and the positively charged active adsorption sites on the surface of the APDC lead to a decrease in the uptake of Ni (II) ion. In contrast, at higher pH values ($pH > pH_{zpc}$) the surface of APDC may acquire a negative charge leading to an increase in Ni (II) ion uptake due to the electrostatic force of attraction. On the other hand neutral surface of adsorbent occur support for the maximum removal of Ni (II) ion from aqueous solution, as the result initial pH value was optimized as pH 6.7.

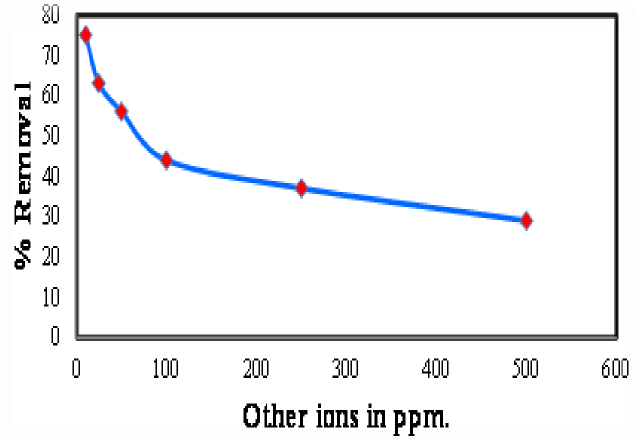


[Ni (II) ion]=10mg/L; Temperature 30°C; Adsorbent dose = 0.025g/50mL.

Fig. 3: Effect of Initial pH on the Removal of Ni (II) ion

3.4. Effect of other ions

The effect of chlorine ions [16] on the adsorption process was studied at different concentrations. The ions added to 50mg/L of Ni (II) ion solutions and the contents were agitated for 60 min at 30°C. The results shown in the fig. 4 reveals that low concentration of Cl^- does not affect the percentage of adsorption of Ni (II) ion on APDC, because the interaction of Cl^- at available sites of adsorbent through competitive adsorption is not so effective. While the concentration of other ion increases, the interference of these ions at available surface sites of the sorbent through competitive adsorption increases that, decreases the percentage adsorption. This is so because ions with smaller hydrated radii decrease the swelling pressure within the sorbent and increase the affinity of the sorbent for such ions.



[Ni (II) ion]=10mg/L; Contact time=60 min.; Adsorbent dose=0.025g/50mL.

Fig. 4: Effect of other ionic strength on the removal of Ni (II) ion

3.5. Adsorption Models

The adsorption equilibrium data were further analyzed into two well-known isotherm models via Freundlich and Langmuir models.

3.5.1. Freundlich model

The Freundlich model [17] which is an indicative of surface heterogeneity of the adsorbent is described by the following equation.

$$\log q_e = \log K_f + \frac{1}{n_f}\log C_e \qquad (3)$$

Where, K_f and $1/n_f$ are Freundlich constants related with adsorption capacity and adsorption intensity respectively. The Freundlich plots drawn between log q_e and log C_e for the adsorption of Ni (II) ion were shown fig.5 and it makes that correlation co-efficient (R^2) values was near unity, as a result temperature studied indicating that Freundlich model was applicable to the present study these values listed in table 2.

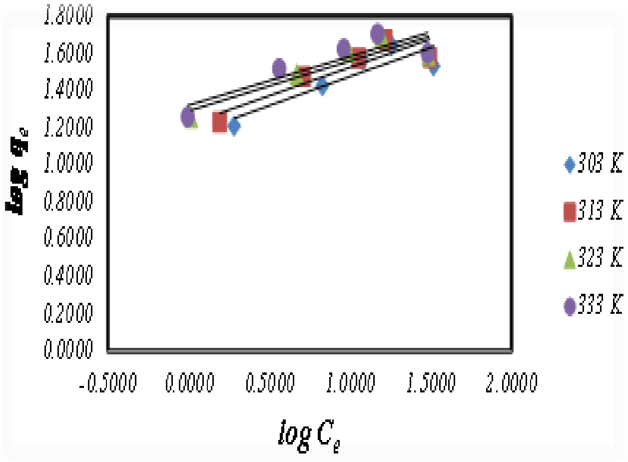


Fig. 5: Freundlich adsorption isotherm for the removal of Ni (II) ion

Table 2: Freundlich and Langmuir isotherm parameter for the adsorption of nickel (II) ion onto APDC

Model	Constant	Temperature (°C)			
		30	40	50	60
Freundlich	K_f(mg/g) (L/mg)$^{1/n}$	14.51	16.53	19.47	20.90
	n_f	3.20	3.28	3.73	3.82
	R^2	0.78	0.82	0.82	0.78
Langmuir	q_m(mg/g)	37.24	40.93	41.21	41.78
	K_L (L/mg)	0.80	0.83	1.76	3.57
	R^2	0.96	0.97	0.98	0.98

3.5.2. Langmuir model

The Langmuir adsorption isotherm [18] equation which is valid for monolayer adsorption on to a surface is given below.

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad (4)$$

Where, q_e (mgg^{-1}) is the amount adsorbed at the equilibrium concentration C_e (mol L^{-1}), q_m (mgg^{-1}) is the Langmuir constant representing the maximum monolayer adsorption capacity and K_L (L mol^{-1}) is the Langmuir constant related to energy of adsorption. The plot drawn between $C_e/q_e$and C_e for the adsorption of Ni (II) ion was found linear and as shown in fig. 6. The correlation coefficient (R^2) values confirm good agreement our experimental results the values with the monolayer capacity (q_m) and equilibrium constant (K_L). These are evaluated from the intercept and slope of langmuir plot and given in table 2. These facts suggest that Ni (II) ion is adsorbed in the form of monolayer coverage on the surface of the prepared adsorbent. In order to find out the feasibility of the isotherm, the essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor R_L by the equation.

$$R_L = \frac{1}{1 + K_L C_0} \quad (5)$$

Where, C_o (mg/L) is the highest initial concentration of Ni(II) ion and K_L (L/mg) is Langmuir isotherm constant. The parameter R_L indicates the nature of shape of the isotherm accordingly.

- $R_L > 1$ -Unfavorable adsorption
- $0 < R_L < 1$ -Favorable adsorption
- $R_L = 0$ -Irreversible adsorption
- $R_L = 1$ -Linear adsorption

The R_L values in the middle of 0 to 1 indicate favorable adsorption for all initial concentration (C_o) and temperatures studied. The calculated R_L values are given in table 3. The values of K_L were increased with increasing the dose of adsorbent for APDC. High K_L values indicate high adsorption affinity the monolayer saturation capacity q_m were around 41.78 mg/L for APDC.

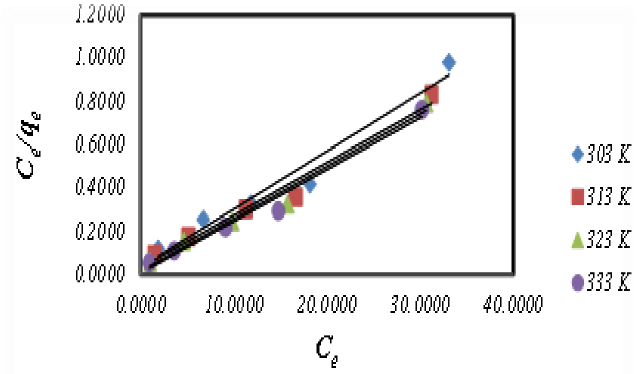


Fig. 6: Langmuir adsorption isotherm for the removal of Ni (II) ion

3.6. Thermodynamic treatment of the adsorption process

Thermodynamic [19] parameters associated with the adsorption, via standard free energy change (ΔG°), standard enthalpy change (ΔH°), and standard entropy change (ΔS°) were calculated as follows. The free energy of adsorption process considering the adsorption equilibrium constant K_0 is given by the equation:

$$\Delta G^0 = -RT\ln K_0 \quad (6)$$

Where, ΔG^0 is the free energy of adsorption (kJ/mol), T is the temperature in Kelvin and R is the universal gas constant (8.314 J mol/K). The adsorption distribution coefficient K_0 for the sorption reaction was determined from the slope of the plot of $\ln(q_e/C_e)$ against C_e at different temperature. The adsorption distribution coefficient may be expressed in terms of enthalpy change (ΔH°) and entropy change (ΔS°) as a function of temperature,

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

Where, ΔH° is the standard heat change of sorption (kJ/mol) and ΔS° is standard entropy change (kJ/mol). The value of ΔH° and ΔS° can be obtained from the slope and intercept of plot of ln K_0 against 1/T. The value of thermodynamic parameter calculated from equation 6 and 7 are shown in table 4. The negative ΔG° values were confirming the spontaneous nature of adsorption Ni (II) ion onto APDC. The lesser values of ΔG° suggest that adsorption is physical adsorption process. The positive value of ΔH° further confirms the endothermic nature of adsorption process. The positive values of ΔS° in table 4, showed increased randomness of the solid solution interface during the adsorption of Ni (II) ionontoAPDC.

Table 3: Dimensionless seperation factor (R_L) for the adsorption of nickel (II) ion onto APDC

(C_0)	Temperature (°C)			
	30°C	40°C	50°C	60°C
10	0.11	0.11	0.05	0.03
20	0.06	0.06	0.03	0.01
30	0.04	0.04	0.02	0.01
40	0.03	0.03	0.01	0.01
50	0.02	0.02	0.01	0.01

Table 4: Thermodynamic parameter for the adsorption of nickel (II) ion onto APDC

(C_0)	ΔG°				ΔH°	ΔS°
	30°C	40°C	50°C	60°C		
10	-3621.19	-4400.84	-5786.81	-6127.33	23.50	89.57
20	-1702.57	-2728.75	-3176.65	-4167.72	22.02	78.50
30	-1069.17	-1306.78	-1919.47	-2287.94	11.87	42.51
40	-454.72	-881.69	-1148.35	-1470.78	9.60	33.28
50	1692.57	1324.13	1235.62	1163.56	6.80	17.13

3.7. Kinetic models

3.7.1. Pseudo-second-order

In order to investigate the mechanism of adsorption, kinetic models [20] are generally used to test experimental data. Pseudo-second-order equations can be used assuming that the measured concentrations are equal to surface concentrations. The linearized form of pseudo second order equation becomes.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \quad (9)$$

Where, q_t (mgg^{-1}) is the amount of adsorbed Ni (II) ionon the adsorbent at time t, q_e the equilibrium sorption uptake and k_2, (min^{-1}) is the rate constant of pseudo-second-order adsorption. The plot t/q_t versus t gives a straight line says second order kinetic model is applicable then q_e and $k_2$are determined from the slope and intercept of the plot, respectively. The high regression value indicate the adsorption reaction exist a pseudo-second-order and these values are shown table 5.

Table 5: Kinetic parameters for adsorption of nickel (II) ion onto APDC

C_0	Temp°C	Pseudo second order				Elovich model			Intraparticle diffusion		
		q_e	k_2	R^2	h	α	β	R^2	α	K_{id}	R^2
10	30	23.19	1.47E-03	0.96	0.79	1.61	1.87E-01	0.96	0.456	12.10	0.99
	40	20.98	2.83E-03	0.98	1.24	3.12	2.31E-01	0.96	0.324	21.78	0.98
	50	19.92	6.24E-03	0.99	2.48	20.75	3.46E-01	0.96	0.185	41.21	0.97
	60	19.87	6.78E-03	0.99	2.68	28.56	3.64E-01	0.96	0.173	5.15	0.97
20	30	40.72	6.86E-04	0.95	1.14	2.30	1.06E-01	0.95	0.504	8.15	0.99
	40	43.28	7.14E-04	0.93	1.34	2.75	1.01E-01	0.93	0.468	10.33	0.97
	50	41.80	9.88E-04	0.97	1.73	3.63	1.06E-01	0.96	0.409	14.03	0.98
	60	40.87	1.36E-03	0.97	2.27	5.56	1.17E-01	0.94	0.334	3.68	0.97
30	30	52.26	5.71E-04	0.86	1.56	3.31	8.56E-02	0.86	0.453	8.67	0.92
	40	50.46	9.24E-04	0.97	2.35	5.03	8.85E-02	0.94	0.387	12.80	0.96
	50	56.65	7.15E-04	0.98	2.29	4.62	7.59E-02	0.97	0.432	11.59	0.98
	60	51.73	1.39E-03	1.00	3.71	8.36	8.95E-02	0.99	0.333	3.54	0.98
40	30	61.94	6.97E-04	0.99	2.68	4.97	6.56E-02	0.97	0.467	8.59	0.96
	40	64.51	7.03E-04	1.00	2.93	5.57	6.44E-02	0.99	0.444	9.89	0.97
	50	64.18	8.39E-04	1.00	3.46	6.70	6.60E-02	0.98	0.408	11.93	0.96
	60	65.46	8.94E-04	1.00	3.83	7.64	6.60E-02	0.98	0.386	3.10	0.97
50	30	43.40	1.31E-03	1.00	2.47	5.31	1.04E-01	1.00	0.365	7.67	1.00
	40	49.14	1.00E-03	0.99	2.42	5.21	9.14E-02	0.98	0.380	7.84	1.00
	50	45.84	1.69E-03	0.98	3.55	12.22	1.19E-01	0.94	0.262	12.88	0.96
	60	48.57	1.49E-03	1.00	3.51	8.71	9.94E-02	1.00	0.313	2.85	1.00

3.7.2. The Elovich equation

The Elovich model [21] equation is generally expressed as

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \qquad (8)$$

Where α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is desorption constant (g/mg) during any one experiment. If Ni (II) ion adsorption fits with the Elovich model, a plot of q_t Vs ln(t) yields a linear relationship with a slope of (1/β) and an intercept of (1/β)ln(αβ). The Elovich model parameters α, β, and correlation coefficient (R^2) are summarized in table 5. This model indicates that the initial adsorption (α) increases with temperature similar to that of initial adsorption rate (h) in pseudo-second-order kinetics models. This may be due to increase in the pore or active site on the APDC adsorbent.

3.7.3. Intra-particle diffusion model

Kinetic data was further analyzed using the Intraparticle diffusion model [22] based on the following equation.

$$\log R = \log K_{id} + \alpha \log t \qquad (9)$$

Where, k_{id} is the intraparticle diffusion rate constant and is related to the thickness of the boundary layer. According to above equation, a plot of log R versus log t gives a straight line that's says the adsorption mechanism follows the intra-particle diffusion process and the evidence of correlation co-efficient values are close to unity.

4. CONCLUSION

This study revealed that *Pergularia daemia* can be used as an alternative adsorbent for heavy metal ions removal in industrial wastewater due to its efficacy of nickel ions adsorption in aqueous solution. The adsorption of Ni (II) ion onto APDC was affected bycontact time, pH, adsorbent dosage, and other ionic strength. The Ni (II) ion uptake percentage by APDC was found to be 90.14% when 0.025 g of adsorbent was shaken with 50mL of Ni (II) ion solution of 10 mg/L for 60 min at pH 6.7. The adsorption data was fitted well by pseudo-second order, Elovich model, and intra particle diffution models that are indicating chemical reaction is involved in the adsorption process. The adsorption process was found to be controlled by three steps of diffusion mechanisms. The isotherm equilibrium data fitted well with Langmuir isotherm model and the monolayer adsorption capacity was found to be 41.78 mg/g at 60°C. Thermodynamic parameters are the negative values of $\Delta G°$ indicated the spontaneity of Ni (II) ion adsorption process and the positive values of $\Delta H°$ and $\Delta S°$ showed the endothermic nature. This study proved that it's possible to remove Ni (II) ion ion from aqueous solution using *Pergularia daemia* stem carbon.

Conflict of interest

None declared

5. REFERENCES

1. Duran-Blanco JM, Lopez-Munoz BE, Olguin MT. *Separation Science and Technology*, 2013; **48:**797-804.
2. Maurya NS, Mittal AK, Corner P, Rothar E. *Bioresour. Technol*., 2006; **97:**512-521.
3. Sugashini S, Gopalakrishnan S. *Research journal of Chemical Sciences*, 2012**; 2(6):**55-59.
4. Rathinam Aravindhan, Jonnalagadda Raghava Rao, Bala chandran Unni Nair. *Journal of Hazardous Materials*, 2006; **142(1-2):**68-76.
5. Namasivayam C, Munisamy N, Gayathri K, Rani M, Renganathan K**.** *BioresTechnol*, 1995; **57:** 37.
6. Arivoli S, Hema M, Parthasarathy S, Manju N.*J. Chem. Pharm. Res.,* 2010; **2(5):**626-641.
7. Arivoli S, Viji Jain M, Rajachandrasekar T. *Mat. Sci. Res. India,* 2006; **3:**241-250.
8. Errais E, Duplay J, Darragi F, M'Rabet I, Aubert A, Huber F, Morvan G. *Desalination*., 2011;**275:**74-81.
9. Itodo AU, Itodo HU. *Life Science J*., 2010; **7:**31-39.
10. Bulut E, Ozacar M, Sengil IA. *MicroporousMesoporous Mater.,* 2008; **115:**234-246.
11. Kumar KV. *J. Hazard. Mater,* 2006; **B137:**638-639.
12. Diaz PV, Medina EC, Nunez FU, Fabila MG. *Fresenius Environmental Bulletin*, 2013;**22:**1432-1440.
13. Arivoli S, Hema M.*Indian Journal of Chemical Technology*, 2009; **16(1):**38-45.
14. Arivoli S, Vijayakumaran V, Ramuthai S**.***E-Journal of Chemistry,* 2009;**6(S1):**S347-S357.
15. Zheng H, Gao Z, Yin F, Ji X, Huang H. *Bioresour Technol.,* 2012; **117:**1-6.
16. Bulgariu D, Bulgariu L. *Bioresour Technol.,* 2012; **103:** 489-493.
17. Park D, Yun YS, Park JM. *Ind Eng Chem Res.,* 2006; **45:** 2405-2407.
18. Pistorius AM, DeGrip WJ, Egorova-Zachernyuk TA. *BiotechnolBioeng.,* 2009; **103:**123-129.
19. Yang L, Chen JP. *Bioresour Technol.,* 2008; **99:** 297-307.
20. Chen S, Yue Q, Gao B, Xu X. *J Colloid Interface Sci.,* 2010; **349:**256-264.
21. Bankar AV, Kumar AR, Zinjarde SS. *J Hazard Mater,* 2009; **170:**487-494.
22. Han X, Wong YS, Wong MH, Tam NF. *J Hazard Mater*, 2008; **158:**615-620.