International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.9, No.07 pp 574-586, 2016

Novel Adsorbent prepared from *Passiflora foetida* seeds for the adsorption of Nickel(II) in aqueous solution

Velumani K*[1], Kumar P E[2], Sivakumar V[1]

[1]Department of Chemistry, Sri Vasavi College, Erode-638316, TN, India
[2]Department of Chemistry, Erode Arts &Science College (Autonomous), Erode-638009, TN, India

Abstract: Water contamination by heavy metals creates lot of illness to human being and animals owing to its bio accumulation. Exploration of a suitable technology for the removal of heavy metals in water and waste water is highly warranted. In this work an activated carbon prepared from *Passiflora foetida* plant seed by chemical activation with KOH is used for the adsorptive removal of Ni(II) in aqueous solution. The effect of various controlling factors like pH, contact time, initial concentration of adsorbate and temperature on the adsorption of Ni(II) was investigated. The Ni(II) adsorption followed the pseudo second order kinetics with good correlation coefficient. The Langmuir model best described the adsorption with high correlation coefficient. The thermodynamic parameters such as Free energy change (ΔG°) Enthalpy change (ΔH°), Entropy change (ΔS°) were evaluated. The negative value of ΔG° confirmed the feasibility and spontaneity of the process.

Key words: Activated carbon, Ni(II), Adsorption, *Passiflorafoetida*, Kinetic models.

1.0 Introduction

Water is essential for the living things to sustain in this world. Swift increase in population and phenomenal industrial revolution imposes severe pollution load onto the waste sources. Especially heavy metal pollution creates lot of imbalance in the life cycle owing to the high toxicity and non-biodegradable nature of heavy metals. Industries like metallurgical, pigment manufacturing, tanneries, battery and fuel cell industries, chemical industries, plating, dyeing industries, etc are the main sources of heavy metals[1]. The presence of nickel in water bodies and its bioaccumulation creates lot of adverse effects on to the human and animal bodies[2]. The heavy metals present in the water bodies interact with other compounds (either organic or inorganic), which results in altered bioavailability and toxicity[3]. As recommended by the World Health Organization(WHO), the maximum permissible level of Nickel (II) in drinking water is 0.07 mg/l[4].

Some of the nickel compounds like nickel carbonyl are carcinogenic and another problem is that they can be easily absorbed by the skin. When the exposure of these compounds exceeds 30 mg/l in the atmosphere for half an hour, is lethal[5]. High concentration of nickel in human bodies causes cancer of lungs, nose and bone[6,7]. The effective removal of heavy metals form wastewater is a real challenging one and at the same time it is highly warranted in the present context. Many methodologies like oxidation, adsorption using activated materials, reverse osmosis, nano filtration, coagulation, ion exchange using natural and synthetic resins were reported in the past for the treatment of waste water containing heavy metals. The applicability of these methods are limited owing to their expensive and ineffective especially for wastewater containing relatively low concentration of metal(1–100 mg/l)[8].

Many researchers are working towards the development of effective and economical method for the treatment of waste water containing heavy metals. Among the technologies available for wastewater treatment, adsorption found be better owing to its wide selectivity, simple technology and low operational costs[9]. Adsorption using activated carbon is a most promising and widely used technology for the removal of pollutants present in waste water. The cost of commercial activated carbon is high and the small scale industries are finding it difficult to spend such a high cost for wastewater treatment. This high capital cost limits the applicability of commercial activated carbon. Recently lot of attention is given on the synthesis of activated carbon from agro-wastes and plants with less economic importance because of their renewable nature, large abundance, comparatively low-cost, high fixed carbon content and presence of porous structure[10].In the present investigation *Passiflora foetida* plant seed is used as a source material for the preparation of an activated carbon and it used for the removal of nickel (II) from aqueous solution. The effect if initial metal ion concentration, pH and temperature were studied. In-order to evaluate the kinetics of adsorption, pseudo-first order, pseudo-second order, Elovich and intra-particle diffusion kinetic model were employed. The isotherm data tested using Langmuir, Freundlich, Tempkin and Dubinin-Raduskevich isotherm models.

2.0 Experimental

2.1 Preparation of adsorbent

The ***Pasiflora foetida*** plant seeds are collected and dried in sun light till they lost their water content. The dried seeds were soaked in 10% KOH solution for 24 hours. At the end of 24 hours, the excess KOH solution decanted off, the material dried and carbonized in muffle furnace at 400°C for 10 minutes. The carbonized material washed several times with distilled water to remove the residual KOH. After washing, the material was dried, crushed, and ground well. Then the material was sieved to obtain average particles of 180-300μ size (ASTM Sieve). The sieved carbon was activated in a muffle furnace at 800°C for 10 minutes and then stored in an air tight container for further adsorption studies. For the Convenience of discussion the adsorbent (***Pasiflora foetida*** Activated Carbon) will be denoted as PAC.

2.2 Adsorption experiments

A stock solution of 1000 mg/l of Ni(II) was prepared by dissolving AR 6.74 g of Nickel Ammonium Sulphate in double distilled water. Experimental solutions of desired concentrations are then obtained by successive dilutions.

Equilibrium adsorption experiments were conducted in batch adsorption mode. Batch adsorption studies were conducted in a 250ml tight lid Borosil glass bottles. For the kinetic studies, 50ml of the Ni(II) solution of specific concentration was agitated with 200mg of adsorbent (PAC) in a temperature controlled orbital shaker (Rivotek Model). The bottle is withdrawn at a particular time and centrifuged using (REMI make) centrifuge at 5000 rpm for 5min. About 1ml of the clear filtrate was added with 1ml Bromine water, 2 mL 1:1 NH_3 and 1 mL of 0.1% DMG to for a Ni-DMG complex. The concentration of Ni(II) was estimated using UV-Vis spectrometers (Elico Make: Model SL-207) at a wavelength of 445 nm. The percentage of metal ion removed and the amount of metal ion adsorbed per gram of adsorbent was evaluated using the following equations.

$$\text{Final Concentration} = C_i - \left[\frac{OD_i - OD_f}{OD_i} \times C_i\right]$$

$$\text{Percentage of dye removal} = \frac{OD_i - OD_f}{OD_i} \times 100$$

$$\text{Amount adsorbed } (q_t) = \frac{OD_i - OD_f}{OD_i} \times \frac{V}{M}$$

Where OD_i and OD_t are the liquid phase concentration of the Ni(II) at initial and concentrations at time t (mg/l), respectively. M is the mass (g) of adsorbent and V is the volume of dye solution (mL).

The pH of solution was measured by using digital pH meter (Elico: Model LI-120). The conductivity is measured by using Digital Conductivity Meter (Deep vision model M-180). Temperature controlled orbital shaker (Rivotek Model) is used for the equilibrium studies. The effect of pH on Ni(II) adsorption was investigated in the initial pH range of 2-12. The initial pH of the solution was adjusted by using 0.1N HCl or 0.1N NaOH. Dried activated carbon (0.2g) was added to 50 mL of solution having 40 mg/l of Ni(II) ions. After adsorption, the solutions were centrifuged and the concentrations of the solutions were determined.

3.0 Results and Discussion

3.1 Adsorbent characterization

The physic-chemical characteristics of PAC are presented in table 1. The pH and pH_{zpc} values of PAC indicate that the adsorbents may contain acidic oxygen functional groups. Moisture content of the carbons has no effect on its adsorptive power, but it dilutes the activated carbons which necessitates the use of additional weight of carbon during the treatment process[11]. The lower bulk density value indicates the highly branched and porous carbons with more void space[11]. Acid soluble matter content was found slightly higher than the solubility in water in the activated carbons because of incorporated carbonate groups in the pores.

Higher specific gravity shows that the activated carbons were used as a good packing purpose for the removal of pollutants from wastewater. The lower ash content and volatile matter attributed to lower inorganic content and higher fixed carbon. Higher value of fixed carbon shows the activated carbons are more efficient and stable. Conductivity values mean that cations and anions in activated carbons may be responsible for the conductivity. The high surface area is considered to be the most suitable for adsorption of activated carbons in aqueous solution. Higher iodine number shows that the activated carbons have high adsorption capacity of inorganic constituents present in the aqueous solution and wastewater[11].

Table 1 –Physico-chemical Characteristics of the PAC

S.No.	Parameters	Adsorbent
1	pH	9.26
2	Conductivity, µS/cm	0.4
3	Moisture, %	1.76
4	Ash Content, %	12.26
5	Bulk density (D), g/mL	0.748
6	Specific Gravity (S), g/mL	1.25
7	Porosity, %	40.2
8	Water Soluble Matter, %	0.645
9	Acid Soluble Matter, %	5.59
10	Iodine Value, mg/g	112.0
11	$pH_{(ZPC)}$	9.2
12	Surface area, m^2/g	129.0

3.2 Effect of pH

The pH is one of the most important parameter which determines the adsorption of metal ion at the liquid-solid interface[12]. As the adsorption of metal ion on the surface of an adsorbent is strongly depends on the pH of the solution[13]. In order to evaluate the effect of pH, adsorption experiments were conducted by varying the pH of the solution from 2.0 to 12.0 using dil. HCL and NaoH solution for a fixed Ni(II) concentration of 50 mg/l.

The density of surface change for electrostatic interactions and relative sites for chemical interaction between the metal ion and the adsorbent surface was determined by the association/disassociation of surface functional groups. The acid oxygen containing surface functional groups favors the adsorption of the cationic species, whereas surface basicity and oxygen free Lewis basic sites favors the adsorption of non-ionic and anionic adsorbate molecules present in the solution[14].

The quantity of these surface functionalities depends upon the nature of precursor and method of activation most of the activated carbons may have both these functionalities there by the carbon can become amphoteric in nature. The dominance of any one of these functionalities depends on the solution pH, which determines the extend of adsorption of the solute molecules. The pH dependent adsorption is related to surface properties of adsorbent as well as the form of metal ion in solution[15].

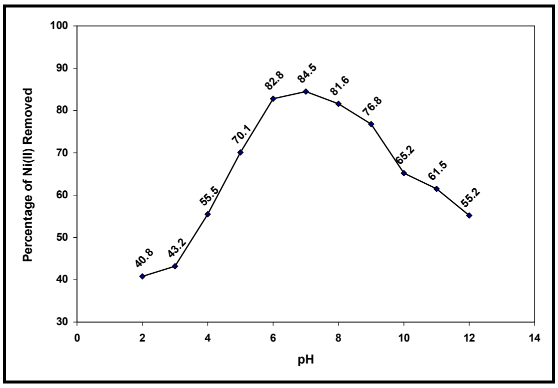

Figure 1 – Effect pH for the adsorption of Ni(II) onto PAC

At lower pH both H^+ and metal ion compete for the surface of adsorbent and there by the adsorption is less. Another fact is that at low pH, the surface of adsorbent is protonated and it repels the positively charged metal ion[16]. As observed from the figure 1, the Ni(II) adsorption is low (40.8%) at a pH of 2.0 and it increases to 84.5% at pH of 7.0. When the solution pH goes above 7.0 the Ni(II) adsorption decreases and it becomes 55.2% at a pH of 12.0. The decrease of adsorption at basic pH is due to the reduced solubility of metal ion and its precipitation[17].

3.3 Effect of Initial metal ion concentration

The effect of initial metal ion concentration on the adsorption of Ni(II) onto PAC is shown in figure 2a. On increasing the initial concentration of Ni (II) for 20 mg/l to 100 mg/l, the amount of Ni(II) adsorption increases from3.82 to 17.00 mg/l. Whereas the percentage of Ni(II) adsorption decreases to from 80.56% to 68.42% on increasing the initial metal ion concentration from 20 to 100 mg/l.

The initial concentration of metal ion provides necessary driving force to overcome the mass transfer resistance created at the solid toe liquid interface[18]. At higher Ni(II) concentrations the number of metal ion competing for the sorption sites are more and there by more solute molecules are adsorbed on the sorption sites. The uptake of Ni(II) by PACis rapid during the beginning of adsorption and then it reaches an equilibrium of 60 min.

3.4 Effect of temperature

The effect of temperature for the adsorption of Ni(II) on the PAC is shown in figure2b. The amount of Ni(II) adsorption decrease from 7.59 to 6.94 mg/l on increasing the solution temperature from 30 to 45°C. The decrease of adsorption of Ni(II) onto PAC at high temperature is attributed to the fact that at high temperature the kinetic energy of Ni(II) ions increase, which results in more desorption at high temperature. The effects of temperature indicates that the adsorption of Ni(II) by PAC is an exothermic process.

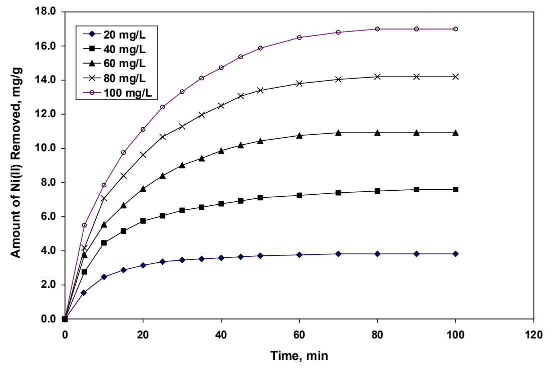

Figure 2a- Effect of Initial concentration on the adsorption of Ni(II) by PAC

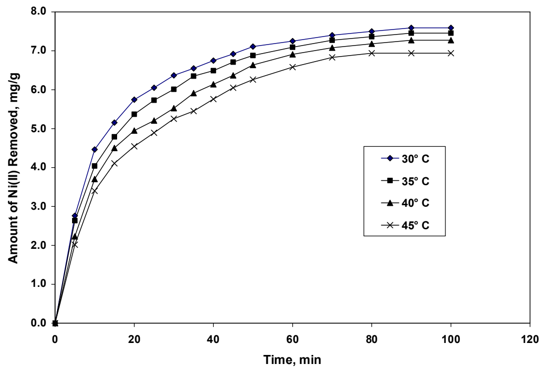

Figure 2b- Effect of Temperature on the adsorption of Ni(II) by PAC

3.5 Kinetic studies

In order to evaluate the performance of adsorbent and to know the real mechanism of adsorption, it is essential to analyze the adsorption kinetics. The existing kinetic models like pseudo-first order, pseudo-second order, Elovich and intra-particle diffusion models were selected to analyze the adsorption data of Ni(II) on to PAC.

3.5.1 Thepseudo-first order kinetics

The pseudo-first kinetics expression suggested by Lagergran (1898) is one of the most widely used rate equation to describe the liquid phase adsorption[19]. The linear form the pseudo-first order expression is

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$

Where, q_e and q_t are the amount of dye adsorbed at equilibrium and at time 't' respectively (mg/g), k_1 is the rate constant of first order adsorption (1/min).

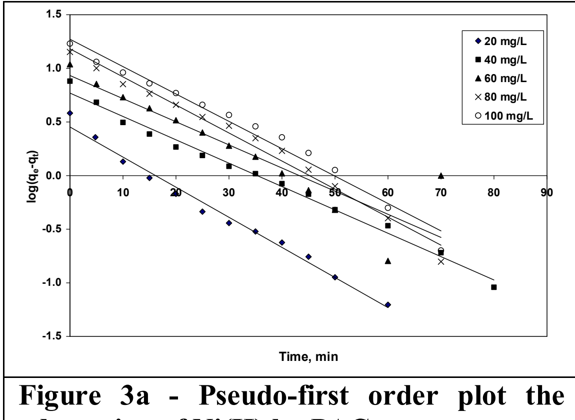

Figure 3a - Pseudo-first order plot the adsorption of Ni(II) by PAC

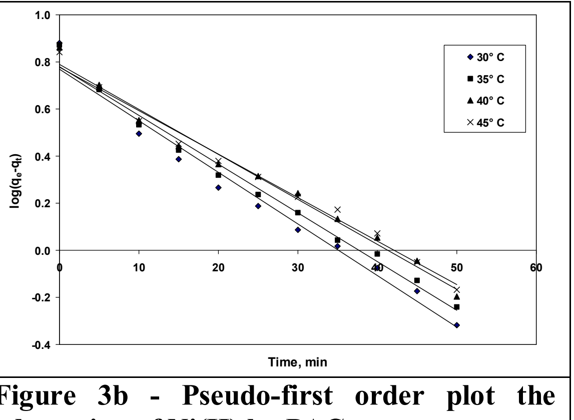

Figure 3b - Pseudo-first order plot the adsorption of Ni(II) by PAC

The values of rate constant (k_1) and adsorption capacity (q_e) were determined from the scope and intercept of the plot of $\log(q_e\text{-}q_t)$ versus t. The pseudo-first order plot for the adsorption of Ni(II) on the PAC at various initial metal ion concentration and temperatures are shown in figure 3a, 3b and the results are presented in table 2. The pseudo-first order rate constant show a decreasing trend on increasing the metal ion concentration as well as the temperature. This indicates that at high concentration and temperature, the rate of backward reaction i.e desorption increases there by the rate constant decreases.

As the q_e calculated from pseudo-first order kinetic model deviates from experimental q_e and the regression coefficient also less for the range of concentration as well as temperatures under investigations. This suggests that the adsorption of Ni(II) by PAC does not follow the first order kinetics during the entire period of adsorption[12].

Table 2 -Calculated kinetic parameters for the adsorption of Ni(II)

	Initial dye concentration, mg/L					**Temperature, °C**			
Parameters	**20**	**40**	**60**	**80**	**100**	**30**	**35**	**40**	**45**
$q_e$exp.(mg/g)	**3.82**	**7.59**	**10.92**	**14.20**	**17.00**	**7.59**	**7.45**	**7.27**	**6.94**
Pseudo first order kinetics									
k_1 x10^{-2} (min $^{-1}$)	6.471	5.021	6.126	6.034	5.873	5.021	4.767	4.399	4.261
$q_e$cal(mg/g)	2.84	5.88	8.58	15.22	18.68	5.88	6.02	6.16	6.00
r^2	0.9862	0.9895	0.8164	0.9853	0.978	0.9895	0.9858	0.9842	0.9868
Pseudo second order kinetics									
k_2 x10^{-2} (g/mg/min)	3.885	1.280	0.697	0.455	0.352	1.280	1.087	0.866	0.794
h	0.662	0.90	1.08	1.23	1.393	0.90	0.758	0.606	0.527
$q_e$cal(mg/g)	4.13	8.36	12.47	16.47	19.88	8.36	8.35	8.37	8.14
r^2	0.9993	0.9998	0.9978	0.9981	0.9979	0.9998	0.9998	0.9989	0.9982
Elovich model									
□ (mg/g/min)	1.414	0.640	0.639	0.286	0.238	0.640	0.614	0.583	0.586
□ (g/mg)	2.377	2.646	1.524	2.734	3.121	2.646	2.03	2.00	2.38
r^2	0.9092	0.9654	0.9656	0.9736	0.9788	0.9654	0.9814	0.9884	0.9908
Intra particle diffusion model									
k_{id}(mg/g/min^{½})	2.592	1.398	0.727	0.577	0.458	1.398	2.520	1.352	1.381
r^2	0.9578	0.9750	0.9911	0.9930	0.9920	0.9750	0.9466	0.986	0.9909

3.5.2 The pseudo-second order kinetics

The linear from of pseudo-second order kinetics is given by the equation[20]

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t$$

where, k_2 (g (mg min)$^{-1}$)is the second order constant for adsorption. The second order rate constants were used to calculate the initial sorption rate, h (mg/g/min) given by the following equation.

$$h = k_2 {q_e}^2$$

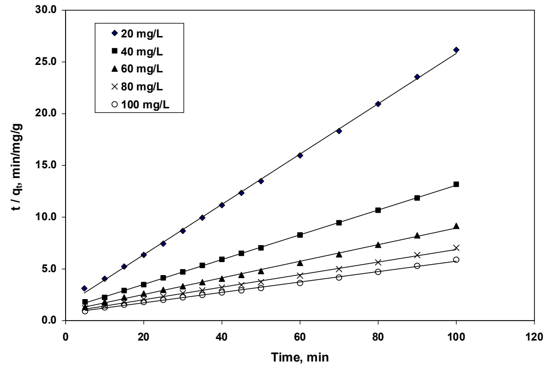

Figure 4a - Pseudo-second order plot the adsorption of Ni(II) (Concentration variation)

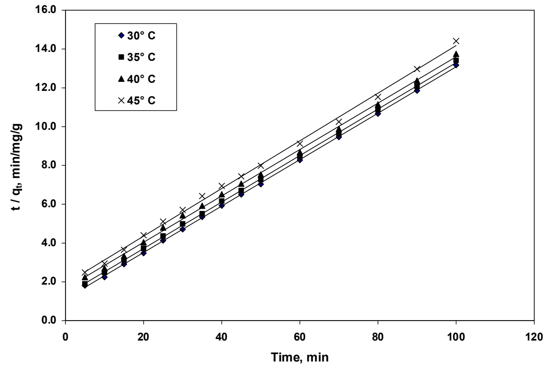

Figure 4b - Pseudo-second order plot the adsorption of Ni(II) (Temperature variation)

A plot of "t/q_t" versus "t" at various concentrations and temperatures are shown in figure 4a and 4b . The pseudo-second order constant calculated from the scope and intercept are given in table 2. The pseudo-second order rate constant decrease from $3.885\text{x}10^{-2}$ to $0.352\text{x}10^{-2}$ (g/mg/min) on increasing the initial Ni(II) concentration from 20 to 100 mg/l and it decreases from 1.28 to 0.794 (g/mg/min) on increasing the temperature from 30 to 40°C. Though the q_e calculated from pseudo-second order deviates from the experimental value substantiates that the adsorption of Ni(II) onto PAC is better represented by pseudo-second order kinetics. This proves that the overall rate of Ni(II) adsorption is controlled by chemical process via ion exchange and or complexation process[21].

3.5.3 Elovich Model

The Elovich kinetic model generally employed to describe the chemisorption type of adsorption[22].The linear from the Elovich kinetic model is

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

where, α represents the rate of chemisorption at zero coverage (mg/g/min) and β is related to the extent of surface coverage and activation energy for chemisorption (g/mg).The constants α and β were calculated from the linear plot of q_t versus ln t at various concentrations and temperatures. The Elovich plot (figure not shown) results are presented in table 2.

The initial sorption rate or chemisorption at zero coverage α decreases from 1.44 to 0.238 mg/g/min on increasing the initial Ni(II) concentration from 20 to 100mg/l and it decreases from 0.640 to 0.586 mg/g/min on increasing the temperature from 30 to 45°C. The desorption constantβ increases with respect to increases in initial metal ion concentration as well as temperature. Among the three kinetic models discussed above, pseudo-second order model best describes the adsorption kinetics of Ni(II) onto PAC.

3.5.4 Intra-particle diffusion model

The intra-particle diffusion model used to evaluate the mechanism of adsorption. During the adsorption of a metal ion by an adsorbent, the following three steps are involved, i) bulk diffusion where the metal ions from the bulk of the solution are transferred to the external surface of the adsorbent, ii) intra-particle diffusion in which the metal ions are transferred to the pores of adsorbent and iii) the metal ions are bonded with the active sites present on the surface of the adsorbent[23].

The linear form of intra-particle diffusion model is[23]

$$q_t = k_{dif} \,.\, t^{1/2} + C$$

Where, q_t is the fraction of metal ion uptake (mg/g) at time t, k_{dif} is the intra particle-diffusion rate constant (mg/g. $\text{min}^{0.5}$) and I is the intercept (mg/g). The results intra-particle diffusion plot (figure not shown) at various Ni(II) concentrations and temperatures are presented in table 2. The linear portion of the plot did not pass through the origin, which indicates that boundary layer diffusion also plays a significant role along with intra-particle diffusion. This is due to the difference in mass transfer between initial and final stages of adsorption.

3.6 Isotherm studies

Adsorption isotherms are used to describe how the adsorbate molecules interact with adsorbent surface and also it describes the rate of change of adsorption with respect to concentration of adsorbate. In-order to analyze the adsorption isotherm for the adsorption of Ni(II) onto PAC, the already existing isotherm models namely Langmuir, Freundlich, Tempkin and Dubinin-Raduskevich (D-R) were used.

3.6.1 Langmuir Model

Langmuir Isotherm is derived based on the assumption of monolayer coverage of adsorbate on the surface of adsorbent[24]. Based on the results of Langmuir isotherm model, maximum adsorption capacity corresponding to complete monolayer coverage on the sorbent surface can be evaluated. The liner form of Langmuir isotherm can be expressed as

$$\frac{C_e}{q_e} = \frac{1}{Q_0 . b_L} + \frac{C_e}{Q_0}$$

Where, b_L is the Langmuir constant, C_e is the equilibrium metal ion concentration in solution, C_e is the initial concentration (mg/l) and Q_0 is a constant related to monolayer adsorption capacity. The Langmuir plot of C_e/q_eversurC_e for the adsorption of Ni(II) onto PAC is shown in figure 5 and the results derived from the slope and intercept of this plot are presented in table 3. The Langmuir monolayer adsorption capacity increases from 22.22 to 26.25 mg/g, which is comparable with the results reported by the past researchers[12].

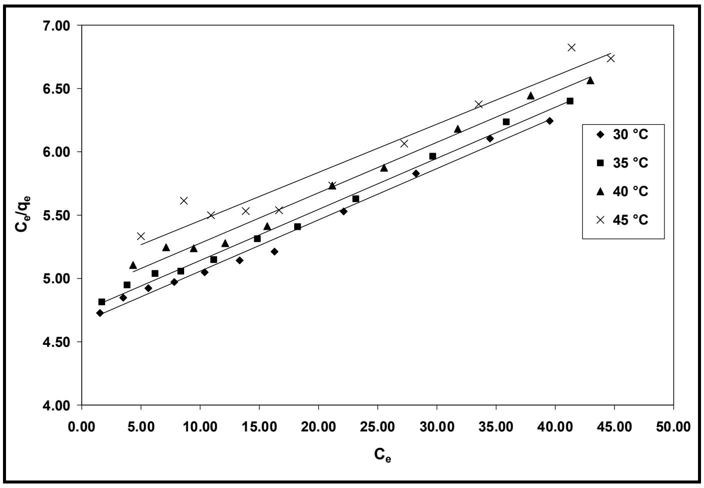

Figure 5 – Langmuir plot for the adsorption of Ni(II) by PAC

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless equilibrium parameter, R_L, also known as the separation factor, which describes the type of isotherm:

$R_L = 1/ (1+b_L . C_0)$

Where b_L is the Langmuir constant and C_0 is the initial Ni(II) concentration (mg/g). In all of the temperatures, the values of R_L were calculated between 0 and 1, indicating the favorable adsorption of Ni(II) on PAC.

3.6.2 Freundlich Model

The Freundlich isotherm model is generally used to describe the surface heterogeneity. The model also derived with a view of adsorption on heterogeneous surfaces with interaction between adsorbed molecules and is not restricted to the formation of a monolayer. The well- known expression for the linear form of Freundlich model is given as[25]

$$\log q_e = \log k_f + \frac{1}{n} \log C_e$$

Where, q_e is the adsorption capacity (mg/g), C_e is the equilibrium concentration of the Ni(II) solution (mg/l), $k_f$is related to overall adsorption capacity and n is related to surface heterogeneity. The Freundlich parameters k_f and n calculated from the slope and intercept of the plot "log q_e" versus "C_e" (Figure 6) are given in table 3.

Table 3 : Results of isotherm studies for the adsorption of Ni(II) onto PAC

Parameters	***Temperature °C***			
	30	***35***	***40***	***45***
Langmuir isotherm				
Q_0 (mg/g)	22.22	24.81	25.13	26.25
b_L x10^{-3}(L/mg)	9.673	8.504	8.157	7.506
r^2	0.9918	0.9938	0.9882	0.9476
Freundlich isotherm				
n	1.55	1.52	1.47	1.40
k_f ($mg^{1-1/n}$ $L^{1/n}$ g^{-1})	1.91	1.73	1.48	1.21
r^2	0.9933	0.9885	0.9634	0.9576
Tempkin isotherm				
b_T (mg/g)	495.27	507.45	515.87	454.92
a_T (L/mg)	1.361	1.517	1.799	2.892
r^2	0.9785	0.9792	0.9784	0.9796
Dubinin-Raduskevich isotherm				
q_D(mg/g)	8.64	15.40	15.09	15.20
B x 10^{-6}(mol^2/J^2)	6.0	7.0	10.0	10.0
E x 10^{-3}(kJ/mol)	2.0	2.0	1.41	1.41
r^2	0.9286	0.9327	0.9463	0.9763

The Freundlich constant related to overall adsorption capacity k_f decreases from 1.91 to 1.21 with increase in temperature. The value of a constant related to surface heterogeneity n is greater than 1.0 indicating that the adsorption of Ni(II) onto PAC is favorable. The correlation coefficient of Langmuir isotherm is more than the Freundlich isotherm, which substantiates that the surface of PAC favors the monolayer adsorption of Ni(II) and the surface of PAC is less heterogeneous during the Ni(II) adsorption.

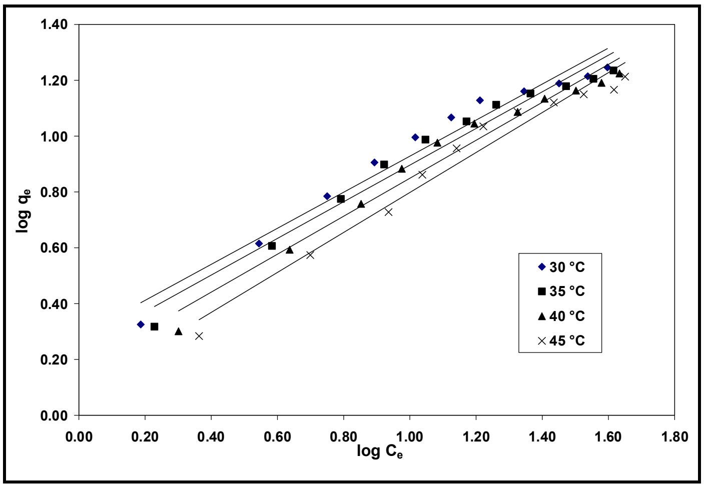

Figure 6 – Freundlich plot for the adsorption of Ni(II) by PAC

3.6.3 Tempkin Isotherm

Tempkin isotherm takes into account of the effect of indirect adsorbate-adsorbate interaction on adsorption and suggests that the heat of adsorption of all molecules in the adsorbent surface layer would decrease linearly with coverage. The linear form of Tempkin isotherm can be expressed as[26]

$$q_e = \frac{RT}{b_T}\ln a_T + \frac{RT}{b_T}\ln C_e$$

The Tempkinsorption potential (a_T) and the Tempkin constant related to heat of adsorption (b_T) calculated from the slope and intercepts of the plot "q_e" versus "C_e" (figure not shown) are given in table 3. The sorption potential (a_T) increases from 1.361 to 2.892 L/mg and constant related to heat of adsorption (b_T) varies from 515.87 to 454.92 for the range of temperatures investigated. However, the applicability of this model to describe the adsorption of Ni(II) onto PAC is not much appropriate owing to its less degree of fitness.

3.6.4 Dubinin-Raduskevich (D-R) Isotherm

The D-R model is applied to determine the physical or chemical nature of the adsorption processes. This isotherm model is more general than Langmuir because it does not assume a heterogeneous surface or a constant adsorption potential. D-R model has commonly been applied in the following form[27]

$$\ln q_e = \ln q_D - B\varepsilon^2$$

Where B is a constant related to the mean free energy of adsorption per mole of the adsorbate ($mol^2\ kJ^{-2}$), q_D is the maximum adsorption capacity (mg/g) and ε is the polyanyi potential, which is equal to

$$\varepsilon = RT\ \ln(1+1/C_e)$$

The values of q_D and B were calculated from the intercept and slope of the plot "lnqe" versus ε^2 (figure not shown).The mean free energy of adsorption E calculated from B using the following equation

$$E = 1/\ (2B)^{1/2}$$

The energy of adsorption E gives information about the mechanism of adsorption (whether physisorption of chemisorption with ion exchange mechanism). The range of mean adsorption energy at 2-20 kJ/mol could be considered physisorption in nature. The magnitude of E ranged between $2.0\ x10^{-3}$ to $1.41x10^{-3}$ kJ/mol indicating the physical nature of bonding between adsorbent and adsorbate.

3.7 Thermodynamics of Adsorption

The inherent energy changes involved during the adsorption were evaluated using the thermodynamic parameters like ΔG^0, ΔH^0 and ΔS^0. The thermodynamic parameters were arrived as per the following equation[28].

$$\ln K_c = \frac{\Delta S^O}{R} - \frac{\Delta H^O}{R}\frac{1}{T}$$

Where, Kc is anequilibrium constant, R is the gas constant ($8.314\ x\ 10^{-3}$ kJ/K/mol) and T is temperature (K). Both ΔH^0 and ΔS^0 were determined from the slope and intercept of the Van't Hoff plots of "lnKc" vs "1/T"(figure 7) is given in table 4. The Gibbs free energy of specific adsorption ΔG° (kJ/mol) is calculated from the following expression,

$$\Delta G° = \Delta H° - T\Delta S°$$

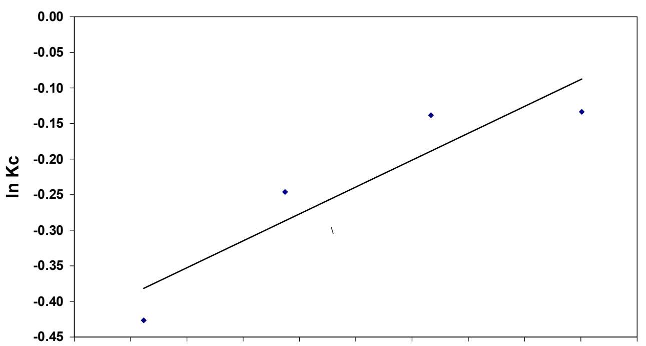

Figure 7 – Thermodynamic plot for the adsorption of Ni(II) by PAC

The enthalpy change for the adsorption Ni(II) by PAC is 15.71 kJ/mol, indicates the weak force of attraction between the sorbent surface and Ni(II) ion. This results coincides with the results of D-R model. The free energy change ΔG° for the Ni(II) adsorption is negative and it becomes more negative when the temperature of the system is increased. The negative free energy change substantiate that the adsorption is favorable and spontaneous. The negative value of ΔS° shows the decreased disorder and randomness at the solid solution interface. As the adsorption progresses, the number of particles in the solution decreases, which ultimately leads to more orderliness.

Table 4 - Thermodynamic parameters

Temp., °C	ΔG°, J/mol	ΔH°, KJ/mol	ΔS°, J/K/mol	Ea, J / mol	A
30	-336.38	-15.71	-52.60	26.64	3.06×10^6
35	-354.58				
40	-640.75				
45	-1127.65				

3.8 Desorption studies

Desorption studies were helpful to regenerate the spent adsorbent and also to helps to know about the mechanism of adsorption (whether the solute molecules or ions held by weak or strong forces of attraction). Based on the nature of eluent used for the regeneration of spent adsorbent, it will be easy to assess the nature of binding between the adsorbate and adsorbent. The Ni(II) loaded PAC was agitated with aqueous solutions of varying pH from 2.0 to 12.0 and the percentage regeneration was estimated. As observed from the figure 8, the desorption was high at low and high pH and it was minimum around the pH of 7.0. At low pH the presence more H^+ creates a repulsive force between the metal ion and the protonated sorbent surface which leads to more desorption of Ni(II). Whereas at higher pH, the precipitation of the adsorbed metal ion leads to more desorption from the sorbent surface. The high amount of desorption at more acidic and more basic conditions indicates the weak association between the sorbent and adsorbate.

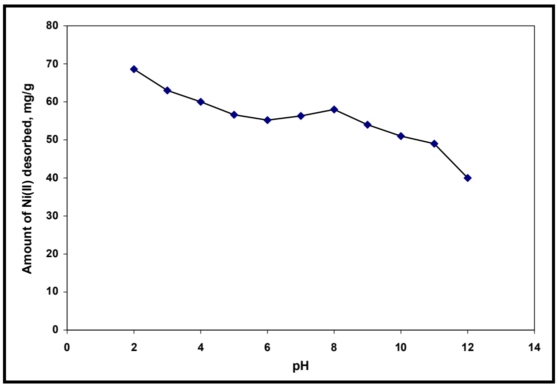

Figure 8 – Effect of pH on the desorption of Ni(II)

4.0 Conclusion

Activated carbon synthesized from the ***Passiflora foetida*** plant seed by chemical activation with KOH is a promising adsorbent with excellent characteristics. The adsorbent characteristics were comparable with that of commercial activated carbon. The maximum adsorption of Ni(II) was found to be at a pH of 7.0. The percentage of removal was decreased and the amount of Ni(II) adsorption increases with increasing the initial metal ion concentration. The pseudo-second order kinetic model is more appropriate describe the kinetics of Ni(II) adsorption that first order. Among the isotherm models, Langmuir model has better correlation coefficient at all temperatures indicating the monolayer adsorption. The negative value of ΔG° confirms the feasibility adsorbent and spontaneity of the adsorption process. The positive ΔH° and negative ΔS° shows the endothermic nature of adsorption and decreased randomness at the solid-solution interface.

4.0 References

1. Gao H.W.,Chen, Fang F., Ling C., Teng Z., Lu-Ting P., Jian-Hua L. andHua-Fei L., A novel detection approach based on chromophore-decolorizing with free radical and application to photometric determination of copper with acid chrome dark blue, Anal. Chim. Acta., 2007, 587, 52–59.
2. Zhao X.T., Zeng T., Hu Z.J., Gao H.W., ZouC.Y., Modeling and mechanism of the adsorption of proton onto natural bamboo sawdust,Carbohydr. Polym., 2012, 87, 1199–1205.
3. Izidoro, Juliana C., Fungaro, Denise A., Abbott, Jennifer E. and Wang S., Synthesis of zeolites X and A from fly ashes for cadmium and zinc removal from aqueous solutions in single and binary ion systems, Fuel, 2013, 103, 827–834.
4. World Health Organisation, Guidelines for Drinking Water Quality. Recommendations, WHO, Geneva, 1984.
5. VieiraM.G.A., NetoA.F.A., GimenesM.L. and da SilvaM.G.C., Sorption kinetics and equilibrium for the removal of nickel ions from aqueous phase on calcinedBofebentonite clay, J. Hazard. Mater., 2010, 177, 362–371.
6. Boujelben N., Bouzid J. andElouear Z., Adsorption of nickel and copper onto natural iron oxide-coated sand from aqueous solutions: study in single and binary systems, J. Hazard. Mater.,2009, 163 (1), 376–382.
7. Katsou E., Malamis S., HaralambousK.J. andLoizidou M., Use of ultrafiltration membranes and aluminosilicate minerals for nickel removal from industrial wastewater, J. Membr. Sci., 2010, 360, 234–249.
8. Ghasemi N., Ghasemi M., Mashhadi S. andTarrafM.H., International Congress on Informatics, Environment, Energy and Applications-IEEA 2012 IPCSIT, 38, IACSIT Press, Singapore, 2012.
9. ChowdhuryZ.Z., ZainS.M. and Atta Khan R. and Ahmed A.A., Equilibrium kinetics and isotherm studies of Cu (II) adsorption from waste water onto alkali activated oil palm ash, Am. J. Appl. Sci., 2011, 8, 230–237.
10. Bhatnagar A. andMinochaA.K., Biosorption optimization of nickel removal from water using Punicagranatum peel waste, Colloid Surface B., 2010, 76, 544–548.
11. Karthikeyan S., Sivakumar P. and Palanisamy P.N., Novel Activated Carbons from Agricultural Wastes and their Characterization, E-J Chem., 2008, 5, 409-426.
12. Manal El-Sadaawy, Ola Abdelwahab, Adsorptive removal of nickel from aqueous solutions by activated carbons from doum seed (Hyphaenethebaica) coat, Alexandria Engg. J., 2014, 53, 399–408.
13. DokeK.M. and KhanE.M., Equilibrium, kinetic and diffusion mechanism of Cr (VI) adsorption onto activated carbon derived from wood apple shell, Arab. J. Chem., 2012, doi: http:// dx.doi.org/10.1016/j.arabjc.2012.07.031.
14. Jagtoyen M. and Derbyshire F., Some considerations of the origins of porosity in carbons from chemically activated wood, Carbon, 1993, 31, 1185–1192.
15. Jain M., GargaV.K. andKadirvelu K., Chromium (VI) removal from aqueous system using Helianthus annuus (sunflower) stem waste, J. Hazard. Mater., 2009, 162, 365–372.
16. Bansal M., Singh D., Garg V.K. and Rose P., Use of agricultural waste for the removal of nickel ions from aqueous solutions: equilibrium and kinetics studies, Int. J. Civil Environ. Eng., 2009, 1(2), 108–114.
17. Gupta R. andMohapatra H., Microbial biomass: an economical alternative for removal of heavy metals from waste water, Indian J. Exp. Biol., 2003, 41, 945–966.
18. Malkoc E., Ni (II) removal from aqueous solutions using cone biomass of Thujaorientalis, J. Hazard. Mater., 2006, 137(2), 899–908.
19. Lagergren S., Zurtheorie der sogenannten adsorption gelosterstoffe 591, Kungliga Svenska Vetenskapsakademiens, Handlingar, 1898, 24(4), 1–39.
20. Ho Y.S. and McKay G., Kinetic models for the sorption of dye from aqueous solution by wood, J. Environ. Sci. Health Part B: Process Saf. Environ. Protect., 1998, 76, 183–191.
21. Wang X.S., Li Z.Z. and TaoS.R., Removal of chromium (VI) from aqueous solution using walnut hull, J. Environ. Manage., 2009, 90, 721–729.
22. Wang X. and Qin Y., Removal of Ni(II), Zn(II) and Cr(VI) from aqueous solution by Alternantheraphiloxeroides biomass, J. Hazard. Mater.,2006, 138, 582–588.
23. Weber Jr W.J. andMorriss J.C., Kinetics of adsorption on carbon from solution, J. Sanitary Eng. Div. Am. Soc. Civ. Eng., 1963, 89, 31–60.

24. Langmuir I., The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc.,1918, 40, 1361–1403.
25. Freundlich H.M., Over the adsorption in solution, Z. Phys. Chem.,1906, 57, 385–470.
26. ReddyD.H.K., Seshaiah K., ReyddyA.V.R., RaoM.M. and WangM.C., Biosorption of Pb^{+2} from aqueous solutions by Moringaoleifera bark: equilibrium and kinetic studies, J. Hazard. Mater., 2010, 174, 831–838.
27. Dubinin M.M., The potential theory of adsorption of gases and vapors for adsorbents with energetically non-uniform surface, Chem. Rev.,1960, 60, 235–266.
28. Gupta V.K., Jain R., Radhapyari K., Jadon N. andAgarwal S., Voltammetric techniques for the assay of pharmaceuticals-A review., Anal.Biochem., 2011, 408, 179–196.

*****