International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064
Index Copernicus Value (2013): 6.14 | Impact Factor (2014): 5.611

Kinetics and Equilibrium Study on the Removal of Ni (II) Using Activated Carbon-Tio_2 Nano Composite

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Abstract: ***The preparation of activated carbon from Typha Angustata L was investigated as adsorbent for removal of Nickel ions from aqueous solution. The surface morphology of activated carbon -Tio_2 Nanocomposite was determined by using XRD, SEM and IR spectroscopy. The Ni(II) was adsorbent dose, contact time, p^H, initial concentration and temperature has been studied. The experimental isotherm data were analyzed using the Langmuir, Freundlich and Tempkin equation. The adsorption kinetic data were tested using pseudo first order, pseudo second order and Elovich model.. The kinetic data fitted for the adsorption process obeyed pseudo second order.***

Keywords: Activated carbon -Tio_2 Nano composite, Ni, adsorption isotherm, Kinetics, Equilibrium, Langmuir

1. Introduction

The pollution of heavy metals has gained worldwide attention due to their toxicity difficult degradation and accumulation the living organisms and found in aquatic environment. Therefore, treatment of wastewater contaminated by heavy metals is an important environmental(1). Nickel was selected as an adsorbate because its compounds have widespread applications in many industrial processes such as non-ferrous metal, mineral processing, paint formulation, electroplating, batteries manufacturing, porcelain enameling, copper sulfate manufacture and steam-electric power plants leading to relatively high concentrations in aquatic environment (2). Some nickel compounds, such as nickel carbonyl, are carcinogenic and easily absorbed by the skin.

The exposure to this compound at an atmospheric concentration of 30mg/l for half an hour. High concentration of nickel causes cancer of lungs, nose and bone (4,5). At very high levels of exposure, nickel salts are known to be carcinogenic (3). Consequently, there is a need to treat industrial effluents polluted with Ni^{2+} ions before their discharge into the receiving water bodies. The presence of heavy metals in the aquatic environment has been of great concern to scientists and engineers because of their increased discharge, toxic nature and other adverse effects an receiving water (6).

Heavy metal ions are reported as priority pollutants, due to the mobility in natural water ecosystem and due to the toxicity(7). Many conventional methods including oxidation, membrane filtration , coagulation, reverse osmosis, absorption, ion exchange, precipitation, have been reported in the literature to remove heavy metals from waste water.

These methods maybe ineffective or extremely expensive especially when the waste steam contains relatively low concentration of metal (1-100mg/l) dissolved in large volume(8). However, adsorption can be regarded as one of the most popular methods for the removal of heavy metals from the wastewater due to its low cost, easy availability, biodegradability, simplicity of design and high removal efficiency(9). Activated carbon has been found the most promising and widely used adsorbent in wastewater pollution control throughout the world and has been successfully utilized for the removal of diverse types of pollutants including metal ions. However, the high capital and regeneration cost of activated carbon limits its large scale application for the removal of metals and other aquatic pollutants, which has encouraged researches to look for low–cost alternative adsorbents.

The effect of initial metal ion concentration was studied and the relationship between pH and removal efficiency was also analysed. The Langmuir, Freundlich, Elkovich models were utilized for analysis of the adsorption equilibrium. Kinetic models were tested to identify the potential adsorption process mechanisms. FTIR study was carried out to understand surface properties and available functional groups involved in sorption mechanism.

2. Materials and Methods

2.1 Preparation of Activated Carbon

The Typha Angustata L flowers was collected from the perundurai, at Erode (Dt) in Tamilnadu. They were cut into small pieces and dried for 25 days . The flowers were dried and burnt the muffle furnace at 450-500$°C$ and kept it for half an hour. To collected the carbonized material was ground well and sieved to a suitable particles size. Activated carbon have been stored in a plastic vessels for the further studies. The patical size of of 0.15 to 0.25mm was used.

2.2 Preparation of Ac- TiO_2-NC

Activated carbon (3g) was allowed to swell in 15ml of water-free alcohol and stirred for 2 hours at 25$°C$ to get a uniform suspension. At the same time, the titanium dioxide

(3g) was dispersed into water-free alcohol 15ml then the diluted titanium dioxide was slowly added by dropping it into the suspension of AC and stirring continued for another 5 hours at $25°C$. Then 5ml alcohol mixed with 0.2ml deionized water was added slowly and stirring continued for another 5 hours at $25°C$.

The suspension was then kept overnight for 10 hours at room temperature and the precipitate obtained was carefully dehydrated in a vacuum oven for 6 hours at $80°C$ to a characteristic of the Ac- TiO_2-NC were determined.

2.3 Adsorbate Solution

A stock solution of Ni^{2+} was prepared by dissolving 4.478g of $NiSo_4 . H_2O$ in completely double distilled water and making upto 1L of nickel solution. Working standards over prepared by diluting different volumes of the stock solution to obtain the concentration. Nickel ions concentrations were determined at characteristic wave length (Max =470 nm) with an double beam UV- visible spectrophotometer.

2.4 Characterization of Adsorbent

Physico-chemical characteristics of the adsorbents were studied as per the standard testing methods. The XRD pattern of pure activated carbon and that of $AC - TiO_2$ Nano composition. Fig 1 (a&b).

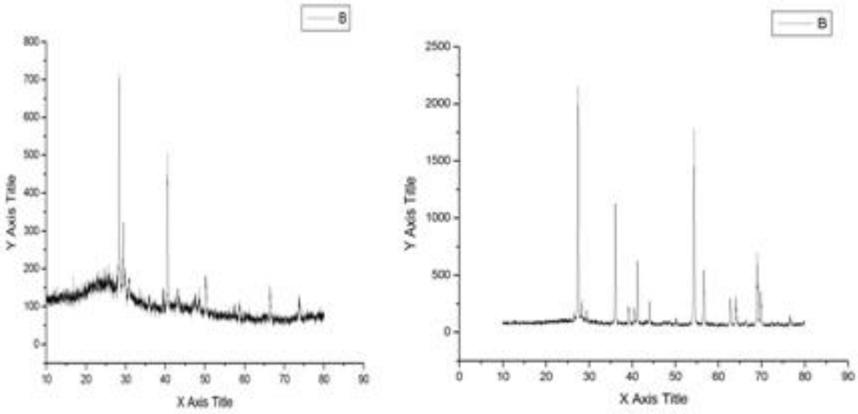

Figure 1(a): Carbon. Figure 1(b). Carbon + TiO_2

Show characteristics peak at 28° and 30°. Which confirm the presence of $AC - TiO_2$ phase in the Nano composite. The recorded patterns were analyzed using to determining peak position, width and intensity. Full-width at half-maxima (FwHm) data was analyzed by Scherer's formula to determine average particle size. $t = \frac{0.9\lambda}{\beta \cos e}$

The surface morphology of the adsorbent was visualized scanning electron microscopy (SEM) figure 2(a&b). the diameter of the composite range $10\mu m$ to 1 μm.

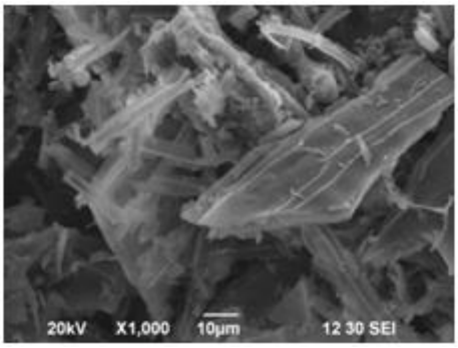

Figure 2 (a): Carbon

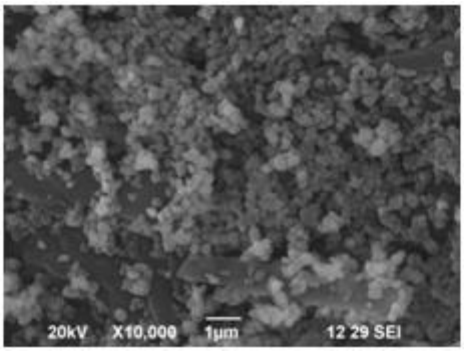

Figure 2 (b): AC-TiO_2 - NC

FT IR Spectroscopy

The absorption bands are due to the stretching and bending vibration of the group. The frequency of carbon peak $3425.58cm^{-1}$ and type of band N-H similarly $617.22cm^{-1}$ and type of band C-H the frequency of TiO_2 peak $655.80cm^{-1}$ is present C-H bonding.

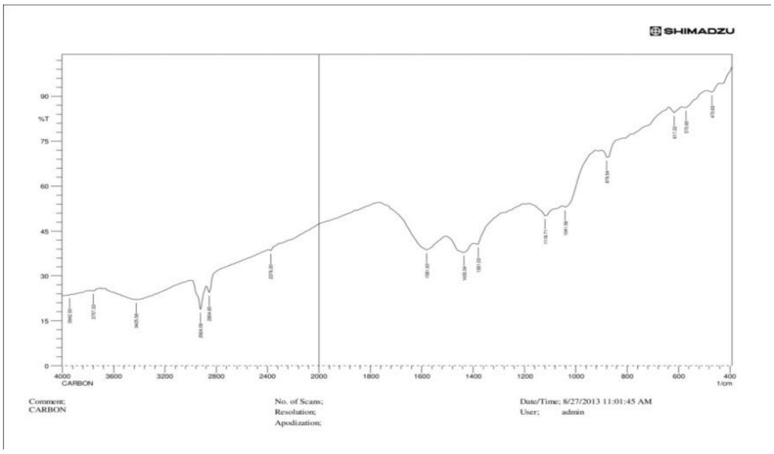

Figure 3 (a): Carbon

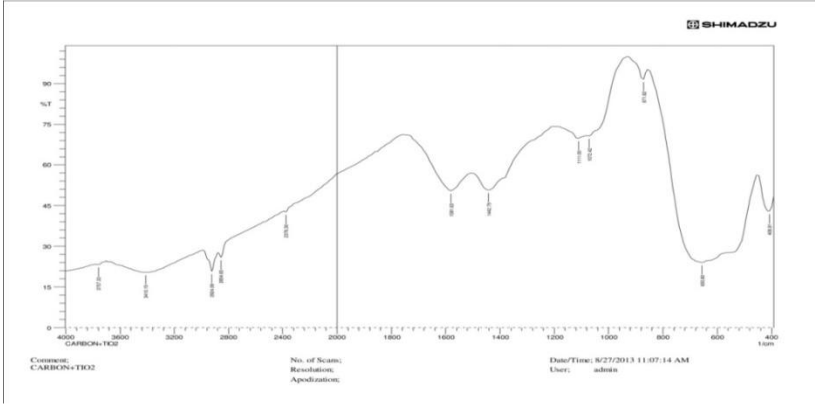

Figure 3 (b): Carbon+TIO$_2$.

3. Batch Adsorption Experiment

Batch adsorption experiments were also performed by agitation 0.1g of the adsorbent with 50ml of nickel solution the P^H containing different initial concentration from 10 to 40mg/L at 30°c. After the established contact time (2h) was attained, the suspension was filtered, and supernatant was analyzed for the metal concentration of 10 to 40mg/L and the adsorbent dosage of 0.1g.was adjusted in the range of 4-11 by using dil Hcl and NaOH solution. Experiments were carried out by varying the adsorbent amount from 0.1to 1.0g with Ni(ll) concentration ranging from 10 to 40mg/L. The concentration of Ni(ll) in the effluent was determined spectrophotometer by developing a rosy red colour using 25·/· Trisodium titrate, DMG and I$_2$ as complexing agent in acidic solution.

The percentage removal of metal and amount of metal adsorbed on AC- TiO$_2$ –NC was calculated by equation respectively.

$$\% \text{ removal} = \frac{100[C_O - C_e]}{C_e}$$

$$q_e = \frac{[C_o - C_e]V}{W}$$

Where q$_e$ is the quantity of metal adsorbed on the adsorbent at the time of equilibrium (mg/l), C$_O$ and C$_e$ are the initial and equilibrium concentration (mg/l). V is the volume of solution, W is the weight of adsorbent.

4. Results and Discussion

4.1 Effect of Contact Time and Initial Metal Concentration

The effect of contact time shows that equilibrium is achieved faster 30 to 210 min with Nano composite. It is observed that in both cases the percentage removal of Ni (ll) ion increase with incease in metal ion concentration Fig (4). The rate of adsorption is very fast initially with about 96·/·of the total nickel being removal within few minutes followed by a increased rate with the approach of equilibrium. The removal rate is high initially due to the presence of the binding sited which gradually become saturated with time resulting in increases rate of adsorption as equilibrium approached finally attain.

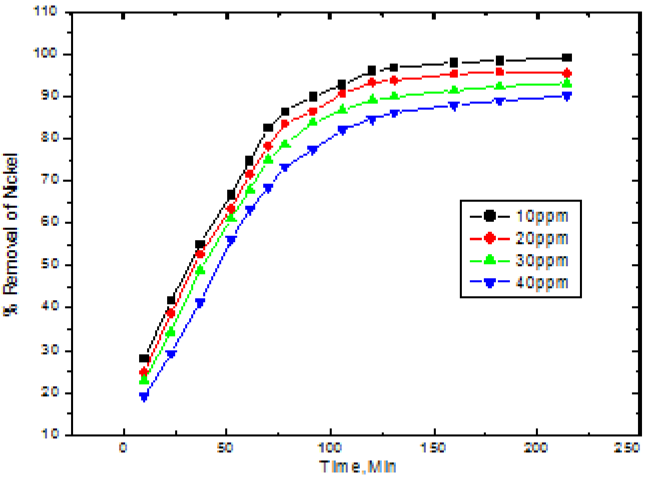

Figure 4: contact time

4.2 Effect of Adsorbent Dosage on Adsorption Process

The effect of dose adsorbents under study on the removal of nickel is shown in fig (5).which illustrates the adsorption of nickel ion with change of the adsorbent dose from 0.1 to 1.0mg. The results showed that within the amount increase in adsorbent concentration there is a increase adsorbed per unit mass of the adsorbent.

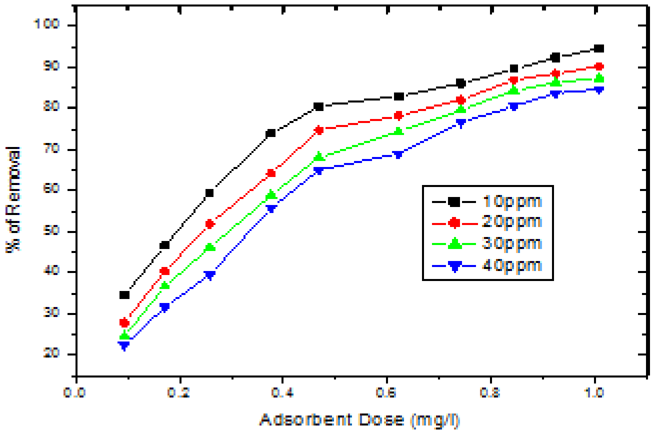

Figure 5: Adsorbent Dosage

4.3 Effect of Temperature

Temperature studies showed fig (6) at different temperature $30°C$, $34°C$, $38°C$, $42°C$ and the results. It is observed that adsorption of nickel ions increases with increasing temperature showing the process to be endothermic.

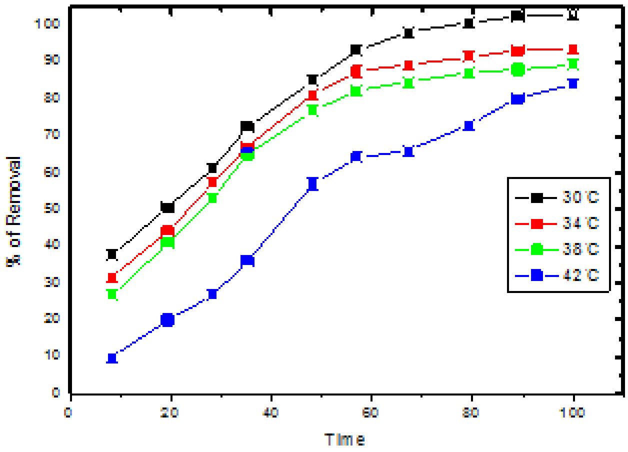

Figure 6: Effect of Temperature

4.4 Effect of P^H

Adsorption of Ni (ll) was studied at various pH values and results are depicted in fig(7). The initial pH of solution was varied from 5 to 11 with the adsorbate various concentration of 10 - 40mg/L maintaining the adsorbent dose at 0.1g and the contact time at 2 hours for nanocomposite. The residual Ni(II) ions were analysed with atomic absorption spectrophotometer. From this figures it is clear that nickel adsorption efficiency is highest at P^H 8-11 with Nanocomption P^{H}_{ZPC} for the Nanocomposition was determined as 8.0.

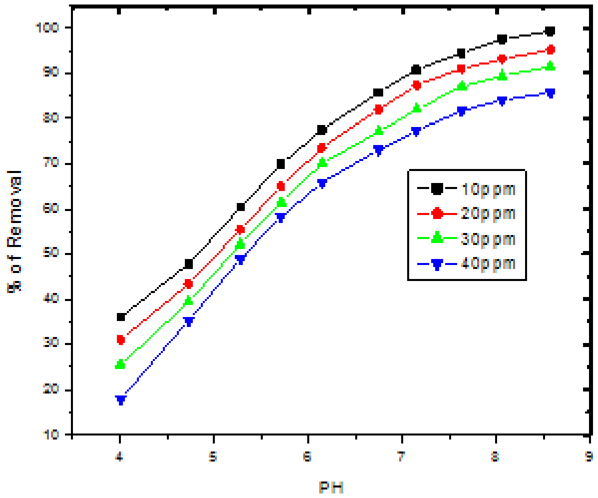

Figure 7: Effect of P^H

4.5 Adsorption Isotherm

The adsorption isotherm were analyzed using Langmuir and freundlich isotherm. 4.5.1 Langmuir adsorption isotherm:

The theoretical Langmuir isotherm is often used to describe adsorption of a solute from a liquid solution as

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{C_e}{Q_0}$$

Where q_e is the amount of metal adsorbed per unit mass of adsorbent (mg/L) and C_e is the equilibrium concentration of the adsorbate (mg/L), and q_0 and 'b' are Langmuir constants related to adsorption capacity and rate of adsorption respectively. As required by equation, plotting C_e/q_e against C_e gave a straight line, indicating that the adsorption of heavy metal on the nanocomposite follow the Langmuir isotherm fig (8). The Langmuir constant 'K_L' and were evaluated from the slope and intercept of the graph.

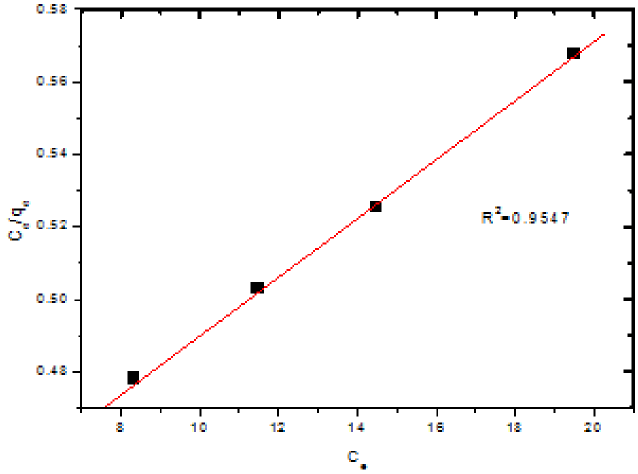

Figure 8: Langmuir adsorption isotherm

From this essential characteristics of Langmuir isotherm are expressed in the term of a dimensionless equilibrium parameters R_L which is defined by

$$R_L = \frac{1}{1+K_L C_0}$$

Where 'c_0' is the initial concentration of adsorbate [mg/L].

'K_L' is the Langmuir adsorption constant (L/mg). R_L value lies between 0 and 1 indicates favourable adsorption(Norrozi B, sorial,G.A, Arami M(2007)).

The value of Langmuir , Freundlich and Tempkin isotherm plot for the adsorption of Nickel by AC-Tio2-NC adsorbent.

4.5.2 Freundlich Isotherm

The freundlich isotherm (1906) is generally used for mathematically description of adsorption in aqueous system and describes heterogeneous surface energies (mckay et al. 2006). The equation can be expressed in logarithmic form as

$$log q_e = log k_f + 1/n \, log \, C_e \, .$$

Where q_e is the amount of metal adsorbed in mgL^{-1}.

C_e is the equilibrium concentration (mgL^{-1}), K_f and n were freundlich constant. (mg/g, L/mg) related to adsorption capacity and adsorption intensity of the sorbent respectively. The plot of $log q_e Vs \, log C_e$ gave straight lines with good regression coefficient indicating that the adsorption of heavy metal follow the freundlich isotherm fig (9).

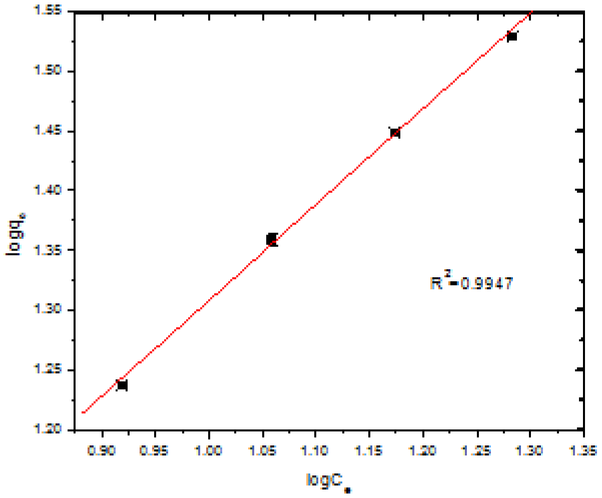

Figure 9: Freundlich Isotherm

4.5.3 Tempkin isotherm

Tempkin isotherm is represented by the following equation

$$q_e = \frac{RT}{b} In[AC_e] \qquad \text{-----------(1)}$$

Equation (1) can be expressed in its linear form as

$$q_e = B \, In \, A + BIn \, C_e \qquad \text{--------- (2)}$$

Where B is a constant related to the heat of adsorption (J/mol) and A is the Tempkin isotherm constant, corresponding to the maximum binding energy (L/mg).A plot of qe vs InCe is shown in Fig(10). The values of A and B calculated from the slope and intercept of the graph are given in Table 1.

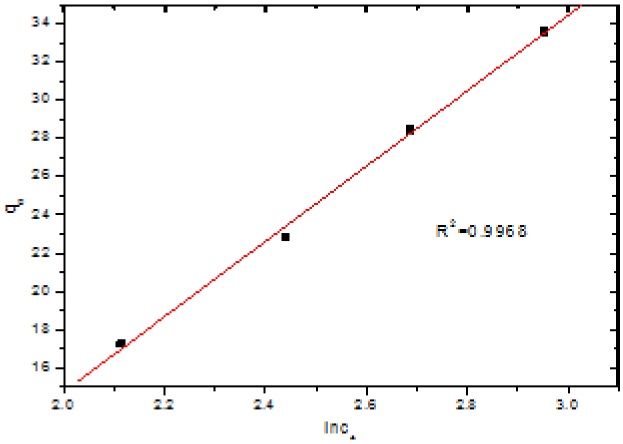

Figure 10: Tempkin isotherm

Table 1: Results of isotherm plots for the adsorption of Nickel on AC-Tio$_{2-}$ AC

Initial metal Concentration	Langmuir isotherm				*Freundlich isotherm*			Temkin isotherm		
	Q_0 (mg/g)	b(L/mg)	R^2	R_L	K_f	1/n	R^2	A (L/mg)	B (J/mol)	R^2
10	123.152	0.01986	0.9546	0.4570	42.66	0.8019	0.9947	24.72	19.72	0.9968
20				0.3862						
30				0.3348						
40				0.2955						

4.6 Adsorption: Kinetics

The kinetics of adsorption of Nickel by the nanocomposite and the kinetic models of pseudo first order, pseudo second order, and Intrapartcles diffusion model were considered.

4.6.1 Pseudo First order kinetics

The pseudo first order kinetics model can be represented as

$$\log(qe-qt)=\log qe-K1/2.303)$$

Where qe is the amount of metal adsorbed at equilibrium (g/mg). qt is the amount of metal adsorbed at time (mg/g) and k_1 is the pseudo first order rate constant k_1 and q_e (ther) can be calculated from the slope and intercept of the graph.

The q_e (ther) and q_e (exp) value are shown in table 2. The adsorption process does not follow first order kinetics.

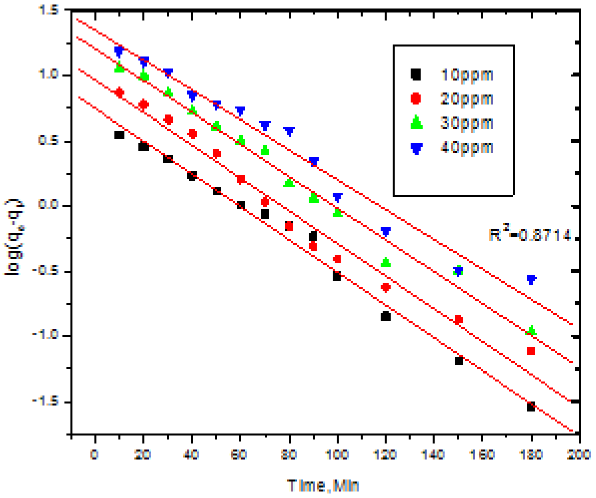

Figure 11: Pseudo First order

4.6.2 Pseudo-second order kinetic model

The linear pseudo second order kinetic equation is given as

$$t/q_t = 1/(k_2 q_e^2) + 1/q_e\ t$$

where k_2 is rate constant of second order adsorption (g $mg^{-1}min^{-1}$). As expected the plot of t/qt vs t Fig (12) was linear. The values of q_e and k_2 can be calculated from the slope and intercept. The q_e(the) and q_e(exp) values are shown in Table 2.

The calculated q_e (the) values are in consonance with q_e (exp) with high correlation coefficient values. The adsorption of NC-Tio2 –AC followed pseudo-second order kinetics.

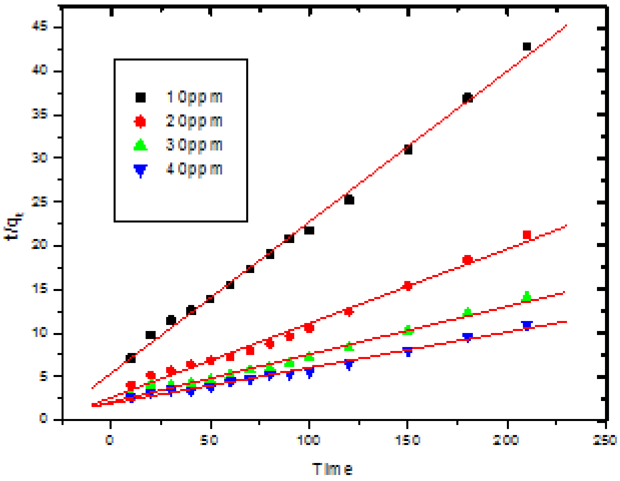

Figure 12: pseudo-second order

4.6.3 Intraparticle Diffusion

The intraparticle diffusion model used here referes to the theory proposed by Weber and Morris based an intraparticle diffusion coefficient K_{id} is defined by the equation,

$$q_t = k_{id}\ t^{1/2} + C$$

Where K_{id} is the intraparticle diffusion rate constant ($mg/gmin^{1/2}$), C is the intercept (mg /g) can be calculated by plotting q_t vs $t^{1/2}$ and the results are given in Fig (13) and Table 2. The linear portion of the plot does not pass through the origin. Such a deviation from the origin indicates that pore diffusion is the only controlling step and not the film diffusion.

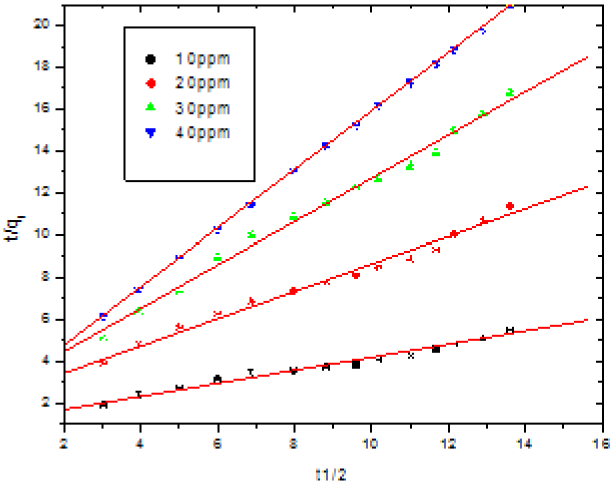

Figure 13: Intraparticle diffusion

Table 2: The Kinetic Parameter for the adsorption of Nickel by AC-Tio$_2$-NC Adsorbent

Initial metal concentration	Pseudo first order				Pseudo second order				Intraparticle diffusion		
	K_1	q_e exp	q_e cal	R^2	K_2	q_e exp	q_e cal	R^2	K_{id}	C	R^2
10	0.2878	4.901	4.3311	0.8882	1.673×10^{-3}	4.901	5.778	0.9962	0.3124	1.0774	0.9326
20	0.2878	9.869	5.5616	0.8763	2.786×10^{-3}	9.869	11.737	0.9878	0.6507	2.1354	0.8958
30	0.0281	14.846	9.5279	0.7858	1.45×10^{-3}	14.846	18.248	0.9848	1.0292	2.4229	0.9133
40	0.02625	19.139	13.6426	0.7714	$.0866\times10^{-3}$	19.139	24.449	0.9854	1.3935	2.0034	0.9335

5. Desorption Studies

Desorption studies with acetic acid revealed that the regeneration of adsorbent was not satisfactory, which confirm the chemisorptive nature of adsorption.

6. Conclusion

The adsorption isotherms evaluated that Ac- TiO$_2$-NC can be used as adsorbent for removal of nickel ion from aqueous solution. The amount of metal adsorbed varied with initial concentration, adsorbent dose, pH and temperature. Adsorption isotherms of the adsorbents under study were evaluated using freundlich, Langmuir and Temkin isotherm. The Kinetic data follows the pseudo second order kinetics model. Desorption studies reveals that not satisfactory Which confirms the chemisorptive nature of adsorption.

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