

# Removal of Nickel (II) using an activated carbon prepared from flower of *TyphaAngustata* L – TiO<sub>2</sub> Nanocomposite - Comparative study

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**Abstract** - The removal of Nickel (II) ion from aqueous solution by Activated carbon (AC) prepared from *TyphaAngustata* L was and AC-TiO<sub>2</sub>nanocoposite by batch adsorption techniques. The nanocomposites were characterized by XRD, SEM and IR spectral studies .The Effect of various parameters such as pH, adsorbent dosage, agitation time and temperature was studied for the removal of Ni (II) ion. Based on linear regression analysis, the data obtained from the batch studies showed a good compliance with the Langmuir, Freundlich and Tempkin isotherm models. The studies showed that the activated carbon- TiO<sub>2</sub>can be used as a good adsorbent for the removal of divalent nickel ion from aqueous solution.

**Keywords** - Activated carbon- TiO<sub>2</sub> - Nanocomposite, adsorption, kinetics, Langmuir and Freundlich isotherm, Nickel ion

## I. INTRODUCTION

Water is a source of life and energy, although millions of people worldwide are suffering from shortage of fresh and clean drinking water. Rapid pace of industrialization, population expansion, and unplanned urbanization have contributed largely to severe water pollution and surrounding soils. This has stimulated a growing research interest in establishing a leading selective, reliable and durable alternative for environmental conservation [1].

The main source of freshwater pollution can be attributed to discharge of untreated sanitary and toxic industrial wastes, dumping of industrial effluent, and runoff from agricultural fields. It is well known that 70–80% of all illnesses in developing countries are related to water contamination; particularly susceptible are women and children [2].

Pollutants discharged in wastewaters can be toxic to aquatic life and cause natural waters to be unfit as potable water sources. Stringent regulations have been introduced by many countries with respect to the presence of these chemicals in water which binds industries to treat industrial effluents properly before discharging it into the natural water-bodies containing clean water. Therefore, it is essential to removal of Ni from industrial wastewaters before discharging it into the environment.

A number of technologies are available with varying degree of success to control water pollution. Some of them are coagulation [3], froth flotation [4], filtration [5], ion exchange [6], aerobic and anaerobic treatment [7, 8], advanced oxidation processes [9], solvent extraction [10], adsorption [11], electrolysis [12], microbial reduction [13] and activated sludge [14].

The chemical precipitation is the most cost-effective treatment technology. The possibility to precipitate metals in the form of insoluble compounds, mostly metal hydroxides, in solutions containing complexing agents depends on the complex stability constant and the hydroxide solubility product [15]. A broad range of biomass types including bacteria, algae, yeast, fungi, activated sludge, anaerobic sludge, digested sludge, peat have been used as bio sorbents to remove Ni(II) metals from aqueous solution [16-27].

The nickel ion, compared with other heavy metal ions, was a more recalcitrant pollutant and many metal tolerant micro-algae had a relatively low Ni-binding capacity. The removal of nickel ions from effluent was far from satisfactory. The bio sorption of nickel by different strains of microorganisms was less than that of other metal ions.

This was probably due to the intrinsic chemical properties of nickel ions leading to steric hindrance of bio sorption.

The present Studies focusing specifically on nickel removal are rare. There is still no satisfactory precedent of employing bio sorbent in the removal of nickel ions and the feasibility of employing micro-algae to remove Ni from electroplating wastewater is uncertain.

## II. MATERIALS AND METHODS

### 2.1 Preparation of activated carbon

In the present study, *Typha Angustata* L flowers were 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 collect the carbonized material was ground well and sieved to a smaller particles size. Activated carbon have been stored in a plastic vessels for the further experiment. The sample was sieved into a smaller particle size of 0.15 to 0.25mm was used.

### 2.2 Preparation of Ac- TiO<sub>2</sub>-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<sub>2</sub>-NC were determined.

### 2.3 Adsorbate solution:

A stock solution of Ni (II) was prepared in 1000ml deionised water using 2.8300g dried K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. The Working solution was obtained by diluting the stock solution with deionised water and pH was adjusted to the desired values according to the following experimental design with 1M HCl and 1M NaOH solution. Nickel ions concentrations were determined at characteristic wave length ( $\lambda_{max} = 393$  nm) with an double beam UV- visible spectrophotometer

### 2.4 Characterization of adsorbent

#### 2.4.1 XRD studies

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<sub>2</sub>Nano composite was shown in figure 1(a&b). The figures show characteristics peak at 28° and 30°, which confirm the presence of AC – TiO<sub>2</sub> phase in the Nano composite.

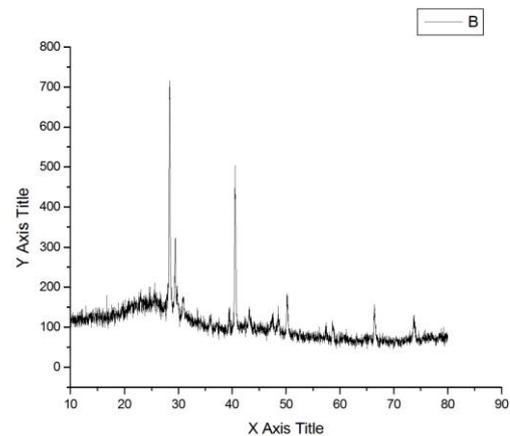


Figure 1(a) Activated carbon

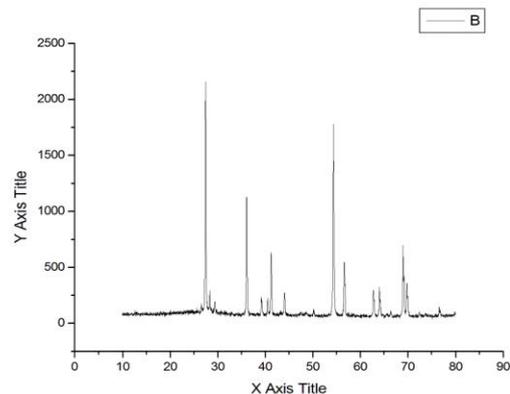


Figure 1(b) Activated carbon+TiO<sub>2</sub> – Nanocomposite

#### 2.4.2 SEM Analysis

The surface morphology of the adsorbent was visualized scanning electron microscopy (SEM) Figure 2(a&b), with the diameter of the composite range 10µm to 1µm. From the study it has been found out that the surface morphology of activated carbon is changed in AC-TiO<sub>2</sub>nanocomposites. The particle like shape was shown by activated carbon nanocomposite compared to bare activated carbon because it do not show any phase structure.

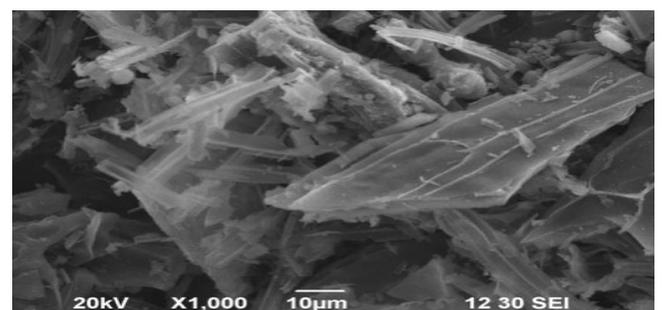


Figure 2 (a) Carbon

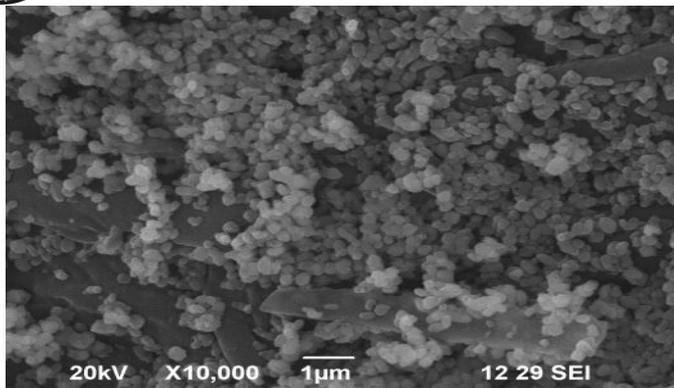


Figure 2 (b) AC-TiO<sub>2</sub> Nanocomposite

#### 2.4.3 FT IR spectral studies

The absorption bands are due to the stretching and bending vibration of the group frequency of carbon peak 617.22cm<sup>-1</sup> and Ti O<sub>2</sub>peak 655.8 cm<sup>-1</sup> (Figure 3 a & b). These spectral studies show that some peaks are disappeared in AC-TiO<sub>2</sub>nanocomposite compared to bare TiO<sub>2</sub>. It indicates the formation of AC-TiO<sub>2</sub>nanocomposite.

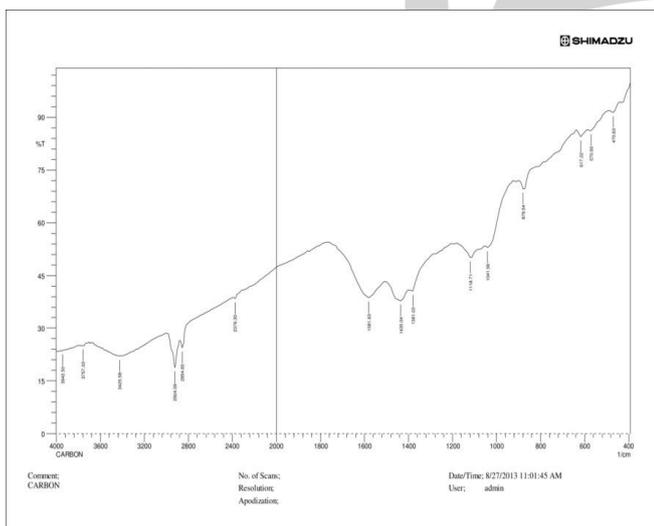


Figure 3 (a) FTIR spectrum of activated carbon

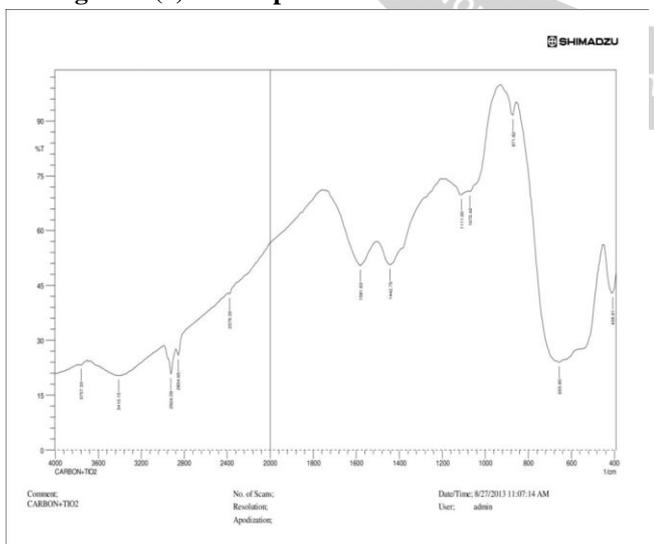


Figure 3 (b) FTIR spectrum of activated carbon +TiO<sub>2</sub> – Nanocomposite

### III. MATERIALS AND METHODS

#### Batch Adsorption Studies

Batch adsorption experiments were also performed by agitation 0.1g of the adsorbent with 50ml of chromium solution the pH containing different initial concentration form 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. The pH values was adjusted in the range of 4-9 by using dil. HCl and NaOH solution. Experiments were carried out by varying the adsorbent amount from 0.1to 1.0g with Ni (II) concentration ranging from 10 to 40mg/L. The concentration of Ni (II)in the solution was determined spectrophotometrically by developing a purple-violet colour with 2drops of phosphoric acid and 1,5-diphenyl carbazide in acidic solution as complexing agent. The absorbance of the purple-violet colored solution is read at 393 nm [28].

The percentage removal of metal and amount of metal adsorbed on AC- TiO<sub>2</sub> –NC was calculated by equation (1) and (2) respectively.

$$\% \text{ removal} = \frac{100 [C_0 - C_e]}{C_e} \text{-----(1)}$$

$$q_e = \frac{[C_0 - C_e]V}{W} \text{----- (2)}$$

Where q<sub>e</sub> is the quantity of metal adsorbed on the adsorbent at the time of equilibrium (mg/g), C<sub>0</sub> and C<sub>e</sub> are the initial and equilibrium concentration (mg/L). V is the volume of solution, W is the weight of adsorbent(g).

### IV. RESULTS AND DISCUSSION

#### 4.1 Effect of contact time

The effect of contact time shows that equilibrium is achieved faster 10 to 210 min with Nano composite. It is observed that in both cases the percentage removal of Ni(II) ion increase with increase in metal ion concentration Fig (4 a & b). The rate of adsorption is very fast initially with about 80 % of the total lead being removal within few minutes followed by an 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 finally attain equilibrium.

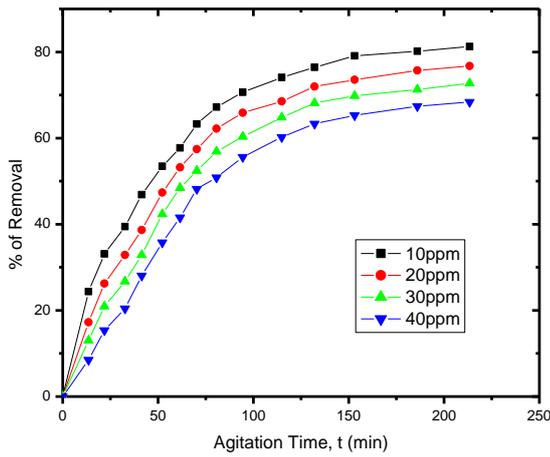


Figure 4a: Effects of agitation time and initial metal ion concentration on the removal of Nickel (II) onto AC

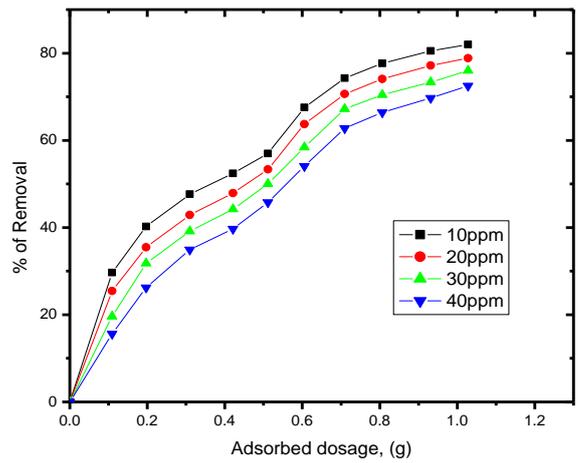


Figure 5 b: Effect of Adsorbent dose and Initial metal ion concentration of Nickel (II) onto AC-TiO<sub>2</sub> - Nanocomposite

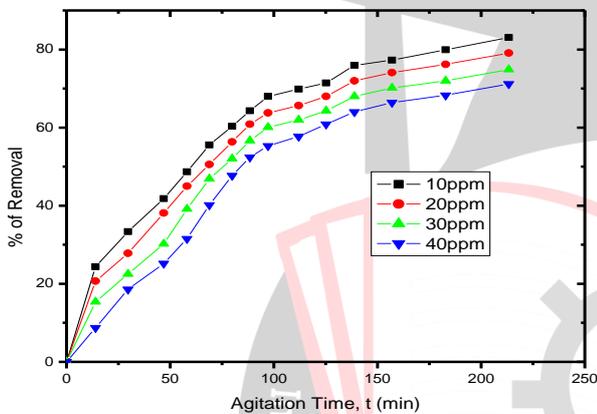


Figure 4b: Effects of agitation time and initial metal ion concentration on the removal of Nickel (II) onto AC-TiO<sub>2</sub> - Nanocomposite

4.2 Effect of adsorbent dosage:

Figure (5a& b) shown the effect of adsorbent dosage on the removal of nickel. It is clear from the figure that as the adsorbent dosage increases, the adsorption also increases. The removal of nickel (about 80 %) was achieved for an adsorbent dosage of 1g of the adsorbent.

4.3 Effect of temperature:

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

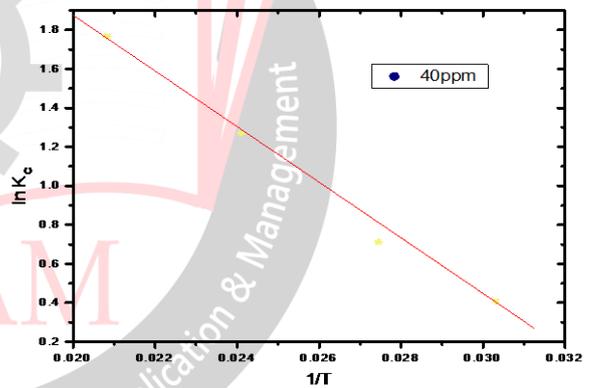


Figure 6a: Effect of Temperature and removal of Nickel (II) onto AC

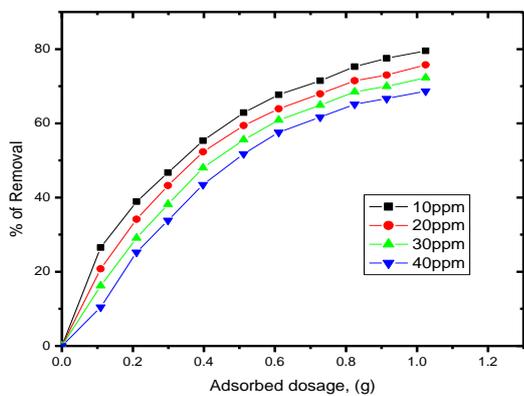


Figure 5 a: Effect of Adsorbent dose and Initial metal ion concentration of Nickel (II) onto AC

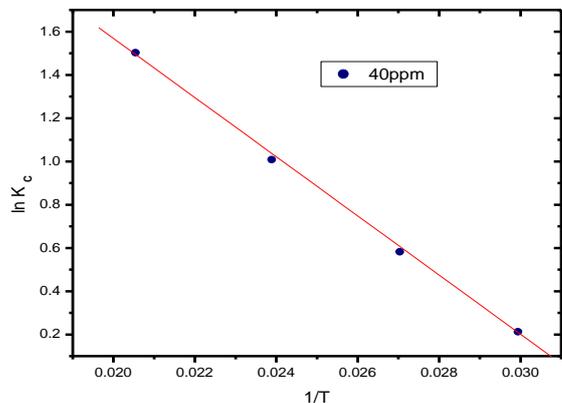


Figure 6b: Effect of Temperature and removal of Nickel (II) onto AC-TiO<sub>2</sub> - Nanocomposite

#### 4.4 Effect of pH:

The effect of pH on the adsorption of Ni (II) by activated carbon was studied at pH values of 3 to 9 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 figure 7 a & b it is clear that nickel adsorption efficiency is highest at pH = 7-9 with nanocomposite.

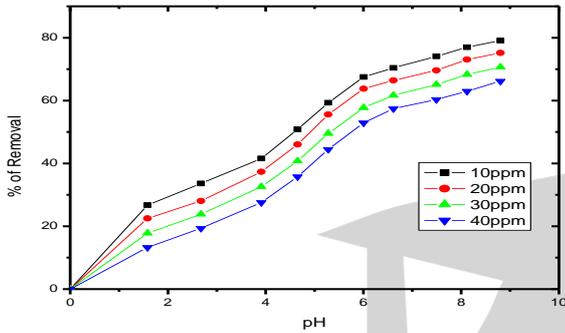


Figure 7 a: Effect of pH and Initial metal ion concentration of Nickel (II) onto AC

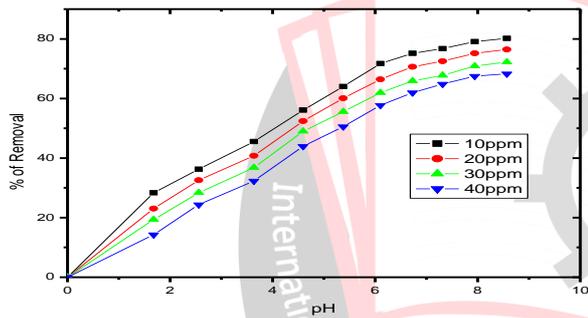


Figure 7 b: Effect of pH and Initial metal ion concentration of Nickel (II) onto AC-TiO<sub>2</sub> – Nanocomposite

#### 4.5 Adsorption Isotherm

The adsorption isotherm were analyzed using Langmuir, Freundlich and Tempkin isotherm.

##### 4.5.1 Langmuir adsorption isotherm:

The Langmuir adsorption isotherm [29] is often used for adsorption of the solute from a liquid solution. The linear form of the Langmuir adsorption isotherm can be expressed by

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

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 ' $K_L$ ' are Langmuir constants related to adsorption capacity and rate of adsorption respectively.  $Q_0$  is the amount of adsorbate at complete monolayer coverage (mg/g) which gives the maximum adsorption capacity of the adsorbent

and  $K_L$ (L/mg) is the Langmuir isotherm constant that related to the energy of adsorption. 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 (8a & b). The Langmuir constant ' $K_L$ ' can be evaluated from the slope and intercept of the linear graph.

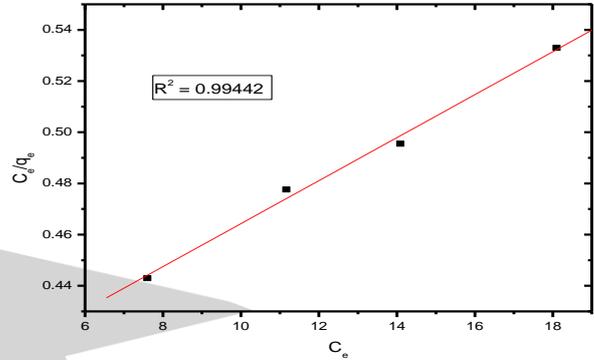


Figure 8 a: Langmuir plot for the adsorption of Nickel (II) onto AC

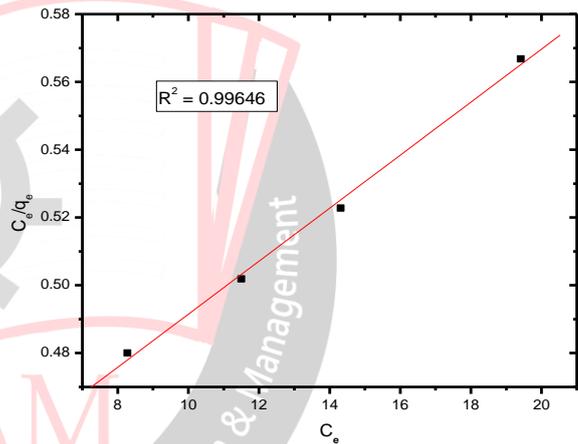


Figure 8 b: Langmuir plot for the adsorption of Nickel (II) onto AC-TiO<sub>2</sub> – Nanocomposite

The essential characteristics of the Langmuir equation can be expressed in terms of dimensionless separation factor,  $R_L$  defined by

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

Where ' $c_0$ ' is the initial solute 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.

##### 4.5.2 Freundlich Isotherm:

The Freundlich isotherm (1906) is earliest known relationship describing the adsorption equation which is often expressed as heterogeneous surface energies [30]

$$q_e = K_f C_e^{1/n}$$

The equation is conveniently used in the linear form by taking the logarithmic of both sides.

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

Where  $q_e$  is the amount of metal adsorbed in per weight of the adsorbent ( $\text{mgL}^{-1}$ ).  $C_e$  is the equilibrium concentration ( $\text{mgL}^{-1}$ ),  $K_f$  and  $n$  were freundlich constant. ( $\text{mg/g}$ ,  $\text{L/mg}$ ) related to adsorption capacity and adsorption intensity of the sorbent respectively. The plot of  $\log q_e$  vs  $\log C_e$  yields a straight lines which indicating the confirmation of the freundlich isotherm for adsorption fig (9a & b). The values of  $n$  indicates favorable adsorption when  $1 < n < 10$ .

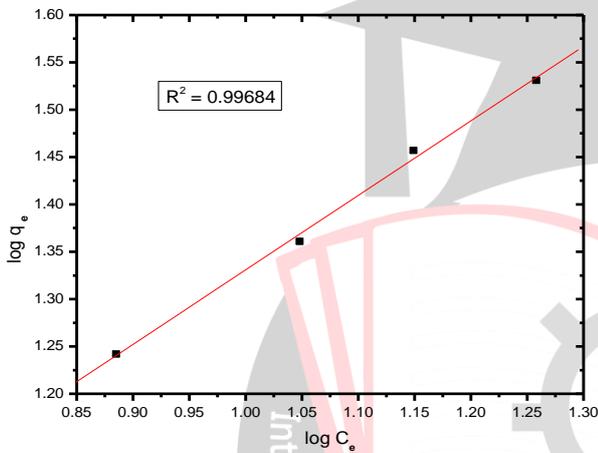


Figure 9 a: Freundlich plot for the adsorption of Nickel (II) onto AC

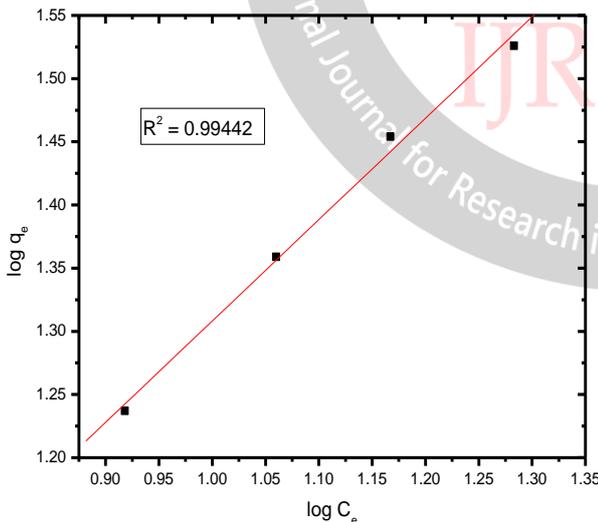


Figure 9 b: Freundlich plot for the adsorption of Nickel (II) onto AC-TiO<sub>2</sub> – Nanocomposite

#### 4.5.3 Tempkin isotherm

Tempkin isotherm is represented by the following equation

$$q_e = \frac{RT}{b} \ln[AC_e]$$

equation can be expressed in its linear form as

$$q_e = B \ln A + B \ln C_e$$

Where  $B$  is a constant related to the heat of adsorption ( $\text{J/mol}$ ) and  $A$  is the Tempkin isotherm constant, corresponding to the maximum binding energy ( $\text{L/mg}$ ) [31]. A plot of  $q_e$  vs  $\ln C_e$  is shown in Figure(10a & b). The values of  $A$  and  $B$  calculated from the slope and intercept of the graph.

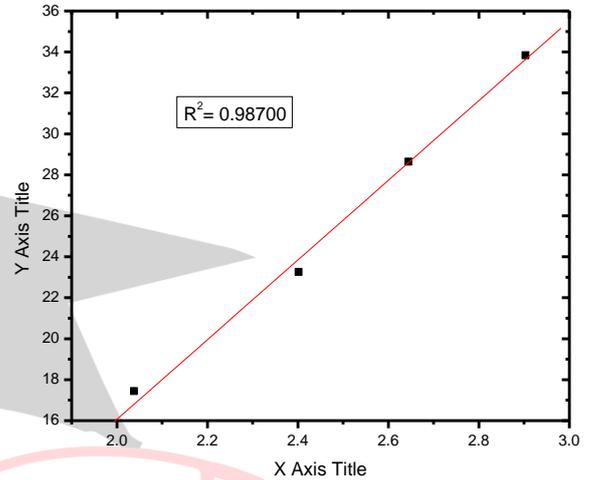


Figure 10 a: Tempkin isotherm for the adsorption of Nickel (II) onto AC

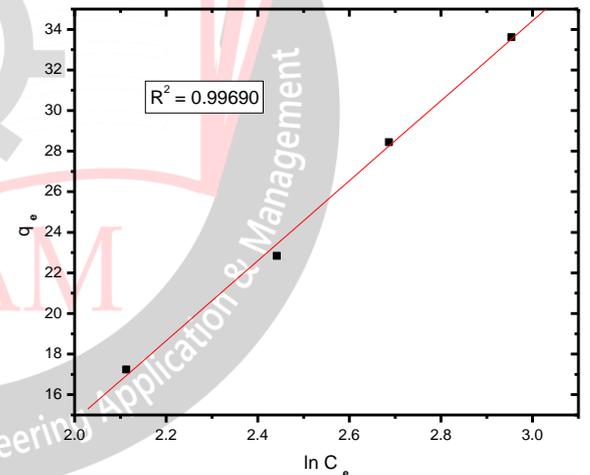


Figure 10 b: Tempkin isotherm for the adsorption of Nickel (II) onto AC-TiO<sub>2</sub> – Nanocomposite

#### 4.5.4 Dubinin-Radhuskevich isotherm:

The equilibrium data was further subjected to the D-R isotherm model to identify the nature of adsorption processes. The linear form of D-R isotherm equation is given by the equation [30].

$$\ln q_e = \ln q_m - \beta \epsilon^2$$

where  $q_e$  is the amount of metal ions adsorbed on per unit weight of adsorbent ( $\text{mol/g}$ ),  $q_m$  is the maximum adsorption capacity ( $\text{mol/g}$ ),  $\beta$  is the activity coefficient related to adsorption mean free energy ( $\text{mol}^2/\text{J}^2$ ) an  $\epsilon$  is the Polanyi potential

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

The D-R isotherm model did not fit the equilibrium data as the R<sup>2</sup> value [Figure 11 a & b].

$$E = 1/\sqrt{2\beta}$$

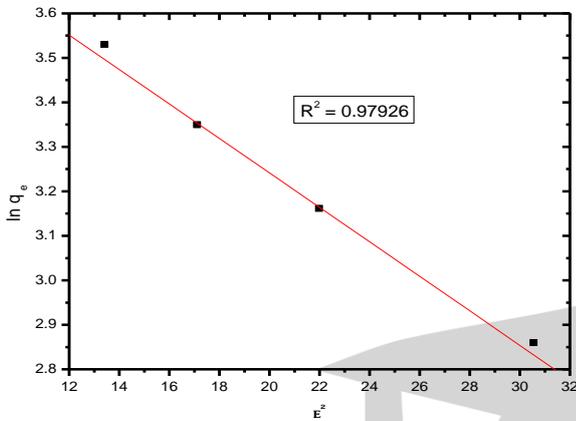


Figure 11 a: Dubinin-Radushkevich isotherm for the adsorption of Nickel (II) onto AC

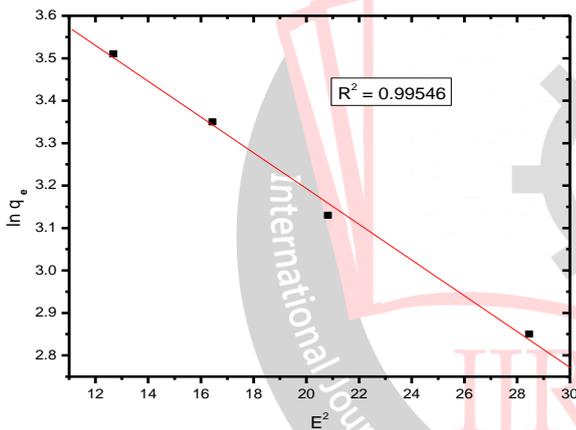


Figure 11 b: Dubinin-Radushkevich isotherm for the adsorption of Nickel (II) onto AC-TiO<sub>2</sub> – Nanocomposite

#### 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 intraparticles diffusion model were considered.

##### 4.6.1 Pseudo First order kinetics

In integrated form of the pseudo first order kinetics model can be represented as

$$\text{Log} (q_e - q_t) = \text{log} q_e - (k_1/2.303)t$$

Where q<sub>e</sub> is the amount of metal adsorbed at equilibrium (g/mg). q<sub>t</sub> is the amount of metal adsorbed at time (mg/g) and k<sub>1</sub> is the pseudo first order rate constant k<sub>1</sub> and q<sub>e</sub>

(ther) can be calculated from the slope and intercept of the graph. The q<sub>e</sub> (ther) and q<sub>e</sub> (exp) value are shown in table. The adsorption process does not follow first order kinetics [figure 12 a & b].

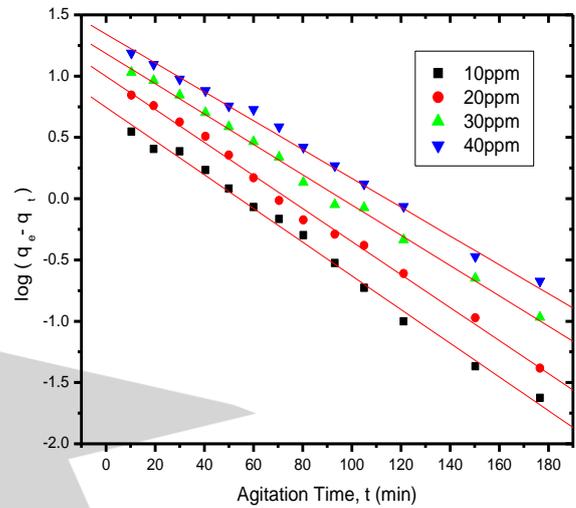


Figure 12 a: Pseudo First order kinetics for the adsorption of Nickel (II) onto AC

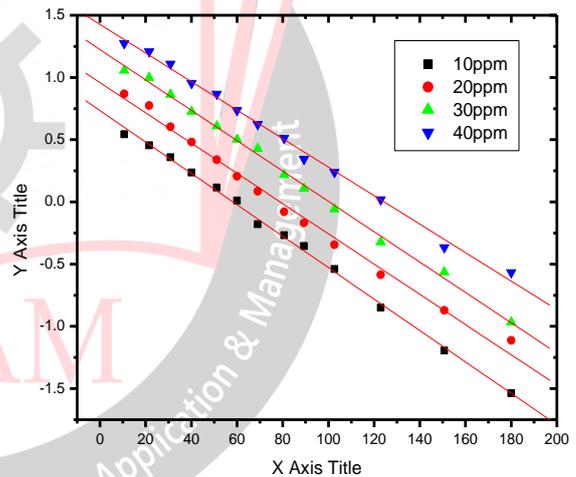


Figure 12 b: Pseudo First order kinetics for the adsorption of Nickel (II) onto AC-TiO<sub>2</sub> – Nanocomposite

##### 4.6.2 Pseudo-second order kinetic model

The integrated form of I order

$$1/q_e + q_t = 1/q_2 + K_2 t$$

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<sub>2</sub> is rate constant of second order adsorption (g mg<sup>-1</sup> min<sup>-1</sup>) [29]. As expected the plot of t/q<sub>t</sub> vs t Figure (13 a & b) was linear. The values of q<sub>e</sub> and k<sub>2</sub> can be calculated

from the slope and intercept. The adsorption of NC-TiO<sub>2</sub> – AC followed pseudo-second order kinetics.

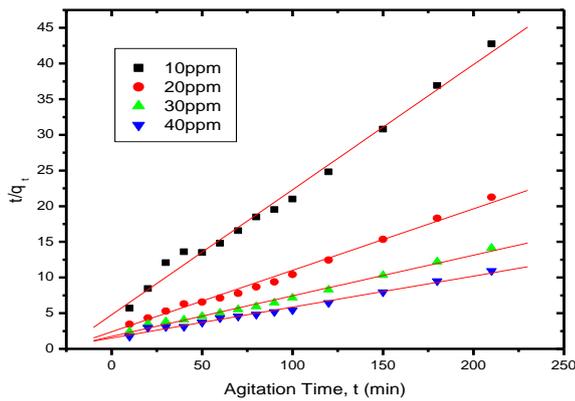


Figure 13 a: Pseudo Second order kinetics for the adsorption of Nickel (II) onto AC

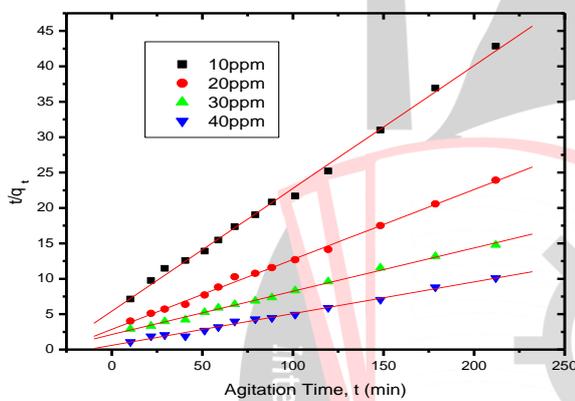


Figure 13 b: Pseudo Second order kinetics for the adsorption of Nickel (II) onto AC-TiO<sub>2</sub> – Nanocomposite

#### 4.7 Intraparticle diffusion

The intraparticle diffusion model used here refers 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 Figure (14 a & b).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.

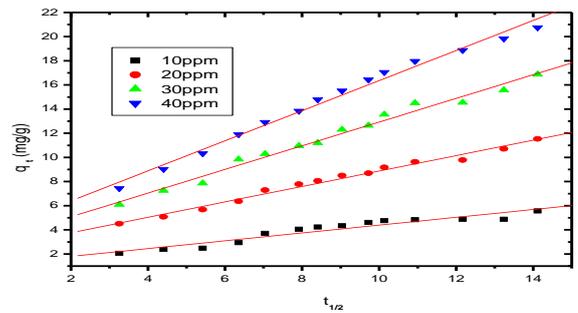


Figure 14 a: Pseudo Second order kinetics for the adsorption of Nickel (II) onto AC

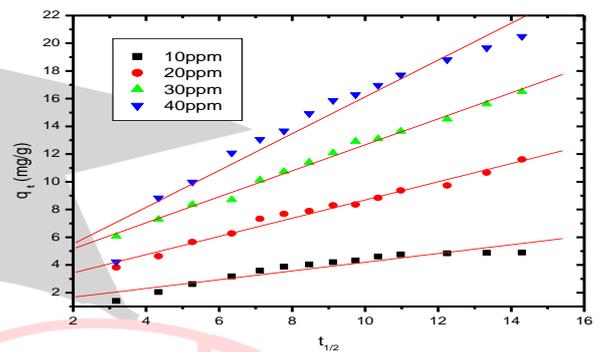


Figure 14 b: Pseudo Second order kinetics for the adsorption of Nickel (II) onto AC-TiO<sub>2</sub> – Nanocomposite

#### 4.8 Thermodynamic parameters:

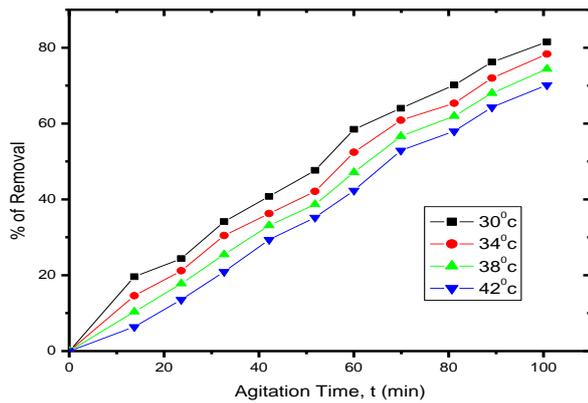
The thermodynamic parameters for the sorption process could be determined from the experimental data obtained at various temperature using the equation

$$\ln K_c = \Delta S^\circ / R - \Delta H^\circ / RT$$

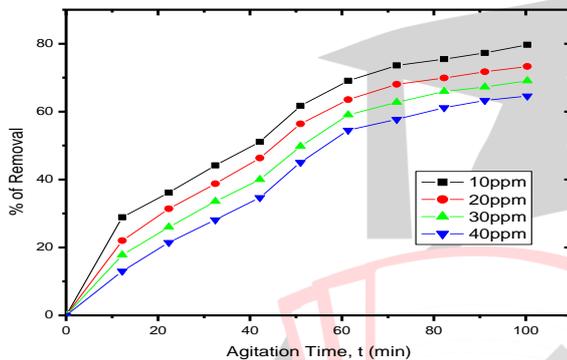
$$\Delta G^\circ = \Delta H - T\Delta S$$

Where  $K_c$  is the Langmuir constant related to the energy of adsorption,  $R$  is the gas constant and  $T$  is the absolute temperature (K).the adsorption process such as free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ).

From the Figure 15 a & b it has been found out that the removal of nickel ion from AC-TiO<sub>2</sub> follows endothermic process.



**Figure 15 a: Thermodynamic parameters for the adsorption of Nickel (II) onto AC**



**Figure 15 b: Thermodynamic parameters for the adsorption of Nickel (II) onto AC-TiO<sub>2</sub> – Nanocomposite**

## V. CONCLUSION

Batch adsorption studies carried out demonstrated the removal of nickel using AC- TiO<sub>2</sub> – Nanocomposite to be strongly dependent on contact time, adsorbent dose, pH and temperature. The experimental data of the adsorption under study were evaluated using Freundlich, Langmuir and Tempkin isotherm. The kinetic results were best described by pseudo second order equation. Thermodynamics data indicated that the adsorption of Ni(II) onto activated carbon is endothermic, chemisorption can be pointed out as the controlling mechanism.

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