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RESEARCH ARTICLE

Studies on the Removal of Ni(II) from Aqueous Solution using Fire Clay-TiO$_2$ Nanocomposite and Fire Clay

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Abstract: Fire clay-TiO$_2$ nanocomposite (NC) and fire clay (FC) was tested as adsorbents for the adsorption of Ni(II) from aqueous solutions. Batch adsorption experiments have been conducted under various operating parameters like initial metal ion concentration, contact time, adsorbent dose, pH and temperature. The equilibrium adsorption data on both clay and nanocomposite fitted well to Langmuir, Freundlich, D-R models and fairly to the Temkin model. The kinetic studies indicated that the adsorption followed pseudo second order, chemisorptive Elkovich and Intraparticle diffusion models. The thermodynamic parameters ΔG^o, ΔH^o and ΔS^o evaluated showed that the adsorptions on both clay and nanocomposite to be exothermic and spontaneous in nature. Ni(II) removal was better with nanocomposite than with clay.

Keywords: Fire Clay, Fire Clay-TiO$_2$ nanocomposite, Heavy metal, Adsorption isotherm

Introduction

Large volumes of waste generates from a variety of industries are one of the main reasons for the contamination of water and other environmental resources. Various techniques including precipitation with lime or sulfide, ion exchange, reverse osmosis, solvent extraction, membrane filtration and electrochemical treatment were tried to these harmful pollutants[1,2]. However these methods suffer from high capital operations costs[3].

In developing countries, there is a pressing need to use the available low cost materials for the treatment of wastes with simple working technology. In wastewater treatments, the process of the adsorption has an edge over other methods, due to its sludge free clean operation[4]. Adsorption of metals on activated carbon derived from different sources has also been studied by some authors[5]. Carbon nanotubes were also used to adsorb heavy metals like lead[6].

Nature clays[7-9] have been used as adsorbents due to their low cost and high removal efficiency. Their sorption capabilities come from their high surface area, porosity and the negative charge on their surfaces.

In the present study fire clay-TiO_2 nanocomposite and fire clay were used as adsorbents for the removal of Ni(II), from aqueous solutions. The effect of pH, adsorbent dose, initial metal ion concentration and contact time and effect of temperature were analysed. The experimental results were applied to Langumuir and Fruendlich, Temkin, D-R adsorption isotherms. Adsorption kinetics was applied in order to understand adsorption mechanism. The physicalchemical characteristic of fire clay+TiO_2 nanocomposite and fire clay were obtained from x-ray diffraction (XRD) and scanning electron microscopy (SEM).

Experimental

Fire clay (3 g) was allowed to swell in 15 mL of water-free alcohol and stirred for 2 hours at 25 °C to get a uniform suspension. At the same time, the titanium dioxide (3 g) was dispersed into water-free alcohol (15 mL). Then the diluted titanium dioxide was slowly added into the suspension of fire clay and stirred for a further 5 hours at 25 °C. Finally, 5 mL alcohol mixed with 0.2 mL deionized water was slowly added. The stirring was continued for another 5 hours at 25 °C and the resulting suspension kept overnight in a vacuum oven for 6 hours at 80 °C.

Absorbate solution

A stock solution of Ni(II) was prepared by dissolving 4.478 g of nickel sulphate (AR) ($NiSO_{4.}H_2O$) in 1000 mL of doubly distilled water.

Characterization of adsorbent

The physicochemical characteristics of the adsorbents were studied as per the standard testing methods[10]. Figures 1 & 2 shows the XRD pattern of pure fire clay and that of fire clay+TiO_2 nanocomposite respectively. The peaks at 28^o (Figure 2) and 30^0 (Figure 1) confirm the presence of fire clay-TiO_2 phase in the nanocomposite. The surface morphology of the adsorbent was visualized via scanning electron microscopy (SEM) Figures 3 & 4. The diameter of the composite range was 50 µm.

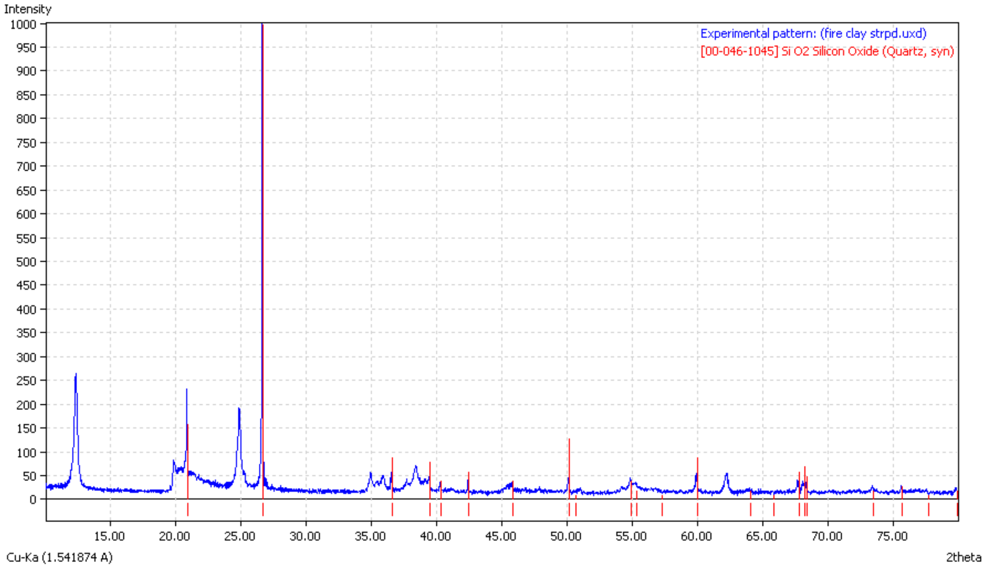

Figure 1. XRD analysis of fire clay

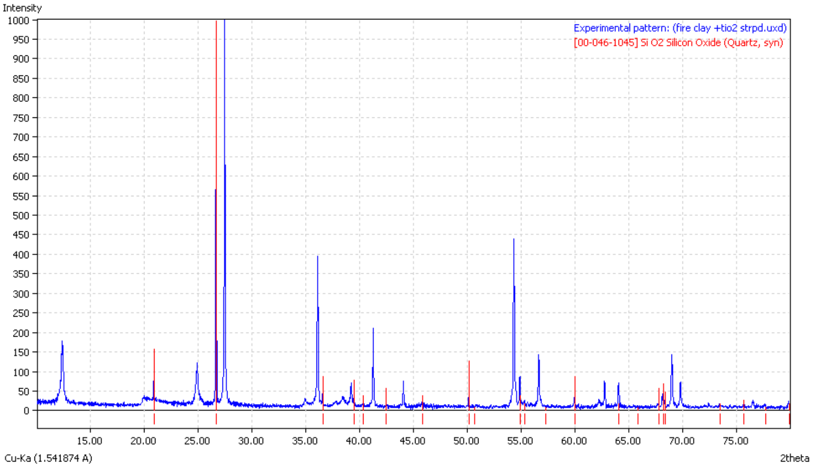

Figure 2. XRD Analysis of fire clay- TiO_2 nanocomposite

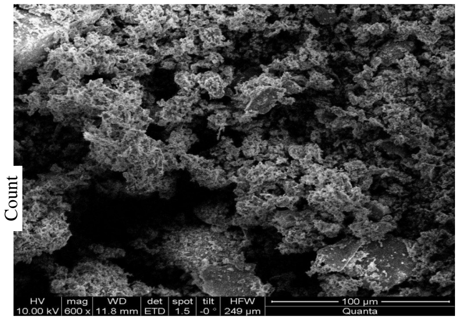

Figure 3. SEM of pure fire clay

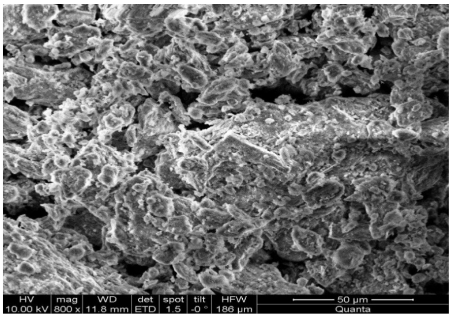

Figure 4. SEM of fire clay –TiO2 composite

Batch adsorption experiments

Batch adsorption experiments were conducted by agitating the flasks for a predetermined time intervals in a thermostat attached with a shaker at a desired temperature. Adsorption isotherm study was carried out with different initial concentrations of Ni(II) ranging from 10 to 40 mg/L while maintaining the adsorbent dosage at 0.1 g. The effect of contact time and pH was studied with Ni(II)concentration of 10-40 mg/L and an adsorbent dosage of 0.1 g. The solution pH was adjusted in the range of 5-11 by using dilute hydrochloric acid and sodium hydroxide solutions. Experiments were carried out by varying the adsorbent amount from 0.1 to 1.0 g with Ni(II) concentration ranging from10 to 40 mg/L. The concentration of free Ni(II) ions in the effluent was determined spectrophotometrically by developing a rosy red color using di methyl glyoxime and tri-sodium citrate and iodine solution.

Results and Discussion

Effect of adsorbent dose

The effect of adsorbent dose on Ni(II)removal was studied by keeping all other experimental conditions constant except that of adsorption dose. The results showed that with increase in adsorbent concentration there is a decrease in the amount adsorbed per unit mass of the adsorbent for both clay and nanocomposite Figures 5 & 6. This may basically be due to adsorption sites remaining unsaturated during the adsorption process.

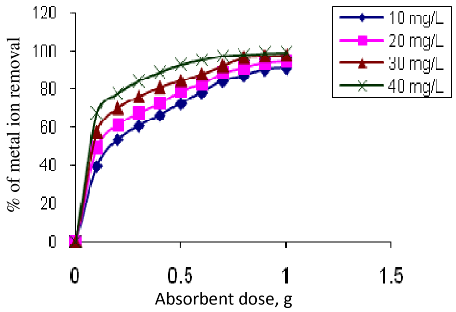

Figure 5. Fire clay-TiO_2 nanocomposite

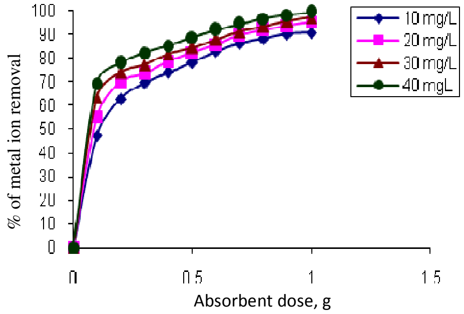

Figure 6. Fire clay

Effect of contact time and initial metal concentration

The effect of contact time and different initial concentrations has been studied using both clay and nanocomposite. It is observed that in both cases the percentage removal of Ni(II) ions increase with increase in metal ion concentration Figures 7 & 8 and attains saturation. The removal rate by adsorption is rapid initially, gradually decreases with time and finally attains equilibrium.

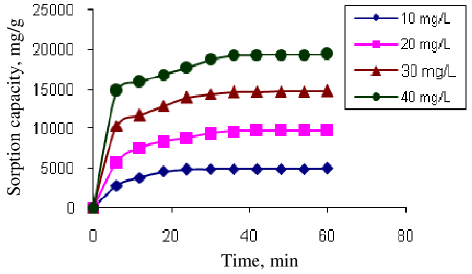

Figure 7. Fire clay-TiO_2 nanocomposite

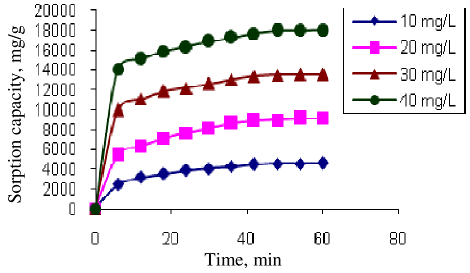

Figure 8. Fire clay

Effect of PH

Adsorption of Ni(II) was studied at various pH values in the range 5-11 and results are depicted in Figures 9 & 10. The adsorbate concentration was varied from 10-40 mg/L maintaining the adsorbent dose at 0.1 g and contact time as 90 min for both clay and nanocomposite. Adsorption efficiency was found to be highest at pH 7.5-10 with nanocomposite and at pH 6.5-10 with clay.

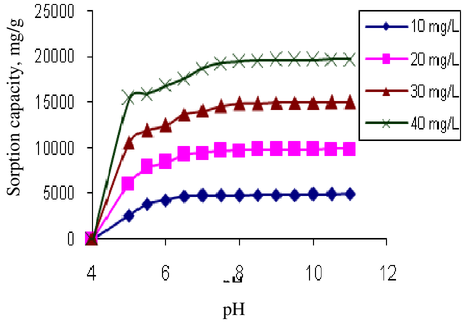

Figure 9. Fire clay-TiO_2 nanocomposite

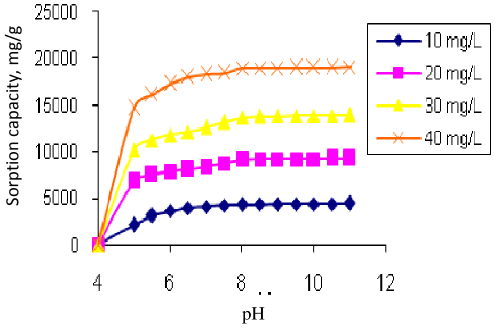

Figure 10. Fire clay

Effect of temperature

Effect of temperature on adsorption of Ni(II) ion was studied at different temperatures *viz.*, 303, 307, 311, 315 K and the results are shown in Figures 11 & 12. It is observed that adsorption of nickel ions decreases[11] with increase in temperature showing the process to be exothermic with both adsorbents.

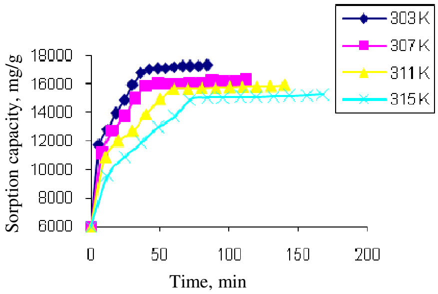

Figure 11. Fire clay-TiO_2 nanocomposite

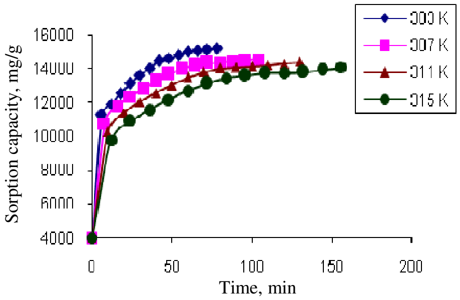

Figure 12. Fire clay

Adsorption isotherm

Langmuir adsorption isotherm

The Langmuir isotherm model commonly used for the adsorption of a solute from an aqueous solution[12]in its linear form can be represented as

$$C_e / q_e = i / bq_0 + C_e / q_0 \tag{1}$$

Where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of metal adsorbed per unit mass of adsorbent (mg/L) and q_0 and 'b' is Langmuir constants related to adsorption capacity and rate of adsorption respectively. As required by equation 1, plotting C_e/q_e against C_e gave a straight line, indicating that the adsorption of heavy metal on both clay and nanocomposite follows the Langmuir isotherm Figures 13 & 14. The Langmuir constants 'b' and q_0 were evaluated from the slope and intercept of the graph. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter R_L which is defined by,

$$R_L = 1/(1 + bC_0) \tag{2}$$

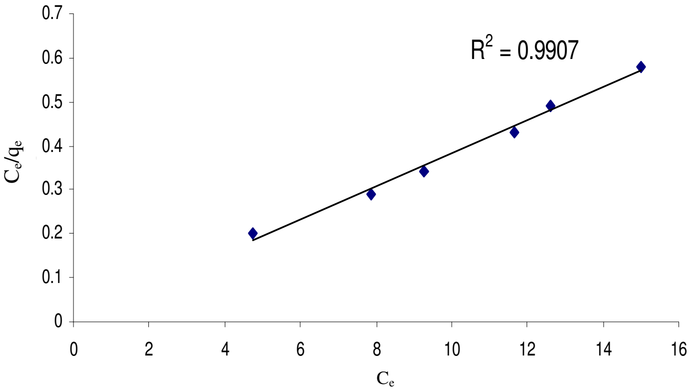

Figure 13. Fire clay-TiO_2 nanocomposite

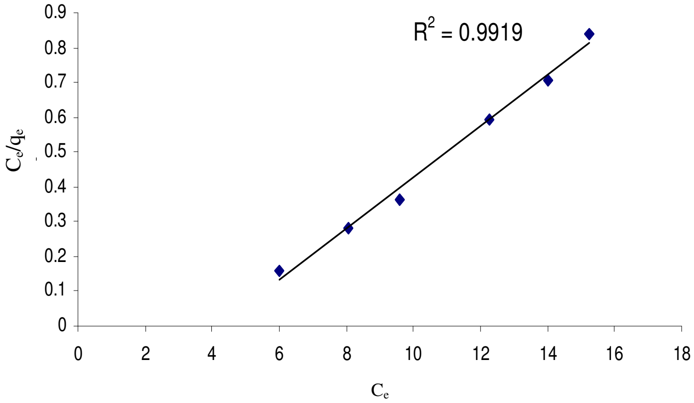

Figure 14. Fire clay

Where, C_o is the initial solute concentration, 'b' the Langmuir adsorption constant (L/mg). R_L value less than one indicates favourable adsorption[13]. The R_L values shown in Table 1 (all<1) confirm that the adsorption of Ni(II) follow Langmuir isotherm.

Table 1. The values of Langmuir constant Q^0 and b in addition to R_L

Metal ion Concentration mg/L	Fire clay + TiO_2 nanocomposite				Fire clay			
	R_L	Q^O	b	R^2	R_L	Q^O	b	R^2
20	0.9988	27.38	0.062	0.9907	0.9938	19.47	0.0031	0.9919
40	0.9976				0.9881			
60	0.9963				0.9817			
80	0.9951				0.9758			
100	0.9938				0.9699			
120	0.9926				0.9641			

Freundlich model

The Freundlich isotherm, in its logarithmic form can be represented as;

$$\log q_e = \log K_f + 1/n \log C_e \qquad (3)$$

Where K_f and 1/n are Freundlich constants related to adsorption capacity and adsorption intensity of the sorbent respectively. q_e is the amount adsorbed at equilibrium (mg/g); C_e is the equilibrium concentration of the adsorbate. The plot of log q_e *versus* log C_e gave straight lines with good regression coefficients (Figure 15 & 16) indicating that the adsorption of heavy metal follow the Freundlich isotherm. The values of K_f and 1/n calculated from the intercept and slope respectively are recorded in Table 2.

Table 2. The values of Freundlich constant K_f and n

Adsobent	K_f	n	R^2
Fire clay + TiO_2 nanocomposite	5.011	1.95	0.9904
Fire clay	4.786	1.93	0.9948

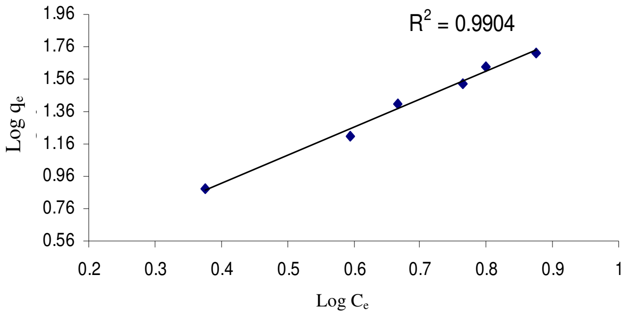

Figure 15. Fire clay-TiO_2 nanocomposite

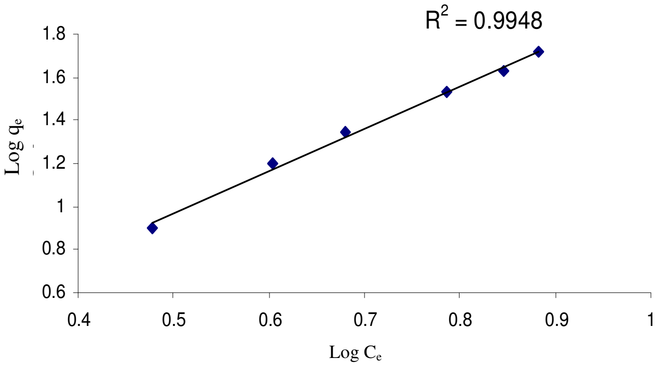

Figure 16. Fire clay

Temkin isotherm model

The Temkin isotherm, in its logarithmic form can be represented as[14]

$$q_e = B \ln A + B \ln C_e \tag{4}$$

Where, B=RT/b, A-equilibrium binding constant corresponding to maximum binding energy and B is related to the heat of adsorption. Temkin Isotherm constants were determined from the plot of q_e *vs*. ln C_e of Figures 17 & 18. The determined values of A, B and 'b' are recorded in Table 3.

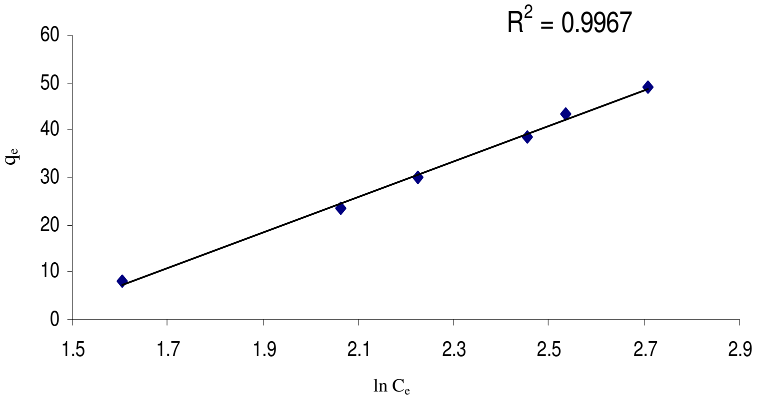

Figure 17. Fire clay-TiO_2 nanocomposite

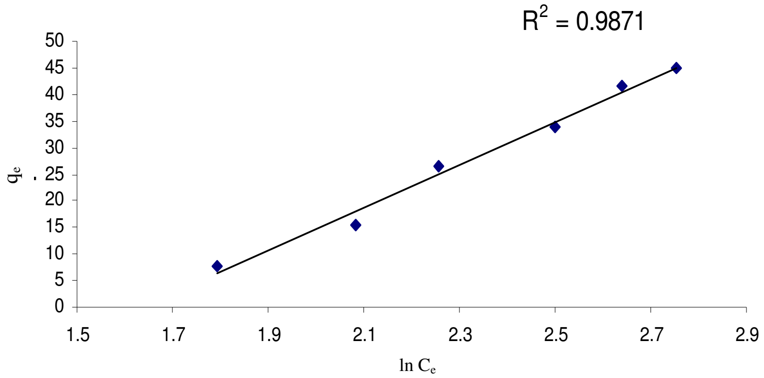

Figure 18. Fire clay

Table 3. The values of Temkin constants

Adsobent	B	A	b	R^2
Fire Clay + TiO_2 Nanocomposite	39.35	4.471	63.59	0.9967
Fire Clay	36.06	3.3100	54.33	0.9871

Dubinin -Radushkevich isotherm model

Dubinin –Radushkevich (D-R)[15] equation can be represented as

$$\ln q_e = \ln q_d - \beta\varepsilon^2 \tag{5}$$

Where, q_d is the D-R constant, β is the constant related to free energy and ε is the Polanyi potential which is defined as;

$$\varepsilon = RT \ln[11/C_e] \tag{6}$$

The constant β is pertained to the mean free energy of adsorption per mole of the adsorbate as it is transferred to the surface of the solid from infinite distance in the solution. This energy can be computed using the following relationship.

$$E = 1/\sqrt{2\phi} \tag{7}$$

D-R isotherm constants were determined from the plot of ln q_e against RTln(1+1/C_e) of Figures 19 & 20. The calculated D-R constants and mean free energy for adsorption are shown in Table 4. The mean adsorption energy was found to be in the range >16 suggested that Ni(II) removal for adsorption process to be chemisorptive nature.

Adsorption kinetics

In order to investigate the mechanism of adsorption of nickel by the nanocomposite and clay pseudo first order, pseudo second order and Elkovich model were considered. It is observed that the data for Ni(II) on both Fire Clay-TiO_2 nanocomposite and Fire Clay does not fit into pseudo first order kinetics.

Pseudo second order kinetics

In linearised form the pseudo second order kinetic model can be represented as

$$t/q_t = 1/k_2 q_e{}^2 + 1/q_e xt \tag{8}$$

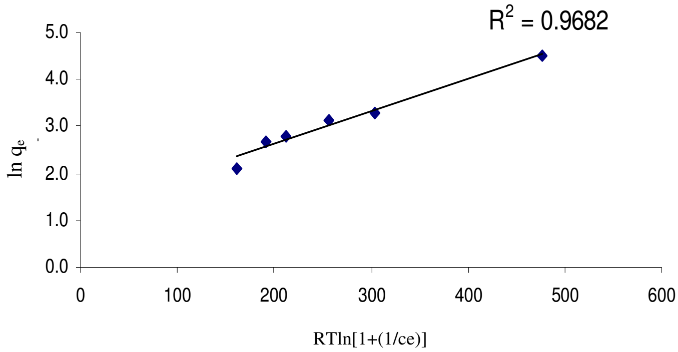

Figure 19. Fire clay-TiO_2 nanocomposite

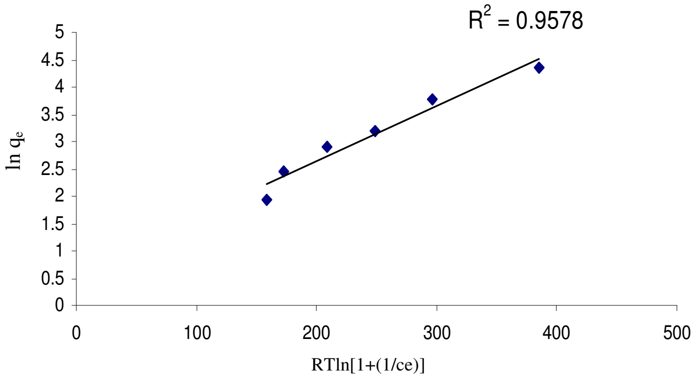

Figure 20. Fire clay

Table 4. The values of D-R constant

Adsorbent	q_d	B	E	R^2
Fire Clay - TiO_2 Nanocomposite	7.00	0.008	19.132	0.9682
Fire Clay	6.95	0.006	17.936	0.9578

Where k_2 is the second order rate constant (g/mg min). A plot of t/q_t and ‘t’ should be linear. q_e and k_2 can be calculated from the slope and intercept of the plot. The linear plots Figures 21 & 22 obtained for the adsorption of Ni(II) on the nanocomposite and clay at various metal ion concentrations clearly show that the adsorption process to follow pseudo second order.

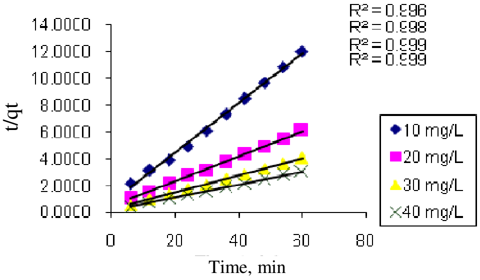

Figure 21. Fire clay-TiO_2 nanocomposite

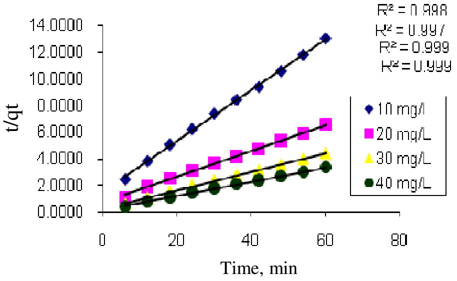

Figure 22. Fire clay

Elkovich kinetic model

The Elkovich equation which is mainly applicable for chemisorption and often valid for systems with heterogeneous adsorbing surfaces[16] is generally expressed in its integrated form as;

$$Q_t = (1/b)\ln(ab) + (1/b)\ln t \tag{9}$$

Where 'a' is the initial adsorption rate (mg/g min) and 'b' is related to the extent of surface coverage and the activation energy for chemisorption (g/mg). A plot of q_t *vs.* ln t should be linear with slope 1/b and intercept log 1/b ln (ab). Figures 23 & 24 show that the plots are linear over a wide range as expected suggesting chemisorption.

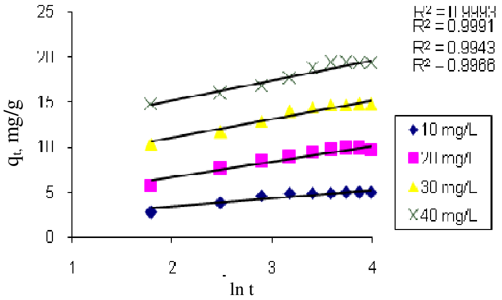

Figure 23. Fire clay-TiO_2 nanocomposite

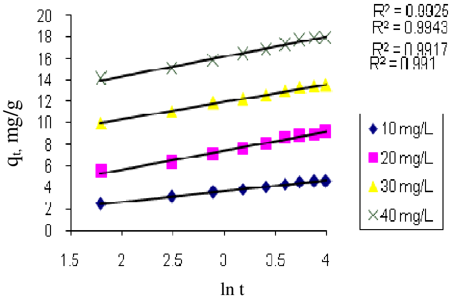

Figure 24. Fire clay

Weber-Morris intraparticle diffusion model

A graphical method (Figure 25 &26) to prove the occurrence of intra-particle diffusion and to determine if it was the rate determining step in adsorption process was introduced by Weber and Morris[17] Intra-particle diffusion was characterized using the relationship between specific sorption (q_t) and the square root of time ($t_{1/2}$) as;

$$q_t = K_{id} t_{1/2} + C \tag{10}$$

Where q_t is the amount adsorbed per unit mass of adsorbent (mg/g) at time 't' and 'K_{id}' is the intraparticle diffusion rate constant. The linear portion of the plot for wide range of contact time between adsorbent and adsorbate does not pass through the origin suggesting that pore diffusion is the only controlling step and not the film diffusion.

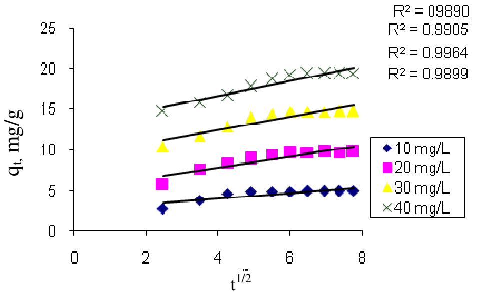

Figure 25. Fire Clay-TiO_2 Nanocomposite

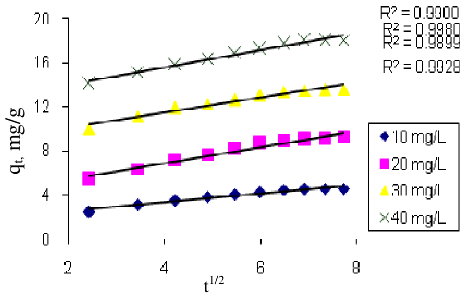

Figure 26. Fire Clay

Thermodynamic parameters

The thermodynamic parameters for the adsorption process such as free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were evaluated using the following equations:

$$\ln K_C = \Delta S^0 / R - \Delta H^0 / RT \quad (11)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (12)$$

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 values of ΔH^0 and ΔS^0 can be calculated, respectively, from the slope and intercept of the Van't Hoff plot of ln K_C *versus* 1/T.

The calculated values of ΔH^0, ΔS^0 and ΔG^0 for adsorption of Ni(II) on both nanocomposite and clay were given in Table 5. Negative values of ΔH^0 confirm the adsorption process to be exothermic. The negative value of ΔG^0 at various temperatures indicates the feasibility and spontaneity of the adsorption process. The positive value of ΔS^0 shows the affinity of adsorbent for Ni(II) and it further confirms a spontaneous increase in the randomness at the solid-solution interface during the adsorption process.

Table 5. Thermodynamic parameters for adsorption of Ni(II)on fire clay+TiO_2 NC & fire clay

Adsorbent	$-\Delta G^0$ kJ/mol				ΔS^0	$-\Delta H^0$
	303 K	307 K	311 K	315 K	J/K/mol	kJ /mol
Fire clay - TiO_2 nanocomposite	18.8	19.2	19.7	20.0	22.14	43.8
Fire clay	18.4	19.0	19.2	19.8	20.1	40.1

Desorption studies

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

Conclusion

This study shows that the fire clay and nanocomposite can be used effectively in the removal of Ni(II) through adsorption. The aqdsorption on both clay and nanocomposite followed Langmuir, Freundlich, D-R models well and fairly fitted well with Temkin model. Pseudo second order kinetic model was followed. Elkovich kinetic model suggested that adsorption process is chemisorptive nature. The adsorption also followed by intraparticle diffusion model. The calculated values of different thermodynamic parameters clearly indicated that the adsorption process with nanocomposite and clay was feasible, spontaneous and exothermic nature. This study also reveals showed that fire clay-TiO_2 nanocomposite exhibited higher adsorption capacity when compared to fire clay in its natural form.

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