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RESEARCH ARTICLE

KINETICS AND THERMODYNAMIC STUDIES ON THE REMOVAL OF Cd (II) FROM AQUEOUS SOLUTION USING FIRE CLAY – TiO_2 NANOCOMPOSITE AND FIRE CLAY

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ABSTRACT

The present study was aimed at investigating the adsorption behaviour of Cd(II) ions onto Fire Clay+TiO_2 Nanocomposite (NC) and Fire Clay (FC). The effects of several parameters such as adsorbent dose, contact time, initial concentration, p^H & temperature had been studied. The adsorption followed pseudo second order, Elovich and intra particle diffusion models. The adsorption of Cd (II) was found to be maximum in the p^H range 6.5-10. The data on the adsorption on both clay and nanocomposite fitted well with Langmuir, Freundlich, D-R isotherms and fairly well with Temkin model. The thermodynamic parameters ΔG^0, ΔH^0, ΔS^0 have also been evaluated. Adsorptions on both adsorbents were found to be exothermic and chemisorptive in nature. The nanocomposite exhibited a better removal efficiency for divalent Cd than the clay.

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INTRODUCTION

Heavy metals such as cadmium, lead, zinc, copper and mercury are extensively used in several industries and naturally the industrial aqueous effluents will certainly contain these metals (Azouaou *et al*., 2008). In the last few decades, industrialization in many regions has increased the discharge of the heavy metals in the environment and aquatic ecosystems (Mahvi *et al*., 2005). Unlike organic pollutants these heavy metal ions do not degrade into harmless end products (Guptha *et al*., 2001). The presence of heavy metals in the environment is a of major concern because of their extreme toxicity and tendency for bioaccumulation in the food chain even at relatively low concentrations (Mohan and Singh, 2002). For Cd in drinking water the World Health Organization (WHO) has set a maximum guideline concentration of 0.003 mg/L (WHO 2003). Several methods utilized to remove metals from aqueous solution / waste water include: reduction followed by electrochemical precipitation, chemical precipitation, chemical oxidation-reduction, ultra-filtration, ion exchange, reverse osmosis, solvent extraction, electro-dialysis, electrochemical, coagulation, evaporation and adsorption (Moussavi and Barikbin, 2010). Adsorption has been developed as an efficient method for the removal of heavy metals from contaminated water and soil. A variety of adsorbents, including clays, zeolites, dried plant parts, agricultural waste biomass, biopolymers, metal oxides, microorganisms, sewage sludge, fly ash and activated carbon has been used for cadmium removal (Tan and Xiao, 2009; Yadla *et al*., 2012). Hence in this study it is proposed to prepare a nanocomposite utilising FireClay and TiO_2 characterize and then evaluate its efficiency in removing divalent cadmium. Similar studies will be carried out using fire clay in natural form so as to compare relative adsorption capacities of both clay and nanocomposite.

MATERIALS AND METHODS

Fire Clay (3 g) 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 (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, 5ml alcohol mixed with 0.2 mL deionized water was slowly added. The stirring was continued for another 5 hours at the same temperature and the resulting suspension kept overnight in a vacuum oven for 6 hours at 80 °C.

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Absorbate Solution

A stock solution of Cd(II) was prepared by dissolving 1.146 g of Cadmium Sulphate ($CdSO_4.8H_2O$) in 1000ml of doubly distilled water.

Characterization of Adsorbent

Physico-chemical characteristics of the adsorbents were studied as per the standard testing methods (Waranusantigul, 2003). Figs.(1,2) shows the XRD pattern of pure Fire Clay and that of Fire Clay+TiO_2 Nanocomposite respectively. The peaks at 28^0 (Fig.2) and 30^0 (Fig. 1) which 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) Figs.(3,4). The diameter of the composite range was 50µm.

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. The effects of contact time, initial concentration and p^H was studied with Cd(II) concentrations in the range 10-40 mg/L and an adsorbent dosage of 0.1 g. The solution p^H 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 Cd(II) concentration ranging from10 to 40 mg/L. The concentration of free Cd(II) ions in the effluent was determined spectro-photometrically by developing a deep blue color using pyronine G and citrate buffer solution.

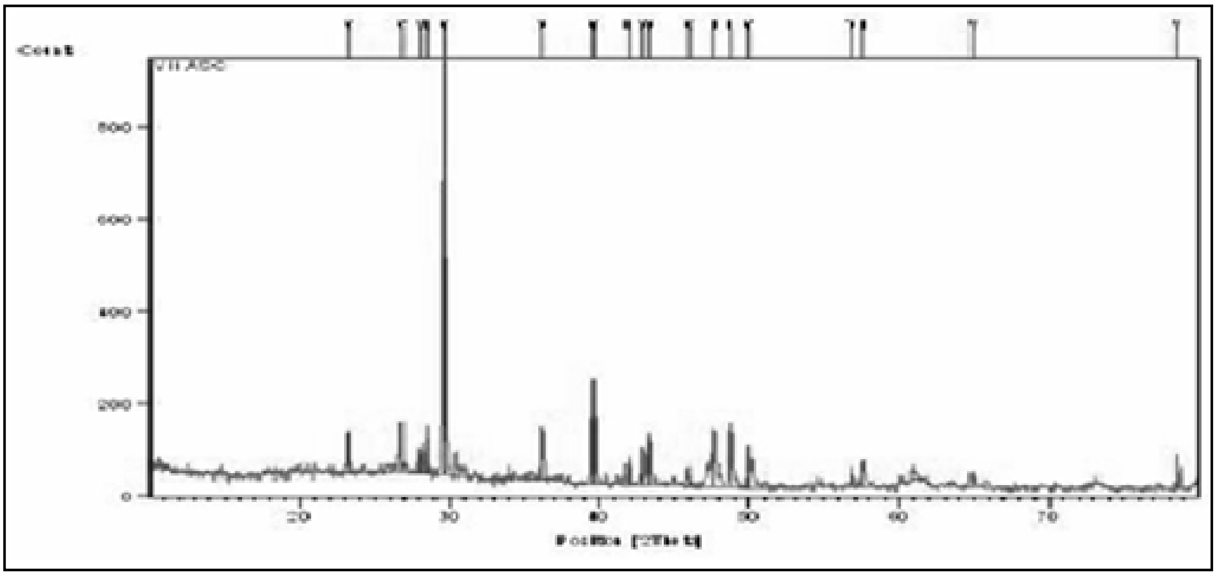

Fig.1. XRD Analysis of Fire Clay

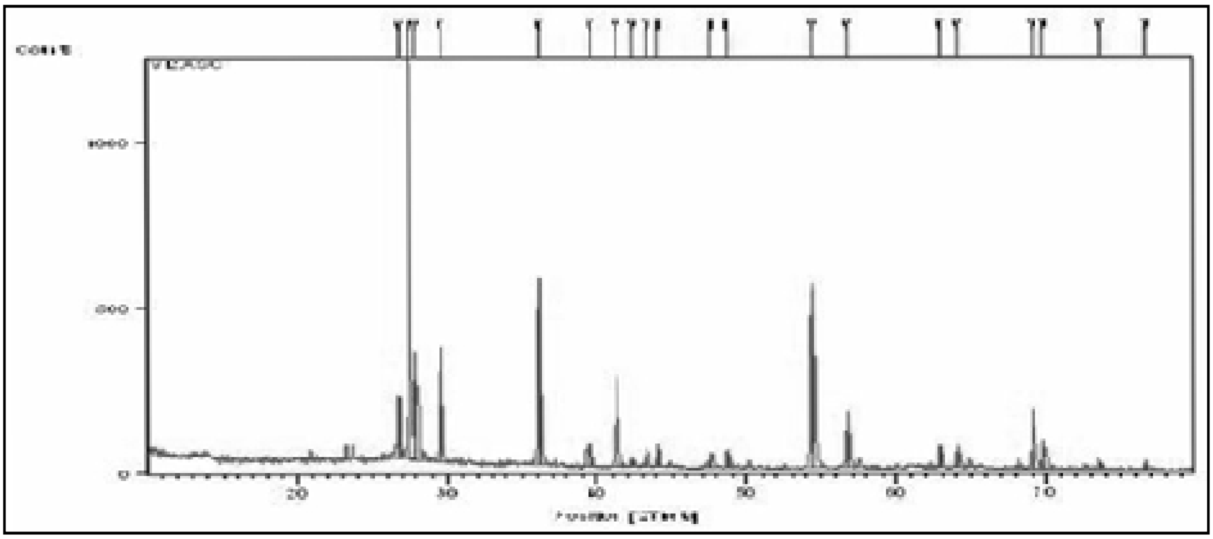

Fig. 2. XRD analysis of stishovite-TiO_2 nanocomposite

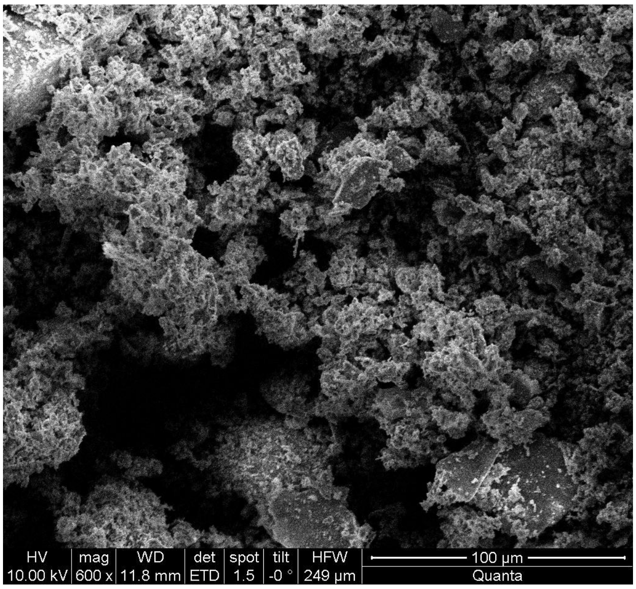

Fig.(3). SEM of Pure Fire Clay

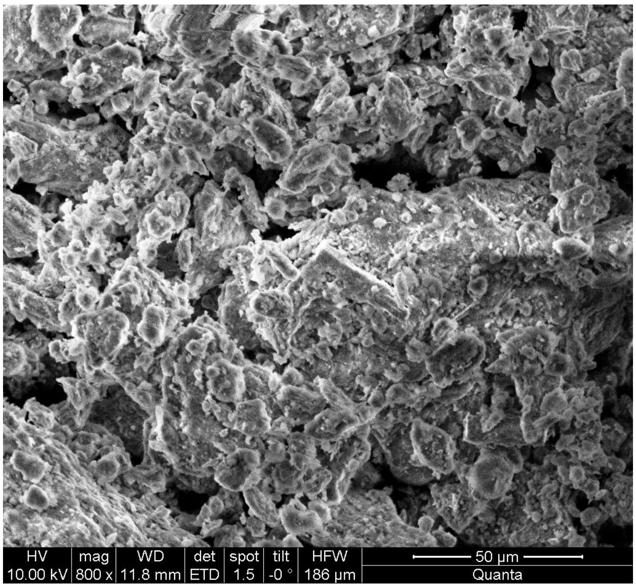

Fig (4). SEM of Fire Clay – TiO_2 Composite

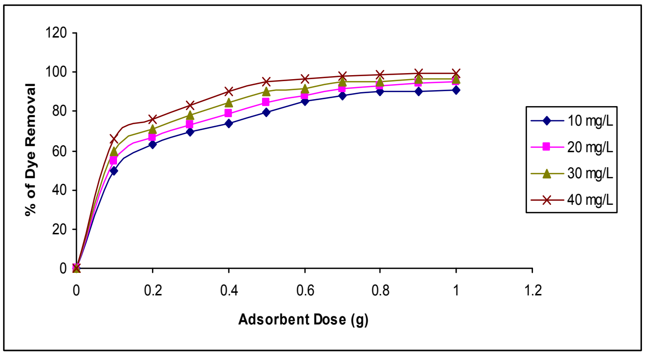

Fig.5. Fire Clay+TiO_2 Nanocomposite

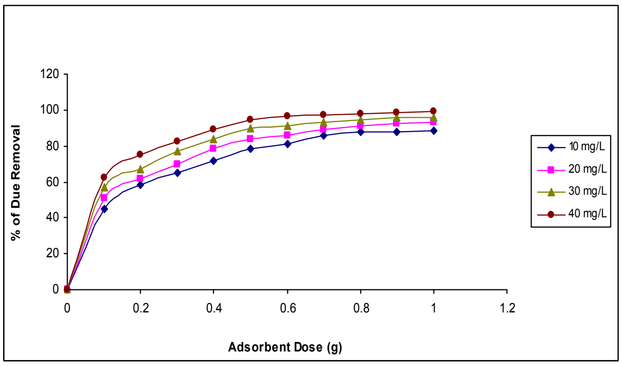

Fig.6. Fire Clay

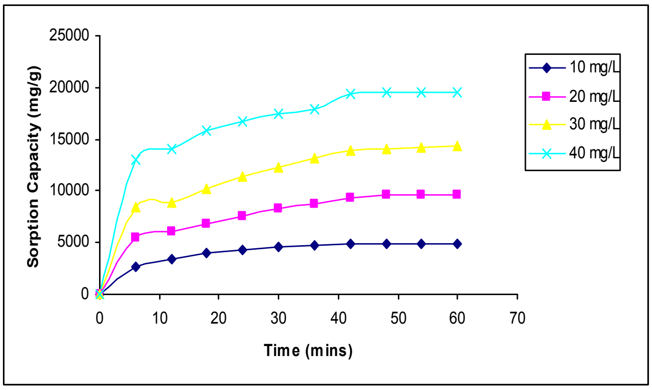

Fig.7. Fire Clay+TiO_2 nanocomposite

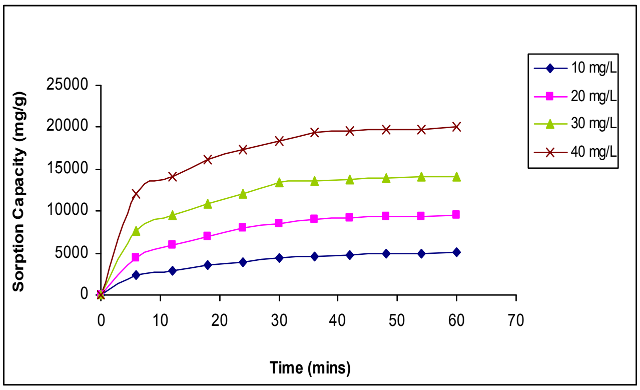

Fig.8. Fire Clay

RESULTS AND DISCUSSION

Effect of adsorbent dose

The effect of adsorbent dose on Cd(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 both clay and nanocomposite Figs. (5, 6). This may be basically due to adsorption sites remaining unsaturated during the adsorption process.

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 Cd(II) ions increase with increase in metal ion concentration Figs.(7,8) and attains saturation in 35 to 55 min with nanocomposite and 40 to 60 min with clay. The removal rate by adsorption is rapid initially, gradually decreases with time and finally attains equilibrium is rapid initially.

Effect of p^H

Adsorption of Cd(II) was studied at various p^H values and results are depicted in Figs (9, 10). The initial p^H of solution was varied 5-11 with the adsorbate concentration varying from 10-40 mg/L maintaining the adsorbent dose at 0.1g and contact time as 90 mins for both clay and nanocomposite. From this Figs. (9, 10) it is clear that cadmium adsorption efficiency is highest at P^H 7.5-10 with nanocomposite and at 6.5-10 with clay.

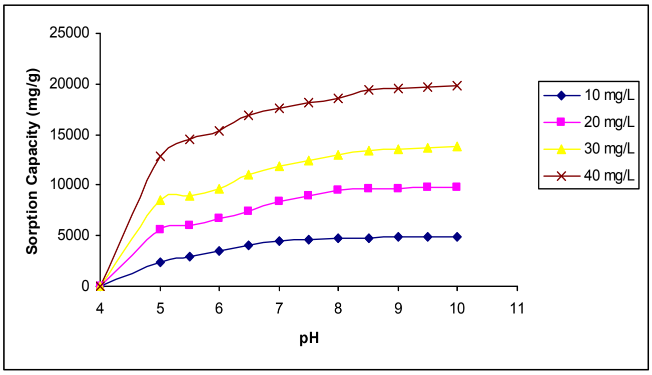

Fig.9. Fire Clay+TiO$_2$ nanocomposite

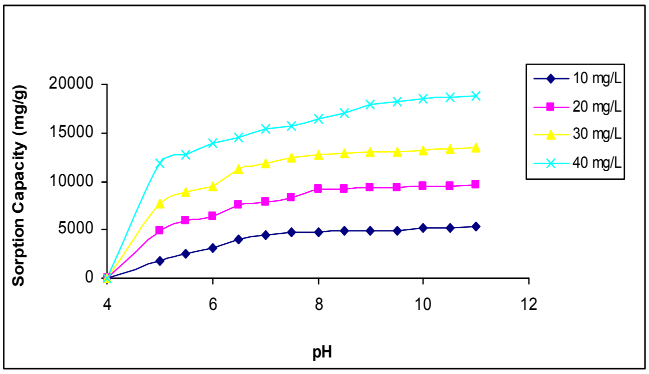

Fig.10. Fire Clay

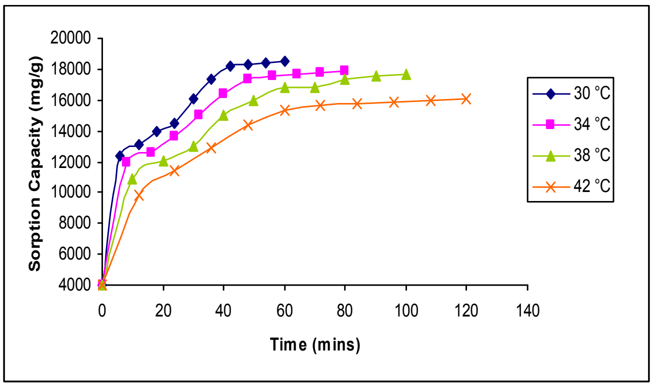

Fig.11. Fire Clay+TiO$_2$ nanocomposite

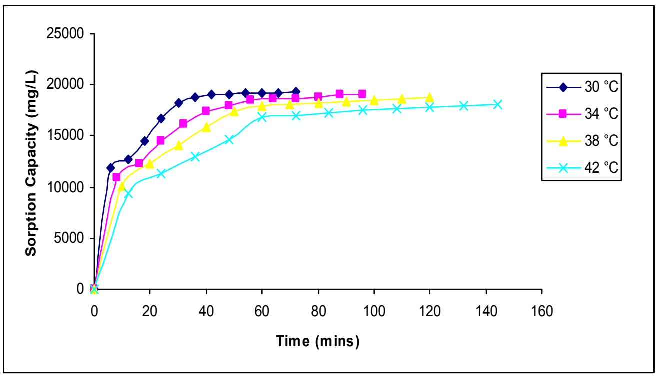

Fig.12. Fire Clay

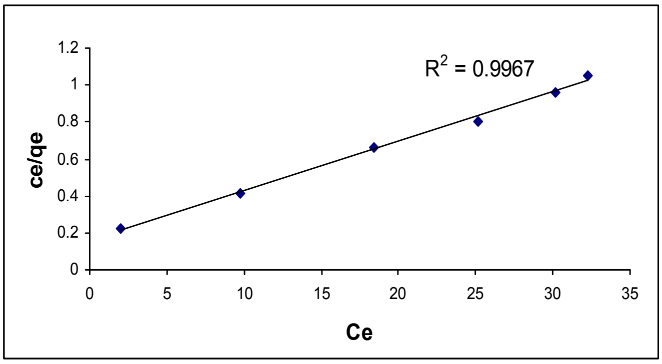

Fig.13. Fire Clay+TiO$_2$ nanocomposite

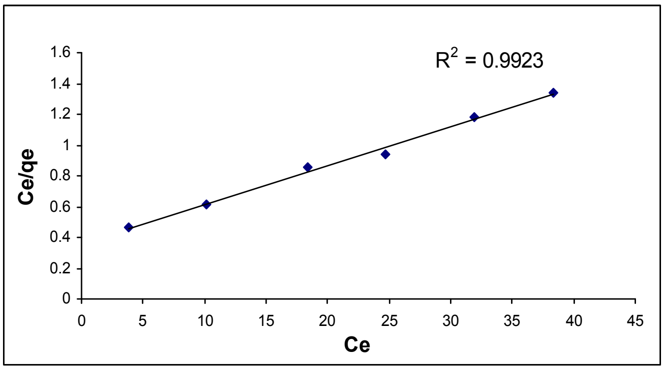

Fig.14. Fire Clay

Effect of temperature

Effect of temperature on adsorption of Cd(II) ion was studied at different temperatures viz., 303, 307, 311, 315K and the results are shown in Figs (11, 12). It is observed that adsorption of Cadmium ions decreases (Pradhan and Thakur, 1999) with increasing temperature showing the process to be exothermic with both adsorbents.

Adsorption isotherm

Langmuir adsorption isotherm

The Langmuir isotherm model commonly used for the adsorption of a solute from a aqueous solution (Langmuir, 1916) in its linear form can be represented as

$$C_e / q_e = i / bq_0 + C_e / q_0 \qquad \text{.............(1)}$$

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' are the 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 follow the Langmuir isotherm Figs.(13,14). The Langmuir constants 'b' and q_0 were evaluated from the slope and intercept of the graph.

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

Concentration of metal (mg/L)	Fire Clay + TiO_2 Nanocomposite				Fire Clay			
	R_L	Q^O	B	R^2	R_L	Q^O	b	R^2
20	0.9788				0.9462			
40	0.9585				0.8979			
60	0.9391				0.8544			
80	0.9204	10.000	0.0108	0.9967	0.8148	8.86	0.00284	0.9923
100	0.9893				0.7788			
120	0.8852				0.7458			

Table 2. The values of Freundlich constant K_f and n

Adsorbent	K_f (L/mg)	n(mg/g)	R^2
Fire Clay+TiO_2 nanocomposite	6.30	1.91	0.9956
Fire Clay	5.495	1.89	0.9908

Table 3. The values of Temkin constants

Adsorbent	b	A	B	R^2
Fire Clay+TiO_2 nanocomposite	9.611	1.227	26.38	0.9914
Fire Clay	7.32	1.082	22.10	0.9897

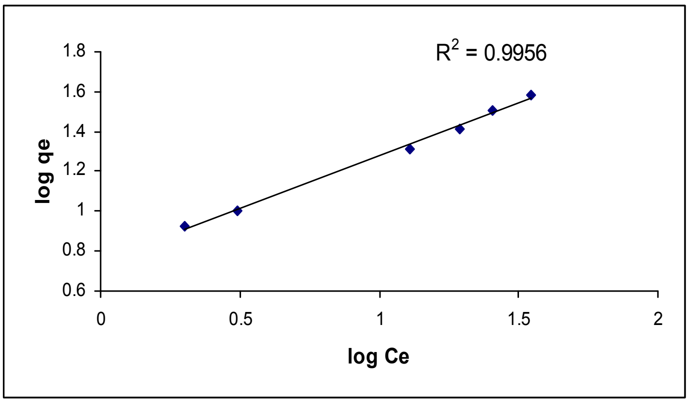

Fig.15. Fire Clay+TiO_2 Nanocomposite

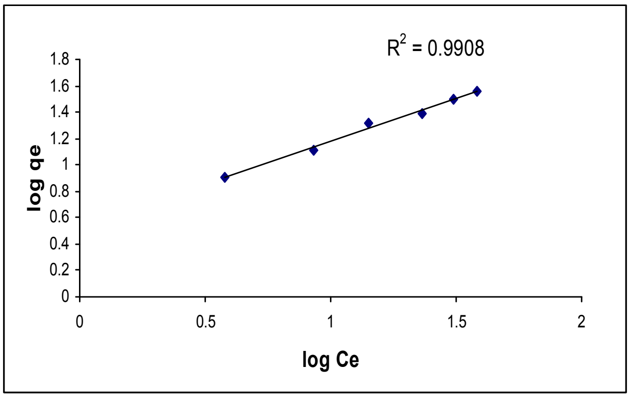

Fig.16. Fire Clay

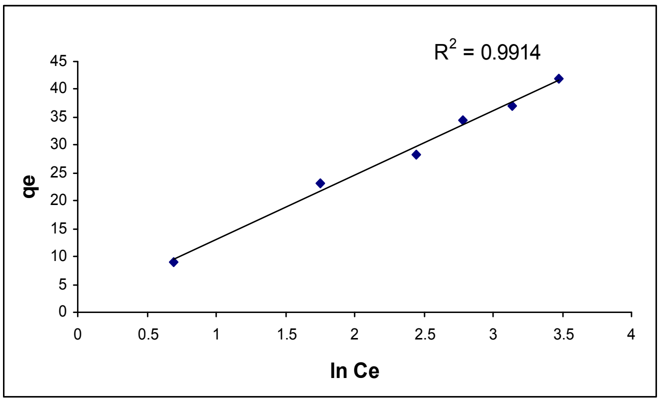

Fig.17. Fire Clay+TiO_2 Nanocomposite

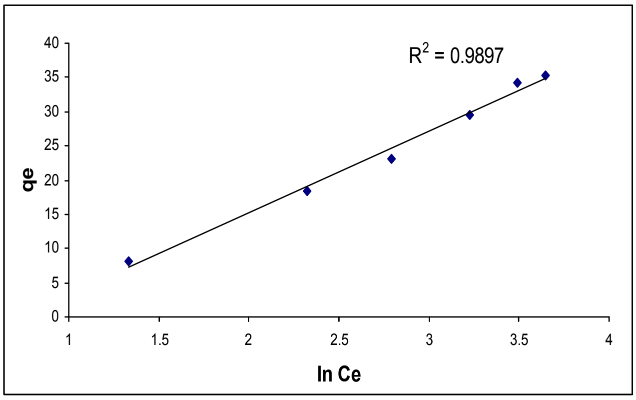

Fig.18. Fire Clay

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter R_L which is defined by,

$$R_L = 1/(1 + bC_0) \qquad \text{………… (2)}$$

Where, C_0 is the initial solute concentration, 'b' the Langmuir adsorption constant (L/mg). R_L value less than one indicates favourable adsorption (Singh *et al*., 2005). The R_L values shown in Table 1 (all<1) confirm that the adsorption of Cd(II) follow Langmuir isotherm.

Freundlich model

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

$$log\, q_e = log\, K_f + 1/n\, log\, C_e \qquad \text{………………(3)}$$

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 indicating that the adsorption of cadmium followed the Freundlich isotherm. The values of K_f and 1/n calculated from the intercept and slope respectively are recorded in Table 2.

Temkin Isotherm Model

The Temkin isotherm, in its logarithmic form can be represented as (Wasewar, 2010)

$$q_e = B \ln A + B \ln C_e \qquad \text{…………………(4)}$$

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 qe Vs ln Ce of Figs. (17, 18). Which enables the determination of isotherm constants A and B. The determined values of A, B and 'b' is recorded in Table 3.

Dubinin -Radushkevich Isotherm Model

Dubinin –Radushkevich (D-R) (Boparai *et al*., 2010)

$$\ln q_e = \ln q_d - \beta\varepsilon^2 \qquad \text{……………(5)}$$

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

$$\varepsilon = RT \ln[1 + 1/C_e] \qquad \text{………………(6)}$$

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.

$$E = 1/\sqrt{2\beta} \qquad \text{………………(7)}$$

Dubinin –Radushkevich isotherm constant were determined from the plot of ln q_e against RTln(1+1/Ce) of Figs. (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 Cd(II) removal for adsorption process to be chemisorptive nature.

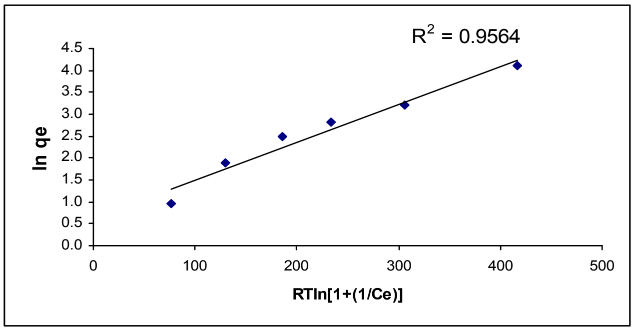

Fig.19. Fire Clay+TiO_2 Nanocomposite

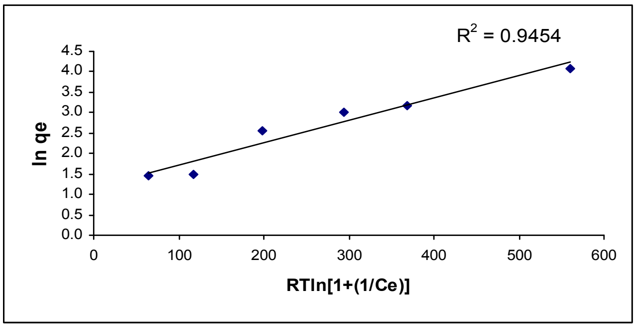

Fig.20. Fire Clay

Table 4. The values of D-R constants

Adsorbent	q_d	B	E	R^2
Fire Clay+TiO_2 Nanocomposite	9.51	0.007	22.72	0.9564
Fire Clay	8.38	0.004	21.0	0.9454

Adsorption kinetics

In order to investigate the mechanism of adsorption of Cadmium by the nanocomposite and clay pseudo first order, pseudo second order and Elkovich model were considered. It is observed that the data for Cd(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

$$t/q_t = 1/k_2 q_e^{\,2} + 1/q_e \times t \qquad \text{......................(8)}$$

Where k_2 is the second order rate constant (g/mg min). Hence 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 Figs.(21,22) obtained for the adsorption of Cd(II) on both adsorbents at various cadmium ion concentrations clearly show that the adsorption process follows pseudo second order kinetics.

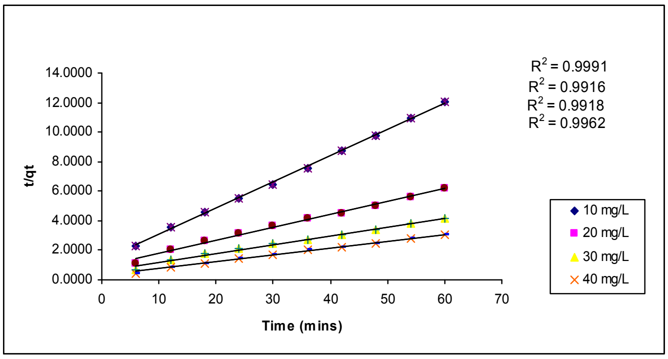

Fig.21. Fire Clay+TiO$_2$ Nanocomposite

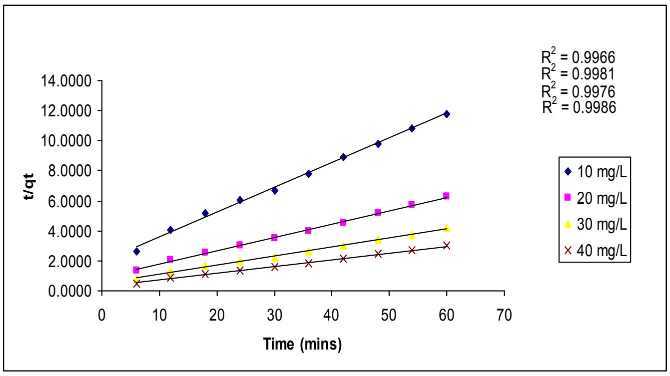

Fig.22. Fire Clay

Elovich kinetic model

The Elovich equation which is mainly applicable for chemisorption and often valid for systems with heterogeneous adsorbing surfaces (Veera *et al*., 2003) is generally expressed in its integrated form as

$$Q_t = (1/b)ln(ab) + (1/b)ln\,t \qquad \text{...................(9)}$$

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). Figs.(23, 24) show that the plots are linear over a wide range as expected suggesting chemisorption.

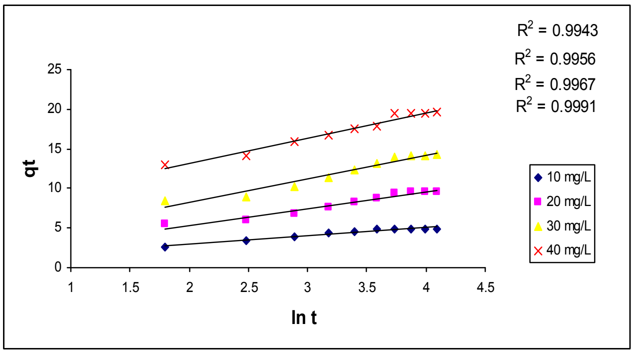

Fig.23. Fire Clay+TiO$_2$ Nanocomposite

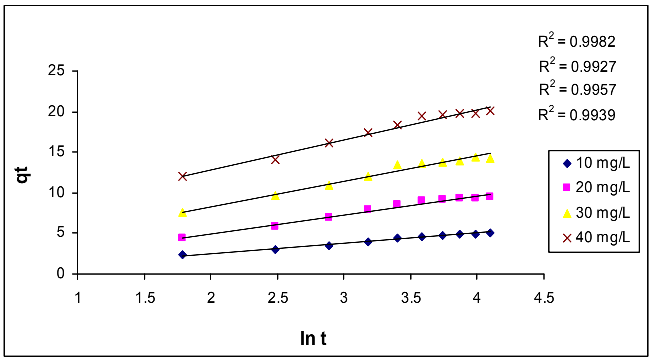

Fig.24. Fire Clay

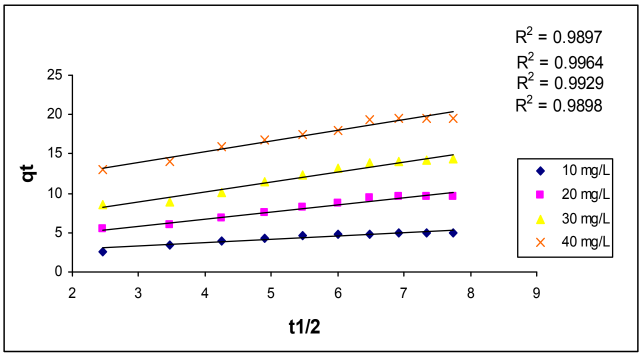

Fig.25. Fire Clay+TiO$_2$ Nanocomposite

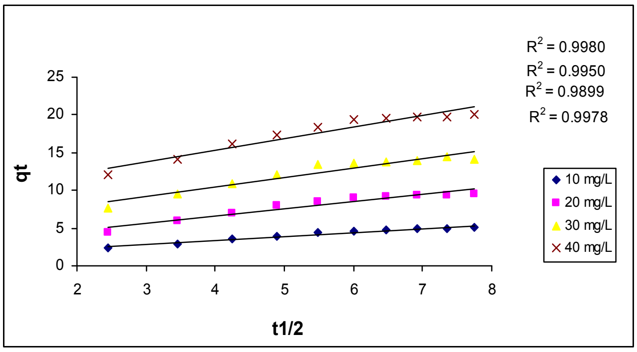

Fig.26. Fire Clay

Table 5. Thermodynamic parameters for adsorption of Cd(II) on Fire Clay+TiO_2 NC & Fire Clay

Adsorbent	- G^0 kJ/mol				S^0	H^0
	303K	307K	311K	315K	kJ/mol	kJ/mol
Fire Clay+TiO_2 Nanocomposite	16.4	16.9	17.7	18.1	23.27	41.3
Fire Clay	16.0	16.7	17.2	17.4	19.3	41.0

Weber-Morris intraparticle diffusion model

A graphical method 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 (Weber and Morris, 1963). Intra-particle diffusion was characterized using the relationship between specific sorption (q_t) and the square root of time ($t_{1/2}$) as

$$q_t = K_{id} t_{1/2} + C \qquad \text{………………………(10)}$$

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.

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:

$$ln\, K_C = \Delta S^0 / R - \Delta H^0 / RT \qquad \text{……………….. (11)}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad \text{…………………(12)}$$

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 Cd(II) on both nanocomposite and clay were given in Table 5. Positive values of ΔH^0 confirms that the adsorption process to be exothermic while 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 Cd(II) and it further confirms a spontaneous increase in the randomness at the solid- solution interface during the adsorption process.

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 Cd(II) through adsorption. Both clay and nanocomposite followed Langmuir, Freundlich, D-R isotherms and, fairly fitted with Temkin model. The adsorption followed pseudo second order kinetic model. Maximum adsorption occurred in basic medium. Elovich kinetic model suggested that adsorption process to be 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 under identical conditions..

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