Adsorption of Methylene Blue on to Fire Clay - MnO_2 Nanocomposite Materials

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Abstract- The present study was aimed to investigate the adsorption behaviour of Methylene Blue onto Fire Clay-MnO_2 Nano Composite. The effect following parameters such as adsorbent dose, contact time, initial concentration, P^H & temperature has been studied. The adsorption of NanoComposite follows pseudo second order, Elkovich kinetic models. The adsorption of Methylene Blue onto Fire Clay - MnO_2 NanoComposite was found maximum in the p^H range 8-11. Adsorption on NanoComposite obeys Langmuir and Freundlich models. In this study thermodynamic parameters ΔG^0 , ΔH^0, ΔS^0 have also been evaluated. Adsorption on removal of Methylene Blue dye using NanoComposite was found to be endothermic and chemisorptive in nature.

Keywords - Fire Clay -$MnO_{2;}$ NanoComposite; Methylene Blue; Adsorbent; Adsorption isotherm.

1. INTRODUCTION:

Our environment is contaminated by organic and inorganic chemicals more important chemical is Dye, because dyes not easily undergoes degradation which is discharged into rivers, lakes etc., as waste water. Because of population has drastically increases, so the requirement for the cloth increases, so discharging the dye wastewater increases. Nearly 7×10^5 tones and 10,000 different types of dyes and pigments are used annually [1-2].Dyes produced by synthetic methods produces more environmental problems like environment hazards and not easy to degrade. Direct disposal of this dye waste water into water bodies' posses' serious threat to aquatic life and produces health problems like mutagenic and carcinogenic to human being [3-5].Treatment of the dye waste water is divided into three main categories they are physical, chemical, and biological methods. In these methods adsorption technology is mostly used because of its quick adsorption of dyes and metals in waste water [6]. Now a day's polymers are also used as an adsorbent to remove dyes from waste water [7].Clays are natural material and it used for manufacture of building materials, dates from antiquity by human. In Ceramic industry clay based materials are used because of their physicochemical properties. It is present in our earth abundantly and it has low mechanical strength. To improve the mechanical strength doping methods was used by Mayans once (300-1600 AD approximately) when they have their clay mixed with indigo [8-9].Doping of MnO_2 with clay gives stiffness of the material and, its influence as an absorbent has been a subject of the research [10].

2. MATERIALS & METHODS

3 gms of Fire Clay suspended in 15 mL of water free alcohol at 25°C and stirred for 2 hrs for suspending the clay for uniform distribution in solvent. Manganese di-oxide 3 gms dispersed in water-free alcohol was prepared in the same time. Solution of Manganese di-oxide was slowly mixed into the Fire Clay suspension at 25°C for 5 hrs. After this process alcohol 5 mL and deionized water 0.2 ml water added slowly. The suspended solution was again stirred for 5 hrs at 25°C and the suspension kept in a hot air oven at 80 °C for 12 hrs [11]. Fire Clay was purchased from local vendor from Coimbatore. The chemicals were used in this preparation of composite was Nice chemicals, Cochin, India.

2.1 Absorbate solution

1 gm of Methylene Blue dye was dissolved in 1000 mL of water and it was taken as stock solution. Different concentrations of dye solution were prepared by diluting stock solution.

2.2 Characterization of adsorbent

The sample prepared was taken into Physicochemical characteristics to determine the composite structure as per the standard testing methods. The XRD pattern of pure Fire clay shown in Fig.1. and that Fire Clay - MnO_2 nanocomposite shown in Fig. 2. It shows the characteristic peaks at 27.2 (Fig.2.) which the presence of Fire Clay- MnO_2 phase in the nanocomposite. The surface morphology of the adsorbents was visualized via scanning electron microscopy (SEM) (Fig.3.&4.). The diameter of the composite range was 0.5 µm.

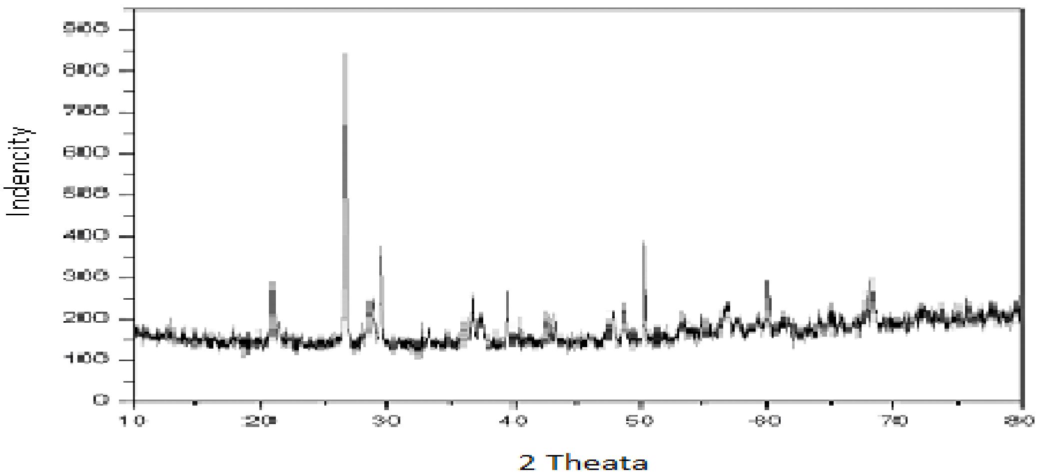

Fig.1. XRD pattern of pure Fire Clay

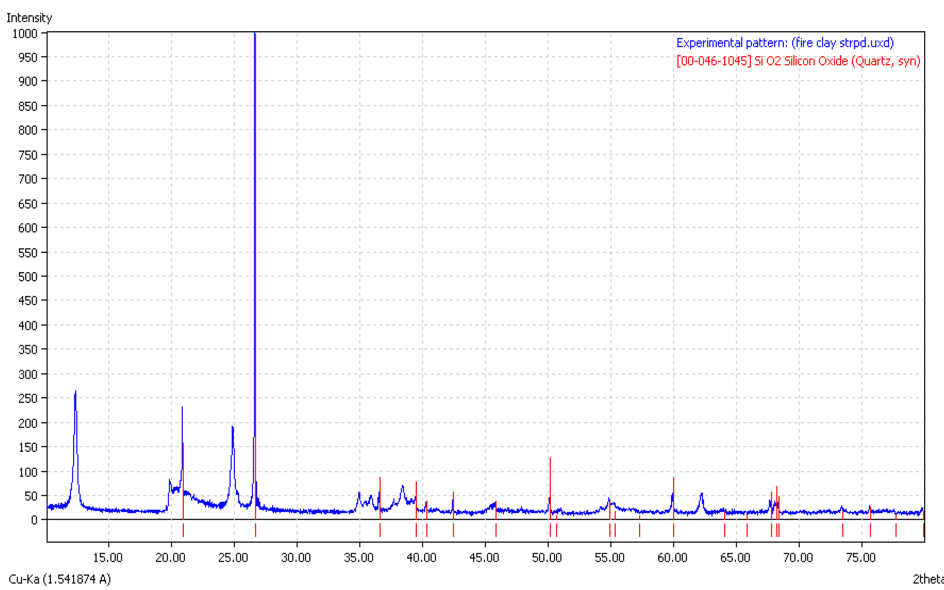

Fig.2. XRD pattern of Fire Clay- MnO_2 nanocomposite

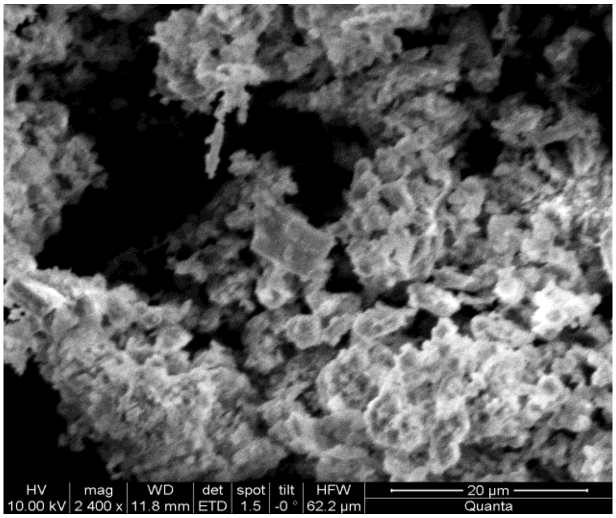

Fig.3. SEM image of Fire Clay

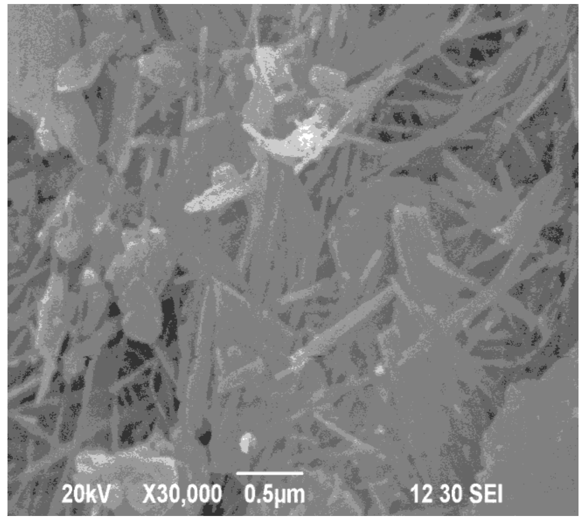

Fig.4. SEM image of Fire Clay - MnO_2 nanocomposites

3. BATCH ADSORPTION EXPERIMENTS

50mL of Methylene Blue dye solution was taken for entire batch mode experiments with known amount of adsorbent in a 100 mL Stoppered Reagent Bottle. The dye solution containing adsorbent was agitated for predetermined time intervals in an Orbital Shaker with thermostat attached at the desired temperature (303 K to 311 K). After the shaking the filtration were carried to separate the adsorbent and adsorbate. The following studies are carried out to study the effects of agitation time, pH, initial dye concentration, adsorbent dose and temperature with 50 mL of dye solution different concentration and with known amount of adsorbent dosage.

4. RESULT AND DISCUSSION

4.1 Effect of contact time and initial dye concentration

To study the effect of initial dye concentration and contact time for the removal of Methylene Blue dye concentration taken varied from 10 to 40 mg/L dye solution was agitated with 100 mg of adsorbent in 50 mL dye solution. Initially the adsorbents adsorption capacity was high finally it becomes constant showing the attainment of equilibrium. The removal of dye is maximum 94%. From the Fig.5. the curves shows monolayer coverage on the adsorbent surface.

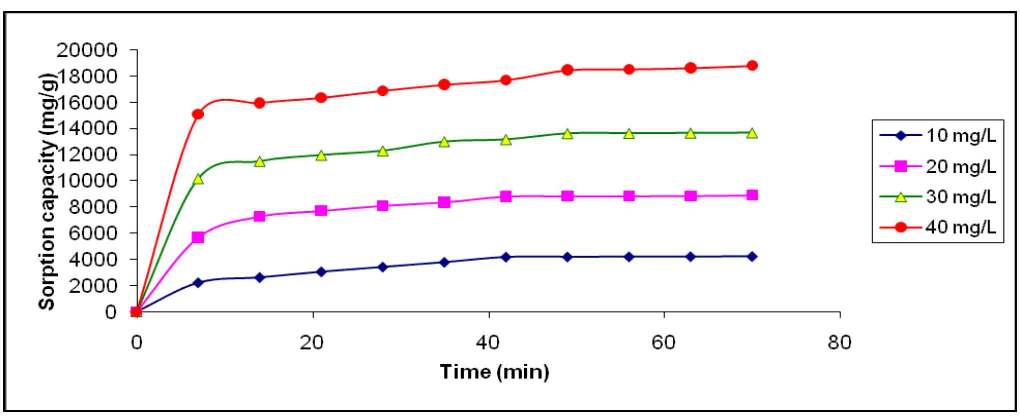

Fig.5. Effect of initial dye concentration

4.2. Effect of adsorbent dosage on adsorption process

To study the effect of adsorbent dosage on Methylene Blue dye removal different amount of adsorbent was taken, and all other experimental conditions are taken as constant. The amount of dye adsorbed by the adsorbent calculated per unit mass of adsorbent and the amount adsorbed per unit mass of the adsorbent decreases with increase in amount of adsorbent Fig.6.. It is due to the adsorption sites remaining unsaturated during the adsorption process.

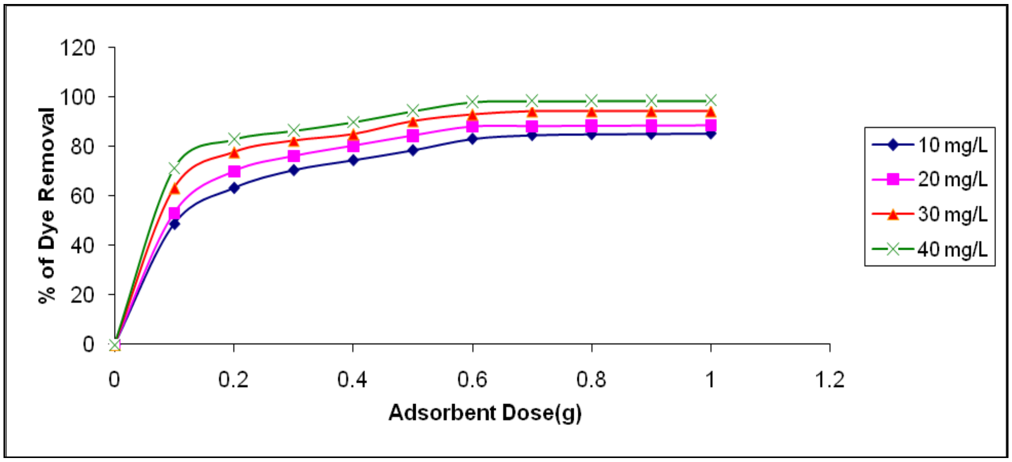

Fig.6**.** Effect of adsorbent dosage

4.3. Effect of pH

Effect of pH on adsorption was carried out at various pH values ranging from 6 to 11 maintaining the required pH by adding necessary HCl (0.5N) / NaOH (0.5N) . The initial pH of solution was varied from 5 to11 with the adsorbate concentration varying from 10-40 mg/L maintaining the adsorbent dose at 0.1g and the contact time as 2 hours. From Fig.7 indicates that maximum dye removal had occurred in basic medium and also observed that as the pH increases the Sorption capacity also increases. The pHzpc for the nanocomposite was determined as 8.0

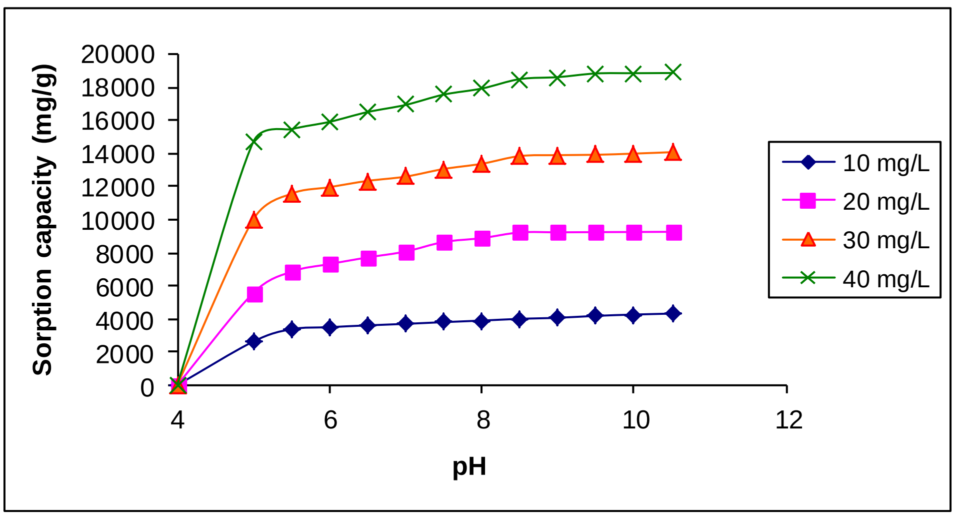

Fig.7. Effect of pH

4.4. Effect of temperature

The adsorption of Methylene Blue with temperature has an important effect on the adsorption on adsorbent. From Fig.8 shows the removal of Methylene Blue by the nanocomposite on different temperature. The amount of basic dye adsorbed increases with increasing temperature from 303K to 311K indicating the adsorption process to be endothermic. This may be due to the fact that as the temperature increases, rate of diffusion of adsorbate molecules across the external boundary layer and internal pores of adsorbent particle increase.

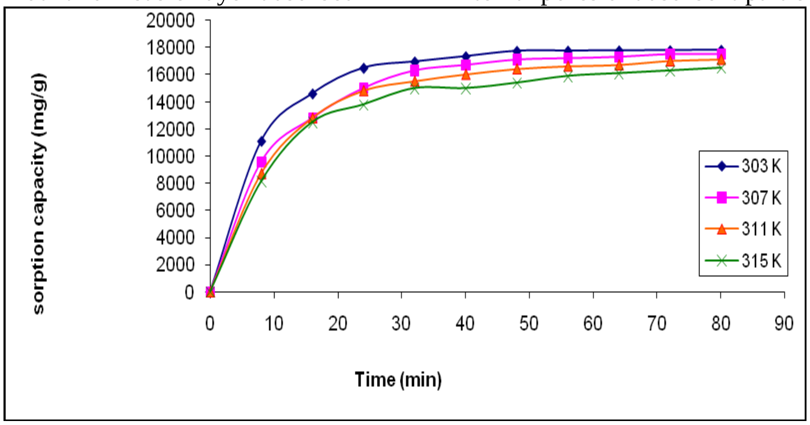

Fig.8. Effect of temperature

4.5. Adsorption isotherm

Langmuir and Freundlich isotherms are used to determine the relationship between the amount of dye adsorbed and its equilibrium concentration was analyzed.

Langmuir adsorption isotherm

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

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

Where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of dye adsorbed per unit mass of adsorbent (mg/L) and q_0 and 'b' are 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 dye o follow the Langmuir isotherm Fig.9.The Langmuir constants 'b' and q_0 were evaluated from the slope and intercept of the graph.

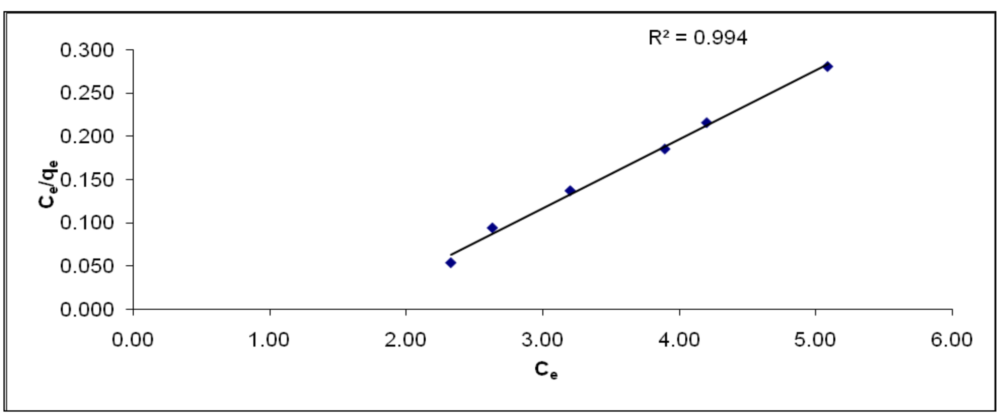

Fig.9: Plot of Langmuir adsorption isotherm

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

Concentration of metal (mg/L)	Fireclay– MnO_2 nanocomposite			
	R_L	b	Q^o mg/g	R^2
20	0.4679			
40	0.4687			
60	0.4851	0.100	25.34	0.994
80	0.4897			
100	0.4954			
120	0.4956			

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

$$R_L = 1/(1 + bC_0) \quad \text{........... (2)}$$

Where, C_0 is the initial solute concentration, 'b' the Langmuir adsorption constant (L/mg).R_L value less than one indicates favorable adsorption [13]. The R_L values shown in Table1 (all<1) confirm that the adsorption of dye follow Langmuir isotherm.

Freundlich model

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

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

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 Dye follow the Freundlich isotherm.Fig.10.The values of K_f and 1/n calculated from the intercept and slope respectively are recorded in Table 2.

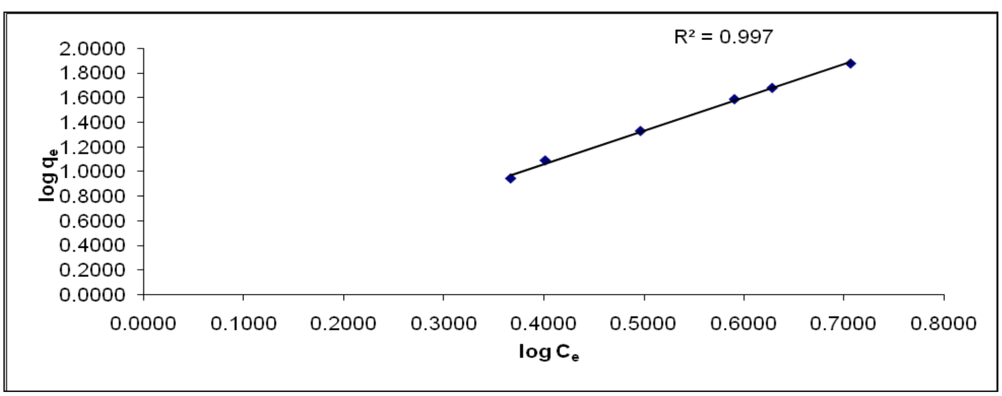

Fig.10: Plot of Freundlich adsorption isotherm

Table 2. The values of Freundlich constant K_f and n

Dye	K_f (L/mg)	n (mg/g)	R^2
Methylene Blue	1.62	1.83	0.997

Temkin isotherm model

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

q_e = B ln A+ B lnC ……….. (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 Fig.11. The determined values of A, Band 'b' are recorded in Table 3.

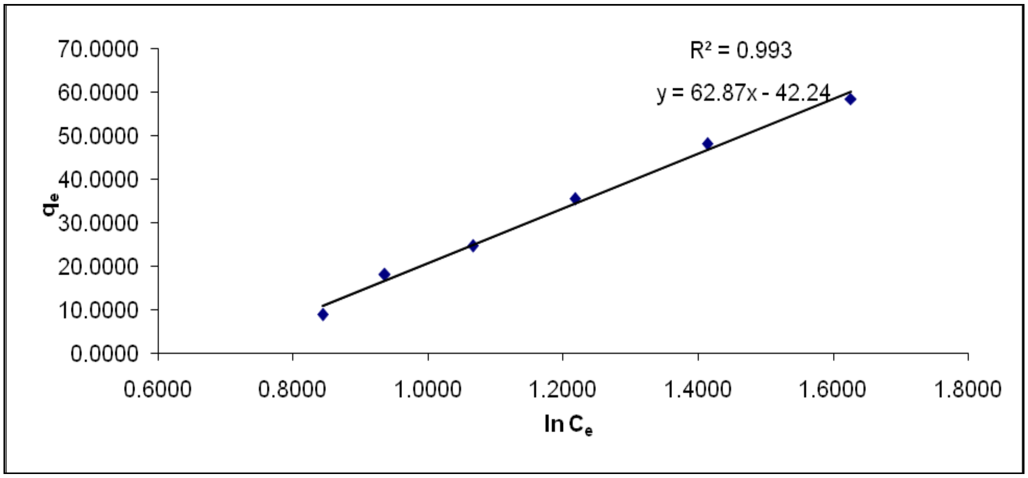

Fig.11. Temkin kinetic model for adsorption of Methylene Blue

Table 3. The values of Temkin constants

B	**A**	**b**	**R^2**
62.87	**1.957**	**39.80**	**0.993**

Dubinin -Radushkevich isotherm model

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

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

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

$$\varepsilon = RT \ln(1+1/Ce) \quad \text{............} \ (6)$$

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.

$$E = 1/\sqrt{2Q} \quad \text{............ (7)}$$

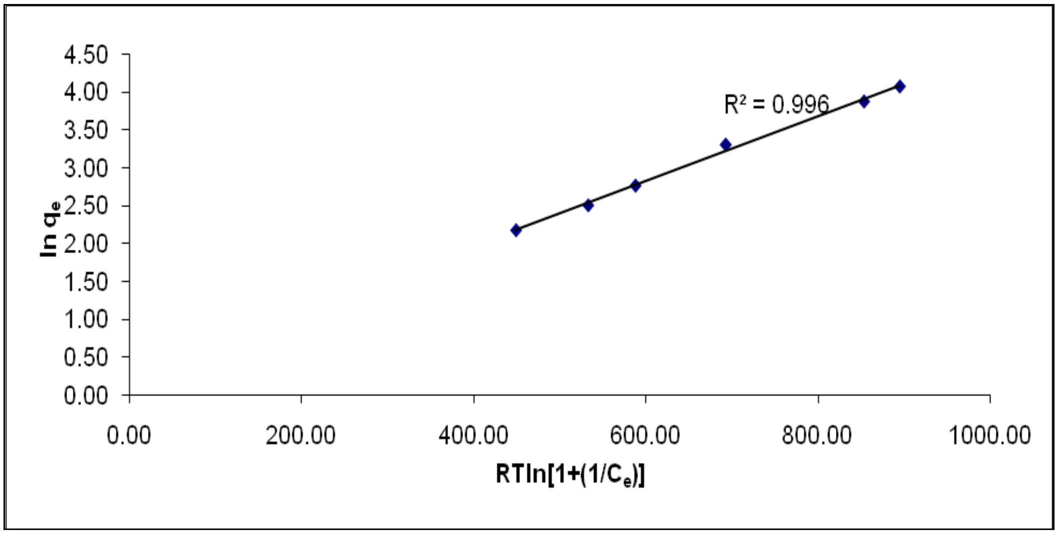

Fig.12. D-R model for adsorption of Methylene Blue

D-R isotherm constants were determined from the plot of lnqe against RT ln(1+1/Ce) of Fig.12. The calculated D-R constants and mean free energy for adsorption are shown in Table 4.

Table 4. The values of D-R constant

q_d	B	E	R^2
1.29	**0.004**	**17.11**	**0.996**

The mean adsorption energy was found to be in the range >16 suggested that Methylene Blue removal for adsorption process to be chemisorptive nature.

Adsorption Kinetics

In order to investigate the mechanism of adsorption of Methylene Blue by the nanocomposite the following kinetic models pseudo first order, pseudo second order Elkovich and intraparticle diffusion model were considered. It is observed that the data for Methylene Blue on Fire Clay - MnO_2 nanocomposite does not fit into pseudo first order kinetics.

Pseudo second order kinetics

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

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

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 Fig.13. obtained for the adsorption of Methylene Blue on Fire Clay - MnO_2 nanocomposite at various dye concentrations clearly show that the adsorption process to follow pseudo second order.

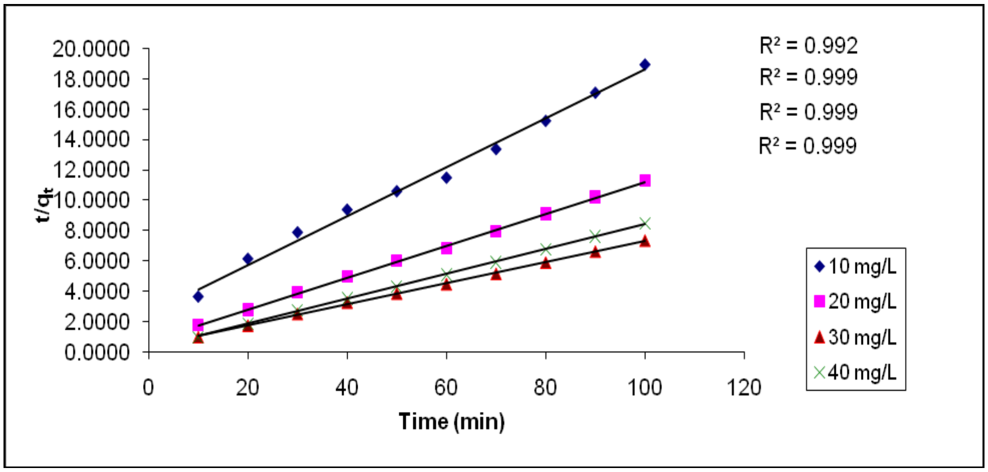

Fig.13**.** Pseudo second order model for adsorption of Methylene Blue

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

$$Q_t = (1/b)ln(ab) + (1/b)lnt \quad \text{.........} (9)$$

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). Fig.14. Show that the plots are linear over a wide range as expected suggesting chemisorption.

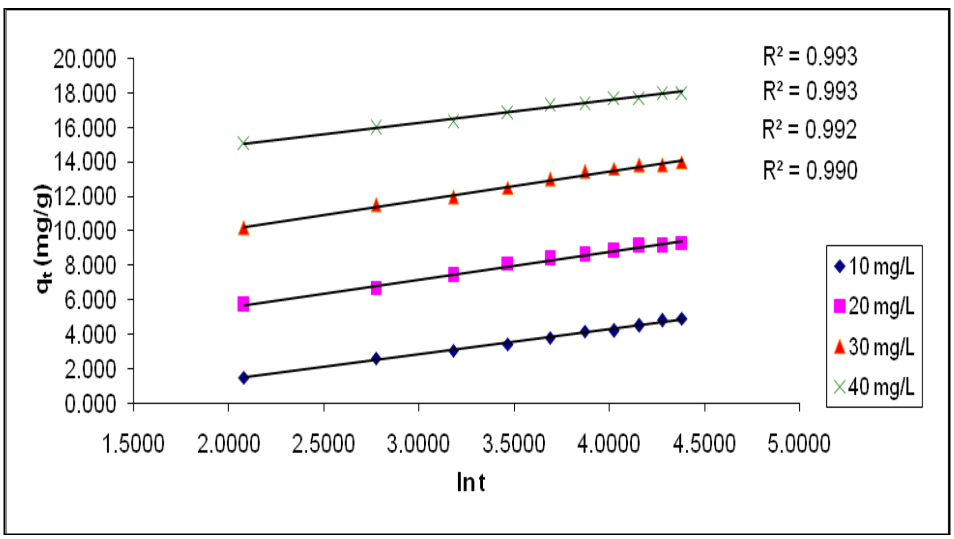

Fig.14. Elkovich kinetic model for adsorption of Methylene Blue

Weber-Morris intraparticle diffusion model

A graphical method (Fig.15.) 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 (qt) and the square root of time (t1/2) as;

$q_t = K_{id}T_{1/2} + C$ ……….. (10)

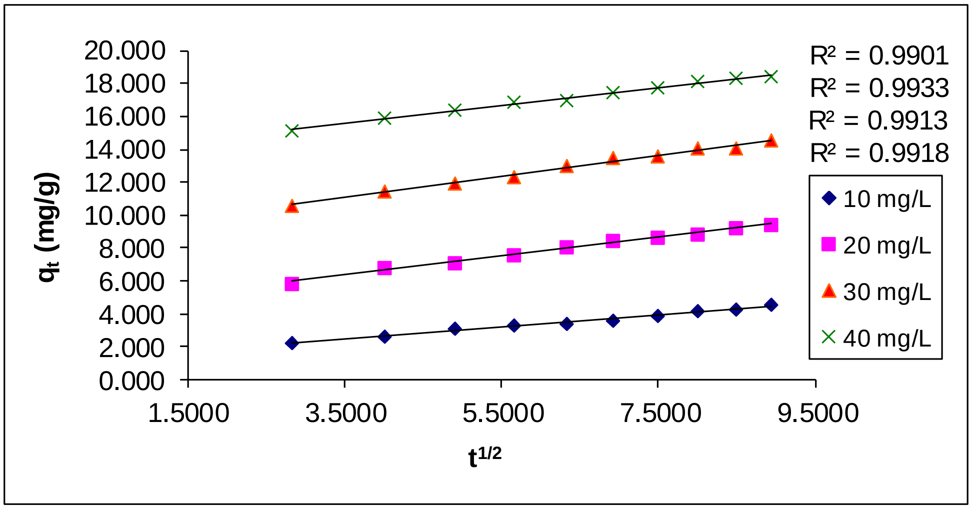

Fig.15. Intraparticle diffusion model for adsorption of Methylene Blue

Where qt is the amount adsorbed per unit mass of adsorbent (mg/g) at time 't' and 'Kid'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:

$$\ln K_C = \Delta S^0 / R - \Delta H^0 / RT$$

……………. (11)

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

…………….. (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 Methylene Blue on Fire Clay - MnO_2 nanocomposite were given in Table 5. Positive values of ΔH^0 confirms that the adsorption process to be endothermic. 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 Methylene Blue 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 Methylene Blue on Fire Clay - MnO_2 nanocomposite

Adsorbent	$-\Delta G^0$ kJ/mol			ΔS^0 kJ/mol	ΔH^0 kJ/mol
	303K	307K	311K		
Fire clay –MnO_2 composite	4766	4829	4892	15.67	18.85

Desorption studies

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

5. CONCLUSION

This study shows that the Fire Clay - MnO_2 nanocomposite can be used effectively in the removal of Methylene Blue through adsorption. Nanocomposite very well fitted with both Langmuir and Freundlich model. Pseudo second order kinetic model was followed. The sorption suggested that the adsorption is high at basic medium. Elkovich kinetic model suggested that adsorption process is chemisorptive nature. The calculated values of different thermodynamic parameters clearly indicated that the adsorption process Fire Clay - MnO_2 feasible, spontaneous and endothermic nature.

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