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Removal of methylene blue by perilite clay-MnO_2 nanocomposite

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Abstract
In this study an attempt has been made to study the feasibility of removal of methylene blue using perilite-MnO_2 nanocomposite as an adsorbent. The commercially available Perilite and MnO_2 are stirred with alcohol, dried and used. Batch adsorption experiments have been conducted under various operating parameters like initial dye concentration, contact time, adsorbent dose and pH. The equilibrium data fitted well with the Langmuir and Freundlich isotherms.

Keywords: Adsorption isotherm, methylene blue, Perilite-MnO_2 nanocomposite

1. Introduction
Various methods like coagulation, oxidation, electrochemical, ion-exchange, biodegradation and ultra-filtration have been applied to overcome the excessive discharges of colourants from petrochemical, textile, leather-making, pharmaceutical as well as food and beverage industries. All these are not comparable to adsorption technique in term of efficiency, operating cost, process flexibility and ease of operation (Shi and Li, 2007; Fathima, 2008; Shen, 2006; Ahmad, 2006; Raghu and Ahmed Basha, 2007; Walker and Weatherley, 2000) [1-6]. Further all these techniques were found to be inefficient and incompetent because of the fairly high solubility and stability of the dyes towards light, oxidizing agents and aerobic digestion. A comprehensive survey indicates that adsorption technique was the most appropriate and efficient one (Ruthven, 1984; Suzuki, 1993) [7-8]. The objective of the present study was to explore the feasibility of the removal of methylene blue using the nanocomposites prepared from perilite clay and MnO_2 as adsorbent.

2. Materials and Methods
Perilite (3g) was allowed to swell in 15 ml of water-free alcohol and stirred for 2 hours at 25 ^{0}C to get a uniform suspension. At the same time, the manganese dioxide was dispersed into water-free alcohol. The diluted manganese dioxide was then added slowly by dropping it into the suspension of Perilite and stirred for further 5 hours at 25^{0}C.Then 5ml alcohol mixed with 0.2 ml deionized water was added slowly and stirring continued for another 5 hours at 25^{0}C. The suspension was then kept over night for 10 hours at room temperature and the precipitate obtained was carefully dehydrated in a vacuum oven for 6 hours at 80^{0}C to a loose dry powder. A stock solution (1000mg/L) of dye was prepared using doubly distilled water. Various dye solutions with different initial concentrations were prepared by diluting the stock dye solution. The adsorbate used in this study is methylene blue.

3. Characterization of Adsorbent
Physico-chemical characteristics of the adsorbents were studied as per the standard testing methods (Waranusantigul, 2003). Fig.1 shows the XRD pattern of Perilite-MnO_2 nanocomposite. The peaks at 28^0 (Fig.2) confirm the presence of Perilite-MnO_2 phase in the nanocomposite. The surface morphology of the adsorbent was visualized via scanning electron microscopy (SEM).The diameter of the composite range was 0.5 µm.

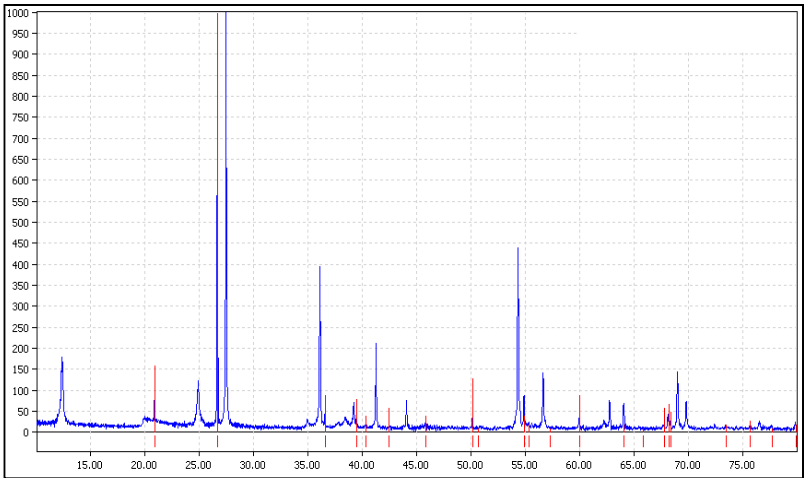

Fig 1: XRD analysis of Perilite-MnO_2 composite

SEM

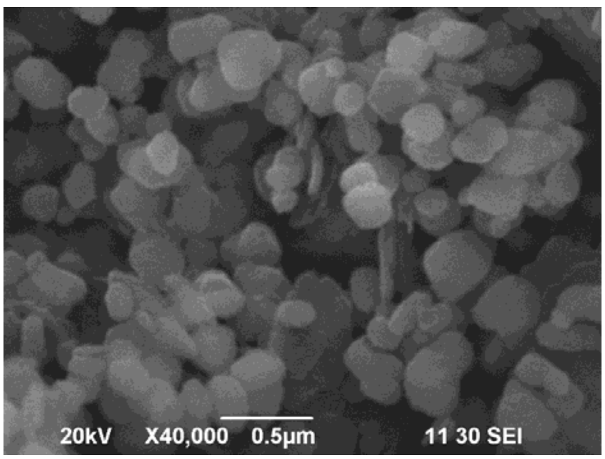

Fig 2: SEM of Perilite-MnO_2 nanocomposite

4. Batch adsorption experiments

Entire batch mode experiments were carried out in the temperature range 303K to 311K by taking 50 ml of the respective dye solution and known amount of the adsorbent in a 100 ml conical flask. The flasks were agitated for determined time intervals in a thermostat attached with a shaker at the desired temperature. The adsorbent and adsorbate were separated by filtration. Studies on the effects of agitation time, pH, initial dye concentration, adsorbent dose were carried out by using known amount of adsorbent and 50 ml of dye solution of different concentrations. Dye solution (50 ml) with different amounts of adsorbent was taken to study the effect of adsorbent dosage on the removal of dyes.

5. Results and Discussion

5.1. Effect of agitation time and initial dye concentration

The effect of initial dye concentration and contact time for the removal of methylene blue is shown in Fig.3. For this study 50 ml of 10 to 25 mg/L of dye solution was agitated with 100 mg of adsorbent. The extent of removal of dye was faster in initial stages, then showed decreasing pattern and finally became constant showing the attainment of equilibrium. The extent of removal was found to be 87%. The curves obtained are single and smooth, indicating monolayer coverage on the adsorbent surface.

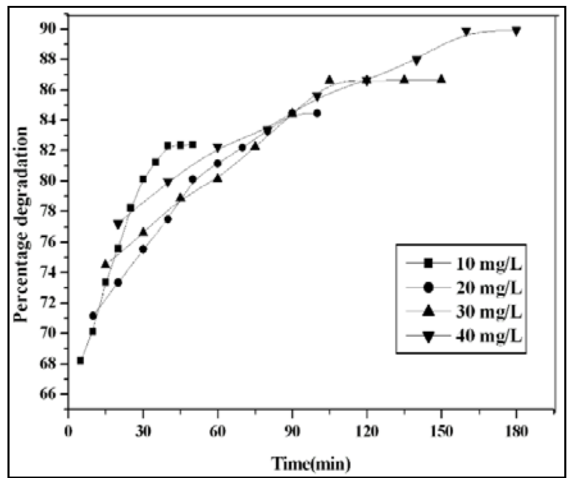

Fig 3: Effect of agitation time and initial dye concentration of Methylene blue on Perilite-MnO_2 nanocomposite

5.2. Effect of adsorbent dosage on adsorption process

The effect of adsorbent dosage on basic dye removal was studied by keeping all other experimental conditions constant except that of adsorption dosage. The amount adsorbed per unit mass of the adsorbent decreased with increase in adsorbent concentration (Fig.4). The decrease in unit adsorption with increasing dose of adsorbent may basically be due to the fact that adsorption sites remaining unsaturated during the adsorption process.

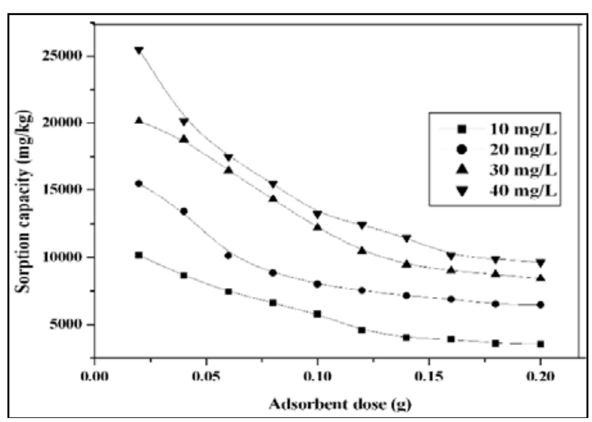

Fig. 4: Effect of adsorbent dose on the removal of Methylene blue on Perilite-MnO_2 nanocomposite.

5.3. Effect of pH

Adsorption experiments were carried out at various p^H values ranging from 5 to 11 maintaining the required p^H by adding necessary amount of dilute hydrochloric acid and sodium hydroxide solutions. A p^H meter calibrated with 4.0 and 9.0 buffers were used. Fig.5 indicates that maximum dye removal had occurred in basic medium. It was observed that as the p^H increases the sorption capacity also increases.

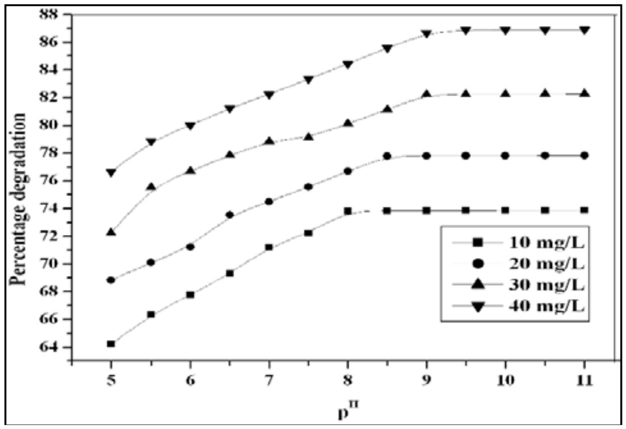

Fig 5: Effect of p^H on the removal of Methylene blue on Perilite-MnO_2 nanocomposite.

5.4. Adsorption isotherm

The relationship between the amount of dye adsorbed and its equilibrium concentration was analysed using Langmuir and Freundlich isotherms.

5.4.1. Langmuir isotherm

The Langmuir adsorption isotherm which assumes that adsorption takes place at specific homogeneous sites within the adsorbent has been used successfully for many systems that involve monolayer adsorptions. The linearized Langmuir equation (Eq.1). Where Ce is the equilibrium concentration of the adsorbate (mg/L), qe is the amount of dye adsorbed per unit mass of adsorbent (mg/L) and qo and b are Langmuir constants related to adsorption capacity and adsorption rate respectively. As required by equation (1) plotting Ce/qe against Ce gave a straight line, indicating that the adsorption of basic dyes on the nanocomposite follow the Langmuir isotherm. The Langmuir constants b and q0 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, (2) Where, C_0 is the highest initial solute concentration, 'b' the Langmuir adsorption constant (L/mg).

$$q_e = \frac{Q^0 b C_e}{1 + bC_e} \quad \text{.................................}(1)$$

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

If the value of R is less than one then it indicates favourable adsorption. The R_L values shown in Table 1 all are less than one indicating the applicability of Langmuir isotherm to this adsorption process.

Table 1: The Langmuir Adsorption isotherm on the removal of Methylene blue on Perilite-MnO_2nanocomposite.

Dye concentration C_o	C_e	q_e (mg/kg)	C_e/q_e
10	3.20	3645	0.0008
20	3.45	4521	0.0007
30	4.24	5012	0.0006
40	5.68	5362	0.0004
50	6.31	5847	0.0002
60	7.89	6211	0.0001

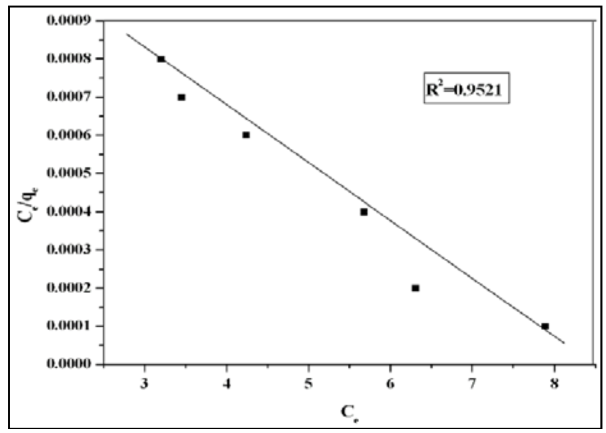

Fig 6: Langmuir adsorption isotherm on the removal of Methylene blue on Perilite-MnO_2 nanocomposite

5.4.2. Freundlich Model

The Freundlich isotherm, an empirical relationship used to describe heterogeneous systems can be expressed in its logarithmic form (Eq.3): (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 values of K_f and 1/n calculated from the intercept and slope respectively are recorded in Table 2. The plot of log q_e versus log C_e gave a straight line (Fig.7) with good regression coefficient indicating that the adsorption of methyl violet follows the Freundlich isotherm.

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

Table 2: The Freundlich adsorption isotherm on the removal of Methylene blue on Perilite-MnO_2 nanocomposite.

Dye concentration C_0	log C_e	log q_e
10	0.4512	3.6478
20	0.5842	3.9965
30	0.6946	4.2337
40	0.7522	4.5678
50	0.7978	4.6888
60	0.8312	4.8875

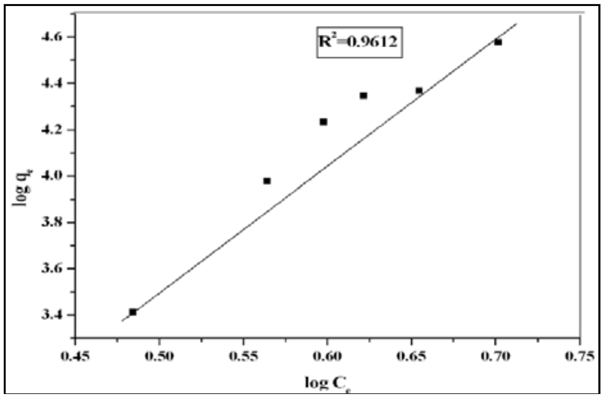

Fig 7: Freundlich adsorption isotherm on the removal of Methylene blue on Perilite-MnO_2 nanocomposite.

6. Conclusion

The present investigation showed that Perilite-MnO_2 nanocomposite can be used as adsorbent for removal of methylene blue. The amount of dye adsorbed varied with initial dye concentration, adsorbent dose and p^H. Removal of methyl violet by nanocomposite obeyed both Langmuir and Freundlich isotherms.

7. References

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