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# Equilibrium and Kinetics of Adsorption of Cationic Dyes by STISHOVITE Clay – TiO2 Nanocomposite

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***Abstract:*** *In this study an attempt has been made to study the feasibility of removal of methyl violet using Stishovite-$TiO_2$ nanocomposite as an adsorbent. The commercially available Stishovite and $TiO_2$ 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, $p^H$ and temperature. The equilibrium data fitted well with the Langmuir and Freundlich isotherms. From these the adsorption efficiency, adsorption energy, adsorption capacity, intensity of adsorption and dimensionless separation factor all are calculated. The experimental data fitted very well with pseudo second order kinetic model and Elcovich model suggesting chemisorption which is substantiated by desorption studies.*

***Keywords:*** *adsorption isotherm, methyl violet, kinetics, Stishovite-$TiO_2$ nanocomposite, desorption*

## I. 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). 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).

The objective of the present study was to explore the feasibility of the removal of methyl violet using the nanocomposites prepared from Stishovite clay and $TiO_2$ as adsorbent.

## II. Materials and Methods

Stishovite (3g) was allowed to swell in 15ml of water-free alcohol and stirred for 2 hours at $25^0$C to get a uniform suspension. At the same time, the titanium dioxide was dispersed into water-free alcohol. The diluted titanium dioxide was then added slowly by dropping it into the suspension of Stishovite and stirred for further 5 hours at $25^0$C.Then 5ml alcohol mixed with 0.2ml deionized water was added slowly and stirring continued for another 5 hours at $25^0$C. The suspension was then kept over night for 10hours 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 methyl violet.

### 2.1. Characterization of Adsorbent

Physico-chemical characteristics of the adsorbents were studied as per the standard testing methods (Waranusantigul, 2003). Fig.1, 2 shows the XRD pattern of pure Stishovite clay and that of Stishovite-$TiO_2$ nanocomposite respectively. The peaks at $28^0$ (Fig. 1) and at $30^0$ (Fig. 2)confirm the presence of Stishovite-$TiO_2$ phase in the nanocomposite.The surface morphology of the adsorbent was visualized via scanning electron microscopy (SEM).The diameter of the composite range was 50 µm.

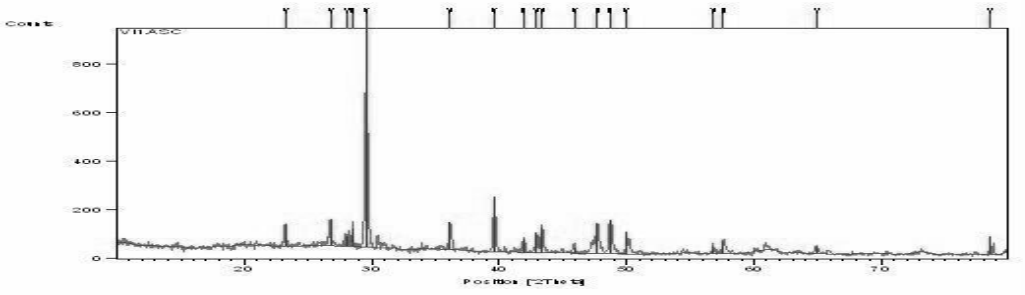

**Fig. 1.** XRD analysis of STISHOVITE

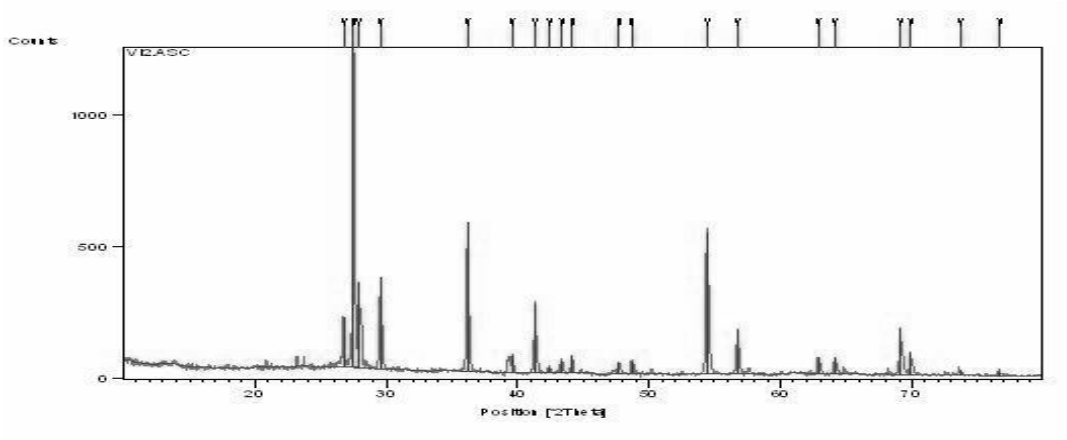


**Fig. 2.** X RD analysis of STISHOVITE-$TiO_2$ COMPOSITE

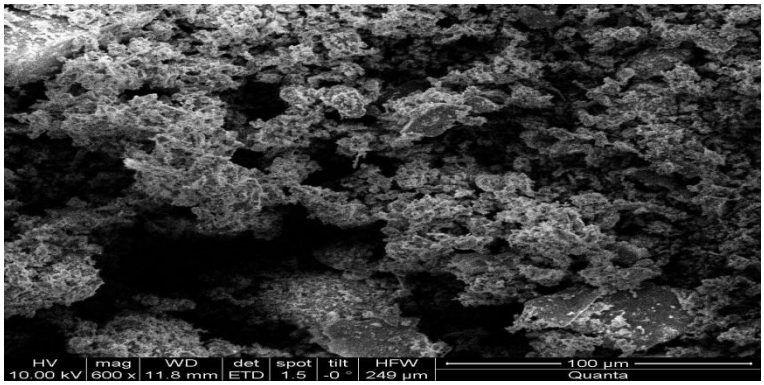


**Fig. 3**.SEM of STISHOVITE

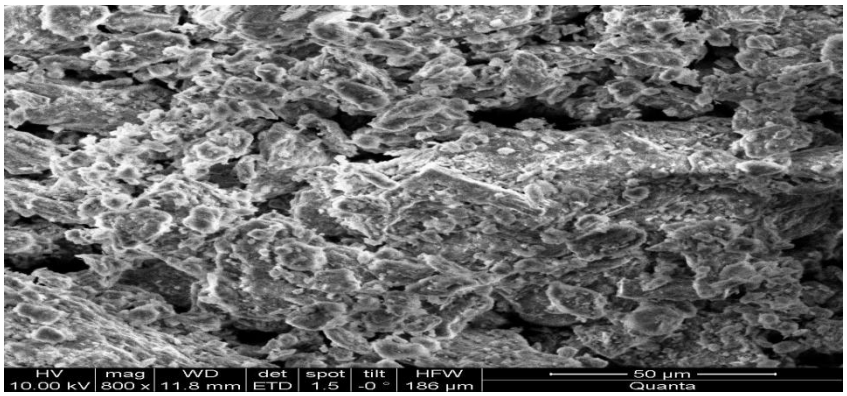


**Fig. 4**. SEM of STISHOVITE – $TiO_2$ COMPOSITE

**IR Spectroscopy:**

Stishovite Clay : Si-O-Si = 1011 $cm^{-1}$, Si-O-Ti = 872 $cm^{-1}$ ,Ti-O-Si = 872 $cm^{-1}$, Ti-O-Ti = 1633 $cm^{-1}$

Stishovite + TiO2 NC : Si-O-Si = 1014 $cm^{-1}$, Si-O-Ti = 873 $cm^{-1}$ ,Ti-O-Si = 873 $cm^{-1}$, Ti-O-Ti = 1796 $cm^{-1}$

## III. Batch adsorption experiments

Entire batch mode experiments were carried out in the temperature range 303K to 311K by taking 50ml of the respective dye solution and known amount of the adsorbent in a 100ml conical flask. The flasks were agitated for pre-

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, $p^H$, initial dye concentration, adsorbent dose and temperature were carried out by using known amount of adsorbent and 50ml of dye solution of different concentrations. Dye solution (50ml) with different amounts of adsorbent was taken to study the effect of adsorbent dosage on the removal of dyes.

## IV. Results and Discussion

### 4.1. Effect of agitation time and initial dye concentration

The effect of initial dye concentration and contact time for the removal of methyl violet is shown in Fig.5. For this study 50ml of 10 to 40 mg/L of dye solution was agitated with 100mg 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 88%. The curves obtained are single and smooth, indicating monolayer coverage on the adsorbent surface.

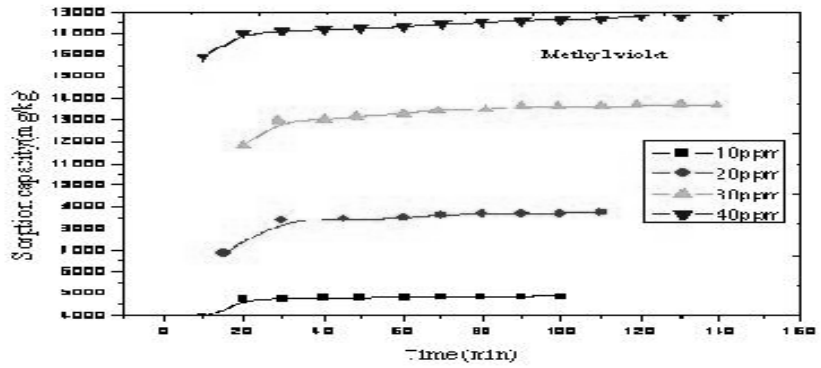


**Fig. 5.** Effect of initial dye concentration

### 4.2. 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.6). 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.

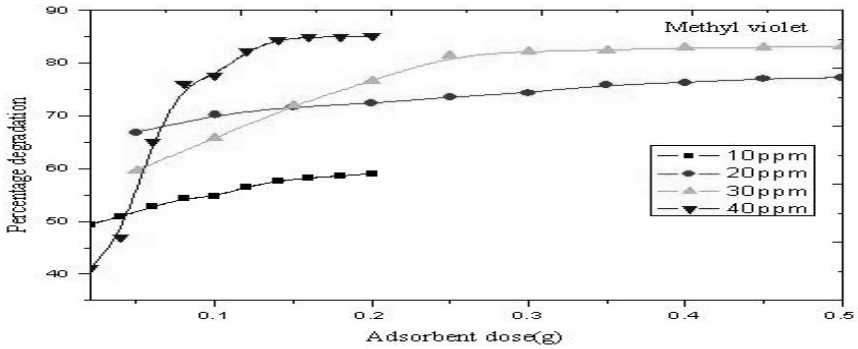


**Fig 6.** Effect of adsorbent dosage

### 4.3. Effect of $p^H$

Adsorption experiments were carried out at various $p^H$ values ranging from 6 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.7 indicates that maximum dye removal had occurred in basic medium. It was observed that as the $p^H$ increases the sorption capacity also increases. The $p^H_{zpc}$ for the nanocomposite was determined as 8.0.

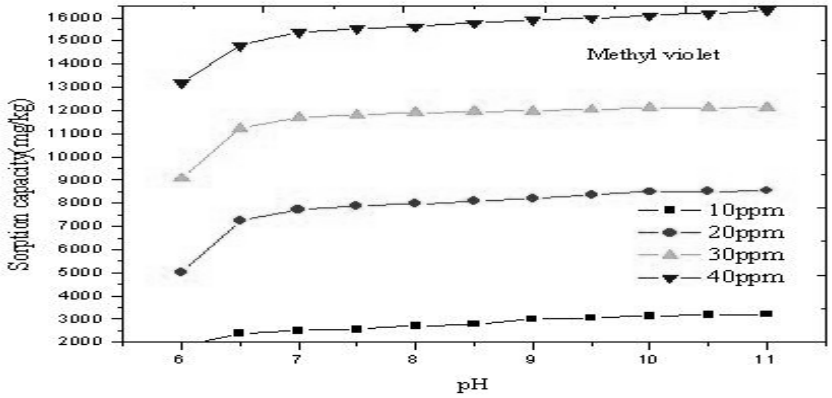


**Fig. 7.** Effect of $p^H$

### 4.4. Effect of temperature

Temperature has an important effect on the adsorption process. Fig.8 shows effect of different temperature on the removal of methyl violet by the nanocomposite. 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**.**

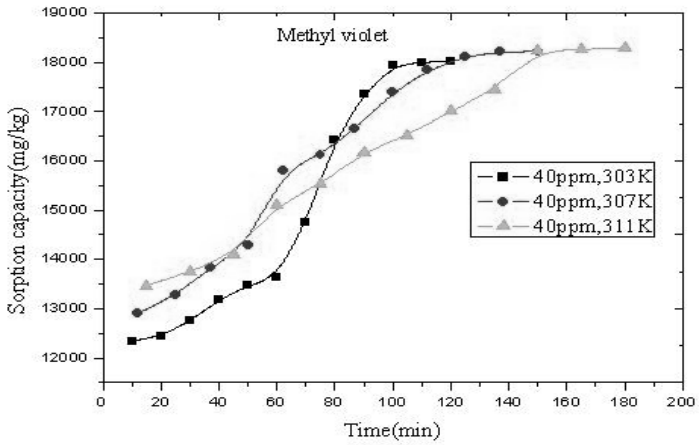


**Fig. 8.** Effect of temperature

### 4.5. Adsorption isotherm

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

#### 4.5.1. 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):

$$C_e / q_e = i / bq_0 + C_e / q_0 \quad (1)$$

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 $q_o$ and b are Langmuir constants related to adsorption capacity and adsorption rate respectively. As required by equation (1) plotting $C_e/q_e$ against $C_e$ gave a straight line, indicating that the adsorption of basic dyes on the nanocomposite follow the Langmuir isotherm. 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,

$$R_L = 1/(1 + bC_0) \quad (2)$$

Where, $C_0$ is the highest initial solute concentration, 'b' the Langmuir adsorption constant (L/mg).

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.

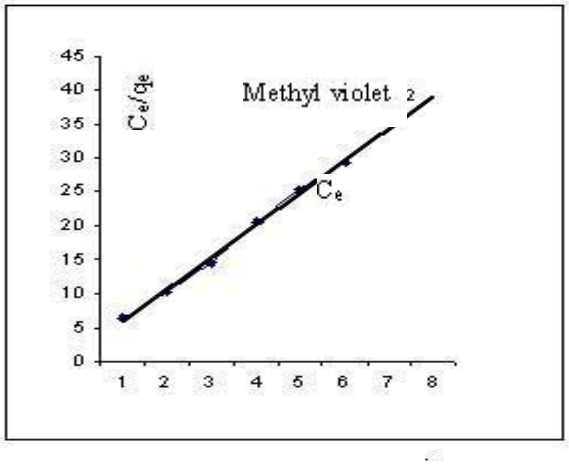


**Fig.9:** Plot of Langmuir adsorption isotherm

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

| *Concentration of dye(mg/L)* | *Methyl violet* | | | |
|---|---|---|---|---|
| | $R_L$ | *b* | $Q^o$ *mg/g* | $R^2$ |
| 20 | 0.9939 | | | |
| 40 | 0.9879 | | | |
| 60 | 0.9819 | 0.000306 | 57.208 | 0.9962 |
| 80 | 0.9761 | | | |
| 100 | 0.9703 | | | |
| 120 | 0.9645 | | | |

**4.5.2. Freundlich Model**

The Freundlich isotherm, an empirical relationship used to describe heterogeneous systems can be expressed in its logarithmic form (Eq.3):

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

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 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.10) with good regression coefficient indicating that the adsorption of methyl violet follows the Freundlich isotherm.

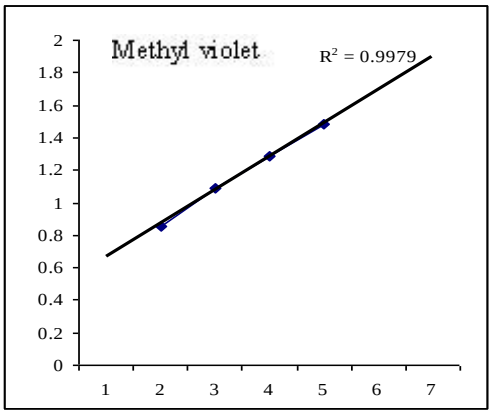

**Fig.10:** Plot of Freundlich adsorption isotherm

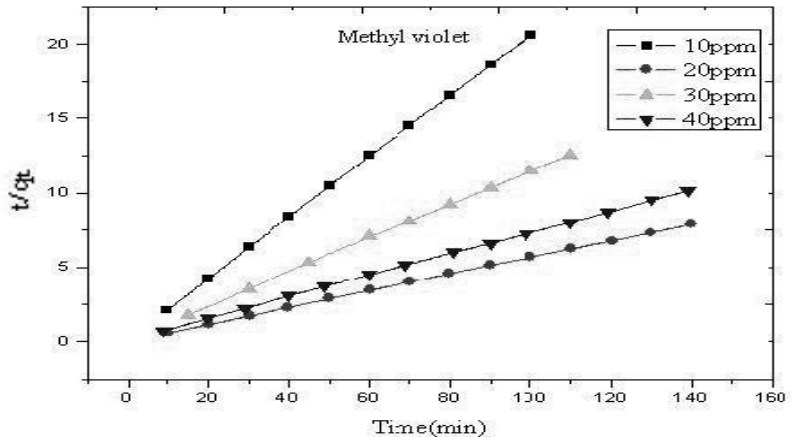


**Table 2 .The values of Freundlich constant $K_f$ and n**

| *Dye* | *$K_f$ L/mg* | *n mg/g* | *$R^2$* |
|---|---|---|---|
| Methyl violet | 10.9647 | 2.0000 | 0.9979 |

**4.6. Kinetics of adsorption**

In order to investigate the mechanism of adsorption of methyl violet by the nanocomposite the following three kinetic models were considered.

**4.6.1. Pseudo first order kinetic model**

The integrated linear form of this model proposed by Lagergren (Eq.4):

$$log(q_e - q_t) = log\ q_e - (k_1 / 2.303)\ t \qquad (4)$$

Where $q_e$ is the amount of dye adsorbed at equilibrium (mg/g), and $q_t$ is the amount of dye adsorbed (mg/g) at time t, $k_1$ is the first order rate constant ($min^{-1}$) and t is time (m).Hence a linear trace is expected between the two parameters log ($q_e$-$q_t$) and t, provided the adsorption follows first order kinetics. It is observed that the data does not fit in to first order equation.

**4.6.2. Pseudo second order kinetics**

The adsorption may also be described by pseudo second order kinetic model .The linearised form of the pseudo second order model (Eq.5):

$$t/q_t = 1/k_2\ q_e^{\ 2} + 1/q_e \times t \qquad (5)$$

Where $k_2$ is the second order rate constant (g/mg min).A plot of $t/q_t$ vs t should be linear if the adsorption follows second order.$q_e$ and $k_2$ can be calculated from the slope and intercept of the plot. methyl violet obeys the pseudo order kinetics.

**4.7. Elovich kinetic model**

The Elovich equation is mainly applicable for chemisorption processes involving heterogeneous adsorbing surfaces. The Elovich model in its integrated form can be

$$Q_t = (1/b)\ln(ab) + (1/b)\ln t \qquad (6)$$

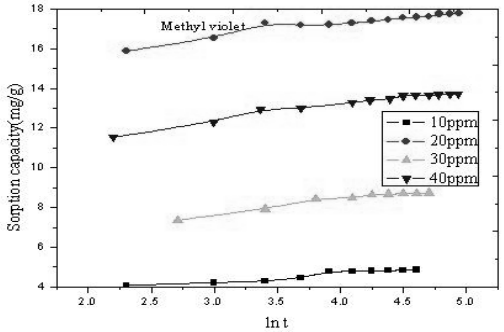

**Fig.12:** Elkovich kinetic model

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 chemisorptions (g/mg). A plot of $q_t$ vs ln t is a straight line, as expected, with a slope of 1/b and an intercept log 1/b ln (ab) with good correlation coefficients confirming the chemisorptive nature of adsorption.

### 4.8. Thermodynamic of Adsorption

Thermodynamic parameters like $\Delta H^0$ and $\Delta S^0$ were evaluated using Van't Hoff's equation:

$$ln\, K_C = \Delta S^0 / R - \Delta H^0 / RT \quad (8)$$

Where $K_C$ is the Langmuir equilibrium constant, $\Delta H^0$ and $\Delta S^0$, are the standard enthalpy and entropy changes of adsorption respectively and their values are calculated from the slopes and intercepts respectively of the linear plot of ln $K_c$ vs 1/T.The free energy change for the adsorption process $\Delta G^0$ (kJ/mol) is derived (Eq.9):

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (9)$$

Negative free energy change and positive entropy change of adsorption (Table 3) indicate that the adsorption process is favourable and spontaneous in nature. The endothermic nature of adsorption is confirmed by the positive $\Delta H^0$ value.

**Table 3: Thermodynamic parameters for adsorption of methyl violet on Stishovite-$TiO_2$ NC**

| *Dyes* | $-\Delta G^0$ *kJ/mol* | | | $\Delta S^0$ *kJ/mol* | $\Delta H^0$ *kJ/mol* |
|---|---|---|---|---|---|
| | *303K* | *307K* | *311K* | | |
| Methyl violet | 1.631 | 1.652 | 1.673 | 5.320 | 19.745 |

## V. Desorption studies

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

## VI. Conclusion

The present investigation showed that Stishovite-$TiO_2$ nanocomposite can be used as adsorbent for removal of methyl violet. The amount of dye adsorbed varied with initial dye concentration, adsorbent dose, $p^H$ and temperature. Removal of methyl violet by nanocomposite obeyed both Langmuir and Freundlich isotherms. The adsorption process followed pseudo second order kinetics. This has been further supported by Elkovich chemisorptive kinetic model. Desorption studies reveals that no satisfactory desorption taking place confirming chemisorptive nature of adsorption. Evaluation of thermodynamic parameters showed the process as endothermic and spontaneous.

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