GLOBAL JOURNAL OF BIOLOGY, AGRICULTURE & HEALTH SCIENCES
(Published By: Global Institute for Research & Education)
www.gifre.org

# EQUILIBRIUM AND KINETIC DATA AND PROCESS DESIGN FOR ADSORPTION OF METHYLENE BLUE ONTO STISHOVITE–$TiO_2$ NANOCOMPOSITE

V.T.Priya[a*], & V.Venkateswaran[b]

[1]Research scholar, Research and development centre, Bharathiyar university, Coimbatore, Tamilnadu
[2]Principal, Sree Saraswathi Thyagaraja College, Pollachi, Tamilnadu
*Corresponding Author

## Abstract

Herein, we report adsorption of Methylene blue onto Stishovite - $TiO_2$ nanocomposite in a batch adsorber method. The experiment was conducted under various operating parameters such as initial dye concentration, contact time, adsorbent dose, pH and temperature respectively. The kinetics of the adsorption process was conducted by the Pseudo second order, the Elovich equation and the intraparticle diffusion equation. Kinetic parameters, rate constants, equilibrium adsorption capacities and correlation coefficients for each kinetic equation were calculated and demonstrated. The final result shows that the adsorption process under study could be best described by the pseudo second order equation. The experimental data fitted well with both Langmuir and Freundlich isotherms. Thermodynamic parameters reveals that the adsorption to be spontaneous and endothermic. A single stage batch adsorber has been designed for various volumes using the Langmuir isotherm.

**Keywords:** Stishovite - $TiO_2$ nanocomposite, Methylene blue, Adsorption kinetics and isotherm, Batch adsorber design

## 1. Introduction

Synthetic dyes in textile and other industries are mostly composed of aromatic rings in their structure, which makes them carcinogenic and mutagenic, inert and non-biodegradable when discharged into waste streams. Hence, the removal of such colored agents from aqueous effluents is significant environmental, technical, and commercial importance (Allen *et al.*, 2004 and Ozacar *et al.*, 2004). Nonetheless several Methods are involved in the color removal from textile effluents such as coagulation, electrocoagulation, flotation, chemical oxidation, filtration, ozonation, membrane separation, ion-exchange, aerobic and anaerobic microbial degradation respectively. However, all of these methods suffer from one or other limitations and none of them were successful in completely removing the color from wastewater (Ozacar *et al.*, 2004 and Lorene-Grabowska *et al.*, 2007).

On the other hand, adsorption of various dyes from aqueous solution using excellent way to treat effluent as a cost effective technique. So far several studies and low cost materials have been applied in the removal of dyes from aqueous solutions successfully. There are numerous materials such as coal, fly ash, wood, silica, shale oil ash, Fuller's earths, zeolite, perlite, alunite, clay materials (bentonite, montmorillonite, etc.) activated slag and agricultural wastes (bagasse pith, maize cob, coconut shell, rice husk, waste fruit residues etc (Mall *et al.*, 2005, Dogan *et al.*, 2000, Parimaladevi *et al.*, 2011 and Parimaladevi *et al.*, 2011) for removal of dyes. To the best of our knowledge only limited application of such data has been directed towards the design of adsorption treatment systems, for example, batch adsorber design (Ozacar *et al.*, 2004 and Dogan *et al.*, 2000).

Utilization of Stishovite – $TiO_2$ nanocomposite in removing methyl violet, auramine yellow, auramine O has been reported earlier (Venkateswaran *et al.*, 2012 and Venkateswaran *et al.*, 2012]. The present study is focused on explaining the efficiency of same adsorbent in removing methylene blue from aqueous solutions. This dye was widely used in paper coloring, dyeing cotton and wool and as temporary hair colorant respectively. It mainly causes to harmful effects like increase in heartbeat, vomiting, shock, cyanosis, jaundice, quadriplegia, and tissue necrosis to the human being (Ho *et al.*, 1998 and Stydini *et al.*, 2004).Equilibrium isotherms and kinetic data have been evaluated. A design analysis method has been developed to predict the required amount of Stishovite – $TiO_2$ nanocomposite at various volumes treated for 95% dye removal.

## 2. Materials and Methods

### Preparation of Stishovite-titanium-di-oxide nanocomposite

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

### Absorbate solution

A stock solution (1000 mg/L) of Methylene blue, the adsorbate used in this study, was prepared using doubly distilled water. Various solutions with different initial concentrations were prepared by diluting the stock dye solution.

## 3. Characterization of Adsorbent

Physico-chemical characteristics of the adsorbents were studied as per the standard testing methods. The XRD

pattern of Stishovite - $TiO_2$ nanocomposite Figure 1 showed characteristic peaks at 28° confirming the presence of Stishovite - $TiO_2$ phase in the nanocomposite. The surface morphology of the adsorbents was visualized via scanning electron microscopy (SEM) (Figure 2). The diameter of the composite range was 50µm.

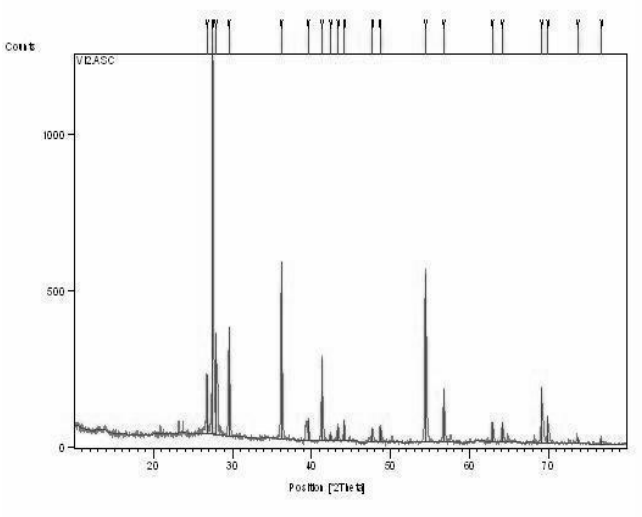


Fig.1: XRD Analysis of Stishovite - $TiO_2$ Composite

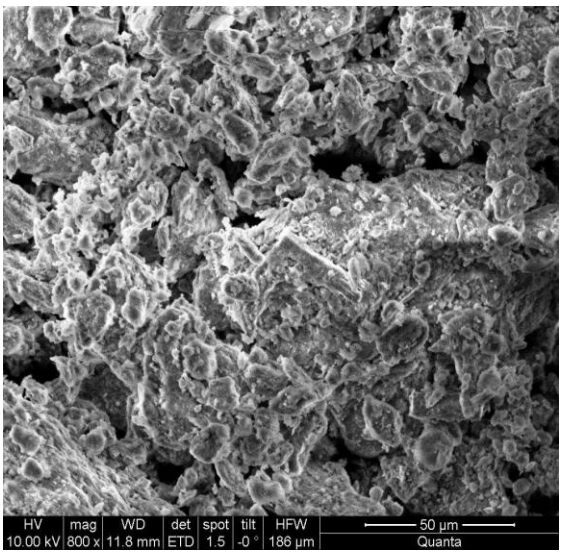


Fig.2. SEM of Stishovite - $TiO_2$ Composite

## 4. Batch Adsorption Experiments

Entire batch mode experiments were carried out by taking 50 mL of the dye solution and a known amount of the adsorbent in a 100 mL conical flask. The flasks were agitated for predetermined time intervals in a thermostat attached with a shaker at the desired temperatures (301 K to 317 K) and then 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 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.

## 5. Results and Discussion

*5.1. Effect of contact time and initial dye concentration*

The experimental results of adsorptions at various concentrations (10, 20, 30 and 40 mg/L) on nanocomposite was shown in Figure 3. It was observed that the percentage removal at equilibrium was found to increase from 60.72 % to 82.51 % as the initial dye concentration was increased from 10 mg/L to 40 mg/L. At lower concentration, the ratio of the initial number of dye molecules to the available surface area is low. Subsequently, the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption become fewer and hence the percentage removal of dye is dependent upon initial concentration (Namasivayam *et al.,* 1996 and Namasivayam *et al.,* 1995).The equilibrium was found to get established at 90,100,120 and 150 minutes with the nanocomposite as the initial dye concentration was increased from 10 mg/L to 40 mg/L. The curves are single, smooth and continuous, leading to saturation, suggesting the possible monolayer coverage of the dye on the adsorbent surfaces (Arivoli *et al.,* 2007).

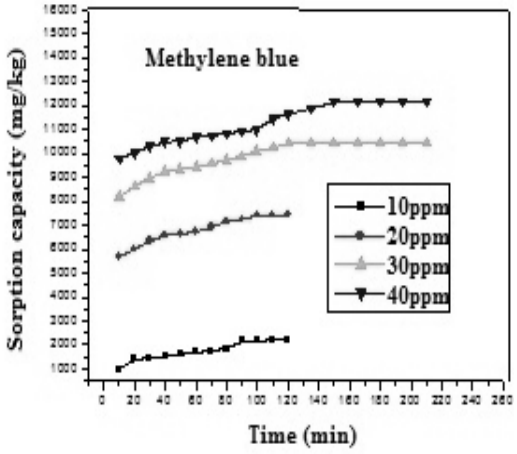


Figure.3 Effect of contact time and initial dye concentration of Stishovite - $TiO_2$ nanocomposite

*5.2. Effect of adsorbent dosage*

The effect of adsorbent dosage on basic dye removal was studied by keeping all other experimental conditions constant except that of adsorption dosage. The results showed that there is an increase in adsorption with increase in adsorbent concentration (Figure 4). This may be attributed to the fact that, as the amount of adsorbent increased the surface area and hence the number of activation sites available for adsorption of dyes increased leading to a higher percentage of adsorption of the dyes.

An increase in the adsorbent concentration after the establishment of equilibrium did not significantly improved the percent removal indicating the establishment of equilibrium between the adsorbed species and those remaining in the solution (Ozer *et al.*, 2007).

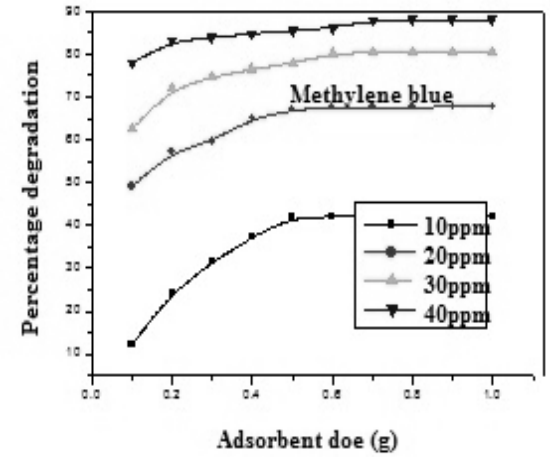


Figure.4 Effect of adsorbent dosage of Stishovite - $TiO_2$ nanocomposite

*5.3. Effect of $p^H$*

Adsorption experiments were carried out at various $p^H$ values in the range 5 to 11, maintaining the $p^H$ by adding required amount of dilute hydrochloric acid and sodium hydroxide solutions. As the $p^H$ increases the sorption capacity also increases. Figure 5 indicate that maximum dye removal had occurred in basic medium.

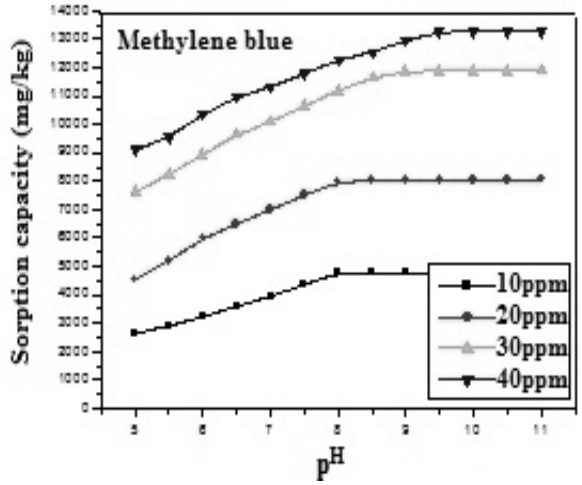


Figure.5 Effect of $p^H$ of Stishovite - $TiO_2$ nanocomposite

*5.4. Effect of temperature*

Temperature has an important effect on the adsorption process. Figure 6 shows the effect of different temperatures on the removal of basic dyes by the nanocomposite. The amount of basic dye adsorbed increases with increasing temperature from 301K to 317K indicating the adsorption process to be endothermic. As the temperature increases, rate of diffusion of adsorbate molecules across the external boundary layer and internal pores of adsorbent particle increases (Norrozi *et al.,* 2007).

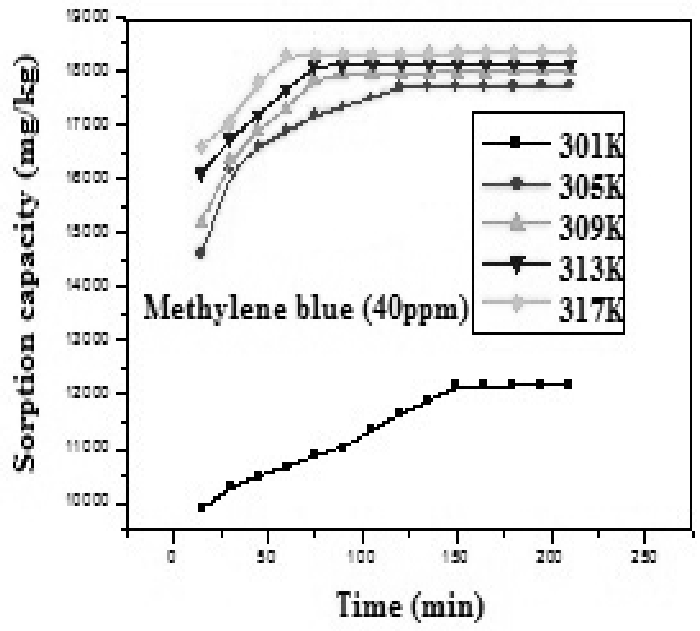


Figure.6 Effect of Temperature of Stishovite - $TiO_2$ nanocomposite

*5.5. Adsorption isotherm*

Langmuir and Freundlich the most frequently used models to describe experimental data on adsorption were employed to analyse the relationship between the amount of dye adsorbed and its equilibrium concentration.

*5.5.1. Langmuir isotherm (*Crini *et al.,* 2007)

The Langmuir isotherm is represented as follows:

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots Eq.(A.1)$$

Where $q_e$ (mg/g) and $C_e$ (mg/L) are the amount of adsorbend dye per unit weight of adsorbent and unadsorbed dye concentration in solution at requilibrium respectively. The $K_L$ (L/g) and $a_L$ (L/mg) are the Langmuir isotherm constants. The Langmuir isotherm constants, $K_L$ and $a_L$ are evaluated through linearization of Eq.(A.1),

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots Eq.(A.2)$$

The adsorption data were analyzed according to the linear form of the Langmuir isotherm Eq.(A.2) the values of the Langmuir constants $K_L$, $a_L$ and $Q^0$ with the correlation coefficient are listed in Table 1 & Figure 7 for the Methylene blue – Stishovite – $TiO_2$ nanocomposite system. The isotherm was found to be linear over the entire concentration range studies with a good linear correlation coefficient ($R^2$ =0.9968), showing that data correctly fit the Langmuir isotherm confirming the monolayer coverage of dye onto Stishovite – $TiO_2$ nanocomposite particles and also the homogeneous distribution of active sites on the adsorbent.

The essential features of the Langmuir isotherm can be expressed interms of a dimensionless separation factor (Ozacar *et al.,* 2004 and Crini *et al.,* 2007) ($R_L$, also called as equilibrium parameter) defined as

$$R_L = \frac{1}{1 + a_L C_0} \ldots\ldots\ldots\ldots\ldots\ldots Eq.(A.3)$$

Where $C_0$ (mg/L) is the initial dye concentration and aL (L/mg) is the Langmuir constant related to the energy of adsorption. The value of RL indicates the shape of the isotherms to be either unfavourable (RL > 1), linear (RL = 1), favourable (0< RL<1) or irreversible (RL = 0).

It was observed that in this study the values are in between 0 and 1 confirming the favourable uptake of the Methylene blue on the adsorbent.

Table.1 Data for langmuir adsorption isotherm for Methylene blue

| Conc. of dye (mg/L) | Methylene blue (Stishovite - $TiO_2$ nanocomposite) | | | |
|---|---|---|---|---|
| | $R_L$ | b | $Q^0$(mg/g) | $R^2$ |
| 20 | 0.294 | | | |
| 40 | 0.172 | | | |
| 60 | 0.122 | 0.134 | 11.885 | 0.9968 |
| 80 | 0.094 | | | |
| 100 | 0.077 | | | |
| 120 | 0.065 | | | |

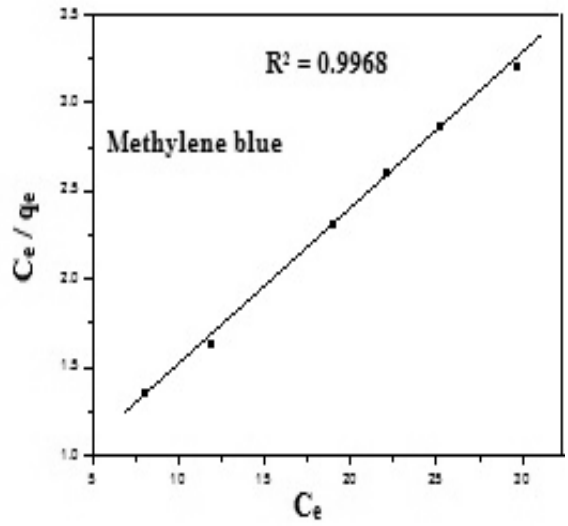


Figure.7 Langmuir model of Stishovite - $TiO_2$ nanocomposite

*5.5.2. Freundlich isotherm (*Ozacar *et al.*, 2003)

In the linear form the Freundlich isotherm can be expressed as

$$logq_e = logK_F + \frac{1}{n} logC_e \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots Eq.(B.1)$$

Where $K_F$ ($mg^{1-1/n}\, L^{1/n}\, g^{-1}$) is the Freundlich constant related to the bonding energy, and n (g/L) is the heterogeneity factor.

As required by Eq. (B.1), the plot of log $q_e$ vs log $C_e$ is linear (Figure 8) with a regression coefficient of 0.9942 showing the data fit well with freundlich isotherm also. The value of n was evaluated as 1.667, indicate that the process was favorable. The value of $K_f$ was found to be 5.370 [$mg^{1-1/n}\, L^{1/n}\, g^{-1}$]

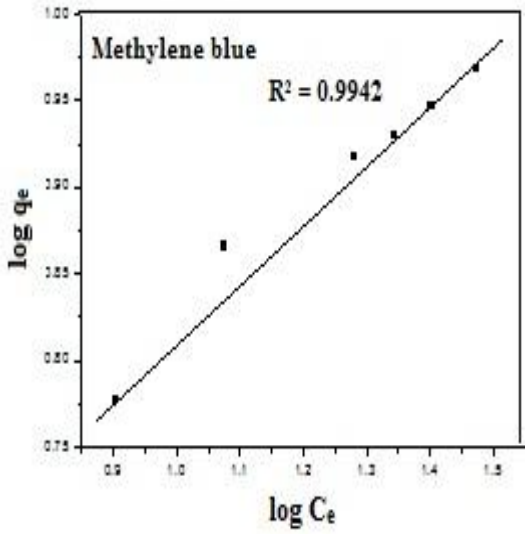


Figure.8 Freundlich model of Stishovite - $TiO_2$ nanocomposite

*5.6. Kinetics of adsorption*

In order to investigate the mechanism of adsorption of Methylene blue by the nanocomposite the following four kinetic models were considered.

*5.6.1. Pseudo-second order kinetic model*

The experimental data does not fit with pseudo first order kinetic model.

The Pseudo second order chemisorptions kinetic rate equation was expressed as (Ho *et al.,* 1999, Ozacar *et al.,* 2004 and Ozacar *et al.,* 2003):

$$\frac{dq_t}{dt} = k_2(q_e - q_t) \quad \ldots\ldots Eq.(C.1)$$

Here $q_e$ and $q_t$ were the adsorption capacity at equilibrium and at time, t, respectively (mg/g) and $k_2$, the pseudo-second order rate constant (g/mg/min). On integrating the Eq.C.1, for the boundary conditions t=0 to t=t and $q_t = q_e$

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad \ldots\ldots Eq.(C.2)$$

which is the integrated law for a pseudo – second order reaction. Eq.C.2 can be rearranged to obtain

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \ldots\ldots Eq.(C.3)$$

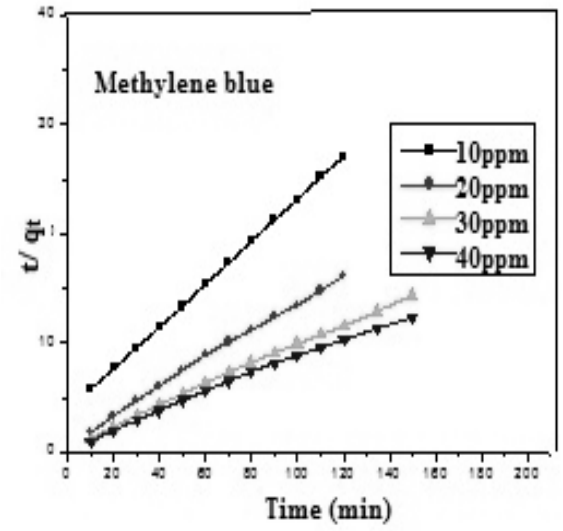


Figure.9 Pseudo-second order kinetic model of Stishovite - $TiO_2$ nanocomposite

Compared to Eq.C.2 and Eq.C.3 had an advantage that $k_2$ and $q_e$ can be obtained from the intercepts and slope of the plot of ($t/ q_t$) vs t and there was no need to know any parameter beforehand (Ho *et al.,* 1998). The results for the adsorption of methylene blue studied on the nanocomposite were shown in Figure 9 and Table 2. The linearity of the plots clearly indicated that the adsorption process followed pseudo second order kinetics.

*5.6.2. Elovich kinetic model (*Low *et al.,* 1960)

The adsorption data may also be analyzed using Elovich equation (Parimaladevi *et al.,* 2011 and Ozacar *et al.,* 2006), which is usually represented as

$$\frac{dq_t}{dt} = a \exp(-bq_t) \quad \ldots\ldots Eq.(D.1)$$

where 'a' was the initial adsorption rate (mg/g min) and 'b' was related to the extent of surface coverage and the activation energy for the chemisorptions (g/mg).

In its integrated form Elovich equation can be represented as

$$q_t = (1/b) \ln (t+t_o) - (1/b) \ln t_o \quad \ldots\ldots\ldots\ldots Eq.\ (D.2)$$

where $t_0 = (1/ab)$

If $t >> t_0$, this equation simplifies to,

$$q_t = (1/b) \ln t - (1/b) \ln t_0$$

$q_t$ = (1/b) ln t +(1/b) ln (ab) ……. Eq. (D.3)

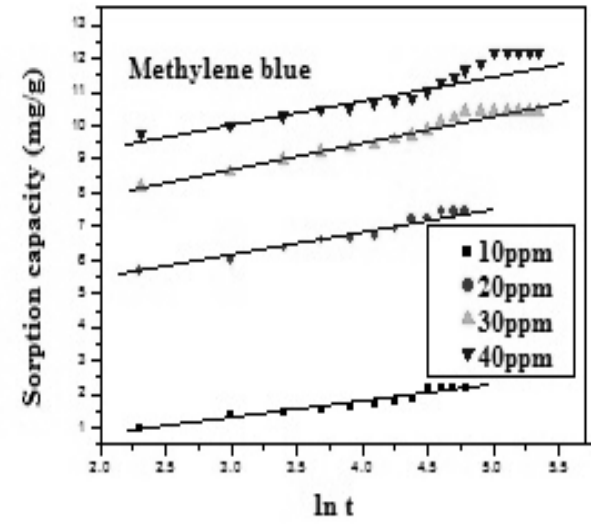


Figure.10 Elovich kinetic model of Stishovite - $TiO_2$ nanocomposite

A plot of $q_t$ vs ln t will be a straight line with a slope of (1/b) and an intercept (1/b) ln (ab). The data obtained in the present study were presented in Figure 10 and Table 2. The linear plots obtained clearly revealed that Elovich model was applicable to the adsorption process under study. Lowering of b values with increase in initial dye concentrations and justification of $t >> t_0$ to predict the behavior of adsorption of dyes over the whole range of variables studied strongly supports the validity of the Elovich equation.

Table.2 Consolidated table for kinetics of adsorption of Methylene blue with Stishovite - $TiO_2$ nanocomposite

| Dye Conc. (mg/L) | $q_e$ exp (mg/g) | Pseudo Second Order | | | | Elovich Kinetic Model | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $q_e$ cal (mg/g) | $k_2$[g/mg/min] | $R^2$ | SSE | $q_e$ cal (mg/g) | 1/b | $R^2$ | SSE |
| 10 | 2.180 | 1.931 | 1.251 | 0.9865 | 0.249 | 1.830 | 0.071 | 0.9984 | 0.350 |
| 20 | 7.430 | 7.055 | 1.626 | 0.9543 | 0.375 | 7.167 | 0.129 | 0.8998 | 0.264 |
| 30 | 10.433 | 10.389 | 1.804 | 0.9328 | 0.044 | 10.401 | 0.196 | 0.8841 | 0.032 |
| 40 | 12.170 | 11.864 | 2.248 | 0.9015 | 0.306 | 11.705 | 1.372 | 0.9982 | 0.465 |

*5.6.3. Intraparticle diffusion equation*

The dye adsorption is governed usually by either the liquid phase mass transport rate or the intraparticle mass transport rate. When the diffusion of dye molecules inside the adsorbent is the rate-limiting step, then adsorption data can be presented by the following equation (Parimaladevi *et al.,* 2011, Crini *et al.,* 2007 and Bhattacharyya *et al.,* 2004):

$q_t = k_{id} t^{1/2} + C$ …….Eq. (E.1)

Where $K_{id}$ is the intraparticle diffusion rate constant and is calculated by plotting qt vs $t^{1/2}$ and the results are given in Figure 11 and Table 3. The linear portion of the plot for does not pass through the origin. This deviation from the origin may be due to the variation of mass transfer in the initial and final stages of adsorption (Aravind *et al.,* 2006). Such a deviation from the origin indicates that pore diffusion is the only controlling step and not the film diffusion.

The plots obtained as seen are multilinear indicating that more than one process affects the adsorption process. As already discussed, the initial sharp portion of the plots represented surface or film diffusion, the linear portion represented gradual adsorption where intraparticle diffusion was rate controlling and the final portion represented equilibrium stage.

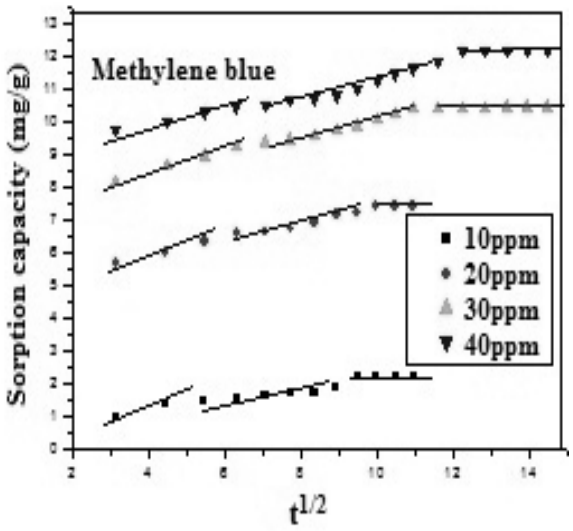


Figure.11 Intraparticle diffusion of Stishovite - $TiO_2$ nanocomposite

Table.3 Intra particle diffusion parameter for Methylene blue with Stishovite - $TiO_2$ nanocomposite at different initial concentrations of solutions

| Conc. of dye (mg/L) | qe exp (mg/g) | qe cal (mg/g) | kid [mg/(g min1/2)] | R2 | SSE |
|---|---|---|---|---|---|
| 10 | 2.180 | 2.064 | 0.501 | 0.9081 | 0.116 |
| 20 | 7.430 | 7.135 | 0.590 | 0.9563 | 0.295 |
| 30 | 10.433 | 10.123 | 0.640 | 0.9931 | 0.310 |
| 40 | 12.170 | 12.035 | 0.780 | 0.9990 | 0.135 |

*5.7. Thermodynamic of Adsorption*

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

$$\ln K_c = \Delta S^0/R - \Delta H^0/R \text{ ……Eq. (F.1)}$$

Where $K_C$ is the Langmuir equilibrium constant, $\Delta H^0$ and $\Delta S^0$ (9.312 kJ/mol), 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 Kc vs 1/T. The free energy change for the adsorption process $\Delta G^0$ (kJ/mol) (2.839 - 2.988 at 301 K – 317 K) is derived using the relation

$$\Delta G^0 = \Delta H^0 - T\,\Delta S^0 \text{ …….....Eq. (F.2)}$$

Negative free energy change and positive entropy change of adsorption indicate that the adsorption process is favourable and spontaneous in nature. The endothermic nature of adsorption is confirmed by the positive $\Delta H^0$ (35.808 kJ/mol) value.

*5.8. Desorption studies*

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

*5.9. Designing batch adsorption from equilibrium data*

A single-stage batch adsorption system can be designed by using the best fit Langmuir adsorption isotherm (Ozacar *et al.*, 2004, Dogan *et al.*, 2000, McKay *et al.*, 1985 and Thomass *et al.*, 1998). A schematic diagram was shown in Figure 12. Consider an effluent containing V $m^3$ of solution and let the dye concentration got reduced from $C_0$ to $C_1$ g dye/metal per $m^3$ solution. The amount of adsorbent was M kg and the solute loading changed from $q_0$ to $q_1$ g dye per kg adsorbent. When fresh adsorbent is used, $q_0$=0 and the mass balance equates the dye removed from the liquid to that picked up by the solid. The mass balance equation for the sorption system in Figure 12 can be written as

$$V\,(C_0-C_1) = M\,(q_0-q_1) = Mq_1 \text{ ---------- Eq. (G.1)}$$

At equilibrium, $C_1 \rightarrow C_e$ and $q_1 \rightarrow q_e$ ---------- Eq. (G.2)

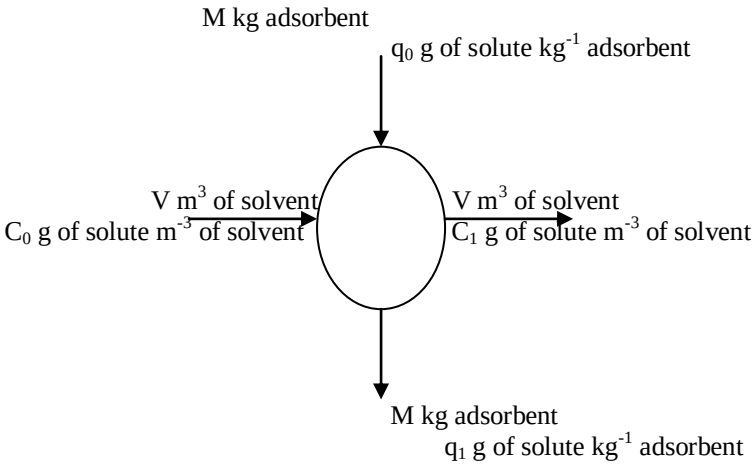


Figure.12 Single stage contacting of a batch of fluid with a batch of adsorbent

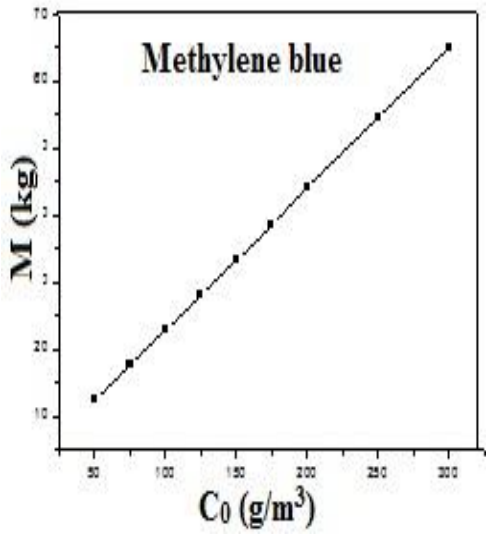


Figure.13 Stishovite - $TiO_2$ nanocomposite required (M) against 50 $m^3$volumes (V) treated for 95% removal at initial dye concentration 50-300g/$m^3$

In the case of the adsorption of Methylene blue used on Stishovite - $TiO_2$ nanocomposite it had been already seen that the Langmuir isotherm gave the best fit to experimental data. Consequently, the Langmuir equation can be best substituted for $q_1$ in the rearranged form of Eq.G.1 giving adsorbent/solution for a given change in dye concentration, $C_0$ to $C_e$, at this particular system

$$\frac{M}{V} = \frac{C_0 - C_e}{q_1} = \frac{C_0 - C_e}{q_e} \equiv \frac{C_0 - C_e}{\frac{K_L C_e}{1 + a_L C_e}} \quad \text{.....(22)}$$

If an initial dye concentration of 50-300 g/$m^3$ was assumed then the amount of Stishovite - $TiO_2$ nanocomposite required for the removal of colour to the extent of 95% at 50 $m^3$ volumes was shown in Figure 13. In the case of a single-stage batch adsorption system, the design procedure can be now outlined. For example let 50$m^3$ of solution was to be treated. Then the amount of Stishovite-$TiO_2$ nanocomposite required for 95% removal can be calculated as 45.96 g for Methylene blue.

The results of present investigation showed that Stishovite - $TiO_2$ nanocomposite have considerable potential for the removal of the dyes selected from aqueous solutions over a wide range of concentrations. It can be concluded that both Stishovite - $TiO_2$ nanocomposite may be used as a viable natural and abundant source for the removal of the dyes and may be an alternative to more costly materials used as adsorbents.

## 6. Conclusion

The present investigation showed that Stishovite-$TiO_2$ nanocomposite can be used as an effective adsorbent for removal of Methylene blue. The amount of dye adsorbed varied with initial dye concentration, adsorbent dose, $p^H$ and temperature. Removal of Methylene blue by nanocomposite obeyed both Langmuir and Freundlich isotherms. The adsorption process followed pseudo second order kinetics. This has been further supported by Elovich 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. Assuming the batch adsorption to be a single staged equilibrium operation, the separation process was defined mathematically using the Langmuir isotherm to estimate the amount of adsorbent required for a desired stage of purification.

The results of the present investigation showed that Stishovite - $TiO_2$ nanocomposite have considerable potential for the removal of Methylene blue from aqueous solutions over a wide range of concentration. It can be concluded that Stishovite - $TiO_2$ nanocomposite may be used as natural and abundant source for the removal of dyes may be an alternative to more costly materials. They may be also effective in removing as well other harmful or undesirable species such as heavy metals, dyes and other hazardous pollutants present in waste effluents.

## References


Allen, S.J McKay, G and Porter, J.F. (2004). Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems, *Jounal of Colloid and Interface Science* 280, pp. 322-333.

Aravind, V and Elango, K.P. (2006). *Indian Journal of Chemical Technology*, 13, pp. 476.

Arivoli, S., Sundaravadivelu, M and Elango, K.P. (2007). *Environmental Science Indian Journal*, 2, pp. 167.

Bhattacharyya, K.G, Sharma, A. (2004). Azadirachta indica leaf powder as an effective biosorbent for dyes: a case study with aqueous congo red solutions, *Journal of Environmental Management*, 71, pp. 217-229.

Crini, G., Peindy, H.N., Gimbert, F and Robert, C. (2007). Removal of C.I. Basic green 4 (malachite green) from aqueous solutions by adsorption using cyclodextrin based adsorbent: kinetic and equilibrium studies, *Separation Purification Technology*, 53, pp. 97-110.

Dogan, M., Alkan, M., and Onguner, Y. (2000). Adsorption of methylene blue on perlite from aqueous solutions, *Water, Air, Soil Pollution* 120, pp. 229-248.

Ho, Y.S and McKay, G. (1998) "a". A comparison of chemisorption kinetic models for the sorption of dye from aqueous solution by wood, *Chemical Engineering Transactions*, 76, pp. 183-191.

Ho, Y.S and McKay, G. (1998) "b". The kinetic of sorption of basic dyes from aqueous solution by sphagnum moss peat, *Canadian Journal of Chemical Engineering* 76, pp. 822.

Ho, Y.S and McKay, G. (1998) "c". A comparison of chemisorption kinetic models for the sorption of dye from aqueous solution by wood, *Chemical Engineering Transactions*, 76, pp. 183-191.

Ho, Y.S and McKay, G. (1999). Pseudo-second order model for sorption processes, *Process Biochemistry*, 34, pp. 451-465.

Low, M.J.D. (1960). Kinetic modeling of liquid phase adsorption of reactive dyes and metal ions on chitosan, *Chemical Reviews*, 60, pp. 267-312.

Lorene-Grabowska, E and Gryglewiez, G. (2007). Adsorption characteristics of congo red on coal-based mesoporous activated carbon, *Dyes Pigments*, 74, pp. 34-40.

Mall, I.D., Srivastava, V.C., Agarwall, N.K., Mishra, I.M. (2005). Removal of congo red from aqueous solution by bagasse fly ash and activated carbon: kinetic study and equilibrium isotherm analysis, *Chemosphere*, 61, pp. 492-501.

McKay, G., Otterburn, M.S and Aga, J.A. (1985). Fuller's earth and fired clay as adsorbents for dyestuffs equilibrium and rate studies, *Water, Air, Soil Pollution*, 24, pp. 307-322.

Namasivayam, C., Muniasamy, N., Gayathri, K., Rani, M and Renganathan, K. (1996). *Bioresource Technology*, 57(1), pp. 37-43.

Namasivayam , C and Yamuna, R.T. (1995). *Environmental Pollution* 89(1), PP. 1-7.

Norrozi, B., Sorial, G.A., Bahrami, H and Arami, M. (2007). Equilibrium and kinetic adsorption study of a cationic dye by a natural adsorbent-silkworm pupa, *Journal of Hazardous Materials B*, 139, pp. 167-174.

Ozacar, M and Sengil, I.A. (2003) "a". Adsorption of reactive dyes on calcined alunite from aqueous solutions, *Journal of Hazardous Materials B*, 98, pp. 211-224.

Ozacar, M. (2003) "b". Equilibrium and kinetic modeling of adsorption of phosphorous on calcined alunite, *Adsorption*, 9, pp. 125-132.

Ozacar, M and Sengil, I.A. (2004) "a". Equilibrium data and process design for adsorption of disperse dyes onto alunite, *Environmental Geology*, 45, pp. 762-768.

Ozacar, M and Sengil, I.A. (2004) "b". Application of kinetic models to the sorption of disperse dyes onto alunite, *Colloids Surface A: Physicochemical Engineering A*spects, 242, pp. 105-113.

Ozer, A., Akkaya, G and Turabik, M. (2005). Biosorption of acid red on enteromorphaprolifera in a batch system, *Journal of Hazardous Materials B*, 126, pp. 119-127.

Ozacar, M. (2006). Contact time optimization of two stage batch adsorber design using second-order kinetic model for the adsorption of phosphate onto alunite, *Journal of Hazardous Materials B*, 137, PP. 218-225.

Parimaladevi, P and Venkateswaran, V. (2011). Kinetics, thermodynamics and isothermal modeling of adsorbtion of triphenyl methane dyes (Methyl violet, Malachite green and Magenta-2) onto fruit waste, *Journal of Applied Technology in Environmental Sanitation* 1(3) pp. 273-283.

Parimaladevi, P and Venkateswaran, V. (2011). Adsorption of cationic dyes (Rhodamine b and Methylene blue) from aqueous solution using treated fruit waste, *Journal of Applied Technology in Environmental Sanitation* 1(3), pp. 285-293.

Stydini, M., Dimitris, I.K and Verykios, X.E. (2004). Visible light-enduced photocatalytic degradation of acid orange 7 in aqueous $TiO_2$ suspensions, *Applied Catalysis Environmental* 47, pp.189.

Thomass, W.J and Crittenden, B. (1998). Adsorption Technology and Design, Butterwort-Heinemann, Woburn.

Venkateswaran, V and Priya, V.T. (2012). Adsorption kinetics and thermodynamics of removal of basic dyes by Stishovite clay - $TiO_2$ nanocomposite, *Journal of Applied Technology in Environmental Sanitation* 2(1), pp. 7-16.

Venkateswaran, V and Priya, V.T. (2012). Equilibrium and Kinetics of Adsorption of Cationic Dyes by Stishovite Clay – $TiO_2$ nanocomposite, *International Journal of Modern Engineering Research* 2(6), pp. 3989-3995.