Removal of Methyl Violet and Auramine Yellow from Stishovite Clay

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Abstract: *The adsorption behaviour of Methyl violet and Auramine yellow from aqueous solution onto Stishovite clay was investigated as a function of parameters such as initial dye concentration, contact time, p^H and temperature. The Langmuir and Freundlich adsorption models were applied to describe the equilibrium isotherms. Adsorption followed pseudo-second order model. The experimental data fitted well with both Langmuir and Freundlich isotherms.*

Keywords: Stishovite clay, Methyl violet, Auramine yellow, Adsorption kinetics and isotherm

1.Introduction

Colored materials and dyes are the cause for many environmental concerns because of their non-biodegradable and polluting nature [1,2]. Thus, prior to their discharge into receiving waters, there is a considerable need to efficiently treat the colored effluents [3]. There are several physicochemical processes for the removal and recovery of colored materials and dyes from effluents, out of which adsorption is one of the most effective one [4-5]. The important aspect of the adsorption process is the ready availability of the adsorbents and less operational cost. Adsorption techniques have proven to be successful in removing the colored organic species but the effectiveness of any adsorption process depends on the choice of the adsorbent.So far several studies on the utility of low cost materials for the removal of dyes from aqueous solutions have been reported. Numerous materials such as coal, perlite, alunite, clay materials (bentonite, montmorillonite, etc.) activated slag and agricultural wastes (bagasse pith, maize cob, rice husk, waste fruit residues etc [6-8] have been used as adsorbents for removing dyes from effluents.

The present study is focused on exploring the efficiency of stishovite clay as an adsorbent in removing Methyl violet and Auramine yellow from aqueous solutions.

2.Materials and Methods

Absorbate solution
A stock solution (1000 mg/L) of Methyl violet and Auramine yellow, 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.

Characterization of adsorbent

Physico-chemical characteristics of the adsorbents were studied as per the standard testing methods. The XRD pattern of Stishovite clay (Fig.1) showed characteristic peaks at 30° confirming the presence of Stishovite phase in the clay. The surface morphology of the adsorbents was visualized via scanning electron microscopy (SEM) (Fig.2).

The diameter of the clay range was 100μm.

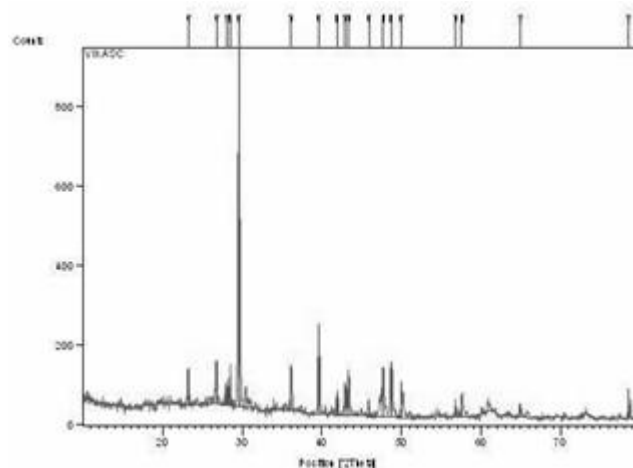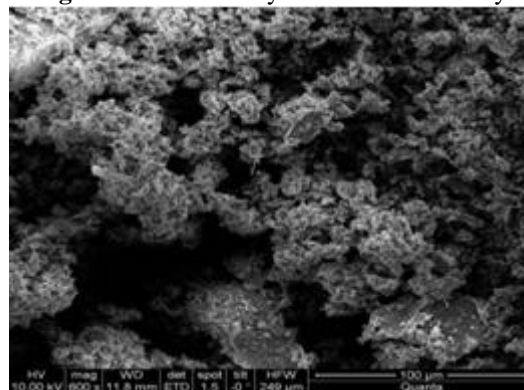**Figure 1:** .XRD analysis of Stishovite Clay

Figure 2: SEM of Stishovite Clay

3.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

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solution (50 mL) with different amounts of adsorbent was taken to study the effect of adsorbent dosage.

4. Results and Discussion

4.1. Effect of contact time and initial dye concentration

The experimental results of adsorptions at various concentrations (10, 20, 30 and 40 mg/L) on clay was shown in Fig.3. It was observed that the percentage removal at equilibrium was found to increase from 64.35 % to 90.44 % for Methyl violet and 57.76 % to 92.88 % for Auramine yellow as the initial dye concentration was increased from 10 mg/L to 40 mg/L. At lower concentrations, 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 higher concentrations the available sites of adsorption become fewer and hence the percentage removal of dye becomes dependent upon initial concentration [9,10].The equilibrium was found to get established at 90,110,185 and 195 minutes for Methyl violet and 80,110,135 and 150 minutes for Auramine yellow with the adsorbent 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 [11].
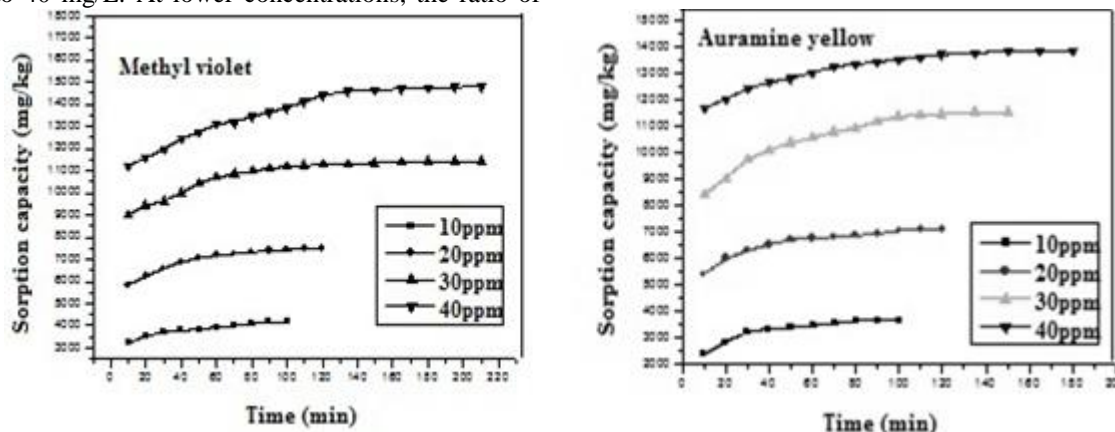

Figure 3: Effect of contact time and initial dye concentration of Methyl violet & Auramine yellow on Stishovite clay
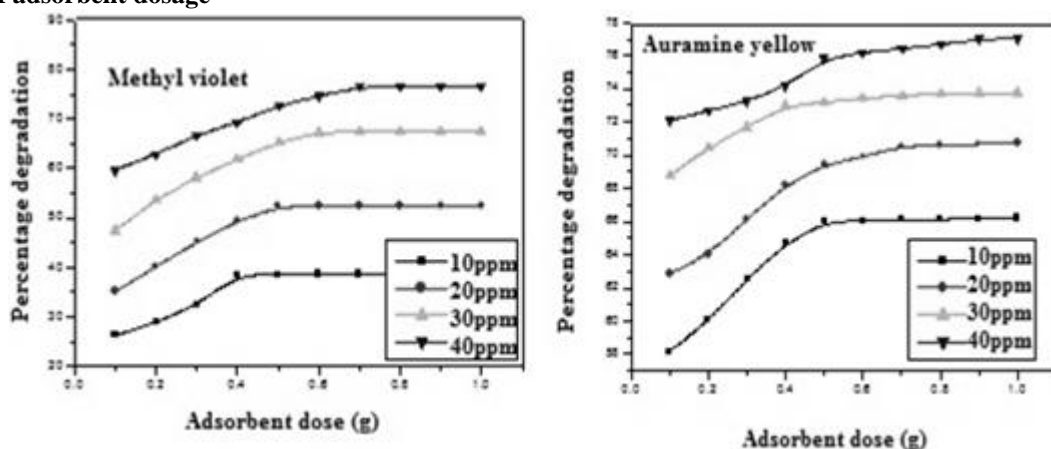
4.2. Effect of adsorbent dosage

Figure 4: Effect of adsorbent dosage of Methyl violet & Auramine yellow on Stishovite clay

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. 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 [12].

4.3. Effect of p^H

Adsorption experiments were carried out at various p^H values ranging from 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. Fig.5 indicates that maximum dye removal had occurred in basic medium.
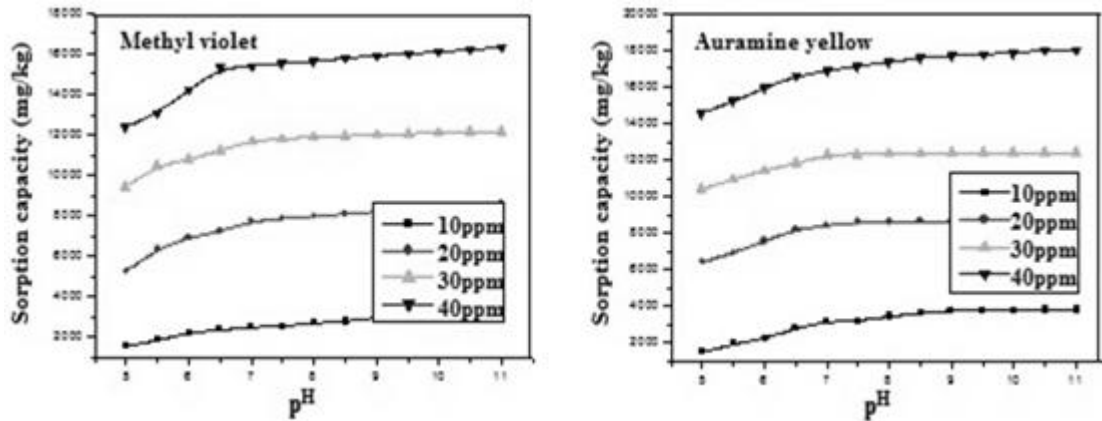
Figure 5: Effect of p^H of Methyl violet & Auramine yellow on Stishovite clay

4.4. Effect of Temperature

Temperature has an important effect on the adsorption process. The amount of basic dye adsorbed increases (Fig.6) with increase in temperature from 301K to 317K, indicating the adsorption process to be endothermic. This may be attributed to the increase in the rate of diffusion of adsorbate molecules across the external boundary layer and internal pores of adsorbent particle [13].
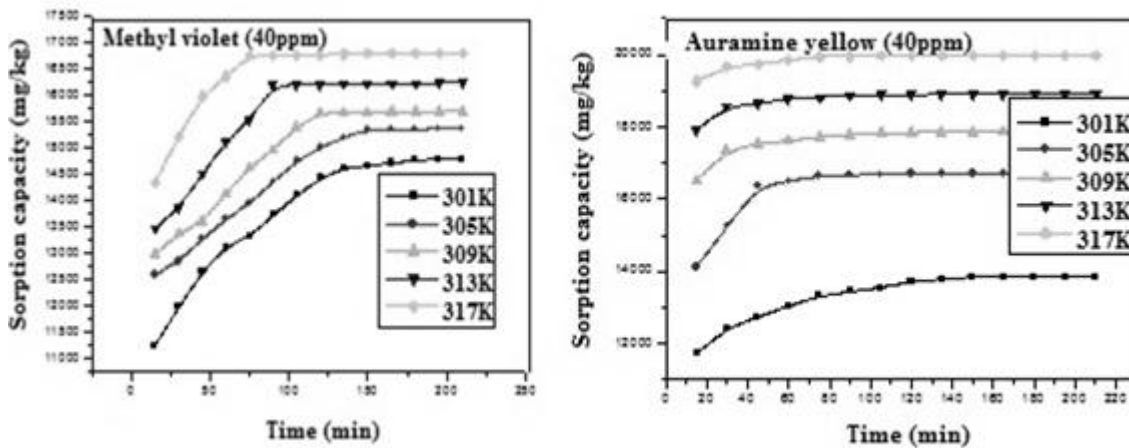

Figure 6: Effect of Temperature of Methyl violet & Auramine yellow on Stishovite clay

4.5. 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.

4.5.1. Langmuir isotherm [14]
The Langmuir isotherm is represented as follows:

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

Where q_e (mg/g) and C_e (mg/L) are the amount of adsorbent dye per unit weight of adsorbent and unadsorbed dye concentration in solution at equilibrium respectively. The K_L (L/g) and a_L (L/mg) are the Langmuir isotherm constants. These 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 isotherm was found to be linear over the entire concentration range studied with a good linear correlation coefficient (R^2 =0.9901 and 0.9901) showing that data correctly fit into the Langmuir isotherm confirming the monolayer coverage of dye onto Stishovite clay and also the homogeneous distribution of active sites on the adsorbent.
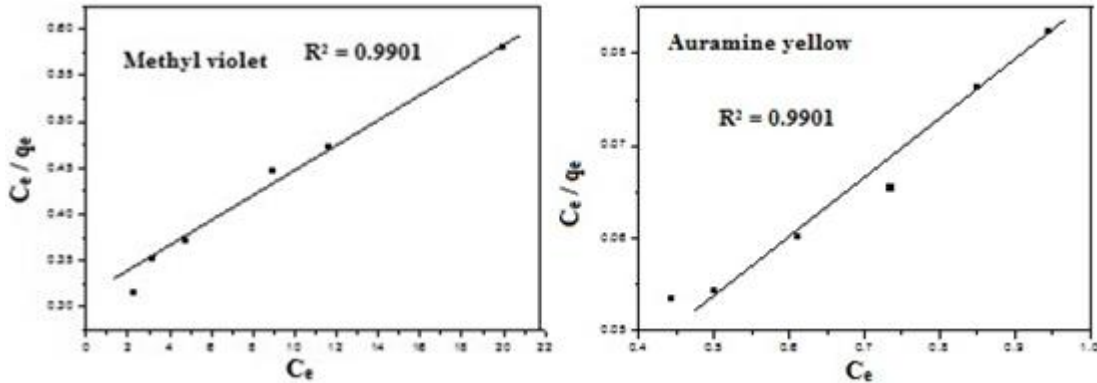
Figure 7: Langmuir model of Methyl violet & Auramine yellow on Stishovite clay

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless separation factor [2,13] (R_L, also called as equilibrium parameter) defined as

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

Where C_0 (mg/L) is the initial dye concentration and a_L (L/mg) is the Langmuir constant related to the energy of adsorption. The value of R_L indicates the shape of the isotherms to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). It was observed that in this study the R_L values are in between 0 and 1 confirming the favourable uptake of both Methyl violet and Auramine yellow on the adsorbent.

4.5.2. Freundlich isotherm [15]

In the linear form the Freundlich isotherm can be expressed as

$$log q_e = log K_F + \frac{1}{n} log C_e \dots \dots \dots \dots \dots \dots \dots Eq.(B.1)$$

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 (Fig.8) with a regression coefficient of 0.9964 and 0.9902 showing the data fit well with freundlich isotherm also. The value of n was evaluated as 1.667 and 1.284 indicate that the process was favorable. The value of K_f was found to be 10.026 and 5.248 [mg$^{1-1/n}$ L$^{1/n}$ g^{-1}] respectively for Methyl violet and Auramine yellow.
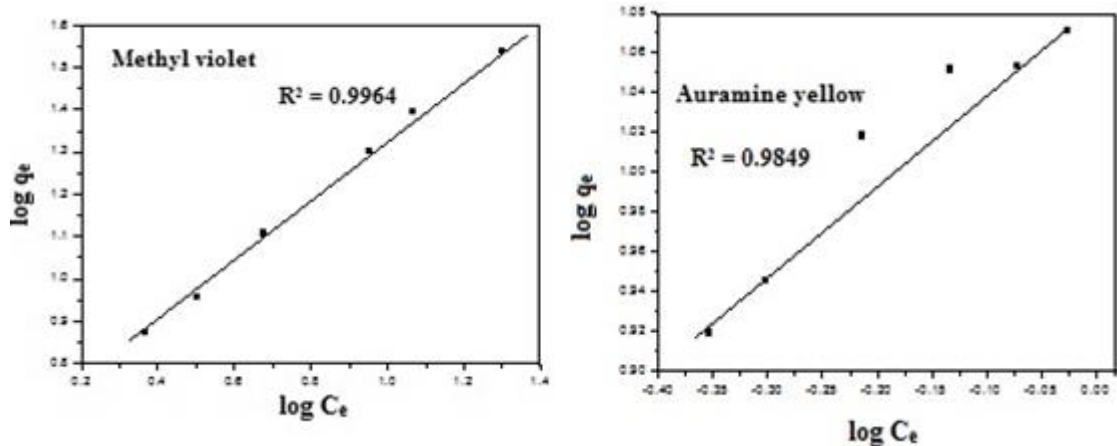

Figure 8: Freundlich model of Methyl violet & Auramine yellow on Stishovite clay

4.6. Kinetics of Adsorption

In order to investigate the mechanism of adsorption of Methyl violet and Auramine yellow by the adsorbent used in this study the following four kinetic models were considered.

4.6.1. Pseudo-Second Order Kinetic Model
The pseudo second order kinetic rate equation was usually expressed as [16-18]:

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

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 $q_t = q_e$

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

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

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

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[19]. The results for the adsorption of Methyl violet and Auramine yellow studied on the clay were

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shown in Fig.9.The linearity of the plots clearly indicated that the adsorption process followed pseudo second order kinetics.
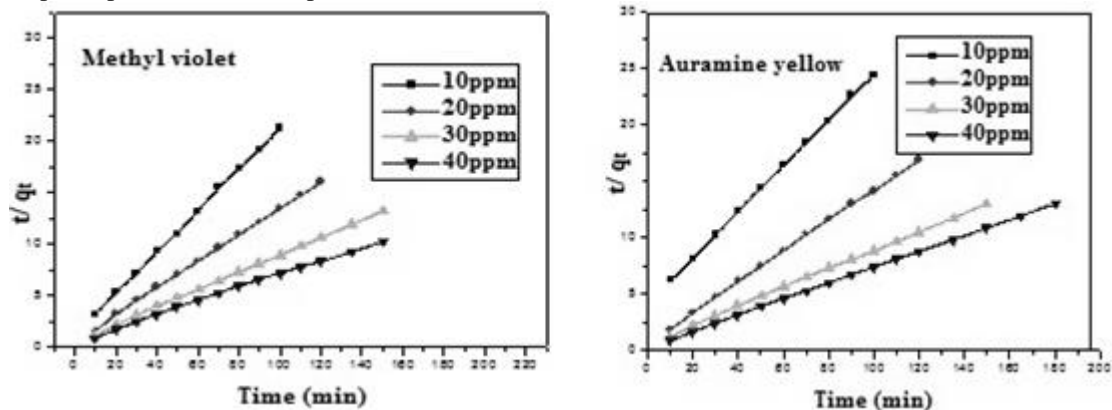

Figure 9: Pseudo-second order kinetic model of Methyl violet & Auramine yellow on Stishovite clay

5.Conclusion

The present investigation showed that Stishovite clay can be used as an effective adsorbent for removal of Methyl violet and Auramine yellow. The amount of dye adsorbed varied with initial dye concentration, adsorbent dose, p^H and temperature. Removal of both basic dyes by stishovite clay obeyed both Langmuir and Freundlich isotherms. The adsorption process followed pseudo second order kinetics.

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