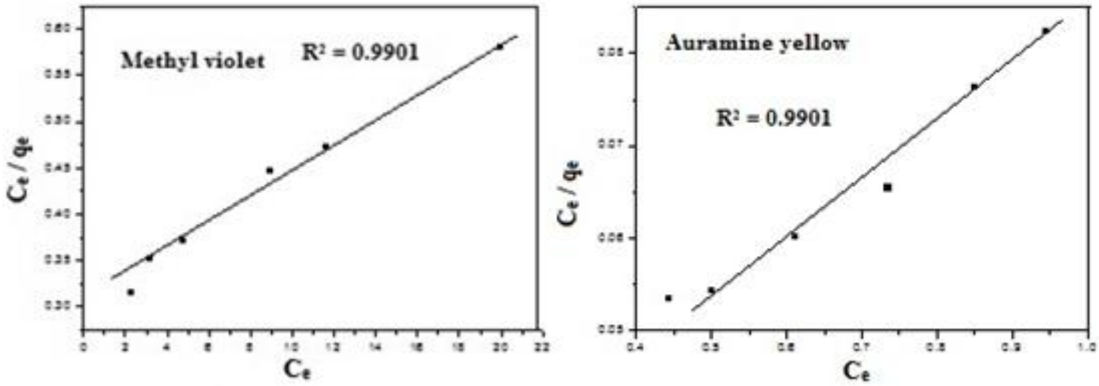

Figure 7: Langmuir model of Methyl violet & Auramine yellow on Stishovite clay

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

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

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.

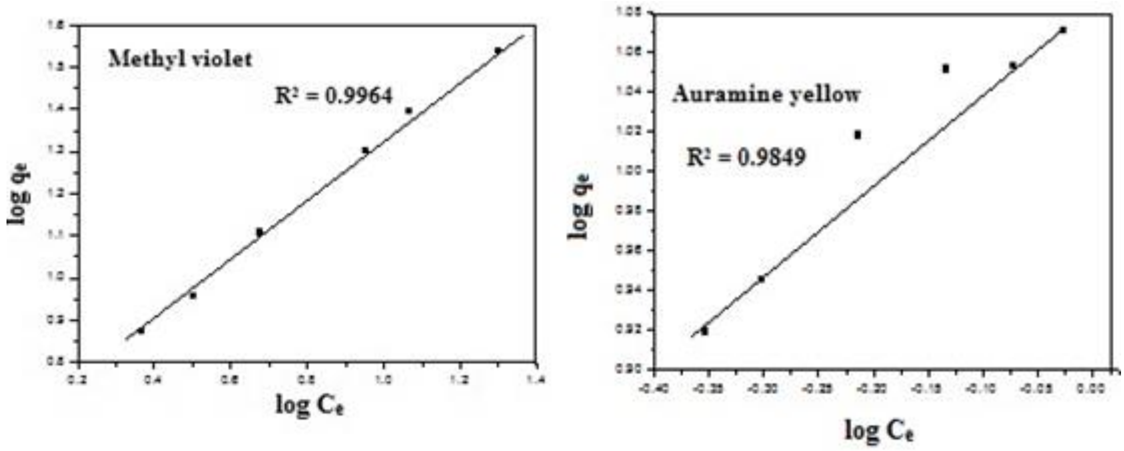

Figure 8: Freundlich model of Methyl violet & Auramine yellow on Stishovite clay

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]:

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

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 $q_t = q_e$

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

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

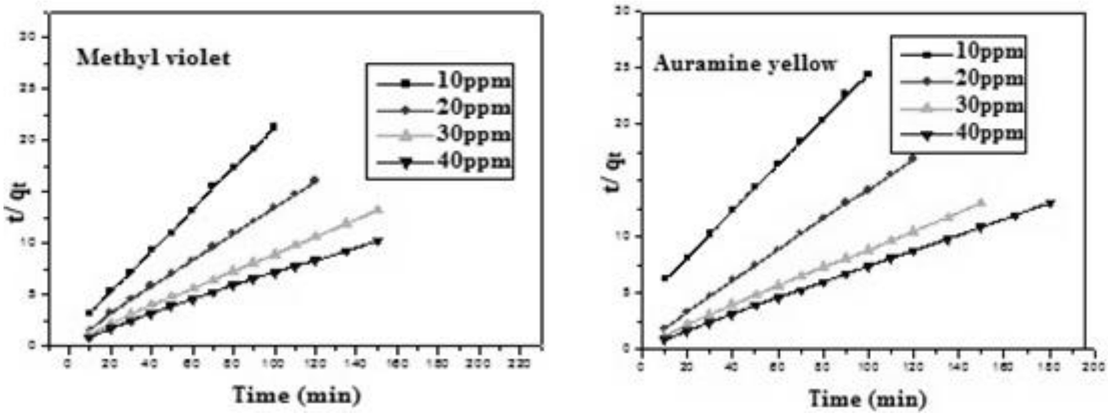

Figure 9: Pseudo-second order kinetic model of Methyl violet & Auramine yellow on Stishovite clay

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.

References

[1] Collins, P., & Downham, A., Coloring our foods in the last and next millennium, International Journal of Food Science and Technology, **35**, 5-22, (2000).
[2] Zollinger, H., Synthesis, properties and applications of organic dyes and pigments, color chemistry, 2^{nd} revised edition, New York: VCH, (1991).
[3] Poots., Removal of acid dye from effluent using natural adsorbents. 1. Peat. Water Research, **10**, 1061-1066, (1976).
[4] Nyholm., Removal of organic micro pollutants at ppb levels in laboratory activated-sludge reactors under various operating conditions-biodegradation, Water Research, **26**, 339-353, (1992).
[5] Mavros., Color removal from aqueous solutions. 1. Flotation. Environmental Technology, **15**, 601, (1994).
[6] Mall, I.D., Removal of congo red from aqueous solution by bagasse fly ash and activated carbon: kinetic study and equilibrium isotherm analysis, Chemosphere **61**, 492-501, (2005).
[7] Dogan , M., Alkan, Y. Onguner, Adsorption of methylene blue on perlite from aqueous solutions, Water, Air, Soil Pollution **120**, 229-248, (2000).
[8] Parimaladevi, P., & Venkateswaran, V., 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)**, 273-283, (2011).
[9] Namasivayam, C ., Bioresource Technology **57(1)**, 37-43, (1996).
[10] Namasivayam, C., & Yamuna, R.T., Environmental Pollution **89(1)**, 1-7, (1995).
[11] Arivoli, S., Environmental Science Indian Journal **2**, 167, (2007).
[12] Ozer, A., Biosorption of acid red on enteromorphaprolifera in a batch system, Journal of Hazardous Materials **B 126**, 119-127, (2005).
[13] Norrozi, B., Equilibrium and kinetic adsorption study of a cationic dye by a natural adsorbent-silkworm pupa, Journal of Hazardous Materials **B 139**, 167-174, (2007).
[14] Crini, G., 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**, 97-110, (2007).
[15] Ozacar, M., & Sengil, I.A., Adsorption of reactive dyes on calcined alunite from aqueous solutions, Journal of Hazardous Materials B **98**, 211-224, (2003).
[16] Ho, Y.S., & McKay, G., Pseudo-second order model for sorption processes, Process Biochemistry **34**, 451-465, (1999).
[17] Ozacar, M., & Sengil, I.A., Application of kinetic models to the sorption of disperse dyes onto alunite, Colloids Surface A: Physicochemical Engineering Aspects **242**, 105-113, (2004).
[18] Ozacar, M., Equilibrium and kinetic modeling of adsorption of phosphorous on calcined alunite, Adsorption **9**, 125-132, (2003).
[19] Ho, Y.S., & McKay, G., A comparison of chemisorption kinetic models for the sorption of dye from aqueous solution by wood, Chemical Engineering Transactions **76**, 183-191, (1998).