Research Journal of Chemical Sciences ISSN 2231-606X
Vol. **3(2),** 65-72, February **(2013)** *Res. J. Chem. Sci.*

Adsorption Kinetics of Methylene Blue onto Clay Fractionated from Bijoypur Soil, Bangladesh

Y. Zaker, M. A. Hossain* and T. S. A. Islam
Department of Chemistry, University of Dhaka, Dhaka-100, BANGLADESH

Available online at: www.isca.in
Received 21st December 2012, revised 14th January 2013, accepted 27th January 2013

Abstract

The adsorption kinetics of methylene blue (MB) from aqueous solution onto clay fractionated from Bijoypur (Netrokona) soil based on particle size (≤53µm) has been investigated. Batch studies were carried out to investigate the effect of contact time, initial dye concentration and temperature on adsorption kinetics. Kinetic studies showed a rapid adsorption during the first thirty minutes. Application of pseudo first order, pseudo second order and intra particle diffusion model equations showed that the experimental results are well expressed by pseudo second order kinetic equation. Adsorption isotherm was constructed from the pseudo second order kinetic data. Maximum adsorption capacity, calculated from well fitted Langmuir equation, is 6.93 mg/g which increased with increase in temperature. The positive value of enthalpy change (ΔH^o=20.98 kJ/mol) and negative free energy change (ΔG^o) indicated that the adsorption of MB on clay is endothermic and involve chemical process. Verification of intra-particle diffusion model showed that intra-particle diffusion could be one of the rate determining steps but pseudo second order mechanism is predominant. Overall adsorption process appears to be controlled by more than one step.

Keywords: Adsorption kinetics, clay, batch study, pseudo first order, pseudo second order, thermodynamic parameters, intra particle diffusion and step-wise adsorption.

Introduction

Wastewaters from textile industries commonly contain moderate concentrations (10-200 mg/L) of dyestuffs, contributing significantly to the pollution of aquatic ecosystem[1]. Various physicochemical and biological techniques can be employed to remove dyes from wastewaters. In comparison with other techniques adsorption is superior in simplicity of design, initial cost, ease of operation and insensitivity to toxic substances. The removal of dye from wastewater by activated carbon[2-4], polymeric resins[5-6], sugarcane baggase[7], clay minerals[8] and several biosorbents[9-10] has been reported widely. A survey of literature revealed that methylene blue (MB) has been used particularly for adsorption studies, not only because of its environmental concern but also for the fact that it has been recognized as a model adsorbate for adsorption of organic because of it known strong adsorption to clay minerals[11]. Despite of many investigations to study adsorption of MB on clay, specific mechanism by which the adsorption of MB takes place on clay is still ambiguous[12]. Kinetics is concern fundamentally with the details of the process whereby a system gets from an initial state to final state and the time required for the transition, hence it gives ideal about the mechanism of adsorption. The availability of the kinetic model equations for the study of adsorption process on activated carbon permits a rational approach to study the mechanism of the adsorption process. It has been reported that over 25 kinetic models has been referenced in available literature, all attempting to describe quantitatively the kinetic behavior during the adsorption process. Each adsorption kinetic model has its own limitation and derived according to certain initial conditions based on certain experimental and theoretical assumptions[13]. Two of the most used empirical equations worth mentioning are the pseudo first and second order. The aim of this present study is to establish the mechanism of adsorption of MB onto the clay fractionated from Bijoypur clay minerals from the kinetic study and evaluate the capacity of a low cost adsorbent to remove MB. Batch studies were carried out involving process parameters such as the initial dye concentration, solution temperature and contact time. Equilibrium and kinetic analysis were conducted to understand adsorption process and optimization of various parameters.

Material and Methods

Adsorbent: Soil sample collected from Bijoypur (Netrokona) was fractionated conducting standard and well known hydrometer method[14] based on particle size to three different fractions such as sand (≥140µm), silt (53-140µm) and clay (≤53µm). Smallest sized fraction is clay which without further treatment was characterized[15] by SEM, LIBS, FT-IR and XRD. This clay was used as an adsorbent.

Adsorbate: Methylene blue (CI: 52015) is a heterocyclic aromatic chemical compound with the molecular formula $C_{16}H_{18}N_3SCl$. The IUPAC name of methylene blue is 3,7-bis(Dimethylamino)-phenothiazin-5-ium chloride and structural formula is shown in figure-1. Its CAS No. is 61-73-4 and molar

mass 319.85 g/mol. Methylene blue is highly soluble in water and the hydrated form has 3 molecules of water per molecule of methylene blue. Laboratory grade methylene blue (MB) supplied by Janssen Chemical, Belgium was used without further purification for the preparation of aqueous solution.

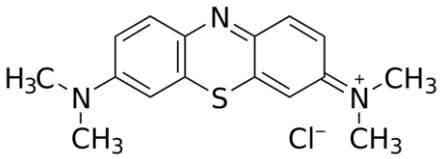

Figure-1
Structural formula of Methylene blue

Adsorption experiments: The stock solution was prepared by dissolving 0.016 g MB in 500 mL of distilled water. Serial dilutions were made to obtain the required lower concentrations of MB in the range of 3.5 to 28.5 mg/L. The pH of each MB solution was maintained at 7.0. For each of the kinetic experiment, 40 mL of MB solution of known initial concentration and 0.1 g of clay were taken in a 60 mL reagent bottles (Pyrex glass, England) with air tight stopper. This mixture was agitated in a temperature controlled water bath shaker (HAAKE SWB20, Fissions Ltd., Germany) at 30°C with a constant shaking speed of 110 rpm. The flasks were agitated for a time interval of 15, 30, 45, 60, 75 and 90 minutes and the clay was separated from the mixture by centrifuge. The concentration of MB in the supernatants was determined by measuring the absorbance at λ_{max} of 663 nm using UV-visible spectrophotometer (UV-1650 PC Shimadzu, Japan). The amount adsorbed (q_e) were calculated in equation (1):

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

where, C_o is the initial concentration of MB (mg/L) and C_e is the equilibrium concentration of MB (mg/L), m is the weight of clay used for the adsorption studies (g) and V is the volume of MB solution (L). Similar kinetic experiments were also performed at 40 and 50°C to determine the effect of temperature on adsorption kinetics.

Results and Discussion

Effect of contact time and initial concentration: Effect of contact time on the adsorption is the fundamental basis of the adsorption kinetics. Figure-2 shows the variation of amount adsorbed of MB on clay with contact time. It shows that the amount adsorbed increased at first thirty minutes to a near constant value with increase of contact time. Again, most of the adsorption occurred within first 60 minutes for different initial concentrations and adsorption became very slow at later. This may be attributed to lack of available active sites required for the high initial concentration of dye[16]. The amount adsorbed increased from 1.29 to 6.93 mg/g within first 60 minutes of contact of MB with clay as the initial concentration increased from 3.5 to 28.5 mg/L.

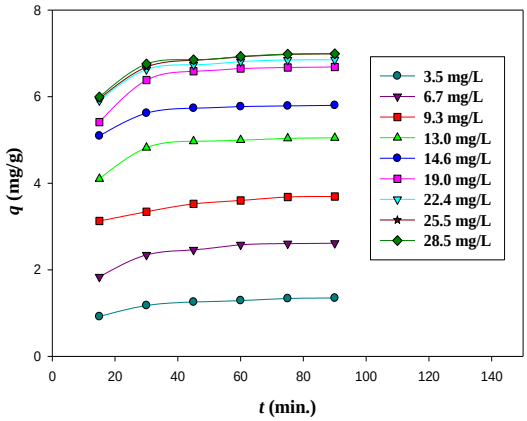

Figure-2
Effect of contact time and initial concentration for adsorption of MB on clay

Different kinetic model equations were applied to the above observation to verify the nature of adsorption kinetics. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficients (R^2, values close or equal to 1).

Largergren pseudo first order equation: Pseudo-first order rate equation is commonly used to the adsorption of liquid/solid system based on adsorbent capacity[17]. According to this model, one adsorbate species reacts with one active site on surface. The differential form of the equation is generally expressed as,

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2)$$

where, q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg/g), k_1 is the rate constant of pseudo first order equation (L/min). Integrating equation (2) for the boundary conditions $t = 0$–t and $q_t = 0$–q_t gives:

$$\ln\left(\frac{q_e}{q_e - q_t}\right) = k_1 t \quad (3)$$

Equation (3) can be rearranged to obtain the following linear form:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

In order to obtain the rate constants, the values of $\ln(q_e - q_t)$ were linearly correlated with t by plot of $\ln(q_e - q_t)$ versus t to give a linear relationship from which k_1 and predicted q_e can be determined from the slope and intercept of the plot, respectively[18]. The variation in the rate should be proportional to the first power of concentration of adsorbate. However, the relationship between initial solute concentration and rate of adsorption will not be linear when pore diffusion limits the adsorption process. The applicability of the pseudo-first order equation to experimental data generally, differs in two ways; the parameter does not represent the number of available sites and the parameter ln q_e is an adjustable parameter and often found

not equal to the intercept of the plot $\ln(q_e - q_t)$ versus t, whereas in true first order, $\ln q_e$ should be equal to the intercept[19]. Figure-3 shows the weak fitness of pseudo-first order plots at different initial concentrations. Values of correlation coefficients and different parameters for different concentration of MB are given in table-1. The results showed that the pseudo first order rate constant, k_1 is irregularly changes with concentration i.e. k_1 independent of initial concentration. Similar result has been presented in literatures[11,18,20]. However, the experimental adsorption capacity was observed to increase with increase in initial concentration.

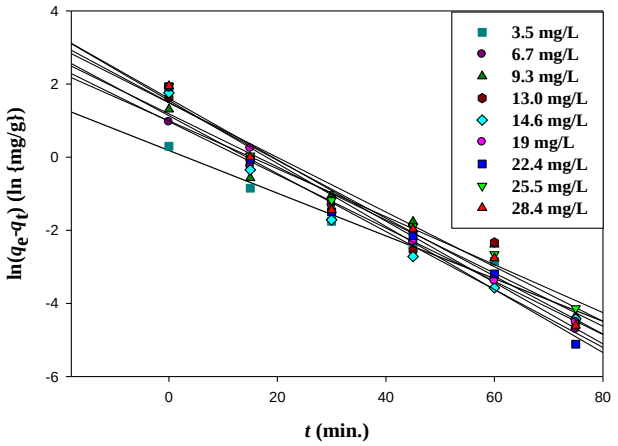

Figure-3
Pseudo first order kinetic model plots for adsorption of MB on clay at different concentrations

Pseudo second order kinetics: Pseudo-second order rate equation was applied to the adsorption kinetics of the present system[21]. The model was derived on the basis of the concentration of the adsorbate in the adsorbent phase[21]. The pseudo second order rate equation is expressed (5) as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (5)$$

where, k_2 is the rate constant of the pseudo second order adsorption (g/mg·min). For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_e$ the integrated form of the equation becomes

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \qquad (6)$$

Equation (6) can be rearranged to the linear form as below (equation 7):

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \qquad (7)$$

If the initial adsorption rate (mg/g·min), $h = k_2 q_e$, then the equation (7) becomes

$$\frac{t}{q_t} = \frac{1}{hq_e} + \frac{t}{q_e} \qquad (8)$$

The plot of t/q_t versus t of equation (7) should give a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively. The linear plots of t/q_t against t, as shown in figure-4, represent the good fit (R^2 = 0.999) over the whole range of initial concentration of MB and contact time. Pseudo-second order rate equation was derived by assuming that two surface sites could be occupied by one divalent adsorbate ion. Thus the equation (7) would be expected to be applicable for the adsorption of methylene blue ions due to the existence of divalent form of methylene blue $(MB^+)_2$ and/or MBH^{2+} in aqueous solution[22]. The pseudo-second order mechanism is found to be predominant during the adsorption kinetics of MB onto clay[23] and *Polyalthia Longifolia* seed powder[24]. The pseudo-second order rate constants, initial rate constant and equilibrium amount adsorbed for different initial concentrations were calculated from the linear plots of t/q_t *vs.* t and are shown in figure-4 and presented in table-2. The value of pseudo second order rate constant k_2 varied from 0.043 to 0.083 as the initial concentration increased from 3.5 to 28.5 mg/L. The equilibrium adsorption capacity calculated from pseudo second order rate equation, $(q_e)_{cal}$ increased from 1.48 to 7.23 as the initial concentration was increased from 3.5 to 28.5 mg/L.

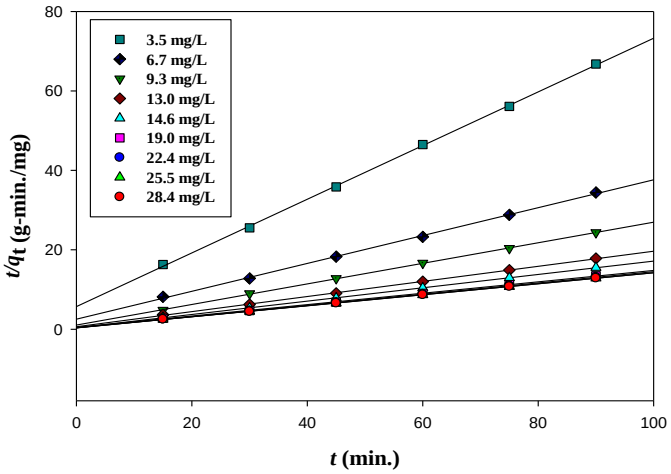

Figure-4
Pseudo second order kinetic plots for adsorption of MB on clay at different concentrations

Test for the fitness of kinetic models: The sum of square of error (SSE, %) is one method which has been used in literature to test the validity of each model that has been used. The sum of square of error is,

$$SSE(\%) = \sqrt{\sum \frac{\{(q_e)_{expt} - (q_e)_{cal}\}^2}{N}} \times 100 \qquad (9)$$

Table-1
Different parameters of pseudo first-order kinetic model for the adsorption of MB on clay at 30°C

C_o (mg/L)	k_1 (1/min)	$q_{e\ (expt)}$ (mg/g)	$q_{e\ (cal)}$ (mg/g)	R^2	SSE (%)
3.5	0.058	1.348	1.704	0.971	1.774
6.7	0.073	2.614	2.647	0.988	
9.3	0.066	3.694	3.369	0.946	
13.0	0.067	5.048	3.264	0.937	
14.6	0.079	5.799	3.108	0.964	
19.0	0.084	6.685	4.963	0.992	
22.4	0.086	6.853	4.716	0.976	
25.5	0.075	6.991	4.419	0.973	
28.5	0.079	6.992	4.464	0.965	

Table-2
The constant parameters of the pseudo second-order kinetic model for the adsorption of MB on clay at 30°C

C_o (mg/L)	k_2(g/mg·min)	$q_{e(exp)}$ (mg/g)	$q_{e\ (cal)}$ (mg/g)	h (mg/g·min)	R^2	SSE (%)
3.5	0.080	1.348	1.480	0.118	0.9996	0.2118
6.7	0.058	2.614	2.849	0.140	0.9991	
9.3	0.063	3.694	3.863	0.243	0.9997	
13.0	0.049	5.048	5.258	0.305	0.9995	
14.6	0.083	5.799	5.945	0.493	0.9998	
19.0	0.043	6.685	6.979	0.300	0.9994	
22.4	0.060	6.853	7.057	0.423	0.9998	
25.5	0.050	6.991	7.225	0.361	0.9998	
28.5	0.056	6.992	7.205	0.404	0.9993	

where, N is the number of data points. The values of SSE (%) for the pseudo first and pseudo second kinetic models are given in table-1 and 2, respectively. It can be seemed that the SSE (%) value is lower for the second order kinetic model (0.2118) than that for the pseudo order first model (1.774). This conform a better applicability of the pseudo second order kinetic model. The correlation coefficient for the pseudo first order ranged between 0.93 and 0.99 whereas the values for the second order are closest to 1 (0.999). The higher the correlation coefficient and the lower the SSE (%) value, the better the fitness to the model. The correlation coefficient indicates that the experimental data best fitted into the pseudo second order suggesting that the process of adsorption follows pseudo second order kinetics. Tables-1 and 2 also showed the $(q_e)_{expt}$ and the $(q_e)_{cal}$ for the two models. It can be observed that the $(q_e)_{expt}$ differs significantly from $(q_e)_{cal}$ for the first order model, whereas the values are much closer for the pseudo second order model. This again, indicated that the experimental data follows the pseudo second order model. Similar reports have been presented in literature for adsorption of MB onto bamboo based activated carbon[11, 25].

Adsorption isotherm: The adsorption isotherm was determined from the amount adsorbed and the equilibrium concentration calculated from well fitted pseudo second order kinetic studies for different concentrations. Figure-5 shows the comparison of the Langmuir type adsorption isotherms of MB on clay constructed based on experimental result and calculated values.

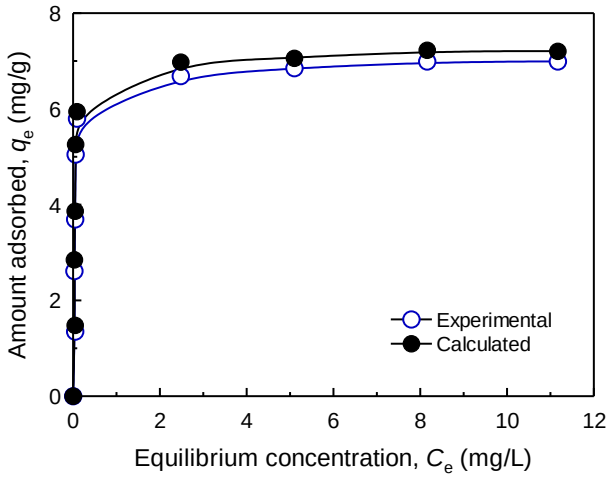

Figure-5
Adsorption isotherm of MB on clay at 30°C constructed from pseudo second order kinetic model

Effect of temperature on adsorption kinetics: Adsorption kinetic experiments were performed at different temperatures for a fixed concentration of 13 mg/L of MB solution. Well fitted pseudo second order kinetic equation was applied to the experimental data as shown in figure-6. Different parameters of pseudo-second order kinetic equation at different temperatures are presented in table-3. The effect of temperature on the adsorption of MB onto clay shows that the amount adsorbed increased with increase in temperature indicating endothermic

nature of adsorption. The endothermicity of the adsorption was also confirmed by the increasing of pseudo second rate constant with increase of temperature. Increase in the value of k_2 with temperature is due to increased mobility and enhanced of MB diffusion at higher temperatures. The decrease in rate of MB adsorption with increasing temperature may be due to the association of MB molecules at the boundary surface.

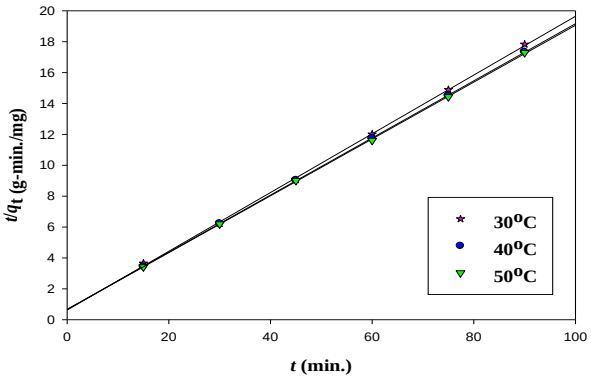

Figure-6
Pseudo second order kinetic plots for adsorption of MB on clay at different temperatures

Table-3
The constant parameters of the pseudo second-order kinetic model for the adsorption of MB on clay at different temperatures

T (K)	k_2 (g/mg·min)	$q_{e\,(expt)}$ (mg/g)	$q_{e\,(cal)}$ (mg/g)	h (mg/g·min)	R^2
303	0.049	5.048	5.258	0.305	0.9995
313	0.051	5.191	5.408	0.276	0.9999
323	0.052	5.208	5.435	0.283	0.9998

The adsorption isotherms at different temperatures were also constructed from the amount adsorbed and equilibrium concentration calculated from well fitted pseudo second order kinetic studies for different concentrations as shown in figure-7. The applicability of Langmuir equation (10) for the adsorption of MB onto clay at different temperatures was verified.

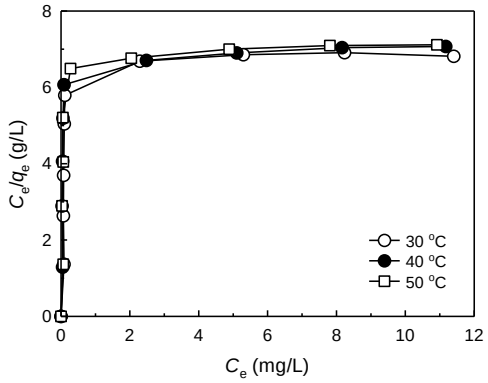

Figure-7
Adsorption isotherm of MB on clay at different temperatures constructed from pseudo second order kinetic studies

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \qquad (10)$$

where, $q_e = x/m$ = amount adsorbed at equilibrium time (mg/g), C_e = equilibrium concentration of adsorbate in solution (mg/L), q_m= maximum adsorption capacity (mg/g) and b = adsorbed intensity (L/mol or L/mg). Figure-8 shows the linear plots of C_e/q_e versus C_e to evaluate the applicability of Langmuir model equation, for the adsorption of MB on clay at different temperatures. The calculated Langmuir constant and their corresponding linear regression correlation coefficient values (R^2) from experimental results at different temperatures are given in table-4. The results show that the adsorption isotherms for different temperatures are well fitted into Langmuir model. The maximum adsorption capacity, q_m obtained from Langmuir isotherm is 6.93 mg/g at 30 °C which is increased to 7.14 mg/g with increasing temperature to 50°C. Again, the adsorption intensity constant, b increased with increase in temperature. Generally, in case of chemical interaction- the amount adsorbed increases with increasing temperature and the adsorption intensity also increases with increasing temperature.

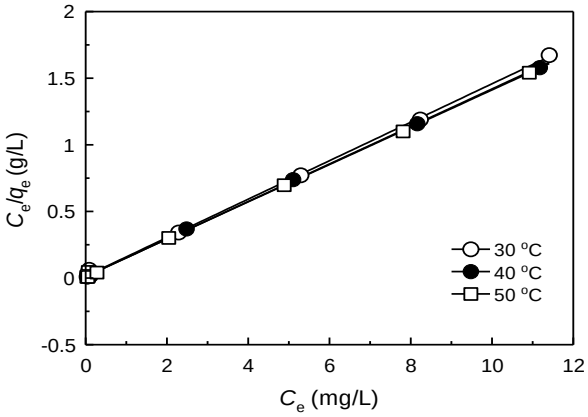

Figure-8
Langmuir isotherm of MB adsorption on clay at different temperatures

Table-4
Langmuir constants for adsorption of MB on clay at different temperatures

T (°C)	Langmuir parameters		
	q_m (mg/g)	b (L/mg)	R^2
30	6.925	9.756	0.9994
40	7.097	12.690	0.9997
50	7.143	11.669	0.9996

Adsorption thermodynamics: Thermodynamic parameters, namely the change of free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) have an important role to determine spontaneity and heat change for the adsorption process. Assuming that the activity coefficients are unity at low concentrations (the Henry's law sense), thermodynamic parameters were calculated from the

apparent equilibrium constant values (K_c) (eq. 11) at different temperatures using the following equations (12 and 13)[25-27]:

$$K_c = C_a/C_e \quad (11)$$

$$\Delta G^o = - RT\ln K_c \quad (12)$$

$$\ln K_c = (\Delta S^o/R) - (\Delta H^o/RT) \quad (13)$$

where, K_c indicates the apparent equilibrium constant, C_a and C_e are the equilibrium concentration of MB on the clay (mg/L) and in the solution (mg/L), respectively. R is the universal gas constant (8.314 J/mol·K) and T is the temperature (K). From equation (12), ΔG^o were calculated using $\ln K_c$ values for different temperatures. The values of ΔH^o and ΔS^o were calculated from the slope and intercept of the linear plot of $\ln K_c$ vs. $1/T$, respectively, as shown in figure-9. The ΔG^o values of MB adsorption on clay under different temperatures as well as ΔH^o and ΔS^o values are presented in table-5. The positive value of ΔH^o (20.98 kJ/mol) indicated that the adsorption of MB on clay was endothermic and chemical in nature. The endothermicity of adsorption of MB was also observed during the adsorption onto clay at temperature from 40 to 60°C, however below this temperature, the exothermic nature was observed[23]. The heat of adsorption varies between 20 and 400 kJ/mol indicating the chemisorptions process[28]. Again, the negative values of ΔG^o decreasing with the increase of temperature indicated more efficient adsorption at higher temperature. Positive ΔS^o values of MB adsorption on clay indicates an irregular increase of the randomness at the clay-solution interface during the adsorption which might be due to the fragmentation of MB molecules or/and structural change on clay surface or surface migration of adsorbed MB molecules[29-30].

Table-5
Equilibrium constant and thermodynamic parameters of MB adsorption on clay at different temperatures

T (K)	K_c (-)	$\ln K_c$	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o (kJ/mol·K)
303	149.54	5.008	-12.615	20.98	0.111
313	223.14	5.408	-14.073		
323	253.90	5.534	-14.861		

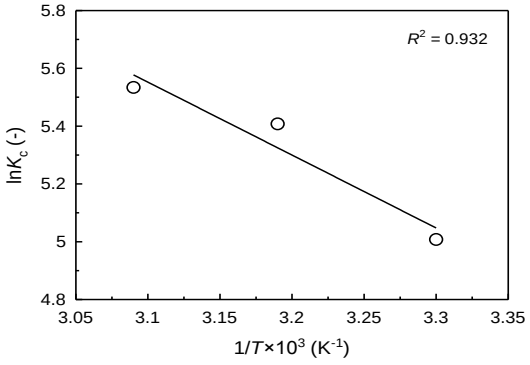

Figure-9
A plot of $\ln K_c$ versus $1/T$ for determination of enthalpy and entropy of MB adsorption on clay

Intra-particle diffusion model: The possibility of intra-particle diffusion of MB onto the clay was investigated using the intra-particle diffusion model (equation 14)[16].

$$q_t = k_p\, t^{1/2} + C \quad (14)$$

where, q_t is the amount of dye adsorbed (mg/g) at time t, C is the boundary layer thickness and k_p is the intra-particle diffusion rate constant (mg/g· $min^{1/2}$). The plots of the amount adsorbed, q_t versus $t^{1/2}$ at different initial concentrations is shown in figure-10. The intra-particle diffusion constants at different initial concentrations are shown in table-6. The correlation coefficients are high but when compared with that observed from pseudo second order kinetic model, the R^2 values of later were found to be much higher than the former. These suggest that pseudo second order kinetic mechanism is predominant and the overall rate of the dye adsorption processes appear to be controlled by chemical interaction. This is agreement with the investigation. The high correlation coefficient indicates the presence of intra-particle diffusion as the rate determining step. The correlation coefficient ranged from 0.72 to 0.96 as the initial concentration varied from 3.5 to 28.5 mg/L.

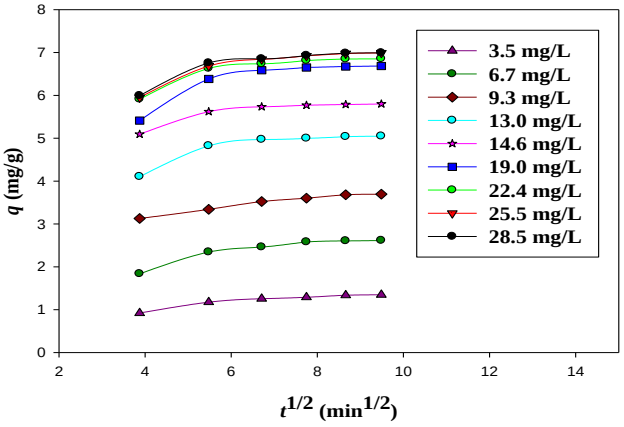

Figure-10
Intra particle diffusion plots for adsorption of MB on clay at different initial concentrations at 30°C, pH= 7.0 and dose = 2.5 g/L

Table-6
Intra particle diffusion constants of MB adsorption on clay at different initial concentrations

C_o (mg/L)	k_p (mg/g-$min^{1/2}$)	C	R^2
3.5	0.072	0.719	0.8766
6.7	0.131	1.492	0.8347
9.3	0.150	2.767	0.9601
13.0	0.104	3.780	0.7329
14.6	0.113	4.843	0.7453
19.0	0.204	4.976	0.7297
22.4	0.151	5.578	0.7494
25.5	0.169	5.543	0.7913
28.5	0.159	5.638	0.7537

Conclusion

Clay fractionated from Bijoypur soil is suitable for adsorption of MB from aqueous solution. The adsorption process is well expressed by pseudo-second order kinetic model. The result showed that intra-particle diffusion is one of the rate determining steps, as such the adsorption mechanism is controlled by particle diffusion. It also observed that the rate of adsorption decreased with increase in experimental temperature. Values of thermodynamic parameters suggested that more MB were adsorbed at higher temperature and implied that the adsorption process was endothermic in nature and involved chemical interaction.

Acknowledgement

The authors are grateful to the Chairman, Department of Chemistry, University of Dhaka, Bangladesh for provided facilities to performed the research. The authors also appreciate the financial support of University Grants Commission, Bangladesh (UGC).

References

1. O'Neill C., Hawkes F.R., Hawkes D.L., Lourenco N.D., Pinheiro H.M. and Delee W., Colour in Textile Effluents - Sources, Measurement, Discharge Consents and Simulation, *J. Chem. Technol. and Biotechnol.,* **74(11),** 1009-1018 **(1999)**

2. Philippe C.V., Bianchi R. and Verstraete W., Treatment and Reuse of Wastewater from the Textile Wet-Processing Industry, *J. Chem. Technol. and Biotechnol.,* **72 (4),** 289-302 **(1998)**

3. Suteu D. and Bilba D., Equilibrium and Kinetic Study of Reactive Dye Brilliant Red HE-3B Adsorption by Activated Charcoal, *Acta. Chim. Slov.,* **52,** 73-79 **(2005)**

4. Iqbal M.J. and Ashiq M.N., Adsorption of Dyes from Aqueous Solutions on Activated Charcoal, *J. Hazard. Materials,* **B139,** 57-66 **(2007)**

5. Hwang M.C. and Chen K.M., The Removal of Color from Effluents Using Polyamide Epichlorohydrin-Cellulose III. Use in Anionic Dye Removal in a Batch Process, *J. Apply. Polym. Sci.,* **50,** 753-744 **(1993)**

6. Suteu D., Nacu A. and Cristian G., Removal of Methyl Violet Tri-Phenyl Methanic Dye Using Ion Exchange Celluloses, *Cellulose Chem. and Technol.,* **35 (5-6),** 451-457 **(2001)**

7. Abdullah G.L., Salleh M.A.M., Mazlina M.K.S., Noor M.J.M.M., Osman M.R., Wagiran R. and Sobri S., Azo Dye Removal by Adsorption Using Waste Biomass: Sugarcane Bagasse, *Int. J. Engg. Tech.,* **2(1),** 8-13 **(2005)**

8. Lagas P., Sorption of Chlorophenol in Soil, *Chemosphere,* **17(2),** 205-216 **(1988)**

9. Kannan N. and Sundaram M.M., Kinetics and Mechanism of Removal of Methylene Blue by Adsorption on Various Carbons: A Comparative Study, *Dyes and Pigments,* **51(1),** 25-40 **(2001)**

10. Filipkwoska O., Klimink E., Grabowski S. and Siedlecka E., Adsorption of Reactive Dyes by Modified Chitin from Aqueous Solutions, *Polish J. Environ. Stud.,* **11(4),** 315-323 **(2002)**

11. Hameed B.H., Din A.T.M. and Ahmad A.L., Adsorption of Methylene Blue onto Bamboo-based Activated Carbon: Kinetics and Equilibrium Studies, *J. Hazard. Materials,* **141(3),** 819-825 **(2007)**

12. Moreno-Castilla C., Adsorption of Organic Molecules from Aqueous Solutions on Carbon Materials, *Carbon,* **42,** 83–94 **(2004)**

13. Santhy K. and Selvapathy P., Removal of Reactive Dyes from Wastewater by Adsorption on Coir Pith Activated Carbon, *Bioresource Technol.,* **97,** 1329-1336 **(2006)**

14. Day P.R., Particle Formation and Particle Size Analysis, In: Methods of Soil Analysis, (eds. CA Black, DD Evans, JL White, LE Ensminger and FE Clark). *Agronomy Monograph,* **Part-I**, 545-567 **(1965)**

15. Zaker Y., Investigation of Bijoypur Clay Fractions as Low Cost Adsorbents, *M.S. Thesis,* Department of Chemistry, University of Dhaka, Dhaka, Bangladesh, **(2010)**

16. Kannan N. and Sundaram M.M., Adsorption of Congo Red on Activated Carbons: A Comparative Study, *Water, Air and Soil Pollution,* **138,** 289 –305 **(2002)**

17. Lagergren S., Zur Theorie der Sogenannten Adsorption Geloster Stoffe Kungliga Svenska Vetenskademiens, *Handinger,* **24,** 1-39 **(1898)**

18. Demirbas E., Kobyab M., Senturk E. and Ozkan T., Adsorption Kinetics for the Removal of Chromium (VI) from Aqueous Solution on the Activated Carbon Prepared from Agriculture Wastes, *Water S.A.,* **30,** 533-539 **(2004)**

19. Ho Y.S. and Mckay G., Comparison of Chemisorption Kinetic Models Applied to Pollutant Removal on Various Sorbents, *Trans IChemE,* **76B,** 332-340 **(1998)**

20. Abechi E.S., Gimba C.E., Uzairu A. and Kagbu J.A., Kinetics of Adsorption of Methylene Blue on to Activated Carbon Prepared from Palm Kernel Shell, *Arch. Apply. Sci. Res.*, **3(1),** 154-164 **(2011)**

21. Ho Y.S. and McKay G., The Kinetics of Sorption of Divalent Metal Ions onto Sphagnum Moss Peat, *Wat. Res.*, **34**, 735-742 **(2000)**

22. Cenens J. and Schoonheydt R.A., Visible Spectroscopy of Methylene Blue on Hectorite, Laponite B, and Barasym in Aqueous Suspension, *Clay and Clay Minerals,* **36(3),** 214–224 **(1988)**

23. Gurses A., Dogar C., Yalcm M., Mcikyildiz M., Bayrak R. and Karaca S., The Adsorption Kinetics of the Cationic Dye, Methylene Blue, onto Clay, *J. Hazard. Mater.*, **131,** 217-228 **(2006)**

24. Mundhe K.S., Gaikwad A.B., Torane R.C. Deshpande N.R. and Kashalkar R.V., Adsorption of Methylene Blue from Aqueous Solution using Polyalthis Longifolia (Ashoka) Seed Powder, *J. Chem and Pharma. Res*., **4(1),** 423-436 **(2012)**

25. Karagoz S., Tay T., Ucar S. and Erdem M., Activated Carbons from Waste Biomass by Sulfuric Acid Activation and Their Use on Methylene Blue Adsorption, *Bioresource Technol.,* **99(14),** 6214–6222 **(2008)**

26. Singha B. and Das S.K. Removal of Pb(II) ions from Aqueous Solution and Industrial Effluent Using Natural Biosorbents, *Environ Sci. Pollut. Res.,* **19,** 2212-2226 **(2012)**

27. Pehlivan E. and Arslan G., Removal of Metal Ions Using Lignite in Aqueous Solution-Low Cost Biosorbents, *Fuel Process. Technol.,* **88,** 99-106 **(2007)**

28. Naiya T.K., Bhattacharya A.K. and Das S.K., Adsorption of Cd(II) and Pb(II) from Aqueous Solutions on Activated Alumina, *J. Colloid and Interf. Sci.,* **333,** 14–26 **(2009)**

29. Chen C., Li X., Zhao D., Tan X. and Wang X., Adsorption Kinetic, Thermodynamic and Desorption Studies of Th(IV) on Oxidized Multiwall Carbon Nanotubes, *Colloids and Surfaces A: Physicochem. Eng. Aspects,* **302,** 449-454 **(2007)**

30. Hossain M.A., Kumita M. and Mori S., SEM Characterization of the Mass Transfer of Cr(VI) During the Adsorption on Used Black Tea Leaves, *African J Pure and Apply. Chem.*, **4(7),** 135-141 **(2010)**