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Kinetics and thermodynamics of methylene blue adsorption by cobalt-hectorite composite

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ABSTRACT

The cobalt-hectorite composite is used for the removal of MB from aqueous solution. Research concerning the effects of pH, composite dose, initial dye concentration and temperature are presented and discussed. Experiment data was analyzed using pseudo-second-order kinetics, intra-particle diffusion, and film diffusion. The characteristic parameters for each model have been determined. Thermodynamic parameters such as activation (E_a), standard free energy (ΔG^o), the enthalpy (ΔH^o) and the entropy (ΔS^o) were also evaluated. The negative value of ΔG^o (kJ/mol) and ΔH^o (kJ/mol) indicates the spontaneous and exothermic nature of the reactions. The data of E_a shows the physisorption process of MB adsorption on Co-hectorite composite.

1. Introduction

Synthetic dyes are extensively used in textile industry but about 20–40% of these dyes remain in the effluents [1–3]. Most of the dyes are toxic and carcinogenic compounds. They are also recalcitrant and thus stable in the recovering environment, posing a serious threat to human and environmental health [4]. Accordingly, to protect humans and recover ecosystem from contamination, the dyes must be eliminated from the dye-contained wastewater before being released into the environment.

During the past three decades, several physical, chemical and biological decolorization methods have been reported (see Table 1) for the removal of pollutants from plastics, dyestuffs, textile, pulp and paper effluents. However, few of them had been accepted by these industries [5–18]. Among the numerous techniques of dye removal, adsorption is the procedure of choice giving the best results as it can be used to remove certain classes of chemical pollutants from water. Adsorption has been found to be superior to other techniques for re-used water in terms of low cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Activated carbon and polymer resins are claimed to be the best adsorbents for removing dyes from relatively concentrated wastewater [19,20]. It is known that activated carbon has a rather low adsorption capacity for some reactive dyes. Thereby, studies have been made on treatment of wastewater using clay/basic [21], chitosan [22], cotton [23], montmorillonite and sepiolite/methylgreen [24] and natural zeolite/basic [18].

Due to their high surface area and molecular sieve structure, natural clay minerals are effective adsorbents for organic contaminants of cations [3]. Hectorite is the most commonly used layered silicate. It has two types of structure: tetrahedral-substituted and octahedral substituted. Hectorite is one of the best adsorbents for removing dyes from relatively concentrated wastewater. This is ascribed to its unique structure with interior channels which allows penetration of organic and inorganic ions bounding together with solutes into the structure of hectorite.

In this paper, we propose the use of a cobalt-hectorite composite for the adsorption of methylene blue (MB). Studies concerning pH value, dose of sorbent, initial MB concentration and temperature are presented and discussed. Experiment data was analyzed using pseudo second-order kinetics, intra-particle diffusion, film diffusion and thermodynamics equations. The characteristic parameters for each model have been determined.

2. Materials and methods

2.1. Sorbent

The sorbent was prepared in one step by ion-exchanged method. Hectorite (2 g) was dispersed in 0.200 L distilled water and

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Table 1
Reviews on existing and emerging technologies for color removal.

Technology/reference(s)
Conventional treatment processes
• Physicochemical treatment (sedimentation/flotation, coagulation/flocculation, Precipitation. Electrokinetic coagulation [5–7]
• Biodegradation (microbiological decomposition, lagoon, enzymatic treatment, integrated treatment processes) [1–8]
• Adsorption (carbon-based adsorbents, silicate-based adsorbents, other materials) [5–8,13,18]
Established recovery processes
• Oxidation (ozonation, electrochemical destruction) [5–7,15,16]
• Membrane filtration (ultra-filtration, ion-exchange) [6,17]
Emerging removal processes
• Bioadsorption [13]
• Biomass [6,14]
• Advanced oxidation process (irradiation, photochemical treatment, photocatalysis, sonication) [6,8,16]

stirred for 2 h. The pH of the colloidal dispersion was adjusted to 6 using 1 M HCl. The calculated amount of $CoCl_2$ solution was added under vigorous stirring for 8 h. The resulting dispersion was washed with distilled water. The product was centrifuged and dried at 80 °C.

2.2. Adsorbate

The adsorption capacity was investigated using MB as the model guest. An accurately weighed quantity of the MB was dissolved in distilled water to prepare the stock solution. The solution for adsorption tests was prepared from the stock solution to the desired concentrations by successive dilutions. A calibration curve was first plotted for MB. This curve was used to convert absorbance data into concentration in kinetic and thermodynamics studies.

2.3. Adsorption process research

Adsorption experiments were carried out in a thermostatic orbital shaker at different temperatures. The shaking was continued till the state of equilibrium was reached. The initial MB concentration and equilibrium concentration were measured using a UV–vis spectrophotometer. This data was used to calculate the adsorption capacity of the adsorbent. The amount of MB adsorbed at equilibrium, q_e was calculated from the mass balance equation given by:

$$q_e = (C_0 - C_e)\frac{v}{w} \tag{1}$$

Where C_0 is the initial MB concentration in liquid phase (g/L); C_e is the liquid phase MB concentration at equilibrium (g/L); v is the volume of MB solution used (L); and w is the mass of sorbent used (g).

The kinetic studies were carried out in 0.050 L MB solution (0.180 g/L) by adding 0.025 g sorbent at different temperatures. At given time intervals, the liquid phase MB concentration was measured.

3. Results and discussion

3.1. Effect of solution pH

The effect of solution pH was studied for MB removal by cobalt-hectorite composite in a range of 2–13 under the conditions given in Table 2. The means of the duplicated experimental results are plotted in Fig. 1, indicating that pH considerably effected MB stability particularly under alkalinous conditions, but less affected the MB adsorption. A similar trend was reported for congo red adsorption from aqueous solution as a function of pH by other researchers, including CTAB-hectorite, ODA-hectorite [25]. As can be seen in Fig. 1, the MB removal without composite increased when the solution pH was below 4 and above 10. The results indicated that the molecular form of MB in solution changed markedly in the pH range from 2 to 4, and above 10. The degree of MB adsorption onto Co-hectorite reached to 95%, when the MB solution pH was 5. In this paper, the optimum pH at which maximum MB adsorption attained was 5, and so the rest of experiments were conducted at this optimum pH.

3.2. Effect of Co-hectorite dose

The effect of Co-hectorite composite dose on MB adsorption was performed in a range of 0.5–2.5 g/L under conditions specified in Table 2. The results are shown in Fig. 2, which indicted the decrease of q_e with the increase of Co-hectorite dose. The reasons were that a large adsorbent dose reduces the unsaturation of the adsorption sites, resulting in comparatively less adsorption at higher adsorbent doses. When the adsorbent dose is small, MB can easily access the adsorption sites and the q_e is high. With the increment in adsorbent dose, the corresponding increment in adsorption per unit mass is less because of lower adsorptive capacity utilization of the adsorbent. Meanwhile, higher adsorbent doses created particle aggregation, resulting in the decrease in the total surface area and activity adsorption sites. In this paper, the optimum Co-hectorite dose at which maximum MB adsorption attained was 0.5 g/L, and so the rest of experiments were conducted at this optimum dose.

3.3. Effect of initial MB concentration and temperature

The dye in the effluent of different industries may have different concentrations, which raises the question of how dye concentrations influence the performance of Co-hectorite composite for removing MB. In this work, the adsorption of 0.150, 0.165, 0.180, 0.195 and 0.210 g/L MB concentrations were investigated for Co-hetorite composite. The means of the duplicate data are depicted in Fig. 3, indicating a considerable influence of MB concentration on Co-hectorite composite adsorption capacity. Based on data illustrated in Fig. 3, by increasing the initial MB concentration, the q_e of

Table 2
Experimental runs and conditions.

Experiment	Conditions				
	Solution pH	Composite dose (g/L)	MB concentration (g/L)	Temperature (K)	Contact time (hour)
Effect of pH	2–13	0.500	0.180	293	1
Effect of composites dose	5	0.500–2.50	0.500, 0.550, 0.600	293	24
Effect of MB concentration	5	0.500	0.150–0.210	293, 303, 313	24
Effect of temperature	5	0.500	0.150–0.210	293, 303, 313	24

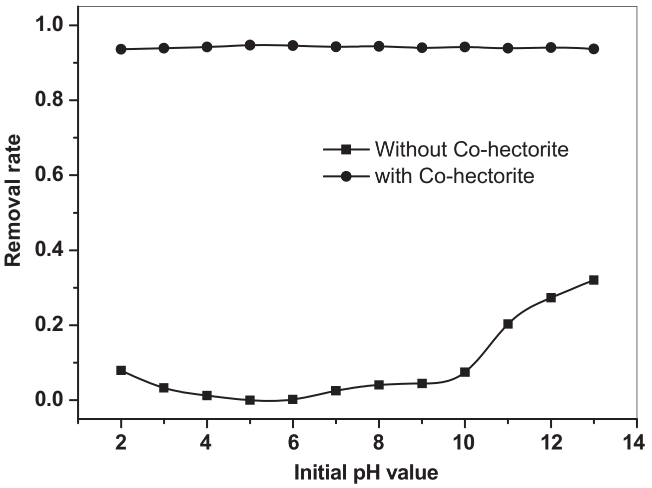

Fig. 1. Effect of pH of MB adsorption on Co-hectorite. Conditions: 0.180 g/L concentration, 0.5 g/L dose and 293 K temperature.

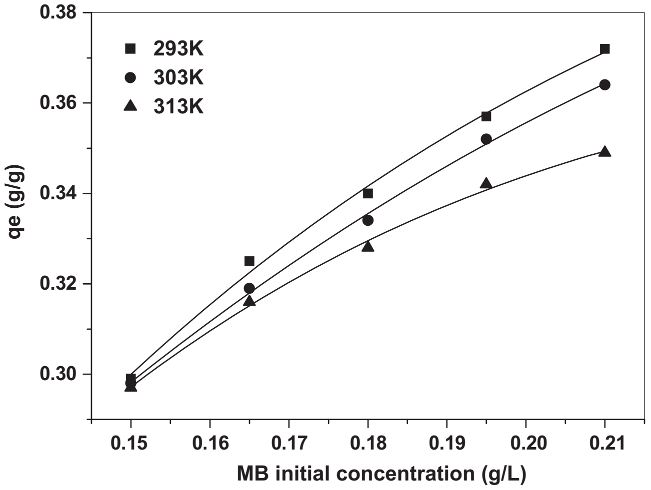

Fig. 3. Amount adsorbed at equilibrium time (q_e) on Co-hectorite at 293, 303, 313, 323 K with different MB concentration.

Co-hectorite composite increased at different temperature. This can be attributed to free adsorption sites available at the initial phase of the test, as well as to a higher mass transfer rate at initial contact time where the MB concentration is high.

Fig. 3 also shows the effect of temperature on the adsorption equilibrium of MB on Co-hectorite composite. It can be seen that the q_e decreased with the increase of the temperature for initial concentration of 0.150–0.210 g/L which indicated the exothermic process. However, at low initial concentration of MB (0.150 g/L), the effect of temperature on the adsorption equilibrium was not significant.

3.4. *Intra-particle diffusion and film diffusion study*

An empirically found functional relationship, common to the most adsorption process, is that the uptake varies almost proportionally with $t^{1/2}$, The Weber–Morris plot [26].

$$q_t = k_{id} t^{1/2} + C \tag{2}$$

where k_{id} is the intra-particle diffusion rate constant. According to Eq. (2), a plot of q_t versus $t^{1/2}$ should be a straight line with a slope k_{id} and intercept C when adsorption mechanism complies with the intra-article diffusion process. The means of the duplicated experimental results is plotted in Fig. 4. From Fig. 4, it may be seen that there are two separate regions. The first straight portion is attributed to the macro-pore diffusion and the second linear portion to micro-pore diffusion. In the first region, it is attributed to the instantaneous utilization of the adsorbing sites on the adsorbent surface. In the second region, it is attributed to a very slow diffusion of the MB from the surface film into the micro-pores, which are the least accessible sites of adsorption. This also stimulates a very slow rate of migration of adsorbates from the liquid phase on to the adsorbent surface. The deviation of straight line from the origin may be due to the difference in rate of mass transfer in the initial and final stages of adsorption. Further deviation of the straight line from the origin indicates that the pore diffusion is not the only rate-limiting step [27].

To confirm the above results, the intra-particle diffusion coefficients, D_p have been calculated using the following equation.

$$D_p = \left(0.03 r_0^2\right) \Big/ t_{0.5} \tag{3}$$

where r_0 (m) is the average radius of the adsorbent particles and $t_{0.5}$ (min) is the time required to complete half of the adsorption.

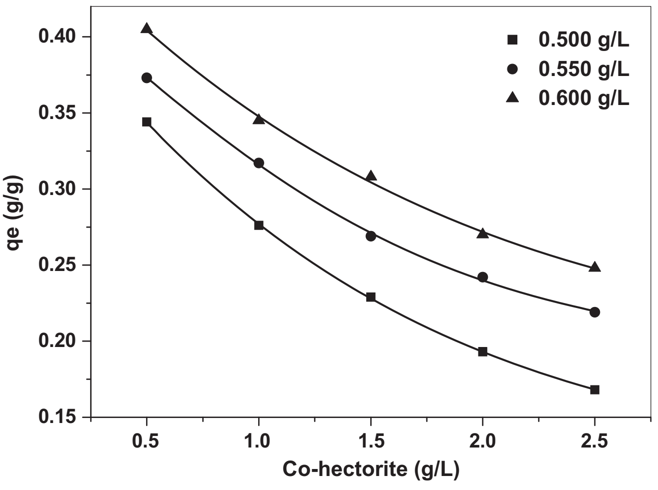

Fig. 2. Amount of MB adsorbed at equilibrium time (q_e) at different Co-hectorite dose at 293 K (initial MB concentration 0.500 g/L, 0.550 g/L, 0.600 g/L, pH = 5.0, time 24 h).

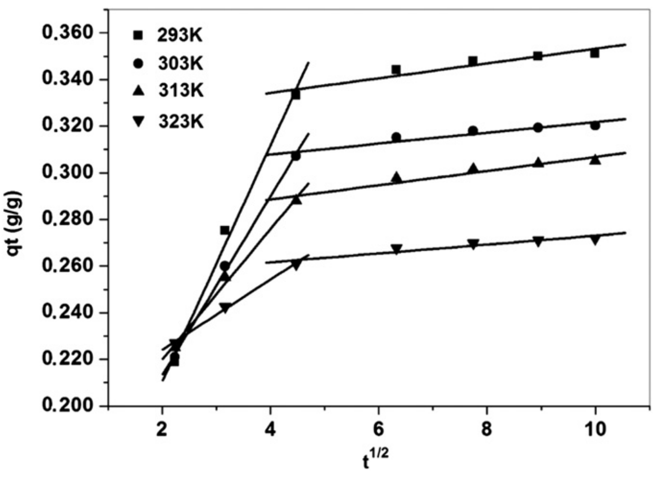

Fig. 4. Werber-Morris kinetic plots of MB adsorption on Co-hectorite at T = 293K, 303K, 313, 323 K.

Table 3
The intra-particle diffusion coefficients (D_P) and the film diffusion coefficient (D_F) of the adsorption process at $T = 293, 303, 313$ K.

T (K)	r_0 (m)	$t_{0.5}$ (s)	D_P (m^2/s)	D_F(m^2/s)
293		81.36	1.71×10^{-14}	3.76×10^{-13}
303	6.81×10^{-4}	64.32	2.16×10^{-14}	4.33×10^{-13}
313		52.92	2.63×10^{-14}	5.02×10^{-13}

According to Michelsen et al. [28], if the calculated intra-particle diffusion coefficient (D_p) value is in the range 10^{-15}–10^{-18} m^2/s, then the intra-particle diffusion will be the rate-limiting step. In this study, the calculated D_p value ranged from 1.71×10^{-14} to 2.63×10^{-14} m^2/s with different temperature (Table 3), which indicated the intra-particle diffusion is not only the rate-limiting step of MB adsorption onto Co-hectorite composite.

In order to study the adsorption kinetics process, the film diffusion coefficients, D_F have been calculated using the following equation.

$$D_F = (0.23 r_0 \delta C_S)/(C_L t_{0.5}) \tag{4}$$

where r_0 and $t_{0.5}$ have the same meaning as above, δ is the film thickness (10^{-5} m) [28], C_S and C_L are the concentrations of adsorbate in solid and liquid phase, respectively. If the rate-limiting step is controlled by film diffusion, the calculated film diffusion coefficient (D_F) value will be in the range from 10^{-10} to 10^{-12} m^2/s.

The calculated values of D_F are found to be in the order of 10^{-13} m^2/s (Table 3), which indicated that the film diffusion was not only the rate-limiting step in the adsorption process.

In this paper, the kinetic process was controlled by Intra-particle diffusion and film diffusion. At the beginning of adsorption process, the MB concentration was high, so the kinetic process was controlled by film diffusion. When MB molecules were adsorbed on the surface of Co-hectorite composite, the MB molecules began to diffuse in the Co-hectorite, the intra-particle diffusion was controlled the adsorption process.

3.5. Thermodynamics research

With respect to the kinetic modeling, the pseudo-second-order [29] model has been examined to find out the adsorption mechanism.

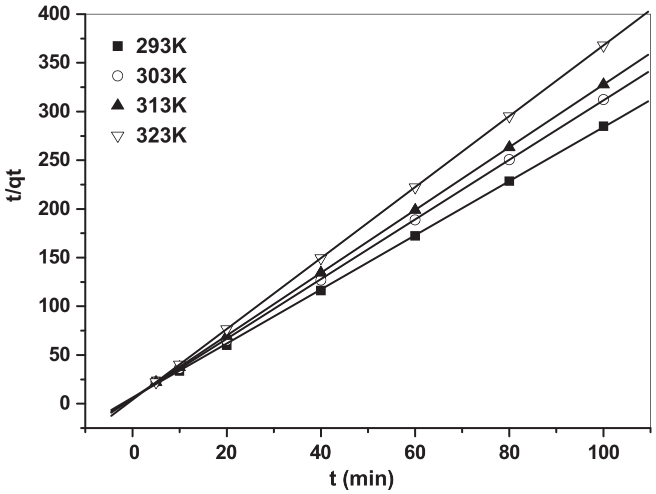

Fig. 5. The pseudo-second-order kinetics for the adsorption of MB onto Co-hectorite at $T = 293, 303, 313, 323$ K.

Table 4
The pseudo-second-order kinetics parameter constants and Arrhenius activation energy (E_a) for the adsorption of MB onto Co-hectorite at $T = 293, 303, 313$ and 323 K.

	Temperature (K)	k_2	q_e (g/g)	r^2	E_a (kJ/mol)
Co-hectorite	293	2.072	0.355	0.9998	20.712
	303	2.885	0.323	0.9999	
	313	3.670	0.308	0.9997	
	323	4.591	0.298	0.9994	

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{5}$$

where q_t is the amount of MB adsorbed (g/g) at time t, q_e is the equilibrium adsorption capacity (g/g), and k_2 is the rate constant of pseudo-second-order adsorption (g/g min). The straight-line plots of t/q_t vs t for the pseudo-second-order reactions have also been tested to obtain rate parameters (Fig. 5). The correlation coefficient r^2, k and q_e under different temperature were calculated and given in Table 4. The pseudo-second-order rate constants are expressed as a function of temperature by the Arrhenius equation.

$$\ln k_2 = -\frac{E_a}{RT} + \ln A \tag{6}$$

where E_a is the Arrhenius activation energy of sorption, representing the minimum energy which reactants must have to be proceed, A is the Arrhenius factor, R is the gas constant and is equal to 8.314 J/mol·K, and T is the solution temperature. The means of the duplicated experimental results is plotted in Fig. 6. From Eq. (6), the E_a is obtained (Table 4). The magnitude of activation energy gives an idea about the type adsorption, which is mainly physical or chemical. The physisorption processes usually have energies in the range of 5–40 kJ/mol, while higher activation energies (40–800 kJ/mol) suggest chemisorptions [29]. It can be inferred from the dispersive interaction between MB and surface of Co-hectorite.

The thermodynamic parameters, i.e., the standard free energy (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o) have been estimated to evaluate the feasibility and exothermic nature of the adsorption process. The Gibbs free energy change of the process is related to the equilibrium constant (K) by the following equation.

$$\Delta G^o = -RT \ln K \tag{7}$$

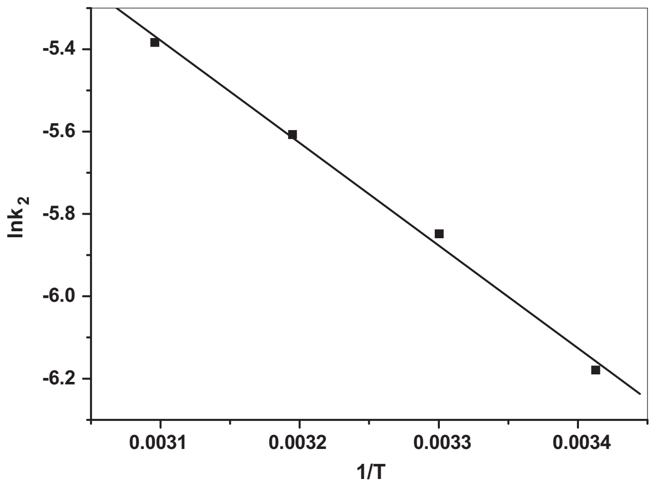

Fig. 6. Arrhenius plots for the adsorption of MB onto Co-hectorite. T is temperature 293, 303, 313 and 323 K.

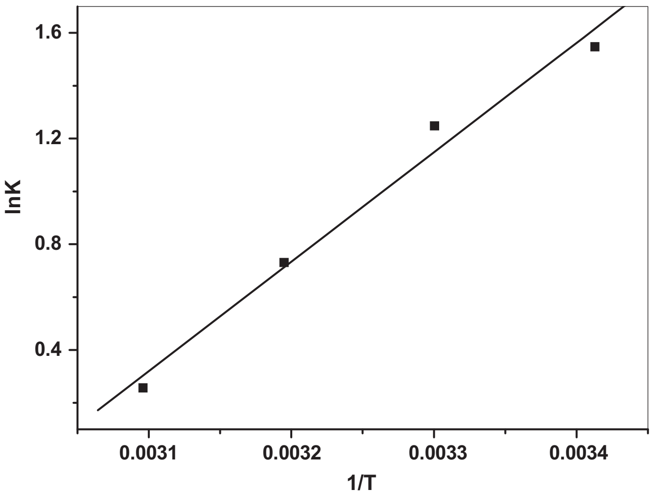

Fig. 7. Plot of lnK vs. 1/*T* for MB onto Co-hectorite.

Table 5
Thermodynamic parameters for the adsorption of MB onto Co-hectorite.

Sample	Temperature (K)	Distribution coefficient (K)	Change in Gibbs free energy ΔG^o (kJ/mol)	Enthalpy ΔH^o (kJ/mol)	Entropy ΔS^o (J/mol K)
Co-hectorite	293	4.699	−3.769	−34.435	−104.083
	303	3.484	−3.144		
	313	2.077	−1.902		
	323	1.292	−0.668		

According to thermodynamics, the Gibbs free energy change is also related to enthalpy change and entropy change at constant temperature by the following equation.

$$\ln K = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \tag{8}$$

The value of ΔH^o and ΔS^o are calculated from the slope and intercept of plots of ln$K$ versus 1/T (Fig. 7). The values obtained are given in Table 5. The Gibbs free energy change (ΔG^o) values are found to be decreasingly negative with temperature which indicated the feasibility and spontaneity of the adsorption process of MB on Co-hecotrite composite. The enthalpy change (ΔH^o) values are found to be negative which indicated the exothermic nature of adsorption process. The (ΔH^o) value is found to be less than 40 kJ/mol, which indicates the adsorption of MB by Co-hectorite composite is physiosorption. The present results are found similar to the results reported by C. L. Xia [25] on adsorption of congo red from aqueous solution by CTAB-hectorite and ODA-hectorite composites.

4. Conclusion

The present study shows that Co-hectorite composite is an effective adsorbent for removal of MB from aqueous solution. The effective pH for MB removal was 5. The optimum composite dose and temperature were 0.5 g/L and 293 K, respectively. The straight lines in plots of t/qt versus t showed good agreement of experimental data with pseudo-second-order kinetic model. The adsorption process was controlled by intra-particle diffusion and film diffusion. The thermodynamic parameters evaluated reveal the spontaneous and exothermic process of MB adsorption on Co-hectorite composite. Adsorption activation energy was found to be 22.103 kJ/mol, which were the typical activation energy range for physisorption. The result would be useful for design of wastewater treatment plants for removal of dye.

Acknowledgments

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References

[1] William AR, Leonard TF. Water and salt reuse in the dyehouse. Textile Chemist and Colourist 1997;29:10–9.
[2] Wu J, Eitman MA, Law SE. Evaluation of membrane filtration and ozonation processes for treatment of reactive dye wastewater. Journal of Environmental Engineering 1998;12:272–7.
[3] Orhan O, Bulent A, Mustafa T, Mehmet SC. Comparison of the adsorption characteristics of azo-reactive dyes on mezoporous minerals. Dyes and Pigments 2004;62:49–60.
[4] Crini G. Kinetic and equilibrium studies on the removal of cationic dyes from aqueous solution by adsorption onto a cyclodextrin polymer. Dyes and Pigments 2008;77:415–26.
[5] Pokhrel D, Viraraghavan T. Treatment of pulp and paper mill wastewater-a review. The Science of the Total Environment 2004;333:37–58.
[6] Robinson T, McMullan G, Marchant R, Migam P. Remediation of dye in textile effluent: a critical review on current treatment technologies with apropsed alternative. Bioresource Technology 2001;77:247–55.
[7] Anjaneyulu Y, Sreedhara Chary N, Samuel Sunan Raj D. Decolourization of industrial effluents-available methods and emerging technologies-a review. Reviews in Environmental Science and Bio/Technology 2005;4:245–73.
[8] Forgacs E, Cserhati T, Oros G. Removal of synthetic dyes from wastewater: a review. Environment International 2004;30:953–71.
[9] Thompson G, Swain J, Kay M, Forster CF. The treatment of pulp and paper mill effluent: a review. Bioresource Technology 2001;77:275–86.
[10] Singh Rai H, Bhattacharyya MS, Singh J, Bansal TK, Vats P, Banerjee UC. Removal of dyes from the effluent of textile and dyestuff manufacturing industry: a review of emerging techniques with reference to biological treatment. Critical Reviews in Environmental Science and Technology 2005;35:219–38.
[11] Pearce CI, Lloyd JR, Guthrie JT. The removal of color from textile wastewater using whole bacterial cells: a review. Dyes and Pigments 2003;58:179–96.
[12] Fu Y, Viraraghavan T. Fungal decolorization of dye wastewaters a review. Bioresource Technology 2011;79:251–62.
[13] Crini G. Non-conventional low-cost adsorbents for dye removal: a review. Bioresource Technology 2006;97:1061–85.
[14] Aksu Z. Application of biosorption for the removal of organic pollutants: a review. Process Biochemistry 2005;40:997–1026.
[15] Vajnhandl S, Majcen le Marechal A. Ultrasound in textile dyeing and the decolouration/mineralization of textile dyes. Dyes and Pigments 2005;65:89–101.
[16] Ma Jun, Jia Yongzhong, Jing Yan, Sun Jinhe, Yao Ying. Synthesis and photocatalytic activity of TiO_2-hectotirte composites. Applied Clay Science 2009;46:114–6.
[17] Hilal N, Al-Zoubi H, Darwish NA, Mohammad AW, Abu Arabi M. A comprehensive review of nanofiltration membrances: treatment, pretreatment, modeling and atomi force microscopy. Desalination 2004;170:281–308.
[18] Yue Duyuan, Jing Yan, Ma Jun, Xia Chenglong, Yin Xiaojie, Jia Yongzhong. Removal of neutral red from aqueous solution by using modified hectorite. Desalination 2011;267:9–15.
[19] Guo Y, Yang S, Fu W, Qi J, Li R, Wang Z, et al. Adsorption of malachite green on micro- and mesoporous rice husk-based active carbon. Dyes and Pigments 2003;56:219–29.
[20] Meshko V, Markovska L, Mincheva M, Rodrigues AE. Adsorption of basic dyes on granular activated carbon and natural zeolite. Water Research 2001;35:3357–66.
[21] El-Geundi MS. Homogeneous surface diffusion model for the adsorption of basic dyestuffs onto natural clay in batch adsorbers. Adsorption Science and Technology 1991;8:217–25.
[22] Juang RS, Tseng RL, Wu FC, Lee SH. Adsorption behavior of reactive dyes from aqueous solutions on chitosan. Journal of Chemical Technology and Biotechnology 1997;70:391–9.
[23] Sawada K, Ueda M. Adsorption behavior of direct dye on cotton in non-aqueous media. Dyes and Pigments 2003;58:37–40.
[24] Rytwo G, Nir S, Crepsin M, Margulies L. Adsorption and interactions of methyl green with montmorillonite and sepiolite. Journal of Colloid and Interface Science 2000;222:12–9.
[25] Xia Chenglong, Jing Yan, Jia Yongzhong, Yue Duyuan, Ma Jun, Yin Xiaojie. Adsorption properties of congo red from aqueous solution on modified

hectorite: kinetic and thermodynamic studies. Desalination 2011;256: 81–7.

[26] Weber Jr WJ, Morris JC. Kinetics of adsorption on carbon from solution. Journal of Sanitary Engineering Division ASCE 1963;89(SA2):31–59.

[27] Mall Indra D, Srivastava Vimal C, Agarwal Nitin K. Removal of orange-G and methyl violet dyes by adsorption onto bagasse fly ash-Kinetic study and equilibrium isotherm analyses. Dyes and Pigments 2006;69:210–23.

[28] Debnath Sushanta, Chand Ghosh Uday. Kinetics, isotherm and thermodynamics for Cr(III) and Cr(VI) adsorption from aqueous solutions by crystalline hydrous titanium oxide. Journal of Chemical Thermodynamics 2008;40: 67–77.

[29] Özcan S, Erdem B, Özcan A. Adsorption of acid blue 193 from aqueous solutions onto Na-bentonite and DTMA-bentonite. Journal of Colloid and Interface Science 2004;280:44–54.