

Adsorption Properties of Methylene Blue on ODA-Hectorite: Equilibrium, Kinetic Studies

Jun MA^{1,a}, Su-Yan TIAN^{1,b}, Shan-Liang MU^{1,b}, Shao-Lei XIE^{2,d}, Rong-Jian YING^{1,e*}

¹ School of Chemistry and Chemical Engineering, Linyi University, 276000, China

² Key Laboratory of Comprehensive and Highly Efficient Utilization of Salt Lake Resources, Chinese Academy of Sciences, 810008, China

^amajun716@163.com, ^btianyan198289@163.com, ^cchem@lyu.edu.cn, ^dxsl2013@isl.ac.cn, ^eyingrongjian@lyu.edu.cn

* Rongjian YING

Keywords: Hectorite, Equilibrium adsorption, Neutral Red, Kinetics.

Abstract. The octadecylamine-hectorite composite (ODA-hectotie) has been designed and synthesized. The composite is used for removal of methylene blue (MB) from aqueous solution. Research concerning the effects of pH, composite dose, initial dye concentration and temperature are presented and discussed. Experiment results showed that the equilibrium adsorption data fitted well with the Langmuir isotherm. Respectively, the experiment data was analyzed using intra-particle diffusion and film diffusion. The characteristic parameters for each model have been determined.

1. Introduction

Contamination of surface water by different organic pollutant is a major factor of environmental problems for a number of years. 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 caused damage not only to aquatic life, but also to human beings, because it is toxic, mutagenic or carcinogenic. 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. Therefore, the removal of dyes from waste effluents was important.

During the past three decades, different methods such as coagulation, electro coagulation, flotation, chemical oxidation, filtration, membrane separation and microbial degradation[4] have been developed for the removal of synthetic dyes from waters and wastewaters to decrease its impact in the environment. These methods might suffer from one or more limitations and could not remove the dyestuff from waster water completely. 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.

Previous research on the adsorption of dyes from aqueous solution revealed numerous economic adsorbents, such as coal, fly ash, wood, biogas waster slurry and polymer resins[5-7]. However, the adsorption capacities of these materials were limited. Activated carbon as an absorbent has been widely investigated for the adsorption of basic dyes[8], but the disposal of the used carbon was very difficult. Thereby, studies have been made on treatment of wasterwater using clay/basic[9], chitosan[10], cotton[11] and natural zeolite/basic[12]. Hectorite is the most commonly used layered silicate. It has two types of structure: tetrahedral-substituted and octahedral substituted. Due to unique structure with interior channels which allows penetration of organic and inorganic ions bounding together with solutes into the structure of hectorite, it is one of the best adsorbents for removing dyes from relatively concentrated wastewater.

In this paper, we propose the use of ODA-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 isotherm models, kinetic and thermodynamics equations. The characteristic parameters for each model have been determined. The results have important significance for the application of hectorite and the treatment of wastewater.

2. Materials and Methods

2.1 Materials

According to our previous research, hectorite and ODA-hectorite were synthesized [13]. The calculated amount of ODA was dissolved at 343.15K in a 1;1(v/v) water: ethanol mixture acidified to pH=3 with HCl solution. The above solution was dropwise added into the dispersion of hectorite (2%). The mixture was mechanically stirred at 343.15K for 8 h, filtered and washed several times with distilled water. The products were dried at 323.15K for 24 h.

2.2 Adsorption Process Research

Adsorption experiments were carried out in a thermostatic orbital shaker at different temperature. 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. These data were 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:

$$q_e = (c_0 - c_e) \frac{v}{w} \quad (1)$$

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)

3. Results and Discussion

3.1 Effect of ODA-hectorite dose

The effect of ODA-hectorite composite dose on MB adsorption was performed in a range of 0.5-2.5 g/L. The result was shown in Fig.1, which indicated the decrease of q_e with the increase of ODA-hectorite dose.

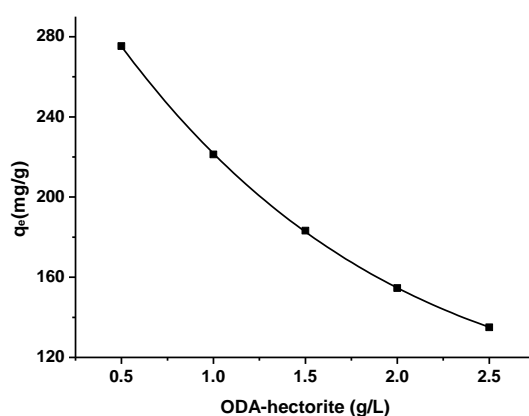


Fig.1 Amount of MB adsorbed at equilibrium time (q_e) at different ODA-hectorite dose at 293.15K (initial MB concentration 0.180g/L, PH=5.0, time 24 h)

The reasons were that a large adsorbent dose reduces the unsaturation of the adsorption sites, resulting in comparatively less adsorption at higher adsorbent dose. 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 adsorbent. Meanwhile, high adsorbent dose created particle aggregation, resulting in the decrease in the total surface area and activity adsorption sites. In this paper, the optimum ODA-hectorite dose at which maximum MB adsorption attained was 0.5g/L, and so the rest of experiments were conducted at this optimum dose.

3.2 Effect of initial MB concentration

The dye in the effluent of different industries may have different concentrations, which raises the question of how dye concentration influence the performance of ODA-hectorite composite for removing MB. In this paper, the MB initial concentration from 0.150 g/L to 0.210 g/L were investigated for ODA-hectorite composite. The means of the duplicate data are depicted in Fig.3, indicating a considerable influence of MB concentration on ODA-hectorite composite adsorption capacity.

Based on data illustrated in Fig.3, by increasing the initial MB concentration, the q_e of ODA-hectorite composite was increased.

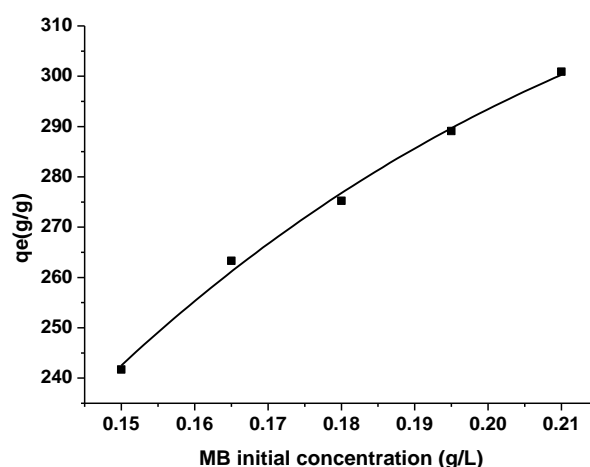


Fig.2 Effect of pH of MB adsorption on ODA-hectorite (Conditions: 0.18g/L MB initial concentration, 0.50 g/L dose and 293K temperature)

3.3 Adsorption Isotherms

An adsorption isotherm showed how the adsorbate molecules partition between the liquid and solid phases when the adsorption process reached equilibrium conditions. Among the available isotherm equations, Langmuir and Freundlich equation were commonly used to describe the adsorption isotherms[14]. The Langmuir isotherm was most widely used for the adsorption of pollutants from liquid solution. The linear form of the Langmuir isotherm was represented as Eq. (2):

$$\frac{c_e}{q_e} = \frac{1}{k_b q_\infty} + \frac{c_e}{q_\infty} \quad (2)$$

Where q_∞ (mg/g) and k_b (L/mg) were the Langmuir isotherm coefficients. The value of q_∞ represented the maximum adsorption capacity.

An essential characteristic of Langmuir isotherm could be expressed by a dimensionless constant called equilibrium parameter R_L , which was indicative of the isotherm shape that predicted whether an adsorption system was favorable or unfavorable. R_L was defined as Eq. (3):

$$R_L = \frac{1}{1 + k_b c_0} \quad (3)$$

where c_0 (mg/L) was initial dye concentration. The value of R_L indicated the type of isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The adsorption of data were analyzed according to Eq.(2). Fig.4 represented Langmuir isotherm for ODA-hectorite, and the values of the Langmuir constants q_∞ , k_b and R_L with the correlation coefficient r_L^2 were listed in Table 1. The isotherm was found to be linear over the entire concentration range with a good linear correlation coefficient ($r_L^2 > 0.999$), showing that the data correctly fitted the Langmuir isotherm. This indicated that the surface of ODA-hectorite was covered by a monolayer of MB molecules. The value of R_L in the range of 0-1 indicated the favorable uptake of the MB process.

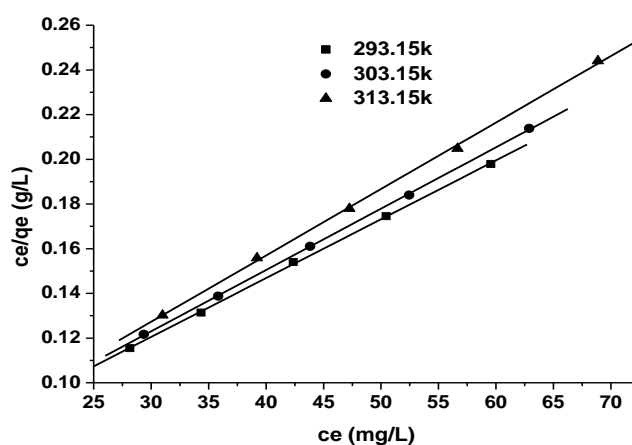


Fig.3 Langmuir isotherm for the adsorption of MB onto ODA-hectorite composite

Table 1 Langmuir constants for the adsorption of MB on ODA-hectorite

ODA-hectorite	Langmuir constants			
Temperature	q_∞ (mg/g)	k_b (L/mg)	R_L	r_L^2
293.15K	380.23	0.0634	0.0699	0.99968
303.15K	363.64	0.0677	0.0657	0.99982
313.15K	336.70	0.0780	0.0575	0.99922

3.4 Adsorption Kinetic

A study of adsorption kinetics was desirable as it provided information about the mechanism of adsorption, which was important for optimising the efficiency of the process[16]. Several kinetic models such as pseudo-first-order, pseudo-second-order, Elovich equation, intraparticle diffusion models and film diffusion study were applied for the experimental data. The amount of MB adsorbed onto ODA-hectorite increased as the time increased. Most of MB molecules adsorption took place at the initial 30 min of the experiment. As the time progressed, there was a weak increase in adsorption even after a long time.

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 model was given as Eq. (4):

$$q_t = k_{id} t^{1/2} + C \quad (4)$$

where k_{id} is the intra-particle diffusion rate constant. According to Eq. (4), 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[15]. The means of the duplicated experimental results is plotted in Fig.7. From Fig.7, 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.

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

$$D_p = (0.03r_o^2) / t_{0.5} \quad (5)$$

where r_o (m) is the average radius of the adsorbent particles and $t_{0.5}$ (min) is the time required to complete half of the adsorption. Coefficient (D_p) value is in the range 10^{-15} - 10^{-18} m²/s, then the intra-particle diffusion will be the rate-limiting step. In this study, the calculated D_p value ranged from 1.15×10^{-14} to 2.41×10^{-14} m²/s with different temperature (Table 2), which indicated the intra-particle diffusion is not only the rate-limiting step of MB adsorption onto ODA-hectorite composite.

Table 2 The intro-particle diffusion coefficients (D_p) and the film diffusion coefficient (D_F) of the adsorption process at different

T(K)	r_o (m)	$t_{0.5}$ (S)	D_p (m ² /s)	D_F (m ² /s)
293.15	7.12×10^{-6}	132.50	1.15×10^{-14}	1.89×10^{-13}
303.15		105.07	1.45×10^{-14}	2.36×10^{-13}
313.15		100.99	1.51×10^{-14}	2.39×10^{-13}
323.15		63.10	2.41×10^{-14}	3.44×10^{-13}

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

$$D_F = (0.23r_o\delta c_s) / c_L t_{0.5} \quad (6)$$

where r_o and $t_{0.5}$ have the same meaning as above, δ is the film thickness (10^{-5} m)[16], 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} m²/s.

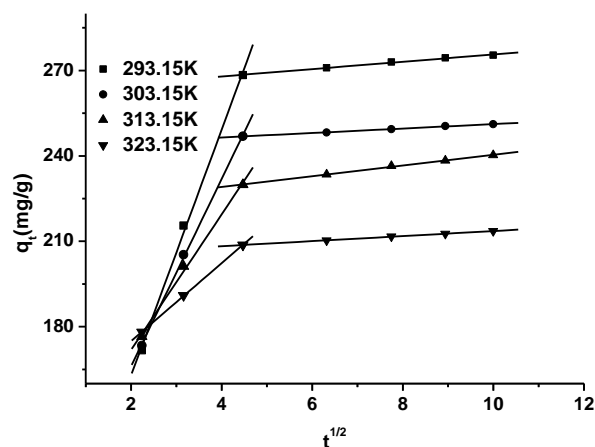


Fig.4 Werber-Morris kinetic plots of MB adsorption on ODA-hectorite at different temperature

The calculated values of D_F are found to be in the order of $10^{-13} \text{ m}^2/\text{s}$ (Table 4), 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 ODA-hectorite composite, the MB molecules began to diffuse in the ODA-hectorite, the intra-particle diffusion was controlled the adsorption process.

Summary

The present study shows that ODA-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/q_t 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.

Acknowledgments

The authors are grateful for the financial support from the National Natural Science Foundation of China (reference 21106171) and Open fund of Key Laboratory of Comprehensive and Highly Efficient Utilization of Salt Lake Resources.

References

- [1] Orhan O, Bulent A, Mustafa T, Mehmet SC. Comparison of the adsorption characteristics of azo-reactive dyes on mesoporous minerals. *Dyes and Pigments*, 62(2004) 49-60.
- [2] Niyaz Mohammad Mahmoodi, Surface modification of magnetic nanoparticle and dye removal from ternary systems, *Dyes and Pigments*, 27(2015) 251-259.
- [3] Jian Zhang, Yan Zhou, Meiyan Jiang, Juan Li, Jiawei Sheng, Removal of methylene blue from aqueous solution by adsorption on pyrophyllite, *Journal of Molecular Liquids*, 209(2015) 267-271.
- [4] Fu Y, Viraraghavan T. Fungal decolorization of dye wastewaters a review, *Bioresource Technology*, 79(2011) 251-262.
- [5] I.D. Mall, V.C. Srivastava, N.K. Agarwall, I.M. Mishra, Removal of congo red from aqueous solution by

bagasse fly ash and activated carbon: kinetic study and equilibrium isotherm analysis, *Chemosphere*, 61(2005) 492-501.

[6] M. Ozacar, I.A. Sengil, A kinetic study of metal complex dye sorption onto pine sawdust, *Process Biochem*, 40(2005) 565-572.

[7] G Annadurai, R.S. Juang, D.J. Lee, Use of cellulose-based wastes for adsorption of dyes from aqueous solutions, *J. Hazard. Mater.*, 92(2002) 263-274.

[8] Andrei Veksha, Puja Pandya, Josephine M. Hill, The removal of methyl orange from aqueous solution by biochar and activated carbon under microwave irradiation and in the presence of hydrogen peroxide, *Journal of Environmental Chemical Engineering*, 3(2015) 1452-1458

[9] Jun Ma, Yongzhong Jia, Yan jing, Equilibrium models and kinetic for the adsorption of methylene blue on Co-hectorites, *Journal of Hazardous Materials*, 175(2010) 965-969

[10] Xin Liu, Lingfang Zhang, Removal of phosphate anions using the modified chitosan bead: Adsorption kinetic isotherm and mechanism studies, *Powder Technology*, 277(2015) 112-119.

[11] K. Thirugnanasambandham, V. Sivakumar, An eco-friendly approach for copper(II) ion adsorption onto cotton seed cake and its characterization: Simulation and validation, 50(2015) 198-204

[12] Meissam Noroozifar, Mozghan Khorasani-Motlagh, Hamidreza Naderpour, Modified nanocrystalline natural zeolite for adsorption of arsenate from wastewater: isotherm and kinetic studies, *Microporous and Mesoporous Materials*, 197(2014) 101-108

[13] Chenglongxia, Yan Jing, Yongzhong Jia, Duyuan Yue, Jun Ma, Adsorption properties of congo red from aqueous solution on modified hectorite: kinetic and thermodynamic studies, *Desalination*, 265(2011) 81-87

[14] Z. Aksu, Application of biosorption for the removal of organic pollutants: a review, *Process Biochem*. 40(2005) 997-1026

[15] Jun Ma, Yongzhong Jia, Yan Jing, Ying Yao, Kinetics and thermodynamics of methylene blue adsorption by cobalt-hectorite composite, *Dyes and Pigments*, 93(2012) 1441-1446

[16] 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*, 40(2008) 67-77