

Adsorption of acid dye from water onto pristine and acid-activated clays in fixed beds

Su-Hsia Lin^{a,*}, Ruey-Shin Juang^b, Yuen-Hua Wang^a

^a Department of Chemical Engineering, Nanya Institute of Technology, Chung-Li 320, Taiwan

^b Department of Chemical Engineering and Materials Science, Yuan Ze University, Chung-Li 320, Taiwan

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Abstract

The adsorption of an acid dye from water onto pristine and HCl-activated montmorillonites in fixed beds was investigated. Experiments were carried out as a function of liquid flow rate, initial dye concentration, and bed height. The adsorption capacity of acid dye onto pristine clay could be largely improved when the clay was activated by HCl. A mass transfer model that involves only two parameters, τ (50% breakthrough time) and k (adsorption rate constant), was proposed. This model could satisfactorily describe the measured breakthrough curves of acid dye in fixed beds (standard deviation <6%). It was shown that the value of τ decreased with increasing liquid flow rate. The effect of the type of clay (pristine, acid-activated) on the values of k , τ , and adsorption capacity was discussed, and the application potential of acid-activated clay for adsorption removal of acid dye from water was also demonstrated.

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1. Introduction

Water contamination resulted from dyeing and finishing in textile industry is a major concern. Discharging large amount of dyes in water resources accompanied with organics, bleaches, and salts can affect the physicochemical properties of freshwater. In addition to their unwanted colors, some of these dyes may degrade to produce carcinogens and toxic products. Hence, the treatment of such effluents does not depend on biological degradation alone [1]. In this work, we focused on the acid dyes, which have wide applications in dyeing wool, polyamide fibers, and blends of both these fibers.

Adsorption is known to be a promising technique, which produces good quality effluents with low levels of dissolved organic compounds such as dyes. Although activated carbons

have been most widely used as adsorbents in wastewater treatment processes [2–4], there is growing interest in using low cost, commercially available materials for the adsorption of dyes. A wide variety of materials such as peat [5], palm-fruit [6], silica fumes [7], natural zeolite [8], montmorillonite, and kaolinite [9] are employed as low cost alternatives to activated carbons. Recently, clay materials have been increasingly paid attention because they are cheaper than activated carbons and their sheet-like structures also provide high specific surface area.

The Ca-type of montmorillonite, which is a 2:1 layered silicate, swells as it contacts by water. The inner layer is composed of an octahedral sheet of general form $M_{2-3}(OH)_6$ (M is typically Al), which is situated between two SiO_4 tetrahedral sheets [10]. Replacement of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} or Zn^{2+} for Al^{3+} in the octahedral layer results in a net negative charge on the clay surfaces. The charge imbalance is offset by the exchangeable cations such as Na^+ or Ca^{2+} on the layer surface. In aqueous phase, water molecules are intercalated into the interlamel-

* Corresponding author. Fax: +886 3 4666902.

E-mail address: sslin@nanya.edu.tw (S.-H. Lin).

Nomenclature

a	constant defined in Eq. (6) ($\text{min}^{-1/2}$)
C	the outlet solute concentration (M)
C_0	the inlet solute concentration (M)
F	liquid flow rate (cm^3/min)
k_1	adsorption rate constant defined in Eq. (2) ($\text{m}^3/(\text{mol min})$)
Q_e	adsorption capacity for a given bed (mol/g)
Q_0	saturated adsorption capacity of the adsorbent (mol/g)
t	breakthrough time (min)
W	the weight of the clay (g)
τ	the breakthrough time when $C/C_0 = 0.5$ (min)

lar space of montmorillonite, leading to an expansion of the clays. The dissolved organic compound can thus diffuse into the interlamellar space of montmorillonite and intercalated. Clays are widely applied in many fields of adsorption technology including the removal of amines [11], metals (Ni, Zn, Pb), phenol and ketones [12,13], phosphates [14], chlorophyll [15], non-ionic contaminants [16], and organic pigments/dyes [17–21]. The wide usefulness of clay materials is essentially a result of their high specific surface area, high chemical and mechanical stabilities, and a variety of surface and structural properties.

In the past, the adsorption of dyes from aqueous solutions onto pristine clays mostly focused on the equilibrium and contact-time kinetic studies in batch modes [17–21]. In addition, the clays modified with surfactants (i.e., the so-called organoclays) have been widely used to improve the adsorption performance [10,15,16]. To our best knowledge, little attention was paid to examining the clays activated with mineral acids. In this work, fixed bed tests were conducted as a function of the flow rate (1.4–2.0 cm^3/min), initial dye concentration (0.003–0.008 M), and bed height (2.5–3.5 cm). Dynamic experiments were performed to obtain breakthrough curves of dye through a fixed bed packed

with pristine and acid-activated montmorillonites. A simplified, two-parameter mass transfer model was proposed to describe the breakthrough data.

2. Materials and methods

2.1. Clays and solutions

Montmorillonite SAz-1 (Cheto, AZ, USA) having an idealized formula of $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot n\text{H}_2\text{O}$ was obtained from the University of Missouri-Columbia, Source Clay Minerals Repository. Its composition is 60.4% SiO_2 , 17.4% Al_2O_3 , 1.42% Fe_2O_3 , 6.42% MgO , 0.063% Na_2O , and 2.82% CaO [22]. The particle size was 0.03 mm and its cation-exchange capacity was 1.2 mol/kg. The BET surface area and average pore size were measured to be 736 m^2/g and 6.81 nm, respectively, from N_2 adsorption isotherms with a sorptiometer (Quantachrome, NOVA 2000). Analytical-grade disazo acid dye, Amido black 10B (C.I. 20470), with a molar mass of 616.5 ($\text{C}_{22}\text{H}_{14}\text{N}_6\text{Na}_2\text{O}_9\text{S}_2$) was supplied by Merck. Fig. 1 shows the structure of this dye. The clays were immersed and activated using 6 M HCl (Merck) for 2 weeks at 60 °C.

2.2. Experimental procedures

The fixed bed tests were carried out in a water-jacketed glass column with an inside diameter of 1.1 cm and a length of 12.8 cm. A typical procedure was as follows. To one end of the column a small glass fiber inserted, aqueous slurry of the clays was then aspirated into the column to obtain the clay bed. A second portion of glass fiber was plugged to another embed the loaded clay in order to prevent the loss of the clay. The aqueous solution with a known dye concentration was fed to the top of the column at a desired flow rate driven by a micro-metering pump (Cole-Parmer, Masterflex 7518-10, USA) until the breakthrough curve was completed. The temperature was controlled at 25 °C. The samples in the outlet were taken at the preset time intervals and the concentrations of dye were analyzed with an UV-vis spectrophotometer (Shimadzu, UV-2550, Japan) at a wavelength of 500 nm.

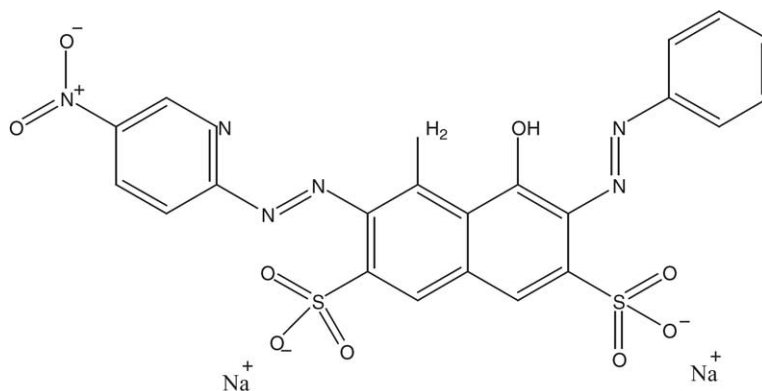


Fig. 1. Structure of the acid dye, Amido black 10B.

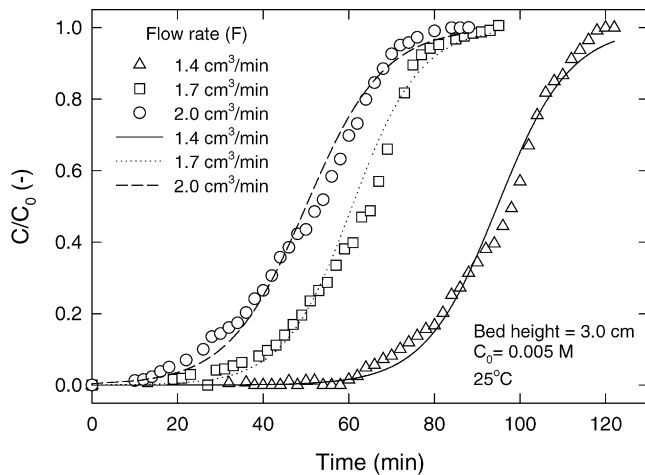


Fig. 2. The measured and modeled breakthrough curves for adsorption of acid dye onto pristine montmorillonite at different flow rates.

3. Results and discussion

3.1. Breakthrough curves using pristine and HCl-activated clays

The measured breakthrough curves of acid dye in the pristine clay bed at different flow rates, initial solute concentrations, and bed heights are shown in Figs. 2–4. Basically, the curves have the same and relatively sharp shape, indicating that the axial dispersion is insignificant. Moreover, the break point (the position at which $C/C_0 = 0.05$) appears more slowly with increasing liquid flow rate and initial dye concentration, but faster with increasing the bed height.

The measured breakthrough curves in the HCl-activated clay bed are shown in Figs. 5 and 6. Similarly, the break point appears more slowly with increasing the initial solute concentration and decreasing bed height. Under comparable conditions, the amount of dye adsorbed in HCl-activated clay

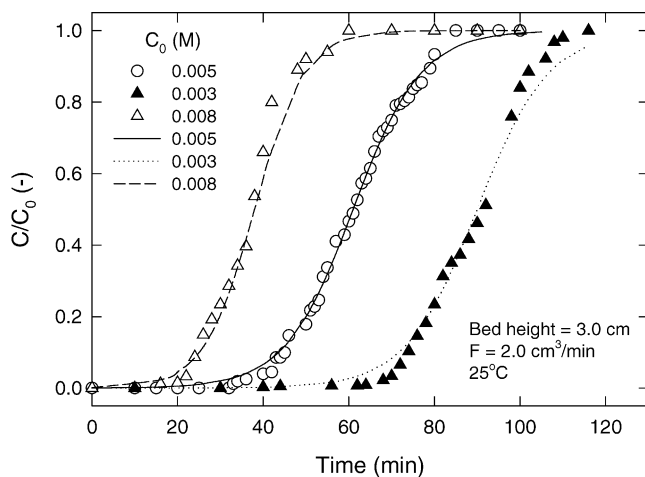


Fig. 3. The measured and modeled breakthrough curves for adsorption of acid dye onto pristine montmorillonite at different feed dye concentrations.

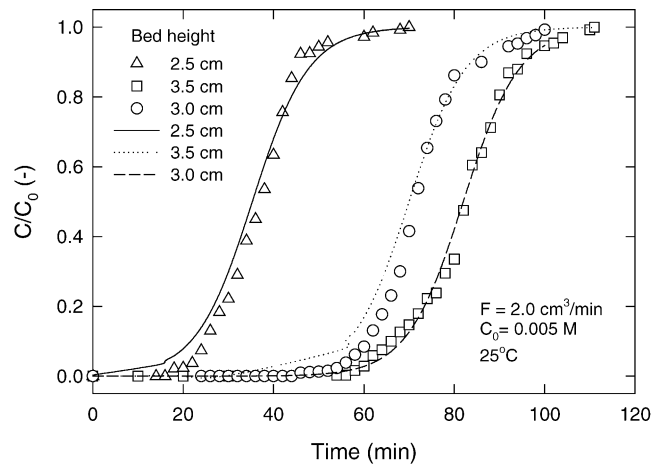


Fig. 4. The measured and modeled breakthrough curves for adsorption of acid dye onto pristine montmorillonite at different bed heights.

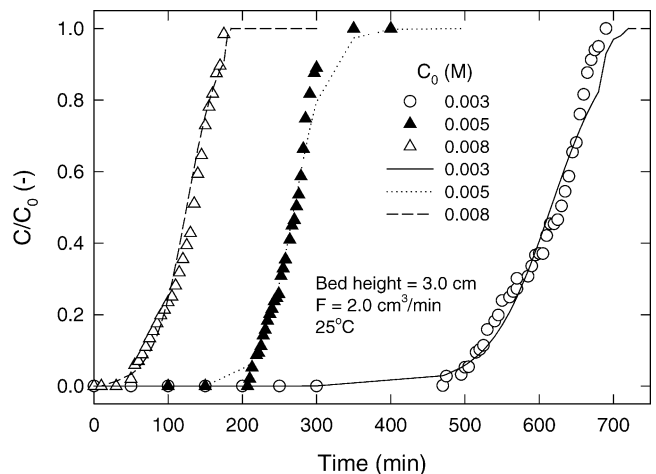


Fig. 5. The measured and modeled breakthrough curves for adsorption of acid dye onto HCl-activated montmorillonite at different feed dye concentrations.

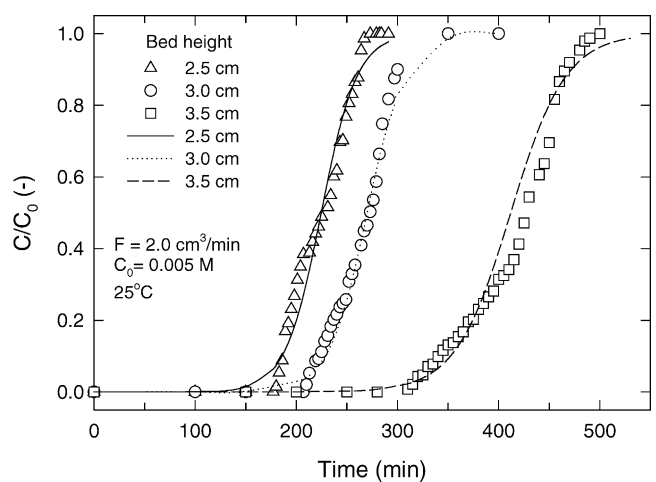


Fig. 6. The measured and modeled breakthrough curves for adsorption of acid dye onto HCl-activated montmorillonite at different bed heights.

bed is much larger than that in pristine clay bed. The same results were reported earlier in the adsorption of anionic dyes on natural and acid-activated bentonites from batch experiments [23]. Compared to the BET surface area and average pore size for the present pristine montmorillonite (736 m²/g and 6.81 nm), the corresponding values of 971 m²/g and 5.31 nm for the HCl-activated clay can explain the significant increase in the amount of adsorption.

3.2. Modeling of the breakthrough curves

Adsorption operation is a complex process and its performance is governed by many variables. The outlet concentration from fixed bed is one of important performance parameters of practical importance to the process designer. Prediction of the outlet concentration is not easy. Usually it involves solving a set of non-linear partial differential equations governing the flow and mass transfer by sophisticated numerical scheme with proper identification of many system parameters. Alternatively, the breakthrough curves of the present beds are analyzed by the following equation that was originally developed by Bohart and Adams from the microscopic model [24]

$$\ln\left(\frac{C_0 - C}{C}\right) = \ln\left[\exp\left(\frac{k_1 Q_e W}{F}\right) - 1\right] - k_1 C_0 t \quad (1)$$

where C is the outlet solute concentration (mol/m³), C_0 is the inlet solute concentration (mol/m³), k_1 is the adsorption rate constant (m³/(mol min)), Q_e is the amount of equilibrium adsorption for a given bed (mol/g), F is the flow rate (m³/min), and W is the weight of adsorbent used (g).

The advantage of this model is its simplicity and reasonable accuracy in breakthrough under various conditions [25,26]. Hutchins [27] has proposed a linear relationship between the service time and the weight of adsorbent. Because the exponential term is usually much larger than unity, the unity term in the brackets in the right-hand side of Eq. (1) is often neglected, leaving

$$\ln\left(\frac{C}{C_0 - C}\right) = -\left(\frac{k_1 Q_e W}{F}\right) + k_1 C_0 t \quad (2)$$

It is noticed that Eq. (2) is essentially the same as the logistic function, which was originally formulated to describe the phenomena of biological growth and decay [25]. Let $k = k_1 C_0$ and $\tau = Q_e W/F$, we have

$$\ln\left(\frac{C}{C_0 - C}\right) = k(t - \tau) \quad (3)$$

or

$$t = \tau + \frac{1}{k} \ln\left[\frac{C/C_0}{1 - (C/C_0)}\right] \quad (4)$$

It is evident from Eq. (4) that τ is the breakthrough time when $C/C_0 = 0.5$.

The two model parameters, τ and k , are normally obtained from the intercept and slope in the plot of $\ln[C/(C_0 - C)]$ ver-

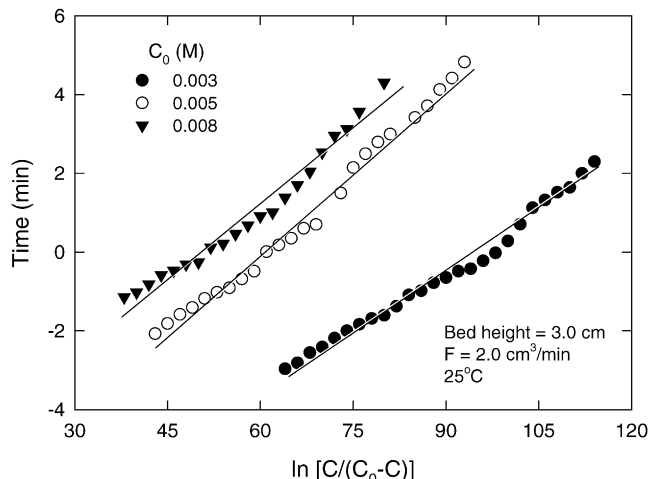


Fig. 7. Linear plots of time vs. $\ln[C/(C_0 - C)]$.

Table 1 Model parameters for the adsorption of acid dye using the pristine clay beds

Bed height (cm)	F (cm ³ /min)	C_0 (M)	τ (min)	k (min ⁻¹)	Q_e (mol/kg)
2.5	2.0	0.005	35.4	0.13	0.14
		0.003	90.5	0.12	0.32
	1.4	0.005	60.8	0.13	0.20
		0.003	50.1	0.14	0.17
3.0	1.7	0.005	90.5	0.12	0.22
		0.008	38.0	0.17	0.13
3.5	2.0	0.005	81.5	0.14	0.23

sus t according to Eq. (3). Fig. 7 shows the results, indicating the validity of this method. Tables 1 and 2 list the calculated values of τ and k . Then, the breakthrough curves calculated from Eq. (2) are shown in Figs. 2–6, and are compared with the measured ones. A close agreement is obtained (standard deviation <6%) under the conditions studied.

3.3. Comparison of model parameters

The derivation of Eq. (3) is based on the definition that 50% breakthrough occurs at $t = \tau$. Thus, the bed would be completely saturated at $t = 2\tau$. Due to the symmetrical nature of the breakthrough curve, the amount of dye adsorbed by

Table 2 Model parameters for the adsorption of acid dye using the HCl-activated clay beds

Bed height (cm)	F (cm ³ /min)	C_0 (M)	τ (min)	k (min ⁻¹)	Q_e (mol/kg)
2.5	2.0	0.005	225	0.037	0.90
3.0		0.003	617	0.024	1.23
3.0	2.0	0.005	270	0.043	0.90
		0.008	125	0.055	0.67
3.5	2.0	0.005	317	0.057	0.91

the clay bed is the half of the total dye entering the fixed bed within the 2τ period. Hence, the following equation holds

$$Q_e W = \frac{1}{2} C_0 F (2\tau) = C_0 F \tau \quad (5)$$

This equation permits an easy determination of Q_e when τ is known.

It is evident that both Q_e and τ values decrease with increasing liquid flow rate (F) (Table 1). However, the flow rate has little effect on the k value. In general, a higher flow rate does decrease the external (film) mass transfer resistance around the surface of adsorbents. At the same time, the residence time of solution within the bed is decreased. Then, the solute molecules have less time to penetrate and diffuse into the center of the adsorbent [28]. According to the present Q_e and k data, the latter effect (residence time) should be dominated, at least for the pristine clay bed.

As shown in Tables 1 and 2, the k value slightly increases with increasing C_0 . This is because the driving force of mass transfer in the liquid film is increased. On the other hand, both Q_e and τ values decrease with increasing C_0 . It is likely that the dye can aggregate due to the van der Waals force between dyes and/or by energy stabilization caused by delocalization of π -electrons in dye aggregates at higher dye concentration. This leads to the result that the sites within the micropore of adsorbent could not be utilized [21].

It is understood that the τ value increases with increasing bed height for both clays. However, increasing bed height does not affect k value for pristine clay bed, but causes an increase of k value for HCl-activated clay bed. This again confirms that the residence time effect is more dominant in these fixed beds, as have been indicated above. On the other hand, the Q_e values for pristine clay bed increases with increasing bed height (Table 1). Such findings are consistent with the previous results in the adsorption of Acid blue 80, Acid yellow 117, and Acid red 114 on activated carbon [28]. Because the adsorption processes in their study are largely diffusion controlled, a correlation between adsorption capacity and a square root of time was proposed (i.e., modified BDST model), which has the following form [28]

$$Q_e = Q_0(1 - \exp(-a\sqrt{\tau})) \quad (6)$$

where a is a constant. Although the number of our experimental data is too few to find the constant a , the trend given in Eq. (6) could reasonably explain the present observations. However, it should be noted that this is not the case for the acid-activated clay bed.

On a quantitative basis, the Q_e value for HCl-activated clay bed is about five times larger than that for pristine clay bed. In fact, Espantaleona et al. [23] have found from batch experiments that the adsorption capacities of Acid yellow 194 are 24.9 and 71.1 mg/g on natural and acid-activated bentonites, respectively, while those of Acid red 423 are 29.1 and 85.2 mg/g, respectively. Besides, the k value for HCl-activated clay is much (two to three times) smaller than that for pristine clay. This is likely a result of the structural

changes of montmorillonite during acidification process. The acidification would lead to an apparent increase in micropore volume/surface area than that of pristine clay, which is supported by higher specific surface area, smaller pore size, and larger adsorption capacity. Treatment of clays with acid at room temperature simply replaces the resident Ca and Na exchangeable ions with protons. However, the treatment with hot acid for 30 min alters the octahedral composition of clay reducing MgO and Fe₂O₃ contents [29,30]. In contrast to pristine montmorillonite, the enhanced adsorption ability of acid-activated clay indicates that the present easy-to-follow activation process is effective and promising for future applications.

4. Conclusions

Fixed-bed adsorption of an acid dye, Amido black 10B, from aqueous solutions using pristine and HCl-activated montmorillonites was experimentally and theoretically studied. The following results were obtained:

1. A mass transfer model (Eq. (3)) involving only two parameters, τ (50% breakthrough time) and k (adsorption rate constant), was successfully used to describe the breakthrough curves of both beds. The parameters could be graphically determined, and this model allowed calculating the adsorption capacity Q_e for a given fixed bed.
2. Both Q_e and τ values decreased with increasing the flow rate. However, the flow rate had little effect on the k value, at least for the pristine clay bed. On the other hand, both Q_e and τ values decreased with increasing the initial dye concentration, whereas the k value slightly increased.
3. Under comparable conditions, the Q_e value for HCl-activated montmorillonite was about five times larger than that for pristine clay but the k value was two to three times smaller. This is likely due to a large increase in micropore volume/surface area for HCl-activated montmorillonite during acidification process. The application potential of acid-activated clays for adsorption removal of acid dye from aqueous streams was highlighted.

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