

Available online at www.sciencedirect.com



Journal of Environmental Sciences 2010, 22(1) 7-14

JOURNAL OF ENVIRONMENTAL SCIENCES ISSN 1001-0742 CN 11-2629/X

www.jesc.ac.cn

# Removal of Methyl Violet from aqueous solutions using poly (acrylic acid-co-acrylamide)/attapulgite composite

Yongsheng Wang<sup>1,\*</sup>, Li Zeng<sup>1</sup>, Xuefeng Ren<sup>1</sup>, Hai Song<sup>1</sup>, Aiqin Wang<sup>2,\*</sup>

Key Laboratory of Resources and Environment Chemistry of West China, Hexi University, Zhangye 734000, China. E-mail: wys@hxu.edu.cn
 Center of Eco-Material and Green Chemistry, Lanzhou Institute of Chemical Physics,
 Chinese Academy of Sciences, Lanzhou 730000, China

Received 16 March 2009; revised 05 May 2009; accepted 14 May 2009

#### Abstract

The adsorption of Methyl Violet (MV) cationic dye from aqueous solution was carried out by using crosslinked poly (acrylic acid-co-acrylamide)/attapulgite (Poly(AA-co-AM)/ATP) composite as adsorbent. The factors influencing adsorption capacity of the composite such as pH, concentration of the dye, temperature, contact time, adsorbent dosage, ionic strength and surfactant were systematically investigated. The equilibrium data fitted very well to the Langmuir isotherm and the maximum adsorption capacity reached 1194 mg/g at 30°C. The thermodynamic parameters including  $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$  for the adsorption processes of MV on the composite were also calculated, and the negative  $\Delta H^0$  and  $\Delta G^0$  confirmed that the adsorption process was exothermic and spontaneous. The kinetic studies showed that the adsorption process was consistent with the pseudo second-order kinetic model and the desorption studies revealed that the regeneration of the composite adsorbent can be easily achieved.

Key words: composite; Methyl Violet; adsorption kinetics; isotherm

**DOI**: 10.1016/S1001-0742(09)60068-1

# Introduction

Removal of dyes from waste effluents is always widely focused because even tiny amount of dye in water is highly colored and toxic to creatures (Pokhrel and Viraraghavan, 2004; Robinson et al., 2001). Various techniques including coagulation and precipitation, ion exchange treatment, adsorption and co-precipitation/adsorption have been used for the removal of dyes from wastewater (Aksu, 2005; Crini, 2006; Forgacs et al., 2004; Qu, 2008). Among them, adsorption exhibited particular advantages over others because it has high treatment efficiency and no harmful byproduct to the treated water. Activated carbon is the most popular adsorbent and has been widely used for the removal of dyes. However, the application of activated carbon is seriously restricted owing to its high production cost. Consequently, many efforts have been done to find cheaper substitutes such as coal, fly ash, silica gel, wool wastes, agricultural wastes, wood wastes and clay minerals (Crini, 2006). Among the clay minerals used, attapulgite (APT) is a crystalline hydrated magnesium silicate with a fibrous morphology, large specific surface area and moderate cation exchange capacity, which is beneficial for the adsorption of dye from aqueous solution (Al-Futaisi et al., 2007; Murray, 2000). However, its adsorption capacity for dyes is limited. Therefore, several attempts have been made to develop more effective adsorbents for the removal of dyes (Crini, 2006; Huang et al., 2007).

In recent years, the polymer/clay hydrogel composite has received great attention because of their relatively low production cost and high adsorption capacity for some dyes (Wang et al., 2008). Hydrogel is a porous threedimensional polymeric network, and the special structure facilitates the diffusion of solutes into the interior network. Also, hydrogels possess numerous ionic or nonionic functional groups, which can absorb and trap ionic dyes from wastewater (Paulino et al., 2006). However, to the best of our knowledge, little information regards to the adsorption of Methyl Violet (MV) by polymer/clay hydrogel composite. On the basis of our previous work on hydrogel composite poly (acrylic acid-co-acrylamide)/attapulgite (Poly(AA-co-AM)/ATP) (Li and Wang, 2005), the adsorption behaviors of MV by the composites was studied in this article. The effects of various experimental parameters such as pH, dye concentration, temperature, contact time, adsorbent dosage, ionic strength and surfactant on the adsorption process were evaluated. Moreover, the equilibrium isotherms and the adsorption kinetics of MV onto the composite were also investigated.

<sup>\*</sup> Corresponding author. E-mail: aqwang@lzb.ac.cn (Aiqin Wang); wys@hxu.edu.cn (Yongsheng Wang)

# 1 Materials and methods

#### 1.1 Materials

Acrylic acid (AA, distilled under reduced pressure before use), ammonium persulfate (APS, recrystallized from distilled water before use), N,N'-methylenebisacrylamide (MBA, used as received) and Methyl Violet (MV, C.I.: 42535, used without further purification) were supplied by Shanghai Reagent Corp., China. Acrylamide (AM, analytical grade, Beijing Chemical Factory, China) was purified by recrystallization from benzene. Attapulgite (APT, Jiangsu Autobang Co., Ltd., China) was milled and sieved through a 320-mesh screen. All MV solutions were prepared with distilled water. Since the dye is difficult to dissolve in water, the dye solution was allowed to stand for 1-2 days until absorbance of the solutions remained unchanged. The molecular formula of MV is C<sub>24</sub>H<sub>28</sub>ClN<sub>3</sub> with the maximum absorbance wavelength at 584 nm. Other reagents used were all analytical grade and all solutions were prepared with distilled water.

# 1.2 Preparation of poly(AA-co-AM)/APT composites and their characterization

Poly(AA-co-AM)/APT composite from AA, AM and APT was prepared according to the methods described previously (Li and Wang, 2005). The IR spectra (Thermo Nicolet NEXUS TM spectrophotometer) showed that the graft copolymerization reaction has taken place among AA, AM and APT. The -OH groups on the surface of APT could react with AA and AM, and then form the composite network in the presence of crosslinker MBA. It has been conformed by previous reports (Li et al., 2004; Xiang et al., 2006) that APT particles act as crosslinking points in the composite network and the excess ATP was only physically filled in the polymeric network. By considering both the production cost and the adsorption properties of the composite adsorbent, the composite containing 30 wt.% APT was selected as the adsorbent and the efficiency of this material for removing MV from aqueous solution was evaluated.

### 1.3 Adsorption equilibrium experiments

Adsorption experiments were performed using the standard batch technique. The composite 0.05 g was placed in a set of 100 mL glass-stoppered Erlenmeyer flasks and 50 mL of dye solutions with various concentrations were introduced, respectively. The pH of each solution was adjusted to the desired value using 0.1 mol/L HCl or NaOH solution. The mixture was agitated in a thermostated shaker (THZ-82) at a constant speed of 120 r/min for a given time, and then the suspensions were centrifuged at 4500 r/min for 10 min. The dye concentration in the solution was analyzed at 584 nm with a spectrophotometer (UNICO 2100). The equilibrium absorption amount of MV,  $q_e$  (mg/g), is calculated using the following Eq. (1):

$$q_e = (c_0 - c_e) \times V/W \tag{1}$$

The percentage of MV removal percentage (R) is calculated according to Eq. (2)

$$R = (c_0 - c_e)/c_0 \times 100\% \tag{2}$$

where,  $c_0$  (mg/L) and  $c_e$  (mg/L) are the initial and equilibrium concentrations of MV, respectively, V (L) is the solution volume and W (g) is the composite mass.

#### 1.4 Adsorption kinetic studies

Present kinetic investigations are carried out to measure the adsorption rate under various experimental conditions such as pH, temperature, inorganic salts and surfactant concentration, and to determine the time required to reach adsorption equilibrium. Fifty milligrams of adsorbent were added to 50 mL of dye solution with desired concentration and definite pH. The mixture was then shaken using a temperature-controlled shaker on a constant agitation speed (120 r/min) at different time intervals. The calculation method of the absorption amount of MV was the same as adsorption equilibrium experiments.

### 1.5 Desorption experiments

The adsorbent was dispersed in 1000 mg/L MV solution as mentioned in the adsorption procedure. The MV-loaded adsorbent was separated from the mixture solution by centrifugation and washed with distilled water to remove any unabsorbed dye. Desorption experiment was performed by transferring the MV-loaded composite into 50 mL of distilled water and stirred for 4 hrs. The pH was adjusted between 2 and 10 by adding 0.1 mol/L HCl or NaOH solution. After regeneration, the adsorbent was again used for the further adsorption of MV. Adsorption and desorption experiments were repeated for 4 cycles.

# 2 Results and discussion

### 2.1 Contact time

The adsorption of MV on Poly(AA-co-AM)/APT composite at different initial concentrations (200–1000 mg/L) and temperatures (30–60°C) was studied as a function of contact time to determine the equilibrium time. As shown

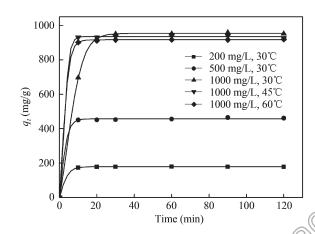


Fig. 1 Removal of Methyl Violet (MV) as a function of contact time Conditions: adsorbent dose 0.05 g; agitation rate 120 r/min.

in Fig. 1, the amount of adsorbed MV increases with prolonging contact time and attains equilibrium at about 90 min for different initial concentrations and temperatures. It indicates that equilibrium time is independent of initial MV concentration and solution temperature. The contact time was chosen as 90 min for the subsequent study.

The initial concentration provides an important driving force to overcome all mass transfer limitations of MV between aqueous and solid phases, therefore, dye removal is highly concentration dependent. The adsorption rate also increases with increasing initial dye concentration due to the increase of driving force. Thus, a higher initial MV concentration could enhance the adsorption process. The information obtained also gave an indication that  $q_{\rm e}$  increased with increasing initial concentration and decreased with increasing temperature. The maximum equilibrium adsorption capacities are 970.9, 934.6 and 917.4 mg/g for 1000 mg/L initial concentration at 30, 45 and 60°C, respectively.

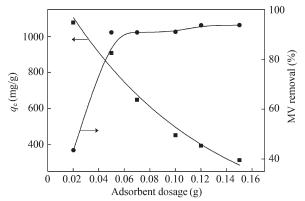
#### 2.2 Effect of adsorbent dosage

In order to investigate the effect of adsorbent amount on MV removal, a series of experiments were performed for a wide adsorbent dosage range 0.02–0.15 g. The relationship between adsorption rate and adsorbent dosage is given in Fig. 2. It can be seen that the removal efficiency rapidly increases with increasing adsorbent dosage when the composite amount was less than 0.05 g, and then tends to constant with further increasing adsorbent dosage. The relationship between the amount of MV adsorbed and the composite dosage is also given in Fig. 2. Obviously, the amount of MV adsorbed decreased rapidly with increasing adsorbent dosage. The results indicated that a higher adsorbent dosage results in a higher MV removal efficiency but corresponds to a lower adsorption capacity. In this system, the optimum dosage of the composite is 0.05 g.

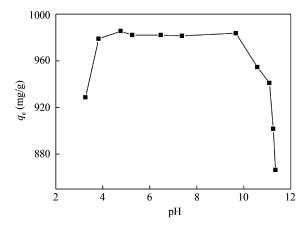
# 2.3 Effect of initial pH

To study the influence of pH on the adsorption capacity of the composite for MV, experiments were performed at initial concentration of 1,000 mg/L and pH range 3–12. During this process, no additional ion was added. Figure 3 shows that the adsorption capacity of the composite for MV is practically independent on pH in the range of 4.5–9.8. However, when pH was lower than 4 and higher than 10, a remarkable decrease in adsorption capacity was observed.

Two possible mechanisms of MV adsorption may be



**Fig. 2** Effect of adsorbent dosage on adsorption capacity of MV. Conditions: initial MV concentration 1000 mg/L; contact time 90 min; agitation rate 120 r/min; temperature 30°C; volume 50 mL.



**Fig. 3** Effect of pH on adsorption of MV. Conditions: initial MV concentration 1000 mg/L; agitation rate 120 r/min; temperature 30°C; volume 50 mL.

considered (Karadağ et al., 2002; Mahdavinia et al., 2004; Şolpan and Kölge, 2006). One is electrostatic interaction between the negative adsorption site of the adsorbent (-COO<sup>-</sup>) and the positively charged dye. The other one is hydrogen bonding interaction between the reactive -OH on the APT surface or -COOH groups of polymer chains and the amine groups -NR<sup>2</sup> of the dye MV. Since polyacrylamide is a non-ionic polymer, ionizable groups on the polymer were increased by the introduction of AA. Therefore, the composite have many carboxyl groups which can increase the interaction between the cationic groups of MV dye and the carboxyl groups of adsorbent. Hydrogen bond will occur between hydroxy or carboxyl group on the repeating unit of the composite and amine groups on the dye molecules (Scheme 1). However, at

Scheme 1 Possible interaction process between dye molecule and Poly(AA-co-AM)/APT composite.

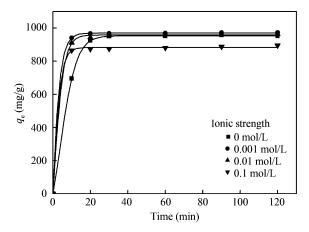
extreme acidic (pH < 4) or basic media (pH > 10), the screening effect of the counter ions, i.e.,  $Cl^-$  and  $Na^+$ , shields the charge of the ammonium cations on the dye or ionization carboxyl group on the composite. As a result, the dye molecule is more difficult to transfer and the adsorption amount of MV dye was obviously decreased.

#### 2.4 Effect of ionic strength

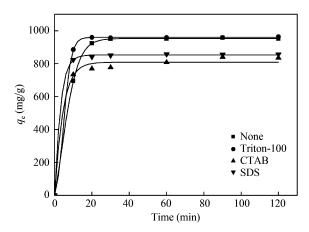
In typical dyeing system, it is well known that salts can either accelerate or retard dye adsorption processes. There are a number of studies showing the changing of the removal order of dye with various types of electrolyte in dye medium (Doğan et al., 2007; van de Ven et al., 2007). Sodium chloride is frequently used as a stimulator in dyeing process. The effect of external ionic strength on the adsorption rate of MV on the composite was investigated in NaCl solutions with the concentration range from 0 to 0.1 mol/L at 30°C (Fig. 4). Generally, increasing ion strength will decrease adsorption capacity when there is the electrostatic attraction between the adsorbent surface and adsorbate. Interestingly, in this study, the raising in ionic strength of solution causes an appreciably increase in the adsorption amounts of MV on Poly(AA-co-AM)/APT composite. However, at high ionic strength (0.1 mol/L), a notable decrease in adsorption capacity for MV was observed. The presence of NaCl in the solution may have two opposite effects. On the one hand, the salt can screen the electrostatic interaction between the composite adsorbent and the dye molecules, and makes the adsorption capacity for MV decrease with increasing NaCl concentration. On the other hand, the salt has the positive effect for the dissociation of dye molecules by facilitating the protonation. The obtained results gave an indication that this adsorption process is mainly governed by the former effect.

# 2.5 Effect of surfactant

Owing to many particular characteristics, surfactants have been used widely in modern industrial processes, and therefore the remnant of them cannot be ignored (Cestari, 2006; Janoš, 2003, 2005). The effects of various



**Fig. 4** Effect of ionic strength on adsorption of MV. Conditions: adsorbent dosage 0.05 g; initial MV concentration 1000 mg/L; agitation rate 120 r/min; temperature 30°C; volume 50 mL.



**Fig. 5** Effect of surfactant on adsorption of MV. Conditions: adsorbent dosage 0.05 g; initial MV concentration 1,000 mg/L; agitation rate 120 r/min; temperature 30°C volume 50 mL.

surfactants on the adsorption capacity were examined as shown in Fig. 5. The surfactant involved anionic sodium dodecylbenzenesulfonate (SDS), non-ionic polyoxyethylene glycol *tert*-octylphenyl ether (Triton X-100) and cationic cetyltrimethylammonium bromide (CTAB). Although there is strong attractive interaction between the MV molecule and the adsorbent surface, a visible decrease in adsorption capacity for MV was observed when the ionic surfactants SDS and CTAB were added into the adsorbate. This tendency may be arisen from the electrostatic repulsion between ionic surfactants and dye or adsorbent (Dakily et al., 2002; Janoš, 2005). Meanwhile, the presence of nonionic surfactant (Triton X-100) affected slightly the dye adsorption.

#### 2.6 Adsorption isotherms

The adsorption isotherm may provide the most important information that reveal how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption process reaching an equilibrium. In order to optimize the design of an adsorption system for removing the dye, it is important to establish the most appropriate correlation for the equilibrium curves. The equilibrium isotherms in this study can be described in terms of Langmuir (Langmuir, 1916) and Freundlich (Butt et al., 2003) isotherms as shown in Eqs. (3) and (4), respectively. The corresponding data obtained are listed in Table 1.

$$c_{\rm e}/q_{\rm e} = 1/Q_{\rm m}K + c_{\rm e}/Q_{\rm m}$$
 (3)

$$\ln q_{\rm e} = \ln K_{\rm F} + 1/n \ln c_{\rm e} \tag{4}$$

The calculated maximum monolayer adsorption

**Table 1** Isotherms constants and correlation coefficients for MV adsorbed on Poly(AA-co-AM)/APT composite

T	Q <sub>m,exp</sub> (mg/g)	Laı	Langmuir model			Freundlich model		
(°C)		Q <sub>m,cal</sub> (mg/g)	K×10 <sup>3</sup> (L/mol)	$R^2$	K <sub>F</sub> (mg/g)	n	$R^2$	
30	1194	1171	21.19	0.998	515.5	8.59	0.635	
45	1167	1120	13.71	0.996	153.4	3.13	0.809	
60	1038	1044	8.86	0.997	165.1	3.50	0.841	

capacity  $Q_{\rm m}$  for MV on the composite is found to be 1171.3 mg/g at 30°C. For predicting the favorability of an adsorption system, the Langmuir equation can be expressed in terms of a dimensionless separation factor,  $R_{\rm L}$ , defined as follows:

$$R_{\rm L} = 1/(1 + Kc_0) \tag{5}$$

Values of  $R_{\rm L}$  calculated at 30, 45 and 60°C were in the range between 0 and 1, suggesting that the adsorption process is favorable. Table 2 lists the comparison of maximum monolayer adsorption capacity of some dyes on various low-cost adsorbents. Compared with some data in the literature, Table 2 shows that the composite studied in this work possesses a larger adsorption capacity.

# 2.7 Thermodynamic parameters

The equilibrium constants obtained from Langmuir equation at 30, 45 and  $60^{\circ}$ C were used to determine the thermodynamic activation parameters such as enthalpy  $(\Delta H)$ , free energy change  $(\Delta G)$  and entropy change  $(\Delta S)$  (Liu, 2006). The change in the Gibbs free energy for a reaction can be expressed as follows:

$$\Delta G = \Delta G^0 + RT \ln Q \tag{6}$$

where,  $\Delta G^0$  and  $\Delta G$  are the standard Gibbs free energy change and reaction quotient, respectively. When the adsorption reaction reaches the equilibrium state,  $\Delta G$  becomes zero so that  $\Delta G^0$  is equal to  $-RT \ln K$ , where, K denotes the equilibrium constant. Table 2 shows the Gibbs free energy values for the adsorption process. The negative value  $\Delta G^0$  indicates the spontaneous nature of MV adsorption onto the composite.

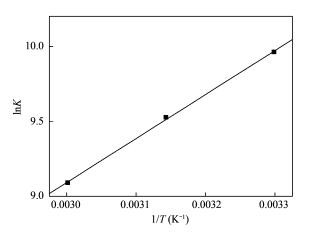
The temperature dependence of the free energy change is given by the following equation (Alkan et al., 2004):

$$d(\Delta G^0/T) = -\Delta H/T^2 dT \tag{7}$$

$$d\ln K/d(1/T) = -\Delta H^0/R \tag{8}$$

Substituting Eq. (6) into Eq. (7) yields Eq. (8) and the equilibrium constant can be expressed in terms of enthalpy change of adsorption as a function of temperature. Assuming that  $\Delta H^0$  is approximately independent of temperature, the slope of  $\ln K$  versus 1/T plot is equal to  $-\Delta H^0/R$ . The change of adsorption entropy can be determined from the equation as  $\Delta G^0 = \Delta H^0 - T \Delta S^0$ .

Figure 6 shows the plots of  $\ln K$  versus 1/T, it can be seen that the linearity of the plots is satisfactory ( $R^2=0.996$ ). Table 3 represents the thermodynamic parameters for MV adsorption on the composite at various temperatures. In



**Fig. 6**  $\ln K$  versus 1/T for the enthalpy change of the adsorption process.

Table 3 Thermodynamic parameters for adsorption of MV at various temperatures

T(K)	$\Delta G^0$ (kJ/mol)	$\Delta H^0$ (kJ/mol)	$\Delta S^0$ (J/(mol·K))
303.15	-25.11	-24.38	2.40
318.15	-25.19		2.57
333.15	-25.18		2.39

general, the change of free energy for physisorption is between -20 and 0 kJ/mol, but chemisorption is in a range of -80 to -400 kJ/mol (Myers, 1999). The results obtained about -25 kJ/mol at different temperature indicates that this is a spontaneous physisorption process. The negative value of  $\Delta H^0$  shows the adsorption is an exothermic process. The positive value of entropy change suggests the increased randomness at the solid-solution interface during the adsorption of MV on the adsorbent.

# 2.8 Adsorption kinetics

In order to investigate the adsorption mechanism, pseudo first-order and pseudo second-order kinetic equations were used to test the experimental data of initial concentration, temperature, ionic strength, surfactant and pH. The first-order kinetic equation was tested but straight lines were not obtained. In many cases, the first-order equation of Lagergren does not fit well to the whole range of contact time and is generally applicable over the initial stage of the adsorption processes (Crini et al., 2007; Bhattacharyya and Sharma, 2004). The adsorption kinetics may be described by a pseudo second-order model (Mckay and Ho, 1999) as following Eq. (9):

$$dq_t/dt = k_2(q_e - q_t)^2 \tag{9}$$

where,  $k_2$  (g/(mg·min)) is the rate constant of the pseudo second-order adsorption,  $q_e$  and  $q_t$  (mg/g) are the amount

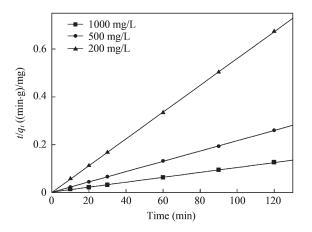
 Table 2
 Comparison of recent reported adsorption capacities of MV for low-cost adsorbents

Adsorbent	$Q_{\text{max}}$ (mg/g)	Isotherms model	T(K)	Reference
Poly(AA-co-AM)/APT	1171.3	Langmuir	303	This work
Amphoteric starch	333.33	Langmuir	293	Xu et al., 2006
Sunflower seed hull	92.59	Freundlich	303	Hameed, 2008
Sugarcane dust	50.40	Langmuir	298	Ho et al., 2005
Bagasse fly ash	26.25	Langmuir	303	Mall et al., 2006
Mansonia wood sawdust	24.6	Langmuir	329	Ofomaja and Ho, 2008

of MV adsorbed at equilibrium and at time t, respectively. Integrating Eq. (9) and applying boundary conditions (t = 0 to t = t and  $q_t = 0$  to  $q_t = q_t$ ) gives the relation shown in Eq. (10).

$$t/q_t = 1/k_2 q_e^2 + t/q_e (10)$$

The rate parameters  $k_2$  and  $q_e$  can be directly obtained from the intercept and slope of the plot of  $t/q_t$  against t. Figure 7 shows the pseudo second-order kinetics of MV adsorption onto the composite for different initial dye concentrations. It is clear that the adsorption kinetics of MV onto the composite follows this model, with regression coefficients higher than 0.999. The calculated values agree with the experimental data very well, indicating that the sorption system studied obeys the pseudo second-order kinetic model. The similar straight-line agreements are also observed for data at different conditions. Table 4 lists the computed results from the second-order kinetic model. The linear correlation coefficients for the second-order kinetic



**Fig. 7** Pseudo second-order kinetics plots for the adsorption of MV at different concentrations. Agitation rate 120 r/min; temperature 30°C.

model are equal to 1 for almost all the cases. According to the pseudo second-order model, the adsorption rate  $dq_t/dt$  is proportional to the second-order of  $(q_e-q_t)$ . Since the composite have relatively high equilibrium adsorption capacity, the adsorption rate becomes very fast and the required equilibrium time is short. Such short equilibrium time coupled with high adsorption capacity indicates a high-degree affinity of the adsorbent with the dye.

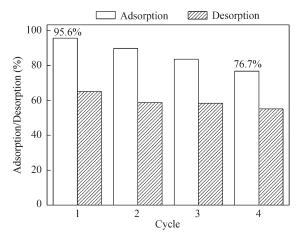
# 2.9 Desorption studies

To check the economical efficiency of this composite adsorbent and to understand the interaction between MV and Poly(AA-co-AM)/APT, desorption experiments were carried out. Wastewater treatment will be economical if the adsorbent can be recovered and repeatedly used. Desorption studies can help elucidating the mechanism of the adsorption process. If the dye adsorbed onto the adsorbent can be desorbed by water, it can be said that the attachment of the dye onto the adsorbent is by weak bonds. The result of desorption showed that desorption efficiency at lower pH (2.31) was found to be greater than that of all other desorption medium. The high desorption in acidic medium indeed reveals that the adsorption of MV onto the composite is mainly controlled by electrostatic attraction, which is consistent with the results obtained previously. Also, this result means that the interaction forces between MV molecule and binding site can be broken down in HCl solution. The regenerated composite was further used for four consecutive adsorption-desorption cycles and results are shown in Fig. 8. It can be noticed that the regenerated composite showed better affinity and satisfactory adsorption capability towards MV even though there is a gradual decrease in adsorption capacity (from 95.6% in first cycle to 76.7% in fourth cycle), and the composite can be used as potential adsorbent for the removal of MV in wastewater treatment.

Table 4 Pseudo second-order kinetic parameters for the removal of MV

Parameter				Pseudo second-order kinetics model				
T (°C)	I <sup>a</sup> (mol/L)	Surf <sup>b</sup> (0.001mol/L)	pН	C <sub>0</sub> (mg/L)	q <sub>e,cal</sub> (mg/g)	q <sub>e,exp</sub> (mg/g)	k <sub>2</sub> (g/mg min)	$R^2$
30	0	None	4.61	1000	970.9	958.4	0.0005	0.9996
30	0	None	4.61	500	465.1	464.7	0.0037	1
30	0	None	4.61	200	178.6	179.4	0.1150	1
45	0	None	4.61	1000	934.6	940.9	0.0051	0.9999
45	0	None	4.61	500	467.3	464.9	0.0056	1
45	0	None	4.61	200	189.4	188.7	0.0052	1
60	0	None	4.61	1000	917.4	918.7	0.0064	1
60	0	None	4.61	500	463.0	460.6	0.0027	1
60	0	None	4.61	200	161.6	162.1	0.0063	0.9997
30	0.001	None	4.61	1000	980.4	973.5	0.0034	1
30	0.01	None	4.61	1000	961.5	960.0	0.0014	1
30	0.1	None	4.61	1000	892.9	890.9	0.0014	1
30	0	Triton	4.61	1000	961.5	963.9	0.0021	1
30	0	SDS	4.61	1000	862.1	958.5	0.0046	1
30	0	CTAB	4.61	1000	854.7	839.6	0.0008	0.9999
30	0	None	6.58	1000	980.4	980.6	0.0062	1
30	0	None	8.22	1000	990.1	986.3	0.0148	1_((
30	0	None	10.09	1000	980.4	977.1	0.0098	1

<sup>&</sup>lt;sup>a</sup> I: ionic strength; <sup>b</sup> surf: surfactant.



**Fig. 8** Four cycles of MV adsorption-desorption with HCl solution (pH 2.31) as the desorbing agent.

# **3 Conclusions**

Methyl Violet was effectively removed from aqueous solutions using Poly(AA-co-AM)/APT as the adsorption agent. Batch adsorption experiments show that the adsorption of MV onto Poly(AA-co-AM)/APT was dependent on many variables including pH, concentration of the dye, temperature, time, adsorbent dosage, ionic strength and surfactant. The maximum adsorption capacity is found to be 1194 mg/g at 30°C. The adsorption process of MV onto Poly(AA-co-AM)/APT follows the pseudo second-order kinetics, and the adsorption is exothermic and spontaneous. The isothermal data obey the Langmuir model better compared to Freundlich model. The regeneration of the spent adsorbent is easily performed with HCl aqueous solution (pH 2.31) and the composite adsorbent can be effectively reused for four cycles consecutively. All results above open up numerous potential application of Poly(AAco-AM)/APT as an effective low-cost adsorption agent to remove dye in industrial process.

# Acknowledgments

This work was financially supported by the Western Action Project of Chinese Academy of Science (No. KGCX2-YW-501), the Taihu Project of Jiangsu Provincial Science and Technology Office (No. BS2007118, BE2008087) and the Key Laboratory of Resources and Environment Chemistry of West China, Hexi University (No. XZ0606).

# References

- Aksu Z, 2005. Application of biosorption for the removal of organic pollutants: A review. *Process Biochemistry*, 40: 997–1026.
- Al-Futaisi A, Jamrah A, Al-Rawas A, Al-Hanai S, 2007. Adsorption capacity and mineralogical and physico-chemical characteristics of Shuwaymiyah palygorskite (Oman). *Environmental Geology*, 51: 1317–1327.
- Alkan M, Demirbaş Ö, Çelikçapa S, Doğan M, 2004. Sorption of Acid Red 57 from aqueous solution onto sepiolite. *Journal of Hazardous Materials*, 116: 135–145.

- Bhattacharyya K G, Sharma A, 2004. Azadirachta indica leaf powder as an effective biosorbent for dyes: A case study with aqueous congo red solutions. *Journal of Environmental Management*, 71: 217–229.
- Butt H J, Graf K, Kappl M, 2003. Physics and Chemistry of Interfaces. Wiley-VCH, Weinheim. 185–193.
- Cestari A R, Vieira E F S, Vieira G S, Almeida L E, 2006. The removal of anionic dyes from aqueous solutions in the presence of anionic surfactant using aminopropylsilica-kinetic study. *Journal of Hazardous Materials*, 138: 133–141.
- Crini G, 2006. Non-conventional low-cost adsorbents for dye removal: A review. *Bioresource Technology*, 60: 67–75.
- Crini G, Peindy H N, Gimbert F, Robert C, 2007. Removal of C.I. Basic Green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: Kinetic and equilibrium studies. *Separation and Purification Technology*, 53: 97–110.
- Dakily M, Khamis M, Manasra A, Takrouri K, 2002. Effect of surfactants on the thermodynamic properties of Methyl Orange dye in buffered solutions. *Color Technology*, 118: 191–197.
- Doğan M, Özdemir Y, Alkan M, 2007. Adsorption kinetics and mechanism of cationic Methyl Violet and Methylene Blue Dyes onto sepiolite. Dyes and Pigments, 75: 701–713.
- Forgacs E, Cserháti T, Oros G, 2004. Removal of synthetic dyes from wastewaters: A review. *Environment International*, 30: 953–971.
- Hameed B H, 2008. Equilibrium and kinetic studies of Methyl Violet sorption by agricultural waste. *Journal of Hazardous Materials*, 154: 204–212.
- Ho Y S, Chiu W T, Wang C C, 2005. Regression analysis for the sorption isotherms of basic dyes on sugarcane dust. *Bioresource Technology*, 96: 1285–1291.
- Huang J H, Liu Y F, Jin Q Z, Wang X G, Yang J, 2007. Adsorption studies of a water soluble dye, Reactive Red MF-3B, using sonication-surfactant-modified attapulgite clay. *Journal of Hazardous Materials*, 143: 541–548.
- Janoš P, 2003. Sorption of basic dyes onto iron humate. *Environmental Science & Technology*, 37: 5792–5798.
- Janoš P, Ömídová V, 2005. Effects of surfactants on the adsorptive removal of basic dyes from water using organomineral sorbent-iron humate. *Journal of Colloid and Interface Sci*ence, 29: 19–27.
- Karadağ E, Šzüm Ö B, Saraydin D, 2002. Swelling equilibria and dye adsorption studies of chemically crosslinked superabsorbent acrylamide/maleic acid hydrogels. *European Polymer Journal*, 38: 2133–2141.
- Langmuir I, 1916. The constitution and fundamental properties of solids and liquids. *Journal of the American Chemical Society*, 38: 2221–2295.
- Li A, Wang A Q, 2005. Synthesis and properties of clay-based superabsorbent composite. *European Polymer Journal*, 41: 1630–1637.
- Li A, Wang A Q, Chen J M, 2004. Studies on poly(acrylic acid)/attapulgite superabsorbent composite. I. Synthesis and characterization. *Journal of Applied Polymer Science*, 92: 1596–1603.
- Liu Y, 2006. Some consideration on the Langmuir isotherm equation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 274: 34–36.
- Mahdavinia G R, Pourjavadi A, Hosseinzadeh H, Zohuriaan M J, 2004. Modified chitosan 4. superabsorbent hydrogels from poly (acrylic acid-co-acrylamide) grafted chitosan with salt- and pH-responsiveness properties. European Polymer

- Journal, 40: 1399-1407.
- Mall I D, Srivastava V C, Agarwal N K, 2006. Removal of Orange-G and Methyl Violet dyes by adsorption onto bagasse fly ash-kinetic study and equilibrium isotherm analyses. *Dyes and Pigments*, 69: 210–223.
- Mckay G, Ho Y S, 1999. Pseudo-second order model for sorption processes. *Process Biochemistry*, 34: 451–465.
- Murray H H, 2000. Traditional and new applications for kaolin, smectite, and palygorskite: A general overview. *Applied Clay Science*, 17: 207–221.
- Myers D, 1999. Surfaces, Interfaces, and Colloids: Principles and Applications (2nd ed.). John Wiley & Sons, Inc., New York. 187–190.
- Ofomaja A E, Ho Y S, 2008. Effect of temperatures and pH on Methyl Violet biosorption by Mansonia wood sawdust. *Bioresource Technology*, 99: 5411–5417.
- Paulino A T, Guilherme M R, Reis A V, Campese G M, Muniz E C, Nozaki J, 2006. Removal of Methylene Blue from an aqueous media using a superabsorbent hydrogel supported on modified polysaccharide. *Journal of Colloid and Interface Science*, 301: 55–62.
- Pokhrel D, Viraraghavan T, 2004. Treatment of pulp and paper mill wastewater – A review. Science of the Total Environment, 333: 37–58.
- Qu J H, 2008. Research progress of novel adsorption processes

- in water purification: A review. *Journal of Environmental Sciences*, 20(1): 1–13.
- Robinson T, McMullan G, Marchant R, Nigam P, 2001. Remediation of dyes in textile effluent: A critical review on current treatment technologies with a proposed alternative. *Bioresource Technology*, 77: 247–255.
- Şolpan D, Kölge Z, 2006. Adsorption of Methyl Violet in aqueous solutions by poly (N-vinylpyrrolidone-co-methacrylic acied) hydrogels. *Radiation Physics and Chemistry*, 75: 120–128.
- van de Ven T G M, Saint-Cyr K, Allix M, 2007. Adsorption of Toluidine Blue on pulp fibers. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 294: 1–7.
- Wang L, Zhang J P, Wang A Q, 2008. Removal of Methylene Blue from aqueous solution using chitosan-g-poly(acrylic acid)/montmorillonite superadsorbent nanocomposite. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 322: 47–53.
- Xiang Y Q, Peng Z Q, Chen D J, 2006. A new polymer/clay nano-composite hydrogel with improved response rate and tensile mechanical properties. *European Polymer Journal*, 42: 2125–2132.
- Xu S M, Wang J L, Wu R L, Wang J D, Li H, 2006. Adsorption behaviors of acid and basic dyes on crosslinked amphoteric starch. *Chemical Engineering Journal*, 117: 161–167.

