

## The adsorption behaviors of the multiple stimulus-responsive poly(ethylene glycol)-based hydrogels for removal of RhB dye

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**ABSTRACT:** In this article, the multiple stimulus-responsive organic/inorganic hybrid hydrogels by combining poly(2-(2-methoxyethoxy) ethyl methacrylate-co-oligo (ethylene glycol) methacrylate-co-acrylic acid) (PMOA) hydrogel with magnetic attapulgite/Fe<sub>3</sub>O<sub>4</sub> (AT-Fe<sub>3</sub>O<sub>4</sub>) nanoparticles were applied to the removal of Rhodamine B (RhB) dye from wastewater. The adsorption of RhB by the hydrogels was carried out under different external environmental, such as pH, temperature and magnetic-field. The results showed that the hydrogels still possessed temperature, pH and magnetic-field sensitivity during the adsorption process, which indicated that the adsorption could be controlled by the hydrogels responsive. The dye adsorption had a significant increment at 30°C and the removal of RhB could reach to over 95%. Besides, the low pH values were also favorable for the RhB adsorption, the removal was over 90% at pH = 4.56. Kinetic studies showed that the pseudo-second order kinetic model well fitted the experimental data. The rate constant of adsorption was 0.0379 g/mg min. Langmuir and Freundlich isotherm models were applied to the equilibrium adsorption for describing the interaction between sorbent and adsorbate. The maximum  $K_L$  and  $K_F$  were 2.23 (L/g) and 0.87 (mg/g) at 30°C, respectively. Under the external magnetic-field, the adsorption rate significantly increased within 250 min and the hydrogels could be separated easily from wastewater. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42244.

**KEYWORDS:** adsorption; applications; clay; composites; dyes/pigments

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### INTRODUCTION

With the development of the industry, water pollution by toxic industrial waste is one of the most serious social and ecological issues. Among those, the pollution from dye wastewater has attracted much attention due to the growing use of a variety of dyes in the textile, plastic, food and pharmaceuticals industries.<sup>1,2</sup> Even tiny amount of dyes in water can generate significant colored effluents, reducing sunlight penetration and thus hindering the process of photosynthesis, and further to disturb aquatic ecosystem.<sup>3,4</sup> Moreover, most of these dyes are known to be toxic or carcinogenic. They not only affect aquatic life but also affect human beings in long time.<sup>5,6</sup> Therefore, removal of dyes from industrial wastewater would play a significant role in environment protection. Nowadays, there have been various physical and chemical methods that were used for the treatment of dye wastewater, such as coagulation, precipitation, ion exchange, membrane extraction, electrolysis, oxidation, and so on.<sup>7-12</sup> However, the conventional adsorption method is still considered as an effective and economic method for water decontamination because of its low cost, controllability, and easily operation with simple design and insensitivity to toxic dye molecules.<sup>13</sup>

Hydrogels that are a class of cross-linked polymeric materials with three-dimensional network structure are able to take up and retain huge amount of water or aqueous solution without dissolving.<sup>14</sup> Due to the solute diffusion easily in porous structure networks, hydrogels usually possess high absorption ability, which makes them gradually become a potential adsorption material. Compared with other adsorbents, hydrogels have their own advantages, such as adsorption-regeneration, economic feasibility and environmental friendly behavior, and hence a lot of researches focus on the application of hydrogels in pollution control.<sup>15</sup> Vesna *et al.*<sup>16</sup> reported the results of a poly(methacrylic acid) based hydrogels for removal of cationic dye basic yellow 28. However, in the practical application, the external condition of wastewater treatment is quite complicated and the adsorption of contamination is required to be controlled by adjusting the external condition. Thus environmental sensitive or smart hydrogels, which are able to change their volume by more than one order of magnitude in response to different parameters, such as temperature, pH value, light, ion, and substance concentrations, gradually attract researchers' attention.<sup>17</sup> Having cationic or anionic pendant groups, pH-responsive hydrogels can be used for treatment of ionic dyes.<sup>18</sup> Rodriguez-

Llansola *et al.*<sup>19</sup> described a new simple urea-based compound capable of forming pH-responsive hydrogels with outstanding dye scavenging properties. Dye solutions could easily permeate into hydrogels upon acidification, and thus the hydrogels showed extraordinary dye removal capabilities. This pH response of the system gives an outstanding added value for potential applications. Ray *et al.*<sup>20</sup> presented a kind of metal-ion-induced, pH-responsive hydrogels formation using amino acid-based bolaamphiphilic molecule containing phenylalanine residues and the application of these gels in removing different types of water-soluble dyes. These metallo-hydrogels can efficiently adsorb various toxic dyes including Crystal Violet and Naphthol Blue Black from water only at a particular pH (6.5–7.2), and this property can be utilized for the removal of different types of toxic dye molecules from wastewater. At present, most of the research focused on the pH-responsive hydrogels or combination with temperature responsive hydrogels in the treatments. However, in some cases the treatments may be carried out in different external environments, such as temperature, pH and magnetic-field. Moreover, in order to collect and separate the sorbent from wastewater, the traditional temperature and pH-responsive hydrogels cannot meet the requirement. In such cases, multiple stimulus-responsive hydrogels would play a significant role in this field.

In our previous work,<sup>21</sup> we introduced AT-Fe<sub>3</sub>O<sub>4</sub> into the poly(ethylene glycol)-based hydrogels to prepare the temperature-, pH- and magnetic-field-sensitive hydrogels (PMOA/AT-Fe<sub>3</sub>O<sub>4</sub>). Here, the purpose of this study was focused on studying the application of this multiple stimulus-responsive hydrogels in dyes wastewater treatment. The adsorption behaviors of Rhodamine B (RhB), a cationic and widely used dye in the industry, by the multiple stimulus-responsive hydrogels were investigated under different temperature, pH environments, and even under an external magnetic field. Furthermore, this hydrogels could be separated from wastewater due to the magnetic-field responsive.

## EXPERIMENTAL

### Materials and Chemicals

2-(2-Methoxyethoxy) ethyl methacrylate (MEO<sub>2</sub>MA, 97%) was purchased from TCI Chemical, Tokyo, Japan. Oligo (ethylene glycol) methyl ether methacrylate (OEGMA, average  $M_n = 475$ , the number of EO units 8–9) was purchased from Sigma-Aldrich. Acrylic acid (AAc), Rhodamine B (RhB), iron dichloride (FeCl<sub>2</sub>), potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), sodium hydroxide (NaOH), phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), acetic acid (CH<sub>3</sub>COOH), and boric acid (H<sub>3</sub>BO<sub>3</sub>) were purchased from Sinopharm Chemical Reagent. All these reagents were used as received. Attapulgate-Fe<sub>3</sub>O<sub>4</sub> (AT-Fe<sub>3</sub>O<sub>4</sub>) was prepared by our research group.

### Preparation of the Multi-Functional PMOA/AT-Fe<sub>3</sub>O<sub>4</sub> Nanocomposite Hydrogels

Multi-response PMOA/AT-Fe<sub>3</sub>O<sub>4</sub> hydrogels were synthesized using the similar method<sup>21</sup> with some modification. According to that previous work, the AT-Fe<sub>3</sub>O<sub>4</sub> contents of 3 wt % was selected to study the adsorption process in this work, because that hydrogels sample showed appropriate magnetic-response and swelling properties. The PMOA/AT-Fe<sub>3</sub>O<sub>4</sub> hydrogels were

prepared by *in situ* free radical polymerization in deionized water, and the redox initiators were composited of FeCl<sub>2</sub> (2 mL, 0.5 wt %) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (2 mL, 0.5 wt %). The component of the hydrogels is 3 wt % AT-Fe<sub>3</sub>O<sub>4</sub>, 55 wt % PMOA and 42 wt % deionized water. The prepared hydrogels were freeze-dried under vacuum condition and then were used in adsorption studies.

### Adsorption Studies of RhB Dyes

Adsorption kinetics studies, the equilibrium adsorption measurements, and the influences of the hydrogels responsive behaviors on the adsorption were performed via bath adsorption technique. A certain amount of hydrogels was added to 25 mL of aqueous dyes solution of a certain concentration and the temperature was maintained constant throughout the duration of experiments using water bath. The concentration of RhB was measured by absorbance (Abs) at the maximum absorption peak using UV spectrophotometer.

In order to investigate the temperature responsive behaviors of the hydrogels, the experiments were carried out at 25, 30, and 35°C. Britton-Robinson buffer solutions with the same ionic strength and different pH values (3.29, 4.56, 5.72, 6.8, 7.96, and 9.15) were measured by pH meter. The pH-responsive behavior of PMOA/AT-Fe<sub>3</sub>O<sub>4</sub> hydrogels was assessed at room temperature (25°C) by immersing hydrogels in different pH buffer solutions. And the magnetic-field responsive was similar to be measured under an external magnetic-field at room temperature (25°C). In addition, the adsorption process models of PMOA/AT-Fe<sub>3</sub>O<sub>4</sub> hydrogels have been investigated.

The percentage dye removal ( $R$ ) has been calculated using the following equation:

$$R = (C_0 - C_e) / C_0 \times 100 \quad (1)$$

where,  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of RhB dye (mg/L).

Amount of dye adsorbed per unit mass of hydrogels (mg/g) has been determined using following equation.

$$Q_t = (C_0 - C_t) \times V / M \quad (2)$$

where,  $C_0$  is the initial concentration of RhB dye (mg/L),  $V$  is volume of the dye solution,  $M$  is the mass of the hydrogels, and  $t$  refers to the treatment time.

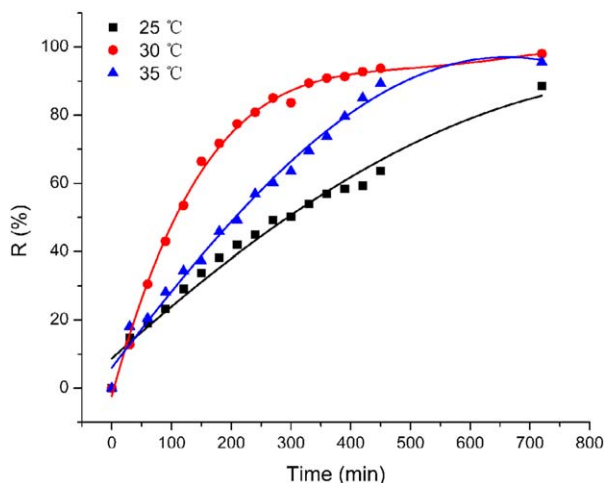
### Fourier Transform Infrared Spectroscopy (FT-IR)

The hydrogels before and after dyes adsorption were tested by a Nicolet Impact NEXUS-8700 FT-IR in the range of 500–4000 cm<sup>-1</sup>. The samples were dried and then were mixed with potassium bromide (KBr) powder and then were compressed into a transparent sheet. Thirty-two scans were conducted to achieve an adequate signal to noise ratio.

## RESULTS AND DISCUSSION

### Effect of Temperature Responsive Behaviors of the Hydrogels on the Adsorption of RhB Dye

It is common knowledge that the adsorption process is inevitable affected by the temperature changing. The PMOA/AT-Fe<sub>3</sub>O<sub>4</sub> hydrogels possess temperature responsive properties, which has the lower critical solution temperature (LCST) (about 33°C) in

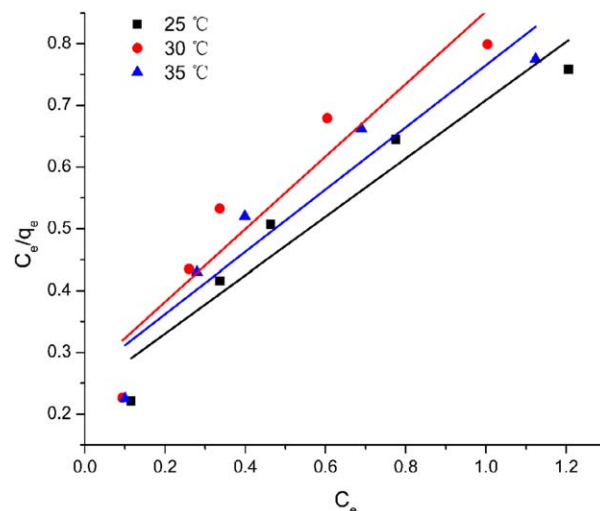


**Figure 1.** The adsorption of the hydrogels for RhB dye at different temperature. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

water and easily adjusts the network structure of the hydrogels.<sup>21</sup> Therefore, the above factors can have a significant influence on the adsorption at different temperature and even control the adsorption process. The influence of external temperature on the adsorption process has been studied at various temperatures at 25, 30, and 35 °C as shown in Figure 1. The dye adsorption has a significant increment from 25 to 30 °C, and then gradually decreases. When temperature exceeds 30 °C, the removal of RhB can reach to over 95% and the dye solution almost is colorless. At temperature below the LCST, the molecular chains of the hydrogels network are stretched, resulting in higher adsorption efficiency. In addition, with the temperature increasing, the thermal motion of the molecule is active, which is helpful for the dye to diffuse into the inner of the hydrogels. However, the temperature cannot be increased indefinitely. The collapse of hydrogels matrix may take place due to the heating effect.<sup>22</sup> When the temperature is above the LCST, the conformational transition of OEGMA side chains decreased the polarity of ethenoxy groups, and the hydration is weakened. The hydrogels begin to shrink, resulting in lower adsorption efficiency, which is lower than that at 30 °C. On the other hand, the thermal motion of the dye molecule will be more active with the temperature increasing, which leads to the dye adsorption capability increasing. Therefore, the adsorption efficiency above 35 °C is still better than that at 25 °C.

Furthermore, the adsorption isotherm models are used to analyze this effect of temperature smart responsive on the adsorption process. Adsorption isotherm models can describe the interaction of a sorbent with a given adsorbate which is essential for its effective application. There are several isotherm models available for analyzing the experimental data and for describing the equilibrium of adsorption. The more commonly used Langmuir and Freundlich isotherm have been used in this work to determine equilibrium relationships between sorbent and adsorbate.

The linear form of the Langmuir equation can be expressed as:



**Figure 2.** Plot of  $C_e/q_e$  vs.  $C_e$  for Langmuir isotherm. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \quad (3)$$

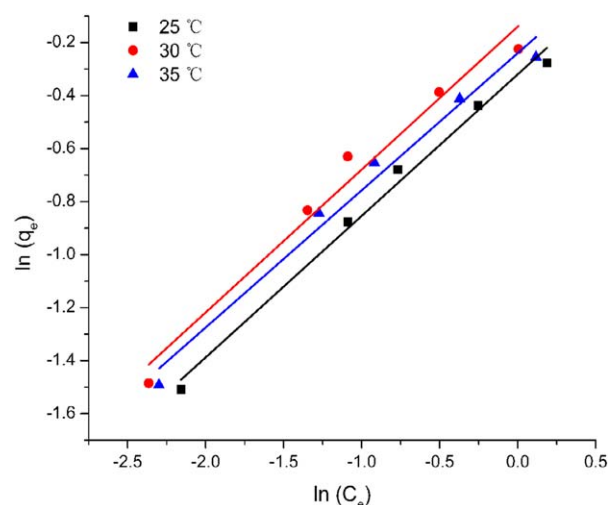
where  $q_e$  (mg/g) is the amount of the dye adsorbed at equilibrium,  $C_e$  (mg/L) is the concentration of the dye solution at equilibrium,  $q_m$  (mg/g) and  $K_L$  (L/g) are the Langmuir constants, which is the maximum sorption capacity at complete monolayer coverage and sorption coefficient, respectively.

Freundlich isotherm is an empirical equation employed to describe heterogeneous systems.<sup>23,24</sup> The Freundlich isotherm is described by equation:

$$\ln q_e = \ln K_F + (1/n) \ln C_e \quad (4)$$

where  $K_F$  (mg/g) and  $n$  are Freundlich's constants indicating sorption capacity and intensity, respectively.

The plot of Langmuir and Freundlich isotherm models are described in Figures 2 and 3. The obtained characteristic



**Figure 3.** Plot of  $\ln q_e$  vs.  $\ln C_e$  for Freundlich isotherm. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table I.** The Parameters of Isotherm Model

Isotherm model	Temperature (°C)		
	25	30	35
Langmuir			
$q_m$ (mg/g)	2.11	1.70	1.98
$K_L$ (L/g)	2.01	2.23	1.93
$R^2$	0.90711	0.85987	0.87233
Freundlich			
$K_F$ (mg/g)	0.726	0.870	0.787
$N$	1.87	1.85	1.93
$R^2$	0.98835	0.96725	0.97578

parameters, as well as the correlation coefficients,  $R^2$ , are summarized in Table I. Based on the comparison results of  $R^2$  presented in Table I, it could be concluded that Freundlich isotherm model fits the equilibrium adsorption data well. This is for the following reasons. For the PMOA/AT-Fe<sub>3</sub>O<sub>4</sub> hydrogels, the adsorption process is contributed by both PMOA network and AT-Fe<sub>3</sub>O<sub>4</sub> nano-particles. And on the other hands, AT-Fe<sub>3</sub>O<sub>4</sub> nano-particles are dispersed not only at the surface of the hydrogels but also into the network inner. Thus the surface of sorbent is not homogeneous. Because of the assumption of the heterogeneous surface energy of the sorbent, Freundlich isotherm model is more suitable for describing the adsorption process of the hydrogels. The adsorption process can be illustrated in Figure 4. AT-Fe<sub>3</sub>O<sub>4</sub> nano-particles are disordered arrangement in the hydrogels network and thus the adsorption is not limited in the surface of the hydrogels. Both PMOA network and AT-Fe<sub>3</sub>O<sub>4</sub> nano-particles can produce the adsorption for the dye to improve the adsorption efficient. In addition, the values of  $1/n$  in Freundlich model indicate the type of isotherm to be irreversible ( $1/n = 0$ ), favorable ( $0 < 1/n < 1$ ) or unfavorable ( $1/n > 1$ ). Results from Table I show that  $n$  is greater than unity. This indicates that the dye can be adsorbed favorably by the hydrogels at the temperature region involved in our work. Furthermore, from the results, it can be seen that the  $K_F$  values also increase before 30°C and reach the maximum at 30°C, and then decrease. Besides, the  $K_F$  values above 35°C are still better than that at 25°C. Those results are well consistent with the temperature response behavior of the hydrogels.

Moreover, the adsorption thermodynamics were also evaluated and the thermodynamic parameters Gibb's free energy ( $\Delta G^\circ$ ) for the adsorption of RhB onto hydrogels were determined using the equation.<sup>25,26</sup>

$$\Delta G^\circ = -RT \ln K_L \quad (5)$$

where  $R$  ( $\text{kJ mol}^{-1} \text{K}^{-1}$ ) is the gas constant,  $T$  (K) is the temperature, and  $K_L$  ( $\text{L mol}^{-1}$ ) is the Langmuir constant.

Therefore, according the equation, the values of  $\Delta G^\circ$  are  $-34.04$ ,  $-35.13$ ,  $-35.00$   $\text{kJ mol}^{-1}$  for 298, 303, 308 K, respectively. The values of  $\Delta G^\circ$  may also give an idea about the nature of adsorption process whether it is chemical adsorption (i.e.,  $-80$  to  $-400$   $\text{kJ mol}^{-1}$ ) or physical adsorption (i.e.,  $-20$  to  $0$

$\text{kJ mol}^{-1}$ ).<sup>25</sup> The  $\Delta G^\circ$  values in our research are within the ranges of  $-34.04$  to  $-35.13$   $\text{kJ mol}^{-1}$ . The obtained results do not fall into a range of pure chemical adsorption process, which indicates the adsorption combine both chemical and physical adsorption.

### Adsorption Kinetics

Adsorption is a physical and chemical process that is the mass transfer process of the solute (adsorbate) from the liquid to the surface of the adsorbent, and the adsorption kinetics research can get the information of the adsorption mechanism.<sup>27</sup> In addition, in order to find out the rate-controlling step of the adsorption process, it is necessary to establish well defined kinetic models. The general adsorption kinetics of dye adsorption may be evaluated by the following kinetic equation.

### Pseudo First-Order Kinetics.

$$\frac{dQ_t}{dt} = k_1(Q_e - Q_t) \quad (6)$$

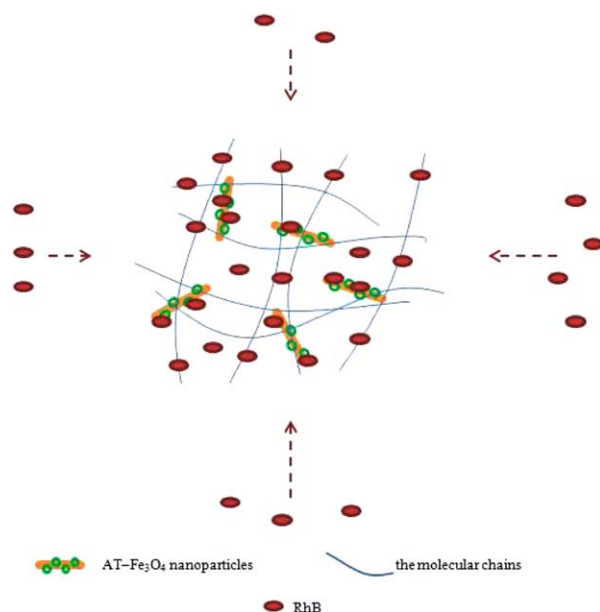
where  $k_1$  (g/mg h) is the pseudo first-order rate constant of adsorption. After integrating eq. (5) with boundary condition of  $Q = 0$  at  $t = 0$  and  $Q = Q_t$  at  $t = t$ , the following linear equation is obtained:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (7)$$

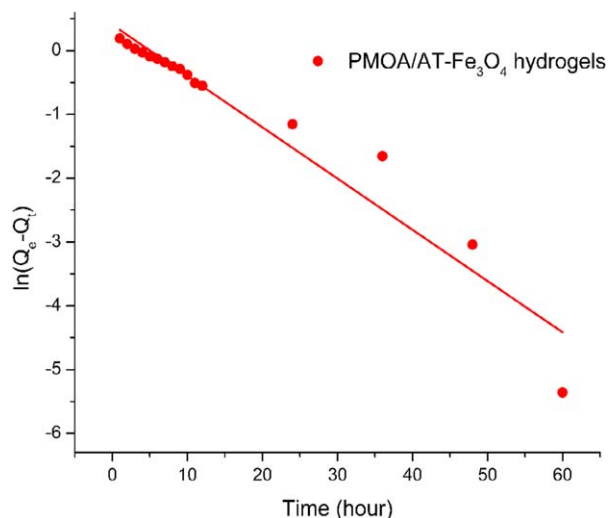
where  $Q_e$  and  $Q_t$  are dye adsorption (mg/g) at equilibrium time and time  $t$  (h), respectively.  $K_1$  is the rate constant of first order sorption ( $\text{L/min}$ ).<sup>28</sup>

### Pseudo Second-Order Kinetics.

$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \quad (8)$$



**Figure 4.** Schematic illustration of the adsorption process by PMOA network and AT-Fe<sub>3</sub>O<sub>4</sub> nanoparticles. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 5.** Adsorption kinetics of RhB dye at different content of AT-Fe<sub>3</sub>O<sub>4</sub> for pseudo first-order kinetic model. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

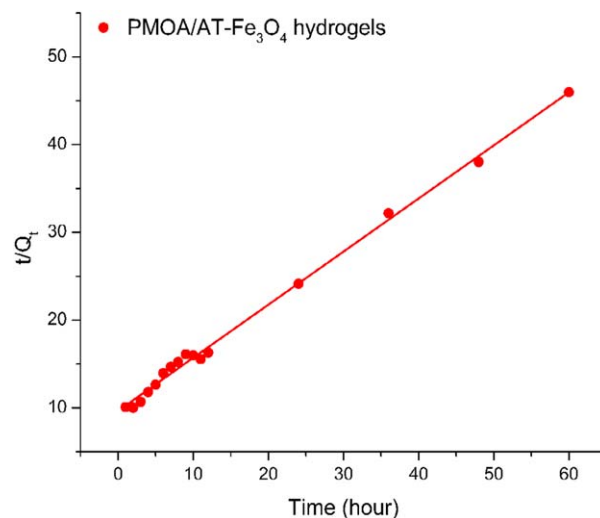
where  $k_2$  (g/mg min) is the pseudo second-order rate constant of adsorption. Integrating the above equation with boundary condition of  $Q = 0$  at  $t = 0$  and  $Q = Q_t$  at  $t = t$  yields:<sup>29</sup>

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (9)$$

Both the pseudo first-order kinetic and pseudo second-order kinetic are investigated as shown in Figures 5 and 6. The validity of the kinetic models evaluated in terms of regression coefficient ( $R^2$ ) is reported in Table II. The results indicate that  $R^2$  for the second-order kinetic models are closed to 1.0 indicating a well fit of the models to the experimental data sets. Therefore, the adsorption of RhB dyes by the PMOA/AT-Fe<sub>3</sub>O<sub>4</sub> hydrogels can be approximated more favorably by the pseudo second-order models. Due to that the first-order kinetic models is related to one reactive substance and the second-order models is related to two reactive substance, which is corresponded to simple and complex sorption kinetic system, respectively.<sup>29</sup> In the PMOA/AT-Fe<sub>3</sub>O<sub>4</sub> hydrogels, because of the incorporation of AT-Fe<sub>3</sub>O<sub>4</sub> nano-particles having adsorption capability, the adsorption is more tends to complex sorption system. It is reveal that the adsorption process of the hydrogels is combined both PMOA chains and AT-Fe<sub>3</sub>O<sub>4</sub> nano-particles. All those factors will influence the adsorption, which is the reason that the second-order models is closer the experiment data.

#### Effect of Magnetic-Field Responsive Behaviors of the Hydrogels on the Adsorption of RhB Dye

Figure 7 shows the separation process of the hydrogels under the external magnetic-field. It can be seen that the hydrogels



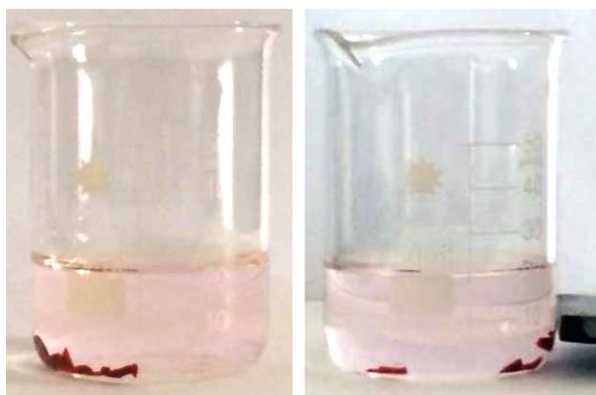
**Figure 6.** Adsorption kinetics of RhB dye at different content of AT-Fe<sub>3</sub>O<sub>4</sub> for pseudo second-order kinetic model. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

adsorbed with RhB dye can be separated easily from wastewater under the magnetic-field. In addition, the influence of magnetic responsive behaviors of the hydrogels on the adsorption process is also studied in a home-made magnetic-field (as shown in Figure 8) at room temperature. Figure 9 shows the adsorption process under the external magnetic-field. The results show that the adsorption process obviously increases the adsorption rate and the concentration of the RhB get a significant decrease within 250 min. Under the external magnetic-field, AT-Fe<sub>3</sub>O<sub>4</sub> nano-particles generate magnetic responsive and directional movement to arrange along the direction of the magnetic from disorder to order. Consequently, this kind of directional movement will stretch the molecular chains of the hydrogels networks, as illustrated in Figure 10. Thus, it is reasonable to suggest that the distance between the molecule chains would increase and lead to a larger space in the hydrogels networks, which allows RhB dye to enter more efficiently. The directional movement of the AT-Fe<sub>3</sub>O<sub>4</sub> nano-particles will cause the thermal motion of the molecule and the external magnetic-field itself will also generate thermal energy in some extent. Both of those effects are favorable for increasing the adsorption capability efficiently.

Furthermore, in order to analyze the effect of magnetic-field on the adsorption, the adsorption kinetics is analyzed (as shown in Figure 11). According to the results of the adsorption kinetics, the pseudo second-order models are selected in this research. From the kinetic constant listed in Table III, it can be seen that the rate constant of adsorption is higher under the magnetic-field. This explains why the concentration of the RhB gets a significant decrease within 250 min. Besides, the values of  $Q_e$  also

**Table II.** Kinetic Constant for RhB Adsorption on the PMOA/AT-Fe<sub>3</sub>O<sub>4</sub> Hydrogels

Sample	First-order kinetic constants			Second-order kinetic constants		
	$K_1$ (L/min)	$Q_e$ (mg/g)	$R^2$	$K_2$ (g/mg min)	$Q_e$ (mg/g)	$R^2$
PMOA/AT-Fe <sub>3</sub> O <sub>4</sub>	0.0803	1.500	0.9339	0.0379	1.653	0.9962

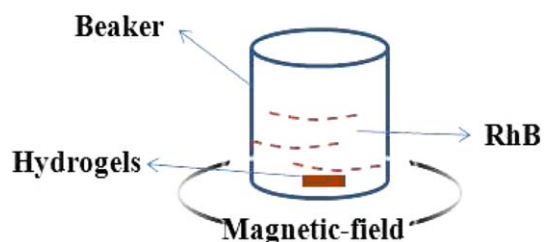


**Figure 7.** The magnetic-field responsive testing of PMOA/AT-Fe<sub>3</sub>O<sub>4</sub> hydrogels. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

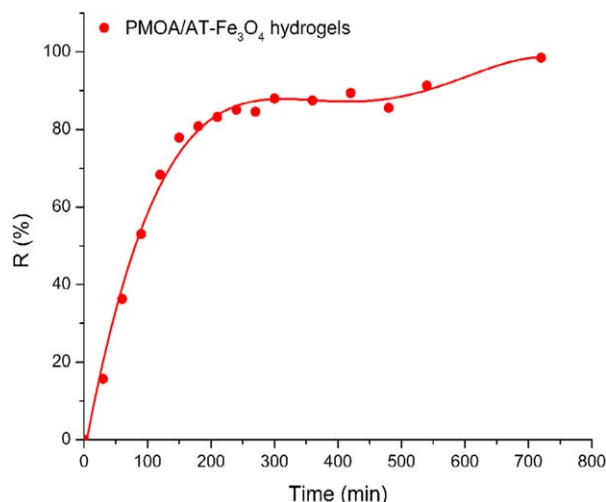
have a significant increasing, which indicates that the magnetic-field response of the prepared hydrogels will improve the adsorption capability efficiently.

#### Effect of pH Responsive Behaviors of the Hydrogels on the Adsorption of RhB Dye

Dye adsorption for PMOA/AT-Fe<sub>3</sub>O<sub>4</sub> hydrogels is studied at pH range from 3.29 to 9.15 with dye concentration of 1 mg/L at room temperature. The adsorption capability of the hydrogels for RhB dye at different pH values are showed in Figure 12, the adsorption capability is first increased and then decreased with the pH value increasing, which can be attributed to the state change of the -COOH group on the hydrogels molecular chains. The similar result has been reported.<sup>13,30</sup> At pH < 4.56, as the pH values increasing, the dye adsorption is increased. This may be attributed to the ionization behavior of -COOH group on the hydrogels molecular chains. At low pH values, there is very low dissociation of -COOH group of the hydrogels, and increasing the pH of dye solution makes fewer protons available to protonate the -COOH group.<sup>21</sup> Those results will increase the dye adsorption due to increase the electrostatic interactions. On the other hand, the point of zero charge of AT is about 3.0. Thus, in this case, the surface of AT-Fe<sub>3</sub>O<sub>4</sub> nano-particles acquires negative charge and there would be an electrostatic interaction between cationic dye molecules and nano-particles, leading a higher cationic dye adsorption. It could be expected that when pH value is above 5 (above the pK<sub>a</sub> value of acrylic acid), the hydrogels would further swell, which should lead to higher adsorption capability. However, due to this decomplexa-



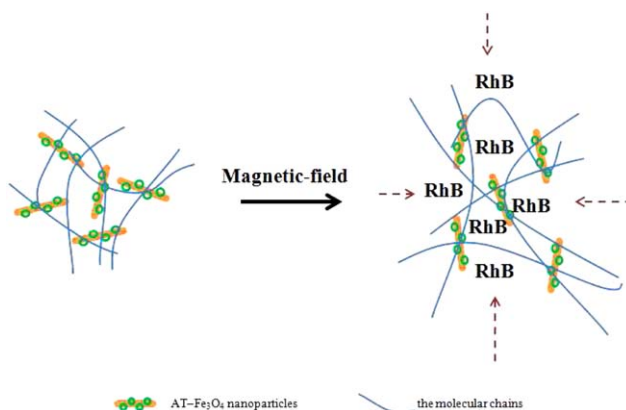
**Figure 8.** Schematic illustration of the adsorption measurement of the hydrogels under the external magnetic-field. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



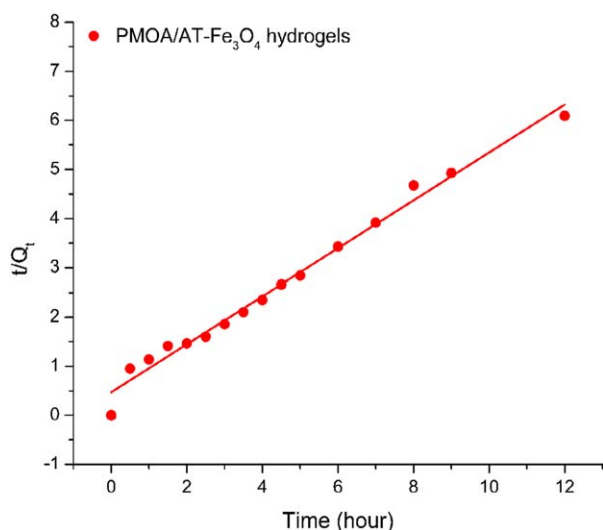
**Figure 9.** The adsorption of the hydrogels for RhB dye as a function of time under the external magnetic-field. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

tion action, the structure of the hydrogels is gradually expanded and the hydrogels is more easily to be broken to lose the adsorption capability (Figure 13), which will cause the fact that the dye molecule is easily to enter into the network and is also easily to depart the network. That means the network of the hydrogels cannot capture the dye molecule. Besides, in alkaline buffer, there is a competition between ions present in the buffer and RhB cations for the same sorption site. The interactions between the buffer ions block the sorption sites and then prevent dye from being absorbed. Thus, the overall adsorption of the dye decreased. All those results are disadvantage to the adsorption processes.

On the other hand, the pseudo second-order kinetic are investigated as shown in Figure 14. From the results of the adsorption kinetics study shown in Table IV, the  $K_2$  and the  $Q_e$  values decrease overall, which corresponds the pH-response effect of the hydrogels. The adsorption capability decrease with the pH values increasing. At high pH values (above the pK<sub>a</sub> value of acrylic acid), the structure of the hydrogels is gradually



**Figure 10.** Schematic illustration of the directional movement of AT-Fe<sub>3</sub>O<sub>4</sub> nanoparticles in the hydrogels network. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 11.** Adsorption kinetics of RhB dye under the external magnetic-field for pseudo second-order kinetic model. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

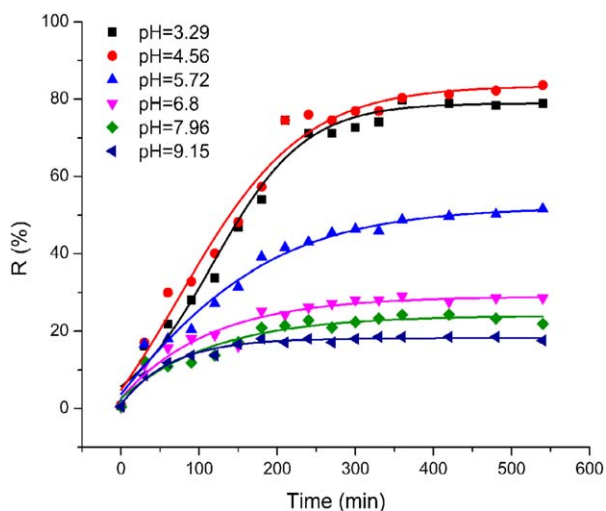
**Table III.** Kinetic Constant for RhB Adsorption Under the External Magnetic-Field

	Second-order kinetic constants	
	$K_2$ (g/mg min)	$Q_e$ (mg/g)
Under magnetic-field	0.5041	2.051
Nonmagnetic-field	0.0379	1.653

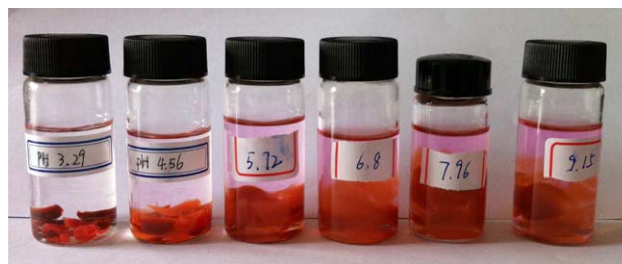
destroyed to decrease the intensity of the hydrogels network, which causes the adsorption efficiency weaken.

#### FT-IR Analysis of the Hydrogels Before and After Dyes Adsorption

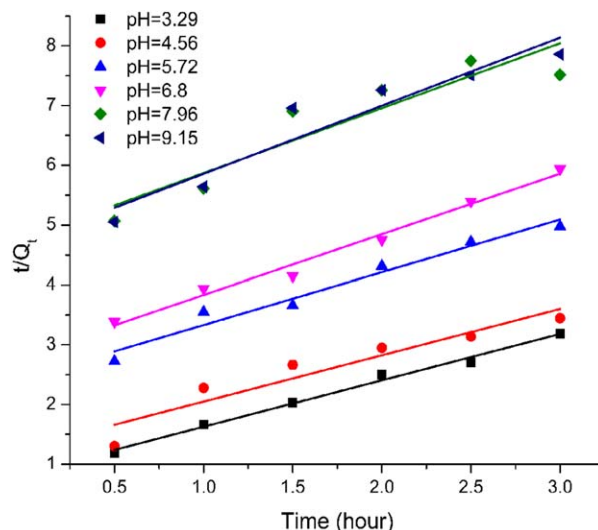
FT-IR spectra of the hydrogels before and after adsorption process are shown in Figure 15. It can be seen that two strong



**Figure 12.** The adsorption of the hydrogels for RhB dye as a function of time at different pH values. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 13.** The PMOA/AT-Fe<sub>3</sub>O<sub>4</sub> hydrogels adsorb RhB dye in different pH buffer solutions. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

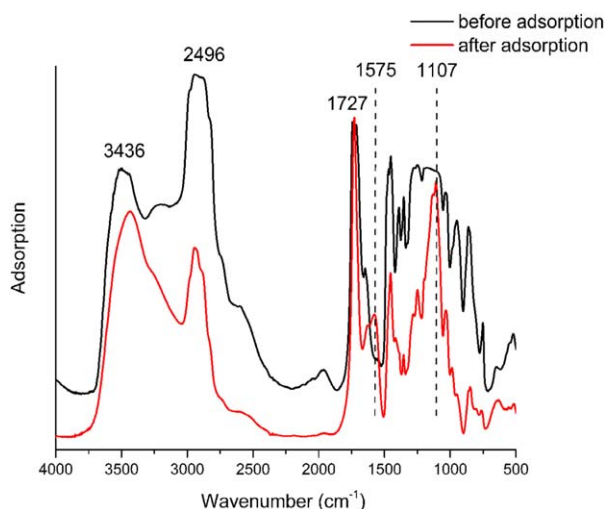


**Figure 14.** Adsorption kinetics of RhB dye at different pH values for pseudo second-order kinetic model. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

adsorption peak ( $1575$  and  $1107\text{ cm}^{-1}$ ) appear after adsorption process, which is attributed to the function group of C=N and C-N in the dyes molecule, respectively. This result can prove that the dyes molecule is absorbed by the hydrogels. On the other hand, the main characteristic of the hydrogels after adsorption is similar with that before adsorption, which implies that the structure of the hydrogels donot change during the adsorption process.

**Table IV.** Kinetic Constant for RhB Adsorption Under the External Magnetic-Field

pH	Second-order kinetic constants	
	$K_2$ (g/mg min)	$Q_e$ (mg/g)
3.29	0.708	1.287
4.56	0.472	1.289
5.72	0.316	1.136
6.8	0.363	0.987
7.96	0.247	0.920
9.15	0.274	0.923



**Figure 15.** FT-IR spectrum of hydrogels (a) before adsorption and (b) after adsorption. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

## CONCLUSION

The multiple stimulus-responsive poly(ethylene glycol)-based hydrogels is successfully applied to deal with the dye wastewater treatment. The pseudo-second-order models and Langmuir isotherm models have better fitted with experimental data corresponding to the kinetic and isotherm models, respectively. The results prove that the adsorption of PMOA/AT-Fe<sub>3</sub>O<sub>4</sub> hydrogels tends to the complex sorption system and heterogeneous surface adsorption. Besides, FT-IR spectrum comparison of the hydrogels before and after dyes adsorption reveals that the structures of the hydrogels do not change during the adsorption process. In addition, the RhB dye adsorption can be affected by the multiple stimulus-responsive behaviors of the PMOA/AT-Fe<sub>3</sub>O<sub>4</sub> hydrogels. The dye adsorption shows a high efficiency around the LCST. The adsorption process also can be controlled by the pH-responsive behaviors of the hydrogels. Despite the temperature/pH sensitivity, the PMOA/AT-Fe<sub>3</sub>O<sub>4</sub> hydrogels also possess considerable magnetic functionality. Under the external magnetic-field, the hydrogels can not only obviously improve the adsorption capability but also show can be separated from wastewater, which is more suitable for the practical application in the treatment of dye wastewater.

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