Highly Selective Removal of Organic Dyes from Aqueous Solutions with Chitin Beads Entrapping Rectorite

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ABSTRACT: By blending chitin with rectorite and organic rectorite in an 8 wt % NaOH/4 wt % urea aqueous solution, we successfully fabricated millimeter-scale chitin/rectorite composite beads (BCRs) and chitin/organic rectorite beads (BCO), respectively, via an optimal dropping technology. The adsorption of the organic dyes on the BCRs and BCOs were investigated to evaluate the selective removal of methylene blue (MB) and methyl orange (MO) of different charges. Adsorption kinetics experiments were carried out, and the data fit a pseudo-second-order equation well. The results reveal that the BCR and BCO sorbents efficiently and selectively adsorbed MO and MB, respectively, from wastewater. The adsorption capacity (Q_e) and removed percentage of MB by BCR were 0.1978 mg/g and 98.90%. The Q_e and R values of MO by BCO were 0.3988 mg/g and 99.70%. Therefore, in this study, we dealt with the development of a clean and safe process for water pollution remediation. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40905.

INTRODUCTION

The efficient removal of dyes from effluents has raised great concerns over the past few years.[1–3] The dyes in wastewater can reduce photosynthetic reactions, and some synthetic dyes are quite toxic and even carcinogenic. This poses a severe health threat to human beings.[4–6] Hence, it is essential to remove dyes from wastewater to alleviate these water problems faced by society. As an effective approach, adsorption processes have been extensively used in water treatment, and a variety of materials have been studied as adsorbents; these include activated carbon,[7,8] clay materials,[9,10] natural zeolite,[11,12] bottom ash,[13,14] and soya.[15] However, there are still some challenges that restrict the adsorption approach; these include a low selectivity and adsorption capacity (Q_e) for the current materials. Therefore, it is of great importance to explore new adsorbents with high adsorption selectivities and capacities.

In recent years, polymer/layered silicates has attracted considerable interest because they combine the structure and physical and chemical properties of both inorganic and organic materials.[10,16,17] Rectorite is another kind of layered silicate with a structure and characteristics much like those of montmorillonite. It is a regularly interstratified clay mineral with alternate pairs of dioctahedral micalike layers and dioctahedral montmorillonite-like layers in a 1:1 ratio.[18] The separable layer thickness and layer aspect ratio of rectorite are larger than those of regular montmorillonite; these enable it to efficiently adsorb many kinds of pollutants.[19] Despite its high Q_e, the use of rectorite on a large scale is limited by process engineering difficulties, including the dispersion of the rectorite powder and the cost of its regeneration. Even if rectorite can be used in granular form, a lack of selectivity in adsorption is observed with rectorite. One solution that has been proposed by several authors is the encapsulation of rectorite powder into biopolymers, such as chitosan and sodium alginate.[20,21] The use of chitin as a carrier material for rectorite has enlightened the possibility of having a selective adsorption of organic molecules; this depends on their electrical charge because of interactions with the hydroxyl and acetyl amino groups on chitin. Chitin can accumulate metal ions and organic dyes; this gives it potential applications in dealing with wastewater containing toxic components.[22–24] Some work has been done to adapt this promising material to industrial fluidized bed processes.[25,26] Chitin is a linear polysaccharide composed of β-(1–4)-linked 2-acetamido-2-deoxy-D-glucose units.[27] Chitin is one of the most extensively investigated biopolymers for the removal of pollutants from aqueous solutions as it is inexpensive, nontoxic, and efficient. However, the high crystallinity of chitin was supported by hydrogen

bonds, mainly through the hydroxyl and acetyl amino groups, which have limited the further utilization of this natural biopolymer to a small area.[28]

In our previous work, an 8 wt % NaOH/4 wt % urea aqueous solution precooled to −20°C was developed to dissolve chitin; this led to the formation of a transparent chitin solution.[29,30] Moreover, chitin/alginate and chitin/cellulose blend membranes have been fabricated successfully from NaOH/urea aqueous solutions; these indicated that the NaOH/urea aqueous solution was a suitable solution for blend materials.[31,32] More recently, we found that magnetic chitin-based gel beads for the removal of methyl orange (MO) could be prepared from a polymer solution with the iron(II) crosslinking method at room temperature.[33] Encouraged by these findings, in this study, we focused mainly on preparation of a composite gel–bead sorbent, in which the rectorite was embedded in the chitin matrix to improve the adsorption selectivity and capacity of organic dyes. Their structure, adsorption behaviors, and factors including the adsorption time, temperature, dye concentration, and ionic strength were investigated to evaluate the desirability of their applications in the water-treatment field. We hoped to provide a green pathway for the fabrication of chitin/rectorite composite beads (BCRs), which have potential applications in the removal of hazardous materials from wastewater.

EXPERIMENTAL

Materials

The chitin sample (crab shell α-chitin) was provided by Shangdong Jinhu Chitin Co., Ltd., powered, and sifted to select particles with a diameter of less than 0.635 mm. Its viscosity-average molecular weight was determined with an Ubbelohde viscometer in NaOH/urea aqueous solution at $25 \pm 0.1°C$ and calculated from the Mark–Houwink equation $[\eta] = 0.26 \, M_w^{0.56 \pm 002}$ (mL/g) to be 2.1×10^6 (where $[\eta]$ is intrinsic viscosities and M_w is average-weight molecular).[30] The degree of acetylation (DA) was measured to be 97% with elemental analysis by the equation:[34]

$$DA = 1 - [(W_C/W_N - 5.14)/1.72] \times 100\%$$

where W_C/W_N is the ratio of carbon to nitrogen.

MO and methylene blue (MB) were purchased from Sinopharm Chemical Reagent Co., Ltd. Calcium rectorite (Ca^{2+}–rectorite, frequently simply termed *rectorite*) refined from clay minerals was provided by Hubei Mingliu, Inc. Co. (Wuhan, China). Sodium dodecyl sulfonate (SDS) was supplied by Aladdin Reagent Co. (Shanghai, China). Other analytical-grade chemical regents were purchased in China and were used without further purification.

Synthesis of Organic Rectorite

The organic rectorite was prepared according to our previous literature as follows.[35] Rectorite (4 g) was dispersed in distilled water to obtain clay suspension with a stirrer and left standing for 24 h after vigorous stirring for 30 min. SDS (2 g) was dissolved in water and then dropped slowly into the rectorite suspension at 90°C under stirring. After stirring for 5 h, the product was washed several times with distilled water, and dried at 90°C to yield organic rectorite.

Preparation of the Gel BCRs (Organic Rectorite)

An approximately 1 wt % chitin solution in 8 wt % NaOH/4 wt % urea was prepared according the previous method. About 4 g of chitin was dissolved in 400 g of an 8 wt % NaOH/4 wt % urea aqueous solution to obtain a clear chitin solution (**I**). Rectorite (1.6 g) was dispersed in 400 g of an 8 wt % NaOH/4 wt % urea aqueous solution to obtain a clay suspension with a stirrer (solution **II**). A precursor solution was prepared by mixing **I** (100 g) and **II** (100 g). The mixture was vigorously stirred with a mechanical stirrer for 1 h and centrifuged for 20 min at 4000 rpm to remove air bubbles. The resulting suspension was then dropped through a 0.45-mm diameter syringe needle at a rate of 1.5 mL/min into a 10 wt % sulfuric acid solution with gentle agitation. The pale gray composite beads, about 2 mm in diameter, formed instantaneously. At the end of the addition, the beads were kept in the solvent for 30 min at room temperature and were then collected by filtration, washed with copious amounts of deionized water until they were neutral, and stored in a distilled water bath. Unless specifically noted, no drying was done, and the beads were used wet to prevent the collapse of the internal structure. Chitin/organic rectorite composite beads (BCOs) were prepared by the same manner.

Characterization

The beads were observed and photographed with a digital camera (Sony α-390). Digitized photographs of the beads were used in combination with image analysis software (Image Analyst 1.0) to obtain their mean diameter and size distribution. To verify the reproducibility of the bead preparation, three different samples (200 beads) were analyzed for each preparation. The observation of the surface section structure of the dry beads was carried out with scanning electron microscopy (SEM). SEM measurements were carried out on a field emission scanning electron microscope (SIRION TMP, FEI) with an accelerating voltage of 20 kV. The samples were coated with Pt to facilitate SEM observation.

Adsorption Experiments

A known weight of BORs (~5.0 g) was added to 20 mL of MO solution at concentrations 120 mg/L and incubated for an appropriate time on a shaking bed at a constant temperature at 130 rpm. The equilibrium pH of the solution was equal to 6.7 ± 0.1 without pH adjustment. In all of the samples, no release of organic rectorite was observed. After 48 h, the beads were removed from the solution. The concentration of MO in the solutions was determined by the measurement of their absorbance at 460 nm by an ultraviolet–visible (UV–vis) spectrophotometer (Shimadzu UV-160A, Japan). The removed quantity of dye (or Q_e; mg/g wet beads) by the beads and the removed percentage (ρ) were then calculated with the following formulas:

$$Q_e = \frac{c_0 - c_e}{m} V \tag{1}$$

$$\rho = \frac{c_0 - c_e}{c_0} \times 100\% \tag{2}$$

where c_0 is the initial dye concentration (mg/L), c_e is the equilibrium concentration of dye remaining in the solution (mg/L), V is the volume of the aqueous solution (L), and m is the
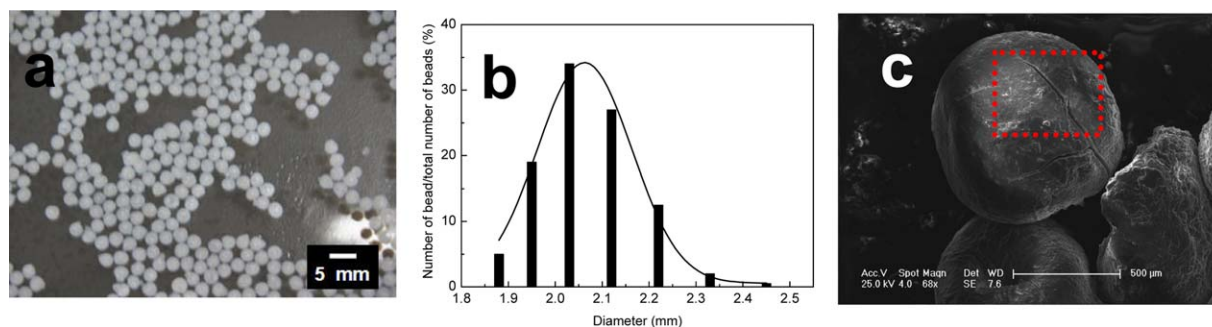
Figure 1. (a) Photograph of the chitin composite beads in the wet state after filtration, (b) size distribution of the beads, and (c) SEM image of the dry beads. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

weight of the wet beads. The adsorption experiment of MB was carried out by the same method described previously. The concentration of MB in the solutions was determined by the measurement of their absorbance at 665 nm, and the initial concentration of MB was 20 mg/L.

Selective adsorption experiments of the two adsorbents (BCR and BCO) on organic dyes were carried out as follows. Accurately weighted amounts (10.0 g) of the beads were placed in a conical flask containing 50 mL of mixed dye solution, in which concentrations of MO and MB were 80 and 40 mg/L, respectively, and these were incubated for an appropriate time on a shaking bed at a constant temperature at 130 rpm. The equilibrium pH of the solution was equal to 6.7 ± 0.1 without pH adjustment. After 48 h, the beads were removed from the solution. The concentration of dyes in the solutions was determined by the measurement of their absorbance from 350 to 800 nm by UV–vis spectrophotometry.

To study the effect of the layered silicate on the removal of dyes by chitin composite gel beads, a series composite beads was prepared with the amounts of layered silicate ranging from 0 to 0.5 g. The adsorption experiments were carried out according to the same methods as described previously.

To study the effect of the temperature on the removal of dyes by chitin composite gel beads, the adsorption properties of the composite beads on organic dyes were studied at 298, 308, and 318 K. The adsorption experiments were carried out according to the same methods as described previously.

The effects of the initial concentrations of dyes were also studied. The initial concentration was changed from 110 to 160 mg/L for MO and from 20 to 70 mg/L for MB. The adsorption experiments were carried out according to the same methods described previously.

The effect of the ion concentration on MB removal by the BCRs was also studied. The experiments were carried out by the addition of different contents of NaCl to a 50 mg/L MB solution. Accurately weighted amounts (10.0 g) of the beads were placed in a conical flask containing 50 mL of MB solution and incubated for an appropriate time on a shaking bed at a constant temperature at 130 rpm. The equilibrium pH of the solution was equal to 6.7 ± 0.1 without pH adjustment. After 48 h, the beads were removed from the solution, the concentration of

dyes in the solutions was determined by the measurement of their absorbance at 655 nm by UV–vis spectrophotometry.

RESULTS AND DISCUSSION

Formation and Structure of the Chitin Beads

Figure 1 shows the morphology of the chitin/layered silicate composite beads. The beads were spherical and gray because of the presence of the layered silicate [Figure 1(a)]. The water containing the beads was clear; this suggested that the layered silicates were immobilized well in the chitin matrix. The beads could be easily removed from the aqueous solution with a filter. The size distribution curve fit a Gaussian distribution and is given in Figure 1(b). The mean diameter of the beads and the polydispersity factor were 2.1 mm and 0.08, respectively; this indicated a successful fabrication of the chitin composite beads. The surface morphology of the dry beads was visualized by SEM [Figure 1(c)]. The spherical beads exhibited a uniform and dense surface. The layered silicate powders as fillers were added to the chitin matrix; this led to the formation of the spherical shape structure. Furthermore, we observed a creased exterior surface, which was different from the smooth and regular surface of the pure chitin beads.[33] This aspect was associated with the presence of inorganic fillers, as was previously observed.[5]

In addition, the layered silicate content of the beads (4 mg/g of wet beads) was close to the amount of rectorites that were initially added to the chitin solution (4 mg/g of wet beads). It was confirmed that the layered silicates were strongly embedded in the chitin matrix, and this led to the formation of the composite materials. It is not hard to imagine that a strong interaction existed between the layered silicate particles and the chitin matrix in the beads. By dropping the layered silicate/chitin solution into a sulfuric acid bath with a height of 5 cm, we fabricated the spherical beads successfully. Therefore, this work provided a green pathway for the preparation of the beads including the layered silicate, and this process is promising for large-scale production.

Selective Adsorption

The adsorption process of the dyes and the adsorption amount as a function of time are shown in Figure 2. The dyes MO [Figure 2(a–c)] and MB [Figure 2(d–f)] were adsorbed by the BCRs and BCOs within 10 h, respectively; this led to the slight orange or blue colors. After 3 h, the wastewater changed to be almost
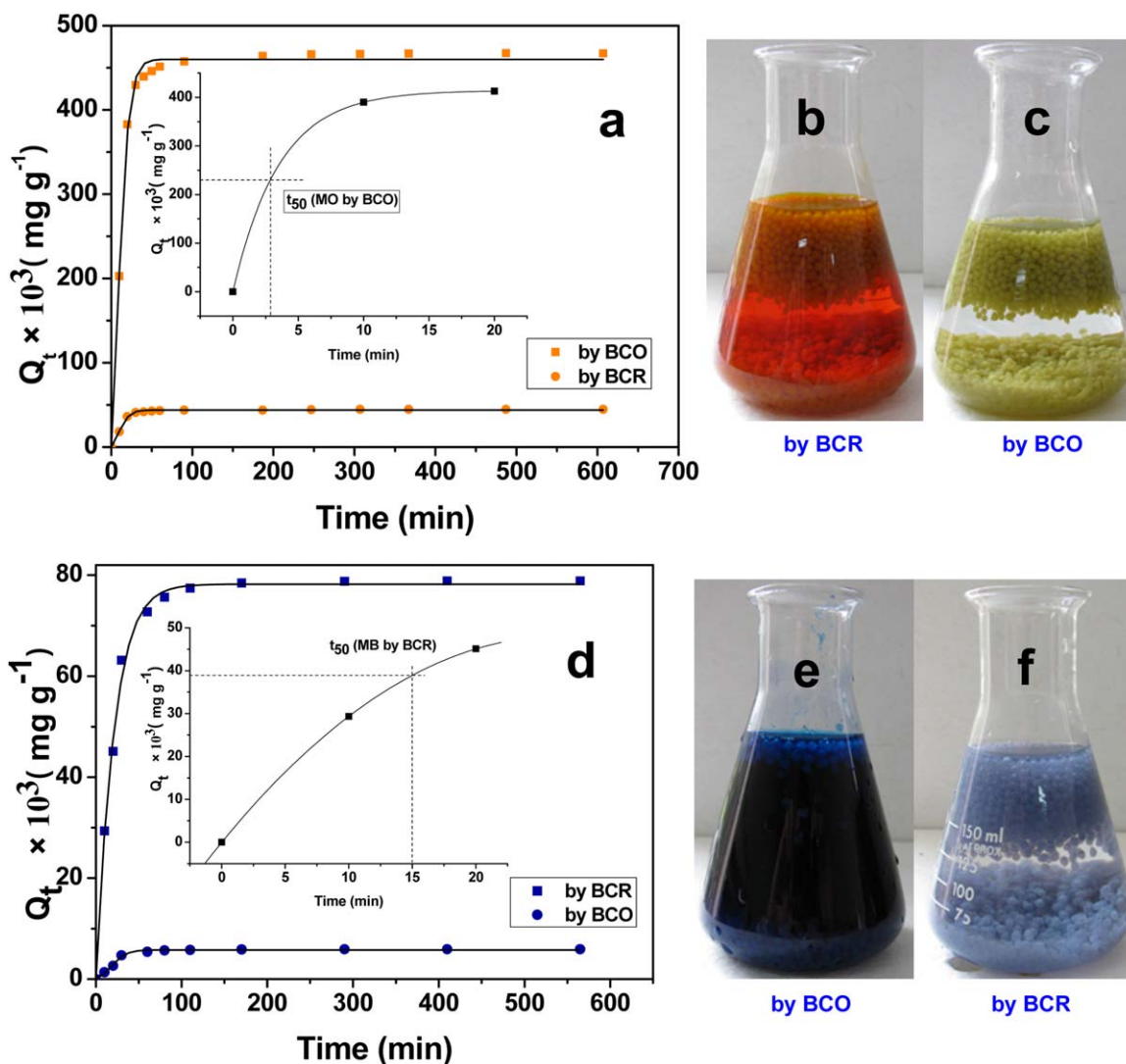
Figure 2. Pictures of the adsorption (right) and Q_t (left) values of the (a–c) MO and (d–f) MB by the BCOs and BCRs, respectively, as a function of the time. The inserts are magnifications of the 1- to 20-min range. t_{50} corresponds to the time when 50% of the dye was adsorbed. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

colorless. Moreover, the blue of MB was not changed remarkably by the BCO, and the orange of MO did not change significantly from the BCRs within 10 h. The results indicate that the chitin beads entrapping the layered silicate could effectively purify water to selectively remove the organic dyes.

The dyes MO and MB were mixed to further study the selective adsorption of the chitin composite gel beads. The adsorption properties of the BCRs and BCOs were investigated on the mixed dyes. The chitin composite gel beads could selectively adsorb MB (for the BCRs) and MO (for the BCOs) from the mixed dyes; this made the color of the mixed dyes changed from their initial green to orange or blue (Figure 3). UV–vis spectrophotometric scanning showed that the mixed dyes had obvious absorptions at 460 and 665 nm, which were the characteristic absorption wavelengths of MO and MB, respectively. However, the characteristic absorption wavelengths of MO and MB disappeared completely after the mixed dyes were processed

by the BCOs and BCRs. This indicated that the layered silicate complex gel beads could be highly selective for the removal of organic dyes. This was attributed to the electrostatic interaction. The rectorite surface is negatively charged, and the charge properties of the organic rectorite surface after modification with SDS were changed. Therefore, the cationic dyes were adsorbed preferentially by the BCRs, and the anionic dyes were adsorbed first by the BCOs. The BCOs and BCRs had higher Q_e values for MO and MB, respectively. This revealed that the negatively charged MO and positively charged MB were easier to bind with the BCOs and BCRs through hydrogen bonds and electrostatic interactions, respectively. So, the chitin composite gel beads indicated a selective adsorption behavior.

Effects of the Adsorption Time

The effect of the contact time on the removal of MB and MO by the BCRs and BCOs is presented in Figure 2(a,d). A rapid uptake of the adsorbed amount of the dyes occurred within the
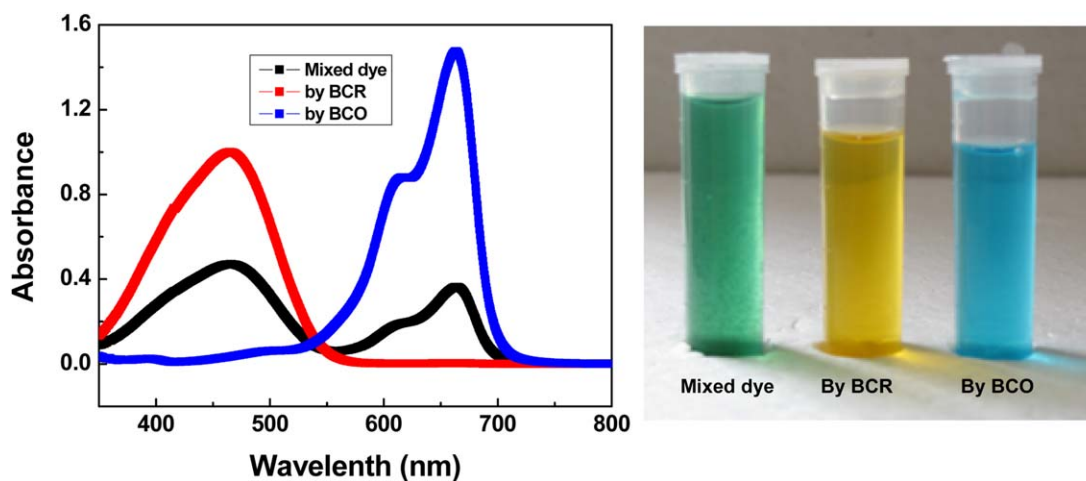
Figure 3. Absorbance in the range 350–800 nm (left) and color (right) of the mixed dyes from MO and MB, and the residual dye solution by the BCR and BCO selective adsorptions, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

first minutes during the adsorption process. About 50% of dye was adsorbed within 3 min for MO and 15 min for MB. Then, this trend gradually slowed down as the adsorption process continued and moved slowly toward a smooth line, namely, the adsorption equilibrium state. However, compared to the adsorption of the BCRs to MB, the adsorption equilibrium time of the MO to the BCOs was not the same; this may have been related to the different adsorbent and adsorbate. From an economical point of view, the contact time required to reach equilibrium is an important parameter in the wastewater treatment. On the basis of these results, we selected 2 and 3 h, respectively, as the adsorption times for the BCRs to MB and the BCOs to MO, respectively.

Effects of the Rectorite Content

The addition of the layered silicates effectively improved Q_e and the selectivity but could also reduce the sorbent cost and increase the industrial value. When the content of the layered silicate was higher than 0.5, the layered silicate was not easily dispersed uniformly in the chitin solution. Table I shows the effect of the content of layered silicate on the removal of MO and MB by the BCOs and BCRs, respectively. A significant effect of the content of layered silicate on dye removal was observed for the two organic dyes. Q_e and the removal rate were improved with the increase in the layered silicate content. This

Table I. Effects of the Layered Silicate Contents on the Adsorption of the Organic Dyes

Mass ratio[a]	$Q_e \times 10^3$ (mg/g)		ρ (%)	
	BCR/MB	BCO/MO	BCR/MB	BCO/MO
1:0	20.29	43.35	10.15	10.84
1:0.2	189.1	362.4	94.55	90.60
1:0.3	195.2	376.3	97.60	94.08
1:0.4	197.8	398.8	98.90	99.70
1:0.5	199.6	399.2	99.80	99.80

[a] Mass ratio of chitin to the layered silicate.

result confirmed that the adsorption was mainly a result of the contribution of the encapsulated layered silicate. Therefore, the layered silicate played an important role in the improvement of
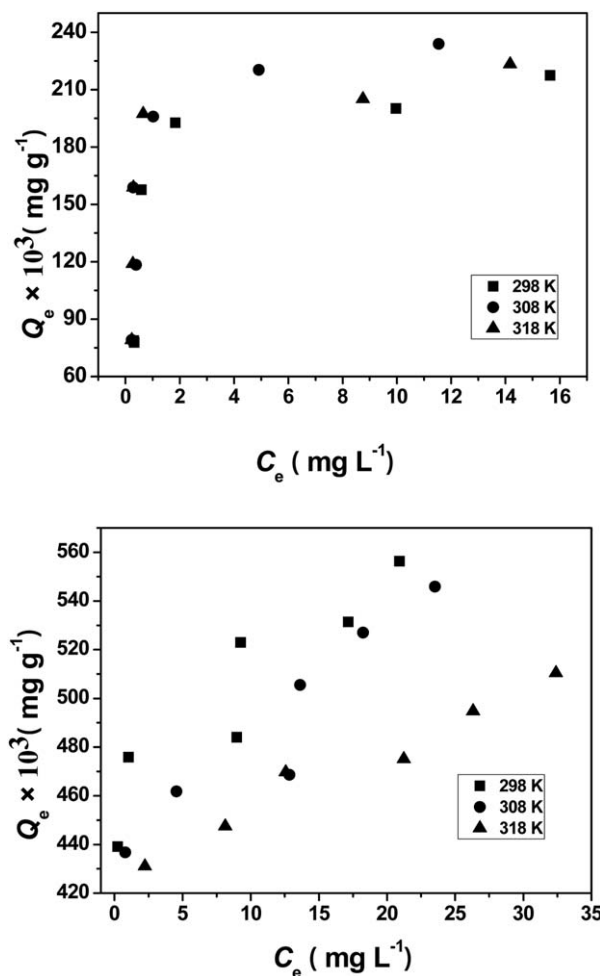

Figure 4. Adsorption isotherms of MB adsorbed onto the BCRs (top) and the MO adsorbed onto the BCOs (bottom) in aqueous solutions at 298, 308, and 318 K.
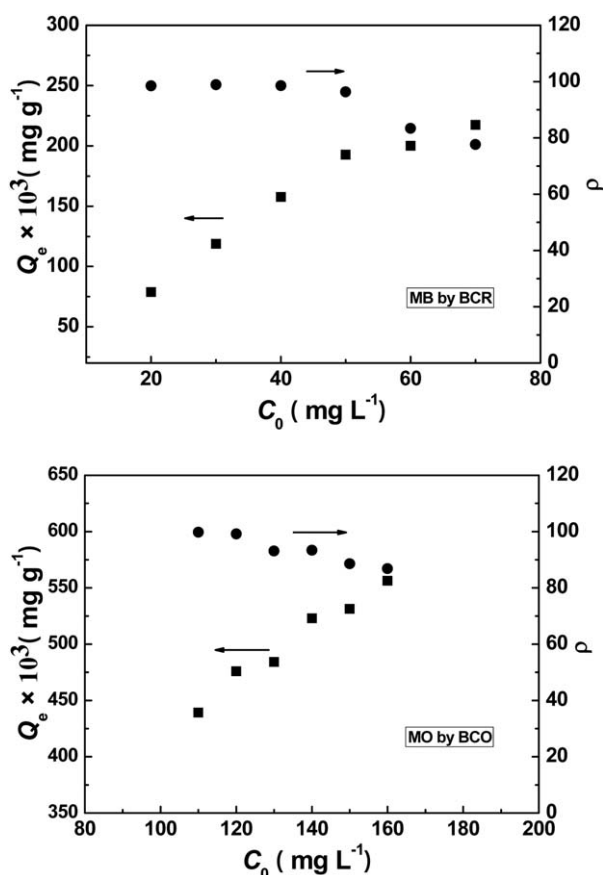
Figure 5. Effect of c_0 on Q_e through the adsorption of MB (top) and MO (bottom).

Q_e of the chitin composite gel beads. Furthermore, the addition of layered silicate decreased the cost of the adsorbent and improved the utilization value in industry.

Effects of the Temperature

Temperature is another important parameter affecting adsorption. The adsorption properties of the chitin composite gel beads on the organic dyes were investigated at 298, 308, and
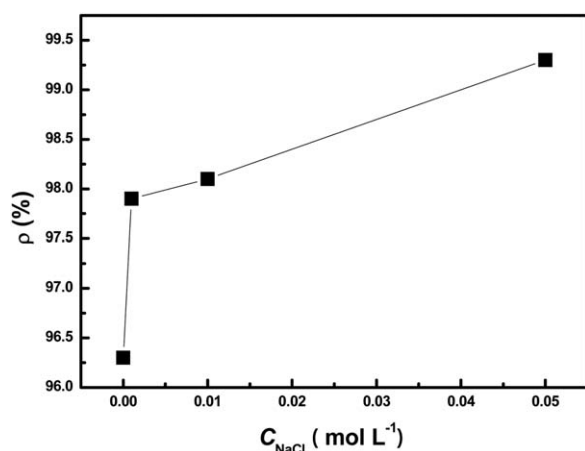
318 K, as shown in Figure 4. Q_e of the BCOs on the MO dye decreased gradually with increasing temperature from 298 to 318 K, but Q_e of the BCRs on dye MB did not seem significantly different. This showed that the BCO gel bead adsorption of MO was an exothermic process, and BCR gel bead adsorption of MB had no effects in the experimental temperature range. The lower temperature was conducive to the adsorption process of the BCOs on MO.

Effects of the Initial Concentration

The initial concentration of the dyes was another important parameter in the adsorption process. The adsorption properties were investigated at room temperature. The results are shown in Figure 5. Q_e increased with the increasing initial concentration of the organic dyes, but the percentage removal of the organic dyes was reduced from 99.8 to 86.9% (for the BCOs to MO) and from 98.5 down to 77.9% (for the BCRs to MB) with increasing initial concentration. This could have mainly been due to the fact that the higher initial concentration meant that the content of dyes was larger. However, the maximum Q_e was constant for a given adsorbent. Therefore, a higher initial concentration did not improve the dye removal percentage. Similar results were reported by Ni.[36]

Effect of the Ionic Concentration

The effect of the ionic concentration on the MB removal by BCR was investigated by changes in the content of NaCl from 0.001 to 0.05 mol/L in a 50 mg/L MB solution. The results are shown in Figure 6. The addition of salt can significantly improve the removal rate of the organic dyes. The removal of MB increased from 96.3 to 99.3% with concentrations of NaCl ranging from 0.001 to 0.05 mol/L. A possible reason for this was that the addition of NaCl produced a salting-out effect, which could have reduced the solubility of the dyes in the aqueous phase. On the other hand, the thickness of the double layer decreased, and as a result, the dye spread more easily to the adsorbent. Therefore, the removal rate of the dyes was improved.

Kinetics of the Sorption Process

The effects of the contact time on the removal of MB and MO by the BCRs and BCOs are presented in Figure 2(a,d). Several
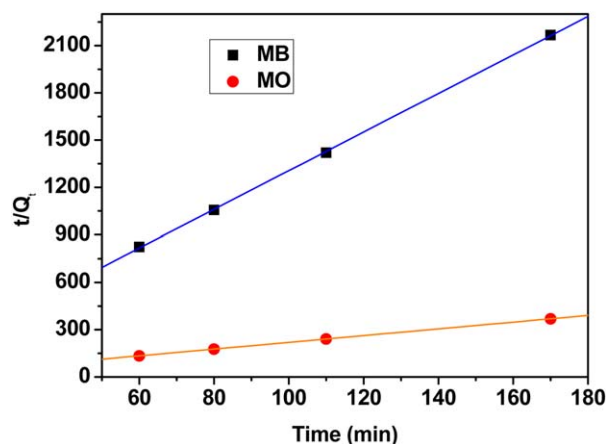

Figure 6. Effect of C_{NaCl} on the uptake of MB by the BCRs. C_{NaCl} = concentration of NaCl

Figure 7. Plots of t/Q_t versus t for MB by the BCRs and MO by the BCOs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Adsorption Kinetic Constants Modeled with a Pseudo-Second-Order Equation

Absorbent/dye	c_0 (mg/L)	t_{eq} (min)	$Q_{eq,exp}$ (mg/g)	$Q_{eq,calc}$ (mg/g)	k (g mg^{-1} min^{-1})	t_{50} (min)	R^2
BCO/MO	120	180	4.67×10^{-1}	4.69×10^{-1}	0.91	3	0.9998
BCR/MB	50	120	7.95×10^{-2}	7.87×10^{-2}	3.38	15	0.9996

kinetic models are available to study the mechanisms of the sorption process and to fit the experimental data. Among them, the pseudo-second-order equation is often successfully used to describe the kinetics of the fixation reaction of pollutants on adsorbents:[5]

$$\frac{dQ_t}{dt} = k(Q_{eq} - Q_t)^2 \qquad (3)$$

where k is the second-order rate constant (g mg^{-1} min^{-1}), Q_{eq} is the amount of dye adsorbed at equilibrium (mg/g of wet beads), and Q_t is the amount of dye adsorbed (mg/g of wet beads) at any time t (min). The integration of this equation for the boundary conditions $t = 0$ ($Q_t = 0$) to t_{eq} ($Q_t = Q_{eq}$) (where t_{eq} time of adsorption equilibrium) followed by linearization leads to

$$\frac{t}{Q_t} = \frac{1}{kQ_{eq}^2} + \frac{1}{Q_{eq}}t \qquad (4)$$

We determined k and Q_{eq} from the slope and intercepts of the plot by plotting t/Q_t versus t. As shown in Figure 7, a linear relationship with high correlation coefficients (R^2s) was observed between t/Q_t and t; this indicated the applicability of the pseudo-second-order model to describe the sorption process. The R^2s, k values, and calculated and experimental equilibrium sorption capacities ($Q_{e,calc}$ and $Q_{e,exp}$, respectively) are summarized in Table II. The values of Q_{eq} showed good agreement with the experimental values, and a good fit of the experimental curve was observed [Figure 2(a,d)]. The results revealed that the chitin composite gel beads possessed a high Q_e for organic dyes, and they could selectively and strongly adsorb MO or MB. It could have been that the presence of the layered silicate and hydroxyl and acetyl amino groups of chitin promoted the dyes with the charges binding into the composite gel beads through hydrogen bonds and electrostatic interaction. For subsequent batch experiments, the equilibrium time was 3 h, which was more than sufficient to establish equilibrium.

CONCLUSIONS

Rectorite and organic rectorite were embedded in a chitin matrix to fabricate a sorbent via a simple and green process. Two dyes, including positively charged MB and negatively charged MO, as model organic dyes were adsorbed effectively by the BCRs and BCOs, respectively. The layered silicate in the chitin composite gel beads played important roles in both the formation of spherical shape beads and the improvement of the selective adsorption. The chitin/layered silicate composite beads exhibited a high Q_e for the two dyes and could more strongly adsorb MB and MO, respectively. The adsorption kinetics were quick, with 3 h needed to reach equilibrium, and the kinetic data fit a pseudo-second-order model well. Furthermore, the

sorbents were composed of biopolymers, and a layered silicate of low cost that is disposable in large amount will allow for the development of a product with a low impact on the environment. This will to the development of a clean and safe process for water pollution remediation. This study provided a new pathway for the preparation of the chitin composite gel beads, including a layered silicate, and this process is promising for large-scale production.

REFERENCES

1. Ozmihci, S.; Kargi, F. *J. Environ. Manage.* **2006**, *81*, 307.

2. Yan, Z.; Tao, S. Y.; Yin, J. X.; Li, G. T. *J. Mater. Chem.* **2006**, *16*, 2347.

3. Ku, Y.; Lee, P. L.; Wang, W. Y. *J. Membr. Sci.* **2005**, *250*, 159.

4. Luo, P.; Zhao, Y. F.; Zhang, B.; Liu, J. D.; Yang, Y.; Liu, J. F. *Water Res.* **2010**, *44*, 1489.

5. Rocher, V.; Siauque, J. M.; Cabuil, V.; Bee, A. *Water Res.* **2008**, *42*, 1290.

6. Yan, Z.; Li, G. T.; Mu, L.; Tao, S. Y. *J. Mater. Chem.* **2006**, *16*, 1717.

7. Gomez, V.; Larrechi, M. S.; Callao, M. P. *Chemosphere* **2007**, *69*, 1151.

8. Luo, X.; Zhang, L. *J. Hazard. Mater.* **2009**, *171*, 340.

9. Vimonses, V.; Jin, B.; Chow, C. W. K.; Saint, C. *J. Hazard. Mater.* **2009**, *171*, 941.

10. Zhou, C. H.; Nitschke, A. M.; Xiong, W.; Zhang, Q.; Tang, Y.; Bloch, M.; Elliott, S.; Zhu, Y.; Bazzone, L.; Yu, D.; Weldon, C. B.; Schiff, R.; McLachlan, J. A.; Beckman, B. S.; Wiese, T. E.; Nephew, K. P.; Shan, B.; Burow, M. E.; Wang, G. D. *Breast Cancer Res.* **2008**, *10*, R105.

11. Karadag, D.; Akgul, E.; Tok, S.; Erturk, F.; Kaya, M. A.; Turan, M. *J. Chem. Eng. Data* **2007**, *52*, 2436.

12. Wang, S. B.; Zhu, Z. H. *J. Hazard. Mater.* **2006**, *136*, 946.

13. Gupta, V. K.; Ali, I.; Saini, V. K.; Van Gerven, T.; Van der Bruggen, B.; Vandecasteele, C. *Ind. Eng. Chem. Res.* **2005**, *44*, 3655.

14. Dincer, A. R.; Gunes, Y.; Karakaya, N.; Gunes, E. *Bioresour. Technol.* **2007**, *98*, 834.

15. Mittal, A.; Kaur, D.; Mittal, J. *J. Colloid Interfaces Sci.* **2008**, *326*, 8.

16. Wang, X. Y.; Tang, Y. F.; Li, Y.; Zhu, Z.; Du, Y. M. *J. Biomater. Sci. Polym. Ed.* **2010**, *21*, 171.

17. Saravanana, D.; Gomathib, T.; Sudha, P. N. *Int. J. Biol. Macromol.* **2013**, *53*, 67.

18. Xin, S. J.; Li, Y. J.; Li, W.; Du, J.; Huang, R.; Du, Y. M.; Deng, H. B. *Carbohydr. Polym.* **2012**, *90*, 1069.

19. Wang, X. Y.; Du, Y. M.; Yang, H. H.; Wang, X. H.; Shi, X. W.; Hu, Y. *Polymer* **2006**, *47*, 6738.

20. Wu, X. T.; Wang, X. Y.; Du, Y. M. *Acta Polym. Sin.* **2009**, *3*, 222.

21. Yang, L. L.; Liang, G. Z.; Zhang, Z. P.; He, S. B.; Wang, J. H. *J. Appl. Polym. Sci.* **2009**, *114*, 1235.

22. Miretzky, P.; Cirelli, A. F. *J. Hazard. Mater.* **2009**, *167*, 10.

23. Mohamed, M.; Ouki, S. *Ind. Eng. Chem. Res.* **2011**, *50*, 9557.

24. Akkaya, G.; Uzun, I.; Guzel, F. *Dyes Pigments* **2007**, *73*, 168.

25. Zhou, D.; Zhang, L.; Guo, S. L. *Water Res.* **2005**, *39*, 3755.

26. Tang, H.; Zhou, W.; Zhang, L. *J. Hazard. Mater.* **2012**, *209*, 218.

27. Rinaudo, M. *Prog. Polym. Sci.* **2006**, *31*, 603.

28. Pillai, C. K. S.; Paul, W.; Sharma, C. P. *Prog. Polym. Sci.* **2009**, *34*, 641.

29. Hu, X. W.; Du, Y. M.; Tang, Y. F.; Wang, Q.; Feng, T.; Yang, J. H.; Kennedy, J. F. *Carbohydr. Polym.* **2007**, *70*, 451.

30. Li, G. X.; Du, Y. M.; Tao, Y. Z.; Liu, Y. T.; Li, S.; Hu, X. W.; Yang, J. H. *Carbohydr. Polym.* **2010**, *80*, 970.

31. Li, G. X.; Li, W. Z.; Deng, H. B.; Du, Y. M. *Int. J. Biol. Macromol.* **2012**, *51*, 1121.

32. Zheng, H.; Zhou, J. P.; Du, Y. M.; Zhang, L. N. *J. Appl. Polym. Sci.* **2002**, *86*, 1679.

33. Li, G. X.; Du, Y. M.; Tao, Y. Z.; Deng, H. B.; Luo, X. G.; Yang, J. H. *Carbohydr. Polym.* **2010**, *82*, 706.

34. Xu, J.; McCarthy, S. P.; Gross, R. A.; Kaplan, D. L. *Macromolecules* **1996**, *29*, 3436.

35. Xu, R. F.; Xin, S. J.; Zhou, X.; Li, W.; Cao, F.; Feng, X. Y.; Deng, H. B. *Int. J. Pharm.* **2012**, *438*, 258.

36. Ni, Z. M.; Xia, S. J.; Wang, L. G.; Xing, F. F.; Pan, G. X. *J. Colloid Interfaces Sci.* **2007**, *316*, 284.