Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.826856

52 (2014) 880–888
January

Taylor & Francis
Taylor & Francis Group

Adsorption property of direct red brown onto acid-thermal-modified sepiolite and optimization of adsorption conditions using Box-Behnken response surface methodology

Cheng-yuan Su[a,b], Wei-guang Li[a,*], Xing-zhe Liu[a], Lei Zhang[a]

[a]*School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China*
Tel. +86 0451 86283003; email: hitlwg@126.com
[b]*School of Environment and Resources, Guangxi Normal University, Guilin 541004, China*

Received 26 February 2013; Accepted 19 March 2013

ABSTRACT

The chemical properties of the acid-thermal-modified sepiolite were investigated. At the same time, the adsorption behaviors of direct red brown onto modified sepiolite were studied. The pH_{ZPC} of the raw sepiolite and the acid-thermal-modified sepiolite was 7.32 ± 0.1 and 6.44 ± 0.1, respectively. The results indicated that the acid-thermal modification increased the surface acidity of the sepiolite and the available surface sites for adsorption. According to the X-ray powder diffraction and Fourier transform infrared spectra, the results showed that the modification improved the purity of the sepiolite. The amount of the direct red brown adsorbed increased from 15.34 to 62.42 mg/g onto the modified sepiolite, as initial dye concentration increased from 50 to 200 mg/L. The amount of direct red brown adsorbed decreased from 18.96 to 13.76 mg/g, as the initial pH of the dye solution increased from 2 to 8. The direct red brown onto modified sepiolite was best described by the pseudo-second-order kinetic model. The experiment data were calculated by the Box-Behnken, and the optimum adsorption conditions were following: the adsorbent dosage 2.53 g/L, pH 4.70, and reaction time 4.46 h. The decolorization rate performed in the optimum adsorption conditions was 91.5%. The initial pH, adsorbent dosage, reaction time, the interaction of adsorbent dosage and reaction time were significant factors for the adsorption.

Keywords: Direct red brown; Acid-thermal-modified sepiolite; Response surface methodology; Adsorption

1. Introduction

Dyes and pigments are used in industries such as textiles, leather, printing, food and plastics, etc [1]. Colored wastewater and dyes can cause a lot of environmental problems in the receiving media [2]. It can create esthetic problems, limit the possible use of water, and obstruct light penetration and oxygen transfer into water bodies, hence affecting the aquatic life [1]. In addition, it contains many chemicals which are toxic, carcinogenic, and mutagenic [3]. Direct red brown, which is characterized by nitrogen to nitrogen double bond (–N=N–), is widely used for dyeing textile fabric

---

*Corresponding author.

Presented at the Fifth Annual International Conference on "Challenges in Environmental Science & Engineering—CESE 2012" Melbourne, Australia, 9–13 September 2012

and leather. It is difficult to biodegrade because it has complex aromatic molecular structure [4]. Conventional methods for removal of dyes from wastewater include chemical oxidation, adsorption, electrolysis, chemical coagulation, photocatalysis, membrane, and biodegradation [3,4]. Adsorption has been found to be an efficient method for the removal of dyes from wastewater because it has a high removal efficiency and does not involve sophisticated instruments, as well offers the potential for regeneration and recycling of the adsorbing material [3,4]. However, the adsorption process is limited by high cost of adsorbents [4]. Therefore, cheap and efficient adsorbents materials have been used including bentonite, sepiolite, fly ash, and so on [4–6]. Sepiolite is a clay mineral with an ideal formula $Mg_8Si_{12}O_{30}(OH)_2$ [7]. The structure of sepiolite is formed by alternative building of blocks and tunnels, which grows up in the fiber direction [8]. High adsorption capacity and corrosion resistance properties of sepiolite are due to this unique fibrous structure. For this reason, sepiolite is widely applied in many fields for the removal of heavy metals, dyes, nitrite, ammonia, and phosphorus [4]. However, the studies about adsorption properties and optimal adsorption conditions of modified sepiolite are limited, while the modification and optimization are important for practical adsorption applications. Response surface methodology (RSM) is a useful mathematical and statistical technique for designing experiments, building models, and determining optimum conditions for desirable responses [9,10].

In this work, the influence of several parameters such as initial dye concentration, initial pH of dye solution, and adsorbent dosage i.e. amount of direct red brown adsorbed onto the acid-thermal-modified sepiolite was firstly investigated. Secondly, the three-factor and three-level Box-Behnken RSM was utilized for modeling and optimizing the adsorption conditions, in which the decolorization rate was selected as response value, while pH, adsorbent dosage, and reaction time were chosen as influential factors.

2. Materials and methods

2.1. Materials

Sepiolite samples were obtained from the Jingteng Mineral Processing Plant in Hebei, China. Direct red brown was purchased from Chunlin Dye Industrial Co., Ltd., in Shangdong, China and was used without purification. All reagents used, including H_2SO_4 and NaOH, were of analytical grade and all solutions were prepared with distilled water.

2.2. Preparation of the acid-thermal modified sepiolite

First, 10 g of raw sepiolite was added into 100 mL 0.5 M H_2SO_4 and was stirred for 6 h at room temperature for activation. Then the acid sepiolite was rinsed to neutral pH with distilled water and dried at 105℃ for 2 h [11]. After the acid-modified sepiolite was calcined at 600℃ for 2 h in muffle furnace, the acid-thermal-modified sepiolite was prepared.

2.3. Characterization of the sepiolite samples

The zeta potential of the sepiolite suspensions was measured using a zeta meter (Malvern). The structures and the mineralogical compositions of the raw sepiolite and the acid-thermal-modified sepiolite samples were characterized by the X-ray diffraction patterns with Cu Kα radiation under operation conditions of 40 kV and 50 mA [12]. The chemical bonds on the surface of samples were recorded in the region 4,000–400 cm^{-1} on a spectrum one Fourier transform infrared spectra (FTIR) spectrometer at a resolution of 4 cm^{-1}. The Brunauer–Emmett–Teller (BET) surface area measurements of the raw sepiolite and the acid-thermal-modified sepiolite were determined by adsorption of nitrogen at 77 K using a Micromeritics, ASAP 2020 surface area analyzer.

2.4. Batch adsorption experiments

Batch adsorption experiments for the removal of direct red brown were performed in a thermostatic shaker at 150 rpm to study the effects of parameters, such as initial dye concentration (50–200 mg/L), initial pH (2–8), and adsorbent dosage (1.0–2.5 g/L). The samples were taken at preset time intervals and the concentrations of direct red brown were rapidly measured. The concentrations of direct red brown in the supernatant solutions before and after adsorption were determined using a T6 spectrophotometer at 480 nm. The adsorption capacity at time t, Q_t (mg/g), was calculated by:

$$Q_t = (C_0 - C_t)V/W \tag{1}$$

Here, C_0 and C_t (mg/L) were the concentrations of direct red brown at initial time and at any time, respectively. V was the volume of the solution (L) and W was the mass of acid-thermal-modified adsorbent used (g).

In addition, the adsorption data were analyzed using pseudo-second-order and intraparticle diffusion kinetic models.

Table 1
Experimental range and levels of independent variables

Independent variable	Factor	Range and levels		
		−1	0	1
The adsorbent dosage (g/L)	X_1	1	2	3
pH	X_2	4	6	8
Reaction time (h)	X_3	2	4	6

2.5. Box-Behnken experimental design

A Box-Behnken experimental design with three factors and three levels was used to fit a second-order response model [13]. Three factors affecting direct red brown adsorption onto acid-thermal-modified sepiolite: the dosage of adsorbent (X_1), pH (X_2), and reaction time (X_3) were selected as the independent variables. The decolorization rate (Y) was considered as the dependent variable. The initial dye concentration was kept constant at 50 mg/L, and the volume was 200 mL at room temperature. Experimental range and levels of independent variables for direct red brown decolorization were presented in Table 1. The experimental results were analyzed using Design Expert 7.0 and Minitab 15.0 software [14].

3. Results and discussion

3.1. The characterization of the samples

The study of the electrochemical properties of the sepiolite interface is important to understand the adsorption mechanism. The variation of the zeta potential with equilibrium pH of the sepiolite suspensions is shown in Fig. 1. The zeta potential value of the acid-thermal-modified sepiolite suspensions decreased as the equilibrium pH increased. The isoelectrical point of the raw sepiolite and the acid-thermal-modified sepiolite appeared in the pH of 7.32 ± 0.1 and 6.44 ± 0.1, respectively. The results show that the pH_{ZPC} of the sepiolite reduced after acid-thermal modified process, which demonstrated that the stability and quantity of the surface of the core acid are increased by modification [15,16]. While after acid-thermal modification, the alkaline of sepiolite decreased due to surface of the part functional group replaced by protons. More adsorption sites were formed and they were useful for direct red brown adsorption onto the modified sepiolite. Meanwhile, the modified could make the sepiolite internal channel connected and increased the surface area of sepiolite [15]. The BET surface area of the raw

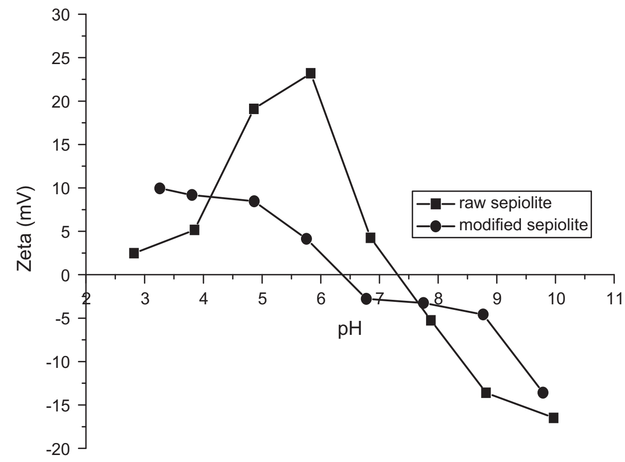

Fig. 1. Variation of zeta potential with equilibrium pH of raw sepiolite and modified sepiolite.

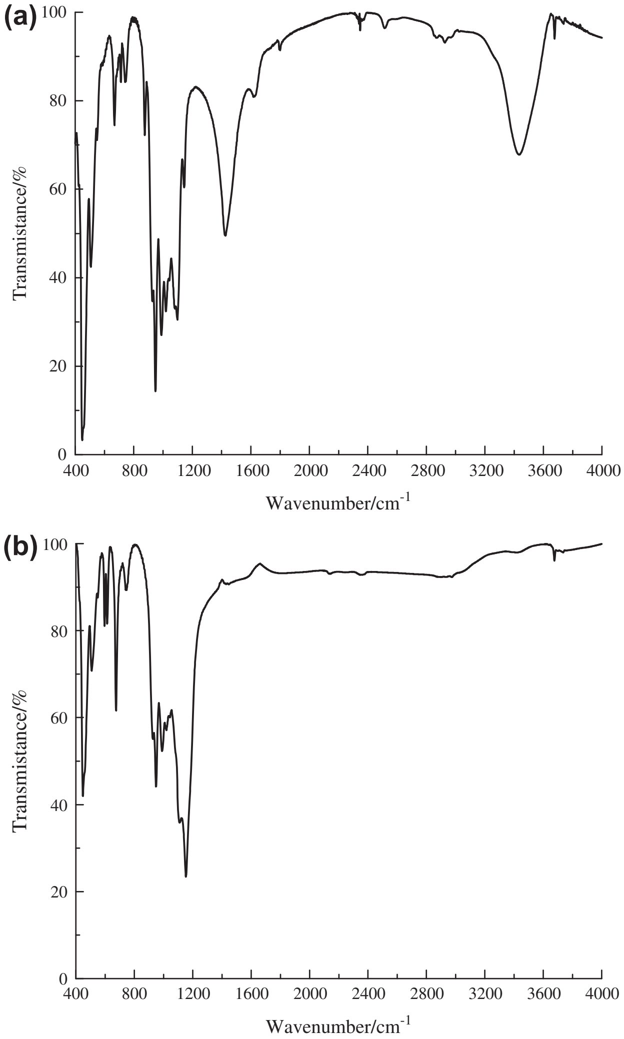

Fig. 2. FTIR spectra of the raw sepiolite (a) and acid-thermal-modified sepiolite (b).

sepiolite and the acid-thermal-modified sepiolite was 14.15 and 88.99 m^2/g, respectively.

The bands in the FTIR spectra of raw sepiolite (Fig. 2) could be summarize as follows [4,17]: (a) the band of group Si–OH stretch at 3,737 cm^{-1}, (b) the band of the triple bridge group Mg_3OH stretch at 3,676 cm^{-1}, (c) the stretch at 3,435 cm^{-1} was associated with zeolitic water, (d) the bands of Si-O combination stretch at 1,144, 1,098 cm^{-1} and the bands of O–Si–O bend at 508 cm^{-1}, (e) the basal plane of the tetrahedral units exhibiting the Si–O–Si plane vibrations at 1,020 cm^{-1} and the Si–O–Mg of the octahedral–tetrahedral linkage vibrations at 448 cm^{-1}, (f) the band of dolomite impurities at 1,427 cm^{-1}. As the raw sepiolite was altered to acid-thermal-modified sepiolite, changes in the FTIR spectra of the sample were noted at 3,435 and 1,427 cm^{-1}. The broad band at 3,435 cm^{-1} is due to the zeolitic water disappeared on acid-thermal-modified process. Also the band at 1,427 cm^{-1} was disappeared because the modification process improved the purity of sepiolite and made the sepiolite internal channels connected.

The X-ray powder diffraction (XRD) patterns of raw sepiolite and acid-thermal-modified sepiolite are presented in Fig. 3. The XRD results showed that the acid-thermal-modified process had caused structural changes in the sepiolite sample. The characteristic diffraction peaks of calcium carbonate ($2\theta = 29.4°$) were disappeared and the characteristic diffraction peaks of SiO_2 were more strengthen [4]. They indicated that the purity of sepiolite was improved by the acid-thermal-modified process. At the same time, a part of magnesium ion was separated [4]. Therefore, the internal pore of sepiolite was opened and the surface area was increased by the acid-thermal-modified process.

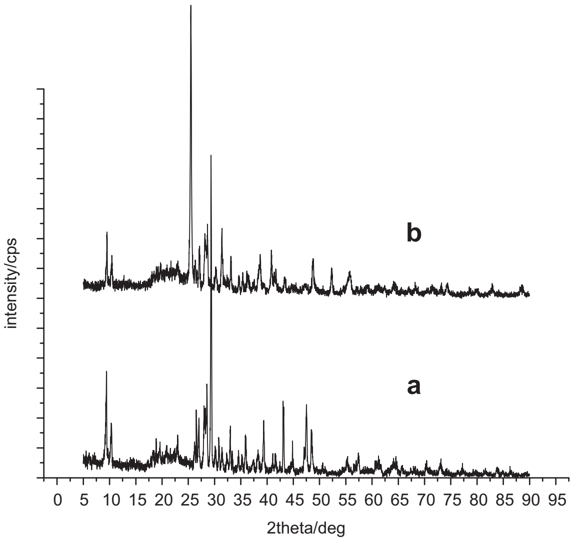

Fig. 3. The X-ray diffraction patterns of the samples ((a) raw sepiolite, (b) modified sepiolite).

3.2. Effect of initial dye concentration on adsorption

The plots of adsorption capacity vs. time at initial dye concentration are shown in Fig. 4. When the initial dye concentration increased from 50 to 200 mg/L at a total volume of 200 mL, 2.5 g/L adsorbent, and room temperature, the amount of direct red brown adsorbed increased from 15.34 to 62.42 mg/g onto the acid-thermal-modified sepiolite. Obviously, the initial dye concentration was an important factor for the adsorption process. When the concentration of direct red brown solution was increased, the speed of the direct red brown molecules through the liquid phase and adsorption on the surface of the adsorbent accelerated, thus increasing adsorption rate. In addition, with the increasing concentration of direct red brown, the active sites on the adsorbent were gradually occupied, so adsorption capacities were varied with the increasing dye concentration.

The linear plot of t/Q_t vs. t, as shown in Fig. 5, has a good agreement between the experimental and the calculated Q_e values [18,19]. At the same time, the linear plot of Q_t vs. $t^{1/2}$ is shown in Fig. 6. The correlation coefficients for the pseudo-second-order kinetic model were greater than 0.979 for all the direct red brown concentrations, indicating the applicability of the pseudo-second-order kinetic model to describe the adsorption process of direct red brown onto the acid-thermal-modified sepiolite. Because the pseudo-second-order kinetic model contained all of the adsorption, such as external liquid film diffusion, surface adsorption, and intraparticle diffusion, the model was more realistic and fully reflected the

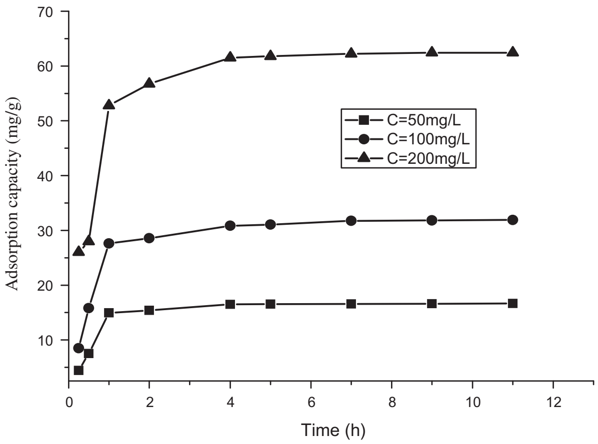

Fig. 4. Effect of initial concentration on adsorption onto the acid-thermal-modified sepiolite.

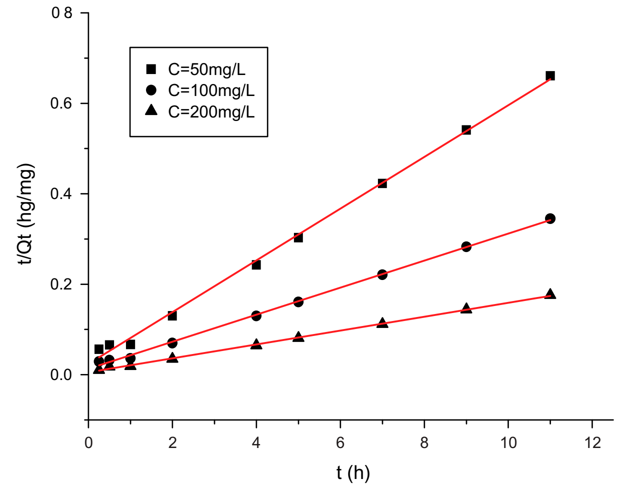

Fig. 5. Pseudo-second-order kinetics for adsorption at different concentration.

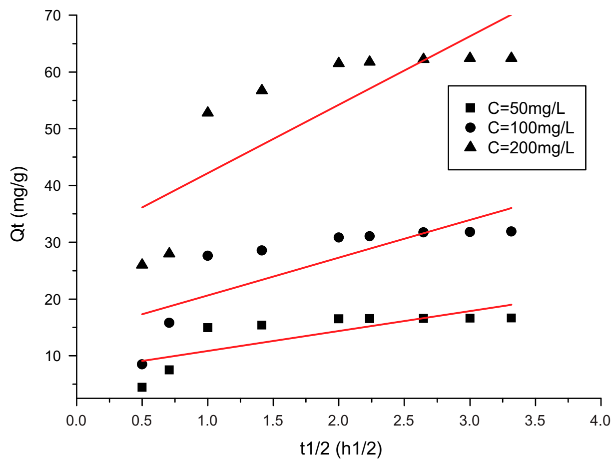

Fig. 6. Intraparticle diffusion kinetics for adsorption at different concentration.

adsorption mechanism of direct red brown on the modified sepiolite [18–21].

3.3. Effect of pH on adsorption

The variation of direct red brown adsorption in initial pH range 2–8 at a volume of 200 mL, initial dye concentration of 50 mg/L, and adsorbent concentration of 2.5 g/L is shown in Fig. 7. The highest direct red brown adsorption capacity was experimentally observed at pH 2, this capacity decreased for higher pH values. When the pH value increased from 2 to 8, the amount of direct red brown adsorbed decreased from 18.96 to 13.76 mg/g. In addition, when the pH value was 2, the adsorption rate was faster than 6 and 8. This result was related to the surface charge of the modified sepiolite and the dye anions [5]. At lower pH values, more hydrogen ions would be available to protonate the surface of the acid-thermal-modified sepiolite and change the Si–O into Si–OH, thus increasing the electrostatic attractions between negatively charged dye anions and positively charged adsorption sites [3,5]. Therefore, pH was an important factor in pursuing a high efficiency of the removal of direct red brown using the modified sepiolite.

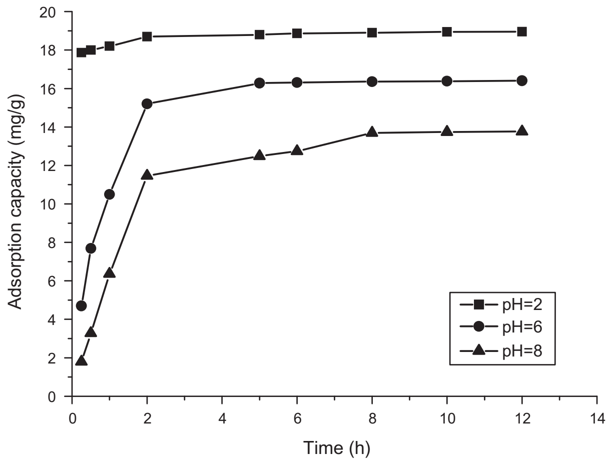

Fig. 7. Effect of initial pH on adsorption onto the acid-thermal-modified sepiolite.

3.4. Effect of adsorbent dosage on adsorption

The effect of adsorbent dosage on the amount of direct red brown adsorbed was investigated by adding 200 mL of dye solution with initial dye concentration

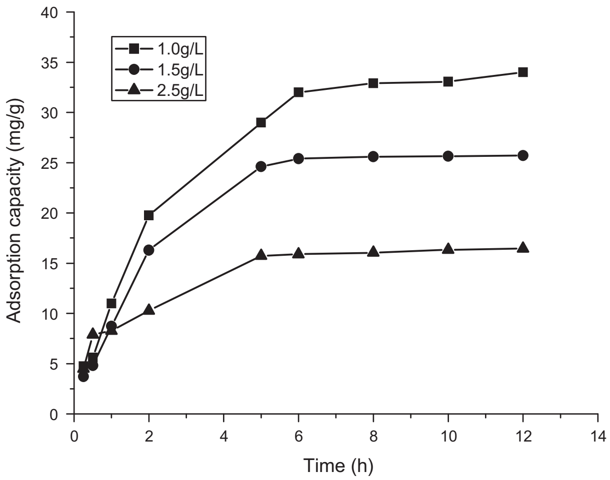

Fig. 8. Effect of adsorbent dosage on adsorption onto the acid-thermal-modified sepiolite.

of 50 mg/L using test solution at pH 6 and room temperature. The plots of dye adsorption capacity vs. time at different adsorbent dosage are shown in Fig. 8. As seen from these figures, the amount of direct red brown adsorbed decreased from 34.00 to 16.44 mg/g with the adsorbent dosage increasing from 1.0 to 2.5 g/L. The decrease in the amount of direct red brown adsorbed with increasing adsorbent dosage was due to adsorption sites remaining unsaturated during the adsorption process [4]. The adsorption kinetic was well described by the pseudo-second-order kinetic model for both dyes.

3.5. *Response surface modeling*

3.5.1. *Experimental design and quadratic model*

Fifteen designed batch runs were performed according to Box-Behnken design (Table 2). A function of the decolorization rate based on the experimental results was evaluated and is given in Eq. (2).

$$Y = 75.8 + 14.6X_1 - 22.7X_2 + 10.5X_3 - 13.2X_1X_1 + 2.5X_1X_2 - 9.9X_1X_3 - 4.6X_2X_2 + 8.1X_2X_2 + 8.1X_2X_3 - 4.0X_3X_3 \quad (2)$$

Table 2
Response surface design arrangement and experimental results

Run	Coded variables			Y_{exp} (%)	Y_{pre} (%)
	X_1	X_2	X_3		
1	0	−1	−1	86.6	87.5
2	0	1	−1	31.1	25.9
3	0	0	0	76.1	75.8
4	1	0	1	81.0	73.9
5	0	0	0	75.5	75.8
6	−1	0	1	61.5	64.4
7	−1	1	0	20.1	18.2
8	0	−1	1	87.1	92.3
9	1	1	0	44.4	52.5
10	0	0	0	75.8	75.8
11	1	0	−1	75.6	72.7
12	0	1	1	64.1	63.2
13	−1	−1	0	76.6	68.5
14	1	−1	0	90.9	92.8
15	−1	0	−1	16.5	23.6

Fig. 9 shows the relationship between the actual and predicted values of Y for adsorption of direct red brown onto the modified sepiolite. It can be seen in Fig. 9 that the developed model was adequate because

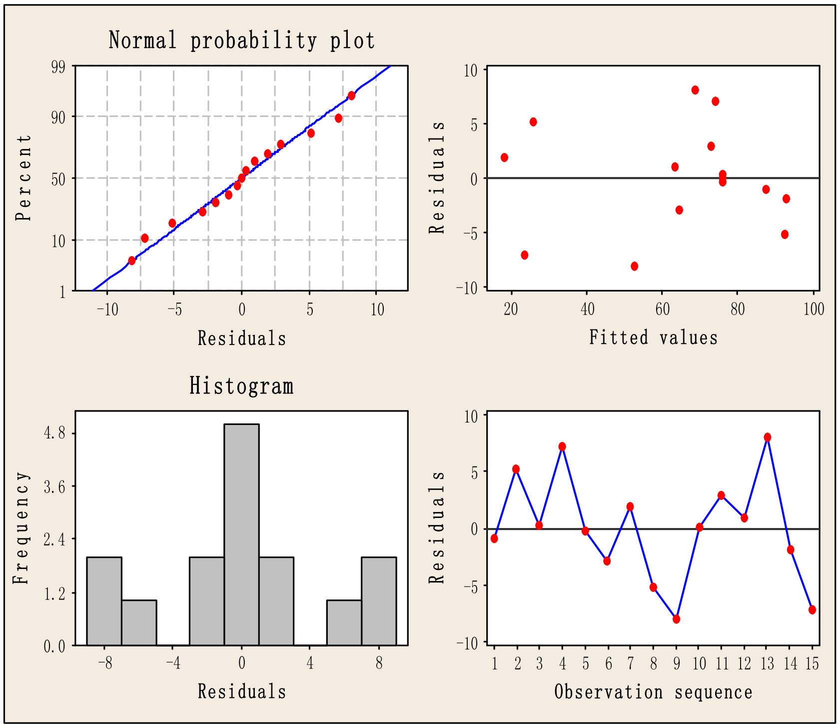

Fig. 9. Normal probability plot of standardized residuals.

the residuals of the responses were less than 10%. The normal probability plot showed how the set of observed values closely followed the theoretical distribution and the residuals tended to be close to the diagonal line [13]. At the same, the experimental points were reasonably aligned, suggesting a normal distribution. The model coefficient of determination (R^2) value was 0.9631. It could provide a well explanation of the relationships between the independent variable and the response [10].

Analysis of variance (ANOVA) tests the significance and the adequacy of the regression model and are presented in Table 3.The model *F*-value of 14.5 implied that the model was significant for decolorization of direct red brown [22]. The values of prob > *F* less than 0.0500 indicated that the model terms were significant, whereas the values greater than 0.1000 were not significant [10]. In the case, the *p*-value of the model was 0.004. It indicated the model term was significant at 95% of probability level [13]. The significance of each independent variable was also evaluated according to its *p*-value [22]. The results indicated that the decolorization of direct red brown was significantly affected by the adsorbent dosage ($p = 0.0033$), the initial pH ($p = 0.0005$), and reaction time ($p = 0.0131$). And the pH had a more significant effect in comparison to adsorbent dosage and reaction time.

Table 3
ANOVA for response surface quadratic model

Source	Sum of squares	Mean square	*F*-value	*p*-value, prob>*F*
Model	8113.02	901.45	14.5	0.0044
X_1	1716.98	1716.98	27.61	0.0033
X_2	4117.78	4117.78	66.22	0.0005
X_3	879.9	879.9	14.15	0.0131
X_1X_2	25	25	0.4	0.5539
X_1X_3	392.04	392.04	6.3	0.0538
X_2X_3	264.06	264.06	4.25	0.0943
X_1^2	642.13	642.13	10.33	0.0236
X_2^2	78.55	78.55	1.26	0.3121
X_3^2	57.97	57.97	0.93	0.3786

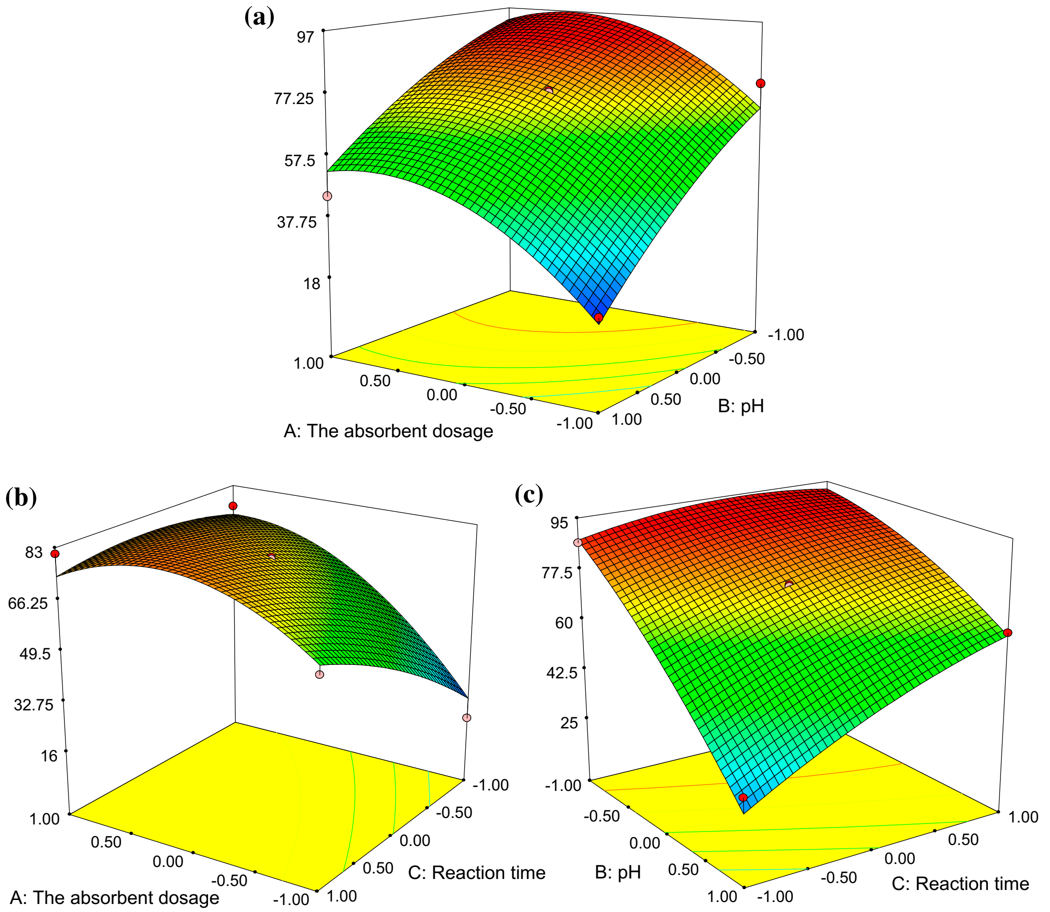

Fig. 10. The response surface plot of the decolorization rate of direct red brown as a function of (a) the absorbent dosage with pH; (b) the absorbent dosage with reaction time; (c) reaction time with pH.

Table 3 also indicates that the interactive effects of adsorbent dosage and reaction time ($p = 0.0538$) had significant influence, while the interactive effects of adsorbent dosage and initial pH had a slight effect on the decolorization of direct red brown onto the modified sepiolite ($p = 0.5539$) [23].

3.5.2. Response surface analysis and optimization conditions

Three-dimensional response surfaces were investigated by the interactive effect of two variables on direct red brown decolorization rate (Fig. 10). The response surface of adsorbent dosage and pH value is shown in Fig. 10(a). It could be infer that the effects of the dosage adsorbent were positive and the pH was negative when changing from level −1 to level +1. In addition, pH had a greater effect on decolorization rate, as was evident that the pH of surface slope was greater than the other factors [21]. The pH value of the initial solution was an important factor as it usually affects the physical and chemical properties of the solution. Fig. 10(b) shows the effects of adsorbent dosage and reaction time on direct red brown decolorization. The interaction of adsorbent dosage and reaction time was a significant factor. It took an important effect on direct red brown adsorption onto acid-thermal-modified sepiolite. By increasing the adsorbent dosage, higher decolorizaiton rates were expected because it increased the adsorbent dosage, hence the availability of more active surface sites of direct red brown for adsorption. Fig. 10(c) shows the effects of reaction time and pH on direct red brown decolorization. As shown in Fig. 10(c), pH had a significant effect on decolorization efficiency of direct red brown; however, the decolorization efficiency was less affected by the reaction time. In the choice of test range, it could be seen that decolorization rate increased with increasing reaction time and decreasing pH [24]. Adsorption after 4 h, the adsorption capacity of direct red brown onto the modified sepiolit nearly achieved adsorption equilibrium. Therefore, an insignificant enhancement in adsorption was effected in 6 h as compared to that in 4 h.

The studies of the contour plot also revealed the best optimal values of the process conditions that the adsorbent dosage 2.53 g/L, pH 4.70 and reaction time 4.46 h. Predicted decolorization rate of 91.5% could be achieved under the optimum conditions. To test the validity of predicted model, additional three runs were performed under the optimum conditions obtained through Box-Behnken RSM. The average decolorization rate was 89.4%. The error of the model predicted and experimental value was 2.1%.

4. Conclusions

The results of the present study showed that the acid-thermal modification could improve the purity and the adsorption capacity of the raw sepiolite. The direct red brown adsorbed onto the modified sepiolite was best described by the pseudo-second-order kinetic model. The Box-Behnken RSM experimental design was effective and reliable for optimizing the adsorption conditions of direct red brown onto the acid-thermal-modified sepiolite. The determinate coefficient of model was 0.9631 and the p-value was 0.0044. The optimum conditions were that the adsorbent dosage 2.53 g/L, pH 4.70, and reaction time 4.46 h. The predicted decolorization rate of 91.5% could be achieved under the optimum conditions. Hence, the acid-thermal-modified sepiolite could potentially be used as a low-cost material for the removal of the direct red brown in aqueous solutions.

Acknowledgments

The authors would like to express their thanks to National Water Special Project of China for financial support by the foundation item No. 2012ZX07205002 and Guang Xi Office of Education for support item no. 201010LX069.

References

[1] H. Hassan, B.H. Hameed, Oxidative decolorization of Acid Red 1 solutions by Fe-zeolite Y type catalyst, Desalination 276 (2011) 45–52.

[2] M. Tekbaş, N. Bektaş, H.C. Yatmaz, Adsorption studies of aqueous basic dye solutions using sepiolite, Desalination 249 (2009) 205–211.

[3] E. Demirbas, M.Z. Nas, Batch kinetic and equilibrium studies of adsorption of Reactive Blue 21 by fly ash and sepiolite, Desalination 243 (2009) 8–21.

[4] E. Eren, O. Cubuk, H. Ciftci, Adsorption of basic dye from aqueous solutions by modified sepiolite: Equilibrium, kinetics and thermodynamics study, Desalination 252 (2010) 88–96.

[5] S. Wang, Y. Dong, M. He, L. Chen, X. Yu, Characterization of GMZ bentonite and its application in the adsorption of Pb(II) from aqueous solutions, Appl. Clay Sci. 43 (2009) 164–171.

[6] S. Wang, Y. Boyjoo, A. Choueib, A comparative study of dye removal using fly ash treated by different methods, Chemosphere 60 (2005) 1401–1407.

[7] A. Tabaka, E. Eren, B. Afsin, Determination of adsorptive properties of a Turkish Sepiolite for removal of Reactive Blue 15 anionic dye from aqueous solutions, J. Hazard. Mater. 161 (2009) 1087–1094.

[8] E. Sabah, M. Majdan, Removal of phosphorus from vegetable oil by acid-activated sepiolite, J. Food Eng. 91 (2009) 423–427.

[9] K.P. Singha, S. Gupta, A.K. Singha, Optimizing adsorption of crystal violet dye from water by magnetic nanocomposite using response surface modeling approach, J. Hazard. Mater. 186 (2011) 1462–1473.

[10] Z. Zhang, H. Zheng, Optimization for decolorization of azo dye acid green 20 by ultrasound and H_2O_2 using response surface methodology, J. Hazard. Mater. 172 (2009) 1388–1393.

[11] X. Guo, Y. Yao, G. Yin, Preparation of decolorizing ceramsites for printing and dyeing wastewater with acid and base treated clay, Appl. Clay Sci. 40 (2008) 20–26.

[12] G. Zhang, Y. Gao, Y. Zhang, Fe_2O_3-Pillared rectorite as an efficient and stable Fenton-like heterogeneous catalyst for photodegradation of organic contaminants, Environ. Sci. Technol. 44 (2010) 6384–6389.

[13] P. Tripathi, V. Srivastava, A. Kumar, Optimization of an azo dye batch adsorption parameters using Box-Behnken design, Desalination 249 (2009) 1273–1279.

[14] C. Zhang, Y. Chen, Simultaneous nitrogen and phosphorus recovery from sludge-fermentation liquid mixture and application of the fermentation liquid to enhance municipal wastewater biological nutrient removal, Environ. Sci. Technol. 43 (2009) 6164–6170.

[15] Y. Xu, X. Liang, G. Sun, Effects of acid and heating treatments on the structure of sepiolite and its adsorption of lead and cadmium, J. Environ. Sci. 31 (2010) 1560–1567.

[16] M. Doğan, A. Türkyilmaz, M. Alkan, Ö. Demirbaş, Adsorption of copper (II) ions onto sepiolite and electrokinetic properties, Desalination 238 (2009) 257–270.

[17] R.L. Frost, O.B. Locos, H. Ruan, J.T. Kloprogge, Near-infrared and mid-infrared spectroscopic study of sepiolites and palygorskites, Vib. Spectrosc. 27 (2001) 1–13.

[18] K.G. Sreejalekshmi, K. Anoop Krishnanb, T.S. Anirudhan, Adsorption of Pb(II) and Pb(II)-citric acid on sawdust activated carbon: Kinetic and equilibrium isotherm studies, J. Hazard. Mater. 161 (2009) 1506–1513.

[19] K. Vasanth Kumar, S. Sivanesan, Equilibrium data, isotherm parameters and process design for partial and complete isotherm of methylene blue onto activated carbon, J. Hazard. Mater. B134 (2006) 237–244.

[20] A. Bahdod, S. El Asri, A. Saoiabi, T. Coradin, A. Laghzizil, Adsorption of phenol from an aqueous solution by selected apatite adsorbents: Kinetic process and impact of the surface properties, Water Res. 43 (2009) 313–318.

[21] D. Bingol, N. Tekin, M. Alkan, Brilliant Yellow dye adsorption onto sepiolite using a full factorial design, Appl. Clay Sci. 50 (2010) 315–321.

[22] S. Sun, A.T. Lemley, P-Nitrophenol degradation by a heterogeneous Fenton-like reaction on nano-magnetite: Process optimization, kinetics, and degradation pathways, J. Mol. Catal. A-Chem. 349 (2011) 71–79.

[23] M. Rajasimman, R. Sangeetha, P. Karthik, Statistical optimization of process parameters for the extraction of chromium(VI) from pharmaceutical wastewater by emulsion liquid membrane, Chem. Eng. J. 150 (2009) 275–279.

[24] S.C.R. Santos, Rui A.R. Boaventura, Adsorption modelling of textile dyes by sepiolite, Appl. Clay Sci. 42 (2008) 137–145.