

RSC Advances

Adsorption behavior of Rhodamine B on nanoporous polymer

Journal:	RSC Advances
Manuscript ID	RA-ART-10-2015-021130.R1
Article Type:	Paper
Date Submitted by the Author:	14-Nov-2015
Complete List of Authors:	Han, Yide; Northeastern university, Chemistry Li, Weiwei; Department of Chemistry, College of Science, Northeastern University Zhang, Jing; department of Chemistry, College of Science, Northeastern University Meng, Hao; Northeastern University, China, Research Center for Analytical Sciences Xu, Yan; Northeastern University, Zhang, Xia; Northeastern university, Chemistry
Subject area & keyword:	Nanoscience - Environmental < Environmental

SCHOLARONE[™] Manuscripts

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/



Yide Han, Weiwei Li, Jing Zhang, Hao Meng, Yan Xu and Xia Zhang^{*}

Nanoporous polymers were successfully synthesized by copolymerization of divinylbenzene and 1-vinylimidazolate (PDVB-VI-x, x= 0.2, 0.33, 0.5, in which x stands for PDVB/VI molar ratio), and used to adsorb Rhodamine B (RhB) from aqueous solution. Characterizations of PDVB-VI were performed by Scanning electron microscopy, N₂ adsorption/desorption isotherms, Fourier transform infrared spectroscopy and Thermogravimetric analysis. PDVB-VI exhibited high surface area, large pore volume and oleophilic nature, which is beneficial to organic dye adsorption. To study the adsorption behavior of PDVB-VI for the removal of RhB in details, PDVB-VI-0.2 was selected as an example. The effects of pH value, adsorbent dosage, contact time and temperature were studied. The results indicated that the maximum adsorption capacity of the adsorbent for RhB was 260.42 mg/g at 298 K. The adsorption behavior could be well described by the pseudo-secondorder kinetics model, and the experimental data followed the Langmuir isotherm model. Thermodynamic parameters indicated that the adsorption process was spontaneous and exothermic. Remarkably, the adsorbent can be reused four times after treating with ethanol. Furthermore, PDVB-VI-0.2 was also used as adsorbent for other dyes removal, such as Acid Blue 1 and Ponceau S, with the adsorption capacity of 90.84 mg/g and 9.62 mg/g, respectively. These results demonstrate that PDVB-VI samples are a new kind of potential industrial adsorbent for the removal of organic dye from aqueous solution.

use.

1. Introduction

In recent years, with the development of industrialization and the increase of population, water pollution is one of the most important issues in the world.¹ Water contamination caused by hazardous chemicals is concerned more and more, since most chemicals are harmful to the environment and human health. For example, industrial effluents from dye industries can cause disease and damage the ecological environment. Therefore, the purification of these industrial effluents is required before discharge. In order to search for a new and better wastewater treatment method to supply clean water, considerable efforts have been made. Among the various methods, adsorption has drawn great attention as one of the most effective, low-cost and easy recycling ways. Porous materials as adsorbents have been widely studied due to their high specific surface area, tunable porosity, and uniform pore sizes, such as zeolites,²⁻⁶ metal-organic frameworks (MOFs),⁷⁻¹¹ activated carbon,¹²⁻¹⁴ adsorption resins.¹⁵⁻¹⁸ However, zeolites and activated carbon with hydrophilic nature are not favorable for removing organic compounds from wastewater. MOFs can be used as adsorbents, but their low stability hinders wider use. Several commercial porous resins are effective adsorbents for the removal of dissolved organic matter, while their



regenerability is poor, making them unsuitable for multicycle

Currently, nanoporous materials with organic frameworks,

an emerging class of porous structures, have attracted much

attention because of their potential applications in catalysis,

environmental technology, drug delivery, separation,

porous structure and large specific surface area, but also exhibit attractive properties in treating organic compounds due to their oleophilic nature. Thus, polymers with nanoporous are frequently used as adsorbents for dyes and oil removal in water. For example, Xiao et al. reported a series of organic mesoporous materials with remarkable adsorption properties for dyes and biomaterials.²³⁻²⁵ More importantly, some functional organic groups, such as carboxyl and amido being responsible for the superior adsorption properties, were successfully introduced into nanoporous polymers. These functionalized mesoporous materials exhibited excellent absorbability in a broad range of applications. Jafari et al. fabricated polydivinylbenzene (PDVB) adsorbents with wettability for siloxane removal from biogas and sewage gases, and found the improvement in adsorption capacity, since imidazole groups were introduced into the samples.²⁶ Hence, it is necessary to investigate PDVB-VI adsorbents for wastewater treatment. However, few examples of the kinetics, isotherm and thermodynamic studies of adsorption of organic dyes from aqueous solutions into nanoporous polymers have been reported.

Department of Chemistry, College of Science, Northeastern University, Shenyang, Liaoning, 110819, P.R. China. E-mail: xzhang@mail.neu.edu.cn; Fax: +86-24-83684533; Tel: +86-24-83684533

Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x

ARTICLE

In this paper, we described the synthesis of nanoporous polymers by copolymerization of monomers of divinylbenzene and 1-vinylimidazole (PDVB-VI-x, x= 0.2, 0.33, 0.5, in which x stands for PDVB/VI molar ratio) under solvothermal conditions, and selected PDVB-VI-0.2 as an example for the removal of RhB from aqueous solution. To evaluate the adsorption performance of the adsorbent, the factors including initial solution pH, initial concentration and contact time, and adsorbent dosage were evaluated during the adsorption process. In addition, the adsorption isotherms, kinetics, thermodynamics of RhB on the PDVB-VI-0.2 were systematically investigated. To give a comprehensive understanding on the adsorption behavior of the adsorbent, other organic dyes (Acid Blue 1 and Ponceau S) were also studied.

2. Materials and Methods

2.1. Reagents

Divinylbenzene (DVB, 80%) and 1-vinylimidazole (VI, \geq 99%) were purchased from Sigma-Aldrich. 2,2'-azobis(2-methylpropionitrile) (AIBN) was purchased from Shanghai No.4 Reagent & H.V. Chemical Co., Ltd. Ethyl acetate (EtoAc) was purchased from Tianjin Bodi Chemical Co., Ltd. All chemicals were used as received.

2.2. Preparation and characterization of the adsorbents

According to the literature,^{20, 26} PDVB-VI were synthesized under solvothermal conditions (as shown in Fig. S1). Typically, PDVB-VI-0.2 was prepared by reaction of a mixture of divinylbenzene, 1-vinylimidazole, 2,2'-azobis(2methylpropionitrile) and ethyl acetate in a molar ratio of 1.0/0.2/0.027/20.8 at 100 °C for 24 h in a Teflon-lined stainless steel autoclave. And then, the samples were obtained by slow evaporation of the solvent at room temperature.

Nitrogen sorption isotherms were measured using a Micromeritics ASAP 2020M system. The samples were outgassed for 10 h at 120 °C before the measurements. The pore size distribution (PSD) was calculated using the Non-local density functional theory (NLDFT) method. Fourier transform infrared spectroscopy (FTIR) spectra were recorded by using a Bruker 66V FTIR spectrometer. Thermogravimetric analyses (TG) were performed on a Mettler Toledo TGA2 (LF) in the air with heating rate of 10 °C/min. Scanning electron microscopy (SEM) images were performed on an ultra plus field emission scanning electron microscope (ZEISS, Germany).

2.3. Adsorption experiment

To determine the adsorption capacity of PDVB-VI-x, 50 mg adsorbent was added into 100 mL of RhB solutions (50 mg/L). The solutions were stirred at room temperature for 5 h, and then the suspensions were filtrated. The absorbance of the resulting filtrate was recorded using a spectrophotometer (model TU-1901, Beijing Purkinje General Instrument Co., Ltd. China) at a wavelength of 555 nm. The concentration of RhB

was then determined from a calibration curve. The adsorption capacity of adsorbents for RhB (Q_e) and the percentage of RhB adsorption (A) were calculated according to eqn (1) and (2), respectively:

$$Q_e = \frac{(C_0 - C_t)V}{m} \tag{1}$$

$$A = \frac{(C_0 - C_t)}{C_0} \times 100$$
 (2)

Where m (mg) is the dosage of adsorbent and V (mL) is the volume of RhB solution. C_0 and C_t (µg/mL) are the initial and final concentration of RhB solution, respectively.

All three adsorbents (PDVB-VI-0.2, 0.33, 0.5) exhibited good adsorption capacities for RhB with removal efficiency of 99.25 %, 97.22 %, 95.49 %, respectively (Fig. S2). Due to displaying the best adsorption capacity for RhB among three adsorbents, PDVB-VI-0.2 was selected as an adsorbent in the following research.

Batch experiments were conducted to obtain the relationship of a desired amount of adsorbent and the known concentration of RhB solution. The effect of pH was carried out with 100 mL of RhB solution (50 mg/L) and 50 mg adsorbent at 298 K and different initial pH of adsorption solution. The pH value of RhB solution was adjusted in the range from 3 to 11 by adding either 0.1 mol/L NaOH or 0.1 mol/L HCl. Thermodynamic experiments were performed at different temperatures (298 K, 308 K, 318 K). To study the effect of contact time, 50 mg of adsorbent was added into 100 mL of RhB solution (50mg/L), then the concentration of RhB left in the solutions was analyzed after different time intervals (15-210 min).

In other dye adsorption experiment, 50 mg of PDVB-VI-0.2 was added into 50 mg/L dye solution (100 mL), and then the solution was stirred at 298 K within 60 min. The residual dye concentration was determined by measuring absorbance at λ max of 639, 508 nm for Acid Blue 1 and Ponceau S, respectively.

3. Results and discussion

3.1. Characterization of the adsorbents

3.1.1. SEM

SEM image of mesoporous polymer PDVB-VI-0.2 is shown in Fig.1, and PDVB-VI-0.33, 0.5 are shown in Fig. S3. All samples have rough surfaces, which is consistent with previous reports.^{20, 26}

3.1.2. FTIR spectra

Fig. 2 presents the FTIR spectra of PDVB-VI-0.2, 0.33 and 0.5. It is outstanding that the stretching vibrations of benzene frame are observed in the region of 1400 cm⁻¹-1600 cm⁻¹. The peaks at 2927 and 2867 cm⁻¹ are ascribed to the stretching vibrations of C-H bond of methylene. The peak at 3020 cm⁻¹ is assigned to the stretching vibration of C-H bond of vinyl. The peaks at 658, 1231 and 1652 cm⁻¹ are caused by the introduction of imidazole groups, and these peaks become





Fig. 1 SEM image of PDVB-VI-0.2.



more intensified with increasing dosage of 1-vinylimidazole, which is in accord with previous research.^{20, 26}

3.1.3. Thermogravimetric analysis

The thermal stability of PDVB-VI nanoporous polymers is shown in Fig. 3. Only around 9% weight loss occurred before 400 $^{\circ}$ C, which suggested that nanoporous polymers have good thermal stability and the solvent in the polymer may be not removed completely.

3.1.4. N₂ Adsorption

Fig. 4 shows N₂ sorption isotherms and PSD of PDVB-VI. All samples showed a typical type IV sorption behavior with a hysteresis loop ($p/p_0 = 0.7$ -1.0), indicating PDVB-VI with nanoporous. PDVB-VI-x (x=0.2, 0.33, 0.5) had Brunauer-Emmett-Teller (BET) surface area in the range from 737 to 681 m²/g, pore volumes from 1.37 to 1.23 cm³/g. The PSD analysis indicates that the dominant pore diameter centers at ca 30 nm and there are two peaks at ca 13 nm and 63 nm. The changes in total pore volume were observed because of different VI contents. Total pore volume decreased with increasing amount of VI in the samples. Additionally, the relatively high specific surface area and large pore size of



Fig. 3 TG of PDVB-VI-x (x=0.2, 0.33, 0.5).



Fig. 4 N_2 isotherms (a) and pore size distributions (b) of PDVB-VI-x (x=0.2, 0.33, 0.5).

PDVB-VI provided larger accommodation space for the dye adsorption.

3.2. Adsorption studies **3.2.1.** Effect of pH

In order to investigate the effect of pH on the adsorption behavior of PDVB-VI-0.2 for RhB, sorption experiments were carried out within the pH range from 3 to 11 at 298 K. 50 mg of PDVB-VI-0.2 was added into the organic dye solution with desired pH value, and then the adsorbed amounts were measured after 60 min. The effect of pH is shown in Fig. 5a, it can be seen that the amount of adsorption was almost constant at various pH values. The results indicated that the pH of the solution was not an important parameter for adsorption of RhB onto PDVB-VI-0.2. This means that PDVB-VI-0.2 is a promising candidate for adsorption removal of dyes from wastewater.

3.2.2. Effects of contact time and temperature

Fig. 5b shows the adsorption capacity of PDVB-VI-0.2 for RhB with varied contact time and temperatures. At 298 K, the adsorption capacity of PDVB-VI-0.2 increased with the increase of contact time before 60 min, and then the equilibrium was achieved with the uptake of 99.01 mg/g. After that, there were no changes on the adsorption. At 308 K and 318 K, the adsorption behavior of PDVB-VI-0.2 showed similar results to that of at 298 K. But the amount of RhB adsorbed at the equilibrium was different, 97.93 mg/g at 308 K and 96.23 mg/g at 318 K, indicating the increase of temperature was not good for the RhB adsorption onto PDVB-VI-0.2, which might be that high temperature hinders the occurrence of RhB adsorption. This implied that the adsorption process is exothermic, which is confirmed by the calculated ΔH of the following application of the thermodynamic analysis. Thus, temperature plays an important role during the adsorption process. For the low temperature leading to higher adsorption capacity, we carried out the following experiments within 60 min at 298 K, if not further specified.

3.2.3 Effect of adsorbent dosage

For a given initial concentration of dyes, the capacity of adsorbents depends on the dosage of adsorbents. To estimate the effect of adsorbent dosage, experiments were conducted at various adsorbent dosages (10-100 mg), fixed the initial RhB concentration (50 mg/L) and the volume of the solution (100 mL). Fig. 5c shows the effect of adsorbent dosage during the adsorption process. It can be easily observed that the percentage of dye adsorption increased with the enhancement of adsorbent dosage, which was ascribed to the increase of available adsorption sites of PDVB-VI-0.2. The percentage of dye adsorption to sage 100% when the adsorbent dosage was 50 mg. Therefore, the appropriate dosage of the adsorbent is 50 mg because of cost concerns.

3.2.4. Adsorption kinetics

Pseudo-first-order rate equation and Pseudo-second-order rate equation are used to investigate the adsorption kinetics, since the kinetic data can give the adsorption rate and potential rate-controlling step. The pseudo-first-order rate



Fig.5 Effects of pH (a), contact time and temperature (b), and adsorbent dosage (c) on adsorptive removal of RhB.

equation is expressed as a linear form by eqn (3):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

Where q_e and q_t (mg/g) are the amount of RhB adsorbed at the equilibrium and at the adsorption time *t* (min), respectively. K₁ is the rate constant of pseudo-first-order model. By linear relationship, k₁ and q_e are calculated from the slope and

C ₀ (mg/L)	Т(К)	Q _{e,ex} (mg/g)	Pseudo-first-order equation		Pseudo-second-order equation				
			Q _{e,c} (mg/g)	K₁(min ⁻¹)	R ²	Q _{e,c} (mg/g)	K ₂ (g/mg min)	R ²	
50	298	99.013	10.53	42.24	0.72682	102.46	0.0024	0.99890	
50	308	97.927	21.19	38.36	0.87657	102.88	0.0019	0.99897	
50	318	96.230	24.06	39.68	0.88218	103.63	0.00189	0.99854	





Fig. 6 Pseudo-second-order kinetics for adsorption of RhB at different temperatures.

intercept of the plot of $ln(q_e-q_t)$ vs. t. The pseudo-second-order rate equation is expressed as a linear form by eqn (4):

$$\frac{t}{q_t} = (\frac{1}{k_2 q_e^2}) + \frac{t}{q_e}$$
(4)

Where q_e is the adsorption capacity of adsorbent at the equilibrium and q_t (mg/g) is the adsorption capacity of adsorbent at the adsorption time t (min). k_2 is the rate constant of pseudo-second-order model. By linear relationship, k_2 and calculated q_e values are determined by the intercept and slope of the plot of t/q_t vs. t.

There are three steps during the adsorption process, including external liquid membrane diffusion, internal diffuse and surface adsorption.^{15, 27} Among three steps, pseudo-firstorder model is majorly determined by the external liquid membrane diffusion, while pseudo-second-order model is determined by the whole three steps. To understand the ratecontrolling step, the plots of " $ln(q_e-q_t)$ vs. t" (Fig. S4) and "t/q_t vs. t" (Fig. 6) were obtained at different temperatures and fitted by pseudo-first-order equation and pseudo-secondorder equation, respectively. The kinetic parameters and correlation coefficients (R^2) are listed in Table 1. The adsorption process did not follow pseudo-first-order equation in terms of correlation coefficients. While the pseudo-secondorder equation gave a good fit to the experimental data (R^2) values above 0.99), suggesting that the adsorption of PDVB-VI-0.2 can be represented by the pseudo-second-order equation.

3.2.5. Adsorption isotherm



Fig. 7 Langmuir (a) and Freundlich isotherm models (b) for RhB adsorption.

Table 3	The c	onstants	of adsorn	tion isc	therms
IANICA	- INC (JULISLALLS	UL ausulu		

Lar	F	Freundlich m	odel		
q _m (mg·g ⁻¹)	K₋(g·mg ⁻¹)	R ²	n	K _F (mg·g⁻¹)	R ²
260.42	0.946	0.99596	3.40	109.15	0.92714

To give insight into the surface properties and adsorption behavior of adsorbent, the adsorption isotherm of RhB was studied. During the adsorption process, 50 mg of PDVB-VI-0.2 was used for the removal of RhB with different concentrations (from 20 mg/L to 160 mg/L). As shown in Fig. S5, it is found that the adsorption capacity increases with the increase of the RhB concentration, and the maximum RhB adsorption capacity

ARTICLE

is reached at concentration of 100 mg/L. The experimental data of RhB adsorption onto PDVB-VI-0.2 were fitted to the Langmuir and Freundlich isotherm models. The Langmuir isotherm is based on the assumption that all adsorption sites are homogeneous within the adsorbent surface and no interaction between adsorbed molecules; while the Freundlich isotherm model is a multilayer adsorption model and describes the heterogeneous adsorption process. Their linear isotherms can be expressed as eqn (5) and (6):

$$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{q_m K_L} \tag{5}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e \tag{6}$$

Where q_e is the equilibrium adsorption capacity of adsorbent (mg/g), q_m is the maximum adsorption capacity (mg/g), C_e is the equilibrium concentration of adsorbate (mg/L), K_L is the Langmuir adsorption constant (L/mg), K_F and n are Freundlich constants. Fig. 7 shows the Langmuir and Freundlich isotherm. The adsorption constants are displayed in Table 2. It can be seen that the correlation coefficient of Langmuir model was higher than that of Freundlich model, suggesting that Langmuir model fitted well with the experimental data. It indicated that the adsorption of RhB into PDVB-VI was monolayer molecule adsorption and followed the Langmuir isotherm. According to the Langmuir model, the maximum adsorption capacity is 260.42 mg/g, which is higher than that of some of the other adsorbents (Table S1).

The dimensionless equilibrium parameter or separation factor R_L , which is an essential characteristic of the Langmuir isotherm, can be expressed as eqn (7):

$$R_L = \frac{1}{1 + K_L C_0} \tag{7}$$

Where K_L is the Langmuir constant and C_0 is the initial concentration of the adsorbate in solution. The values of R_L indicate the type of isotherm to be favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). The values of R_L in this work were found to be between 0 and 0.05 for PDVB-VI-0.2 at 298 K (Fig. S6), confirming that the adsorption behavior is favorable.

3.2.6. Adsorption thermodynamics

Gibbs free energy change, enthalpy change and entropy change are important thermodynamics parameters. They can be used to investigate the effect of temperature on adsorption

Table 3 Thermodyna	mic para	ameters for the	removal of Rh	۱B
Tomporatura	Δц	Δc	۸c	

remperatur		J	
(К)	(kJ∙mol ⁻¹)	(J·mol ⁻¹ ·K ⁻¹)	(kJ·mol ⁻¹)
298			-12.96
308	-51.39	-128.96	-11.67
318			-10.38
R ²		0.9996	

of dyes. The relationship between ΔG , ΔH and ΔS is expressed as the following eqn (8), (9) and (10):

$$K_L = \frac{q_e}{c_e} \tag{8}$$

$$G = -RT \ln K_L \tag{9}$$

$$\ln K_L = -\frac{H}{RT} + \frac{S}{R} \tag{10}$$

Where q_e is the amount of RhB adsorbed onto adsorbent at equilibrium (mg/g), Ce is the equilibrium concentration of the adsorbate in solution (mg/L), K_L is the Langmuir adsorption constant (L/g). R is the gas constant (8.314 J/mol·K) and T is the solution temperature (K). Thus, the values of ΔH and ΔS were calculated from the slope and intercept of the plots of InK_{L} versus 1/T. Table 3 summarizes the thermodynamics parameters from the experimental data. It may be noted that the negative values of ΔG increased with the rise of temperature, which can be attributed to the occurrence of spontaneous adsorption within the test temperature. This result indicated that the adsorption process was more favorable at low temperature. The negative value of ΔH suggested that RhB adsorption into adsorbent was an exothermic process, which was in agreement with the low adsorption capacity of RhB at high temperature. Besides, the negative value of ΔS was consistent with the decreasing randomness at the solid-solution interface during the adsorption process, which meant that the mobility of RhB onto the surface of adsorbent may be restricted.⁷ The parameters including ΔG , ΔH and ΔS illustrated that PDVB-VI-0.2 is a promising adsorbent for the removal of RhB from wastewater.

3.2.7. Regenerability

Regenerability is one of the most important factors for industrial adsorbents. To evaluate the reusability of PDVB-VI-0.2, the solvent elution experiments were carried out. The used PDVB-VI-0.2 was soaked in ethanol solution for 60 min, and then the adsorbent was further used for adsorption test. Fig. 8 shows the adsorption capacity of PDVB-VI-0.2 in different regeneration times. It can be easily observed that the adsorption capacity decreased after the regeneration times comparing with pristine PDVB-VI-0.2. The adsorption capacity of PDVB-VI-0.2 at the fourth cycle was around 88.39 mg/g. The results revealed that PDVB-VI-0.2 is an efficient and durable adsorbent for the removal of RhB from wastewater after reuse of four cycles.

3.2.8 Other organic dyes adsorption

Other organic dyes, such as Acid Blue 1 and Ponceau S, were also studied to estimate the adsorption capacity of PDVB-VI-0.2. Fig. 9 shows the adsorption capacity of PDVB-VI-0.2 for RhB, Acid Blue 1 and Ponceau S after an adsorption time of 60 min. Its adsorption capacity reached 99.01, 90.84, 9.62 mg/g for RhB, Acid Blue 1 and Ponceau S, respectively. It is worth noting that both cationic RhB and anionic Acid Blue 1 were removed from wastewater by using PDVB-VI-0.2 as adsorbent.



Fig. 8 Adsorption capacity of PDVB-VI-0.2 in different cycles.



Fig. 9 Comparison of the adsorption capacity of PDVB-VI-0.2 for RhB, Acid Blue 1 and Ponceau S.

Namely, PDVB-VI-0.2 was an effective adsorbent for various dyes with counter charges. Selective adsorption investigation for the binary mixture of RhB and Acid Blue 1 was performed (Fig S7), and the result indicates that PDVB-VI-0.2 has better adsorption capacity for RhB. According to the previous report,^{15,27} there exist different mechanisms for the adsorption removal of anionic and cationic dyes. Generally, for cationic RhB dye, dispersive and electronic interactions play key roles during the adsorption process; while for anionic Acid Blue 1 and Ponceau S dyes, the interaction between the surface basicity of adsorbent and the free electrons of dye molecule is dominant. Hence, the aforementioned three interactions, including dispersive interactions, electronic interactions and the interaction between the surface basicity of adsorbent and the free electrons of dye molecule, can explain well the adsorption mechanism of PDVB-VI-0.2 for RhB, Acid Blue 1 and Ponceau S. Because of large molecular size and stereochemical structure, Ponceau S might be adsorbed on the surface of PDVB-VI-0.2, which makes dye molecules difficult to diffuse

into the pore. As a consequence, PDVB-VI-0.2 exhibited a lower adsorption capacity for Ponceau S. These results revealed that PDVB-VI-0.2 with basic sites and larger pore size is an excellent adsorbent for the removal of RhB from wastewater.

4. Conclusions

In this paper, nanoporous polymers PDVB-VI based on the copolymerization of divinylbenzene and 1-vinylimidazolate were successfully synthesized. Using PDVB-VI-0.2 as adsorbent, we studied systematically its adsorption behavior toward removal of RhB from aqueous solution. The results indicated that PDVB-VI-0.2 possessed great dye adsorption capacity for RhB. It was also observed that this capacity was not significantly affected by the value of pH in the range from 3 to 11. In the kinetic studies, the kinetics data can be well fitted with pseudo-second-order kinetics model than pseudo-first-order kinetics model. In addition, the adsorption isotherms can be best represented by Langmuir model in terms of regression coefficient. Thermodynamic parameters, such as Gibbs free energy (Δ G), enthalpy (Δ H) and entropy (Δ S), were calculated by the Gibbs free energy function, which indicated that the adsorption process was spontaneous and exothermic. Further studies suggested that PDVB-VI-0.2 could be easily regenerated after treating with ethanol and reused for at least four times. Besides, PDVB-VI-0.2 can be used as adsorbent to adsorb and remove other dyes (Acid Blue 1 and Ponceau S).

Acknowledgements

This work was supported by National Natural Science Foundation of China (Grant: 21301024) and Fundamental Research Funds for the Central Universities (N120305003).

Notes and references

- M. A. Shannon, P. W. Bohn, M. Elimelech, J. G. Georgiadis, B. J. Marinas and A. M. Mayes, *Nature*, 2008, **452**, 301-310.
 - A. Martucci, E. Rodeghero, L. Pasti, V. Bosi and G. Cruciani, *Microporous Mesoporous Mater.*, 2015, 215, 175-182.
 - C. Lu, S. Yu, T. Yao, C. F. Zeng, C. Q. Wang and L. X. Zhang, J. Porous Mater., 2015, **22**, 1255-1263.
 - Z. B. Guo, J. Liu and F. L. Liu, *Microporous Mesoporous Mater.*, 2015, **213**, 8-13.
 - Y. H. Shu, Y. M. Shao, X. Y. Wei, X. Wang, Q. Q. Sun, Q. Y. Zhang and L. S. Li, *Microporous Mesoporous Mater.*, 2015, **214**, 88-94.
 - M. Delkash, B. E. Bakhshayesh and H. Kazemian, Microporous Mesoporous Mater., 2015, **214**, 224-241.
 - S. Lin, Z. Song, G. Che, A. Ren, P. Li, C. Liu and J. Zhang, Microporous Mesoporous Mater., 2014, **193**, 27-34.
 - Y. Xu, J. Jin, X. Li, Y. Han, H. Meng, T. Wang and X. Zhang, Rsc Advances, 2015, **5**, 19199-19202.
 - Q. He, Q. Chen, M. Lu and X. Liu, *Chin. J. Chem. Eng.*, 2014, **22**, 1285-1290.

2

3

4

5

6

7

8

9

ARTICLE

- 10 X. B. Luo, L. Ding and J. M. Luo, J. Chem. Eng. Data, 2015, 60, 1732-1743.
- 11 S. H. Huo and X. P. Yan, J. Mater. Chem., 2012, 22, 7449-7455.
- 12 Y. X. Wang, H. H. Ngo and W. S. Guo, Sci. Total Environ., 2015, **533**, 32-39.
- F. J. Garcia-Mateos, R. Ruiz-Rosas, M. D. Marques, L. M. 13 Cotoruelo, J. Rodriguez-Mirasol and T. Cordero, Chem. Eng. J., 2015, 279, 18-30.
- 14 N. Bakhtiari, S. Azizian, S. M. Alshehri, N. L. Torad, V. Malgras and Y. Yamauchi, Microporous Mesoporous Mater., 2015, 217, 173-177.
- 15 T. Wang, K. Kailasam, P. Xiao, G. Chen, L. Chen, L. Wang, J. Li and J. Zhu, Microporous Mesoporous Mater., 2014, 187, 63-70.
- J. Fu, Z. Chen, M. Wang, S. Liu, J. Zhang, J. Zhang, R. Han 16 and Q. Xu, Chem. Eng. J., 2015, 259, 53-61.
- 17 G. Yang, H. Han, C. Du, Z. Luo and Y. Wang, Polymer, 2010, **51**, 6193-6202.
- 18 X. S. Wang, J. Liu, J. M. Bonefont, D. Q. Yuan, P. K. Thallapally and S. Ma, Chem. Commun., 2013, 49, 1533-1535.
- 19 F. Liu, R. K. Kamat, I. Noshadi, D. Peck, R. S. Parnas, A. Zheng, C. Qi and Y. Lin, Chem. Commun., 2013, 49, 8456-8458.
- F. Liu, W. Li, Q. Sun, L. Zhu, X. Meng, Y. H. Guo and F. S. 20 Xiao, ChemSusChem, 2011, 4, 1059-1062.
- 21 P. Kuhn, K. Krueger, A. Thomas and M. Antonietti, Chem. Commun., 2008, 5815-5817.
- 22 N. B. McKeown and P. M. Budd, Chem. Soc. Rev., 2006, **35**, 675-683.
- 23 S. Wei, Y. L. Zhang, H. Ding, J. Liu, J. Sun, Y. He, Z. Li and F. S. Xiao, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2011, 380, 29-34.
- 24 S. Wei, D. X. Lu, J. Sun, Y. He, L. Zhu, Y. L. Zhang and F. S. Xiao, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2012, 414, 327-332.
- 25 Y. Zhang, S. Wei, F. Liu, Y. Du, S. Liu, Y. Ji, T. Yokoi, T. Tatsumi and F. S. Xiao, Nano Today, 2009, 4, 135-142.
- 26 T. Jafari, I. Noshadi, N. Khakpash and S. L. Suib, Journal of Materials Chemistry A, 2015, 3, 5023-5030.
- 27 R. S. Juang, F. C. Wu and R. L. Tseng, J. Colloid Interface Sci., 2000, 227, 437-444.

Graphical Abstract

This study demonstrates that nanoporous materials possess good adsorption capacities for Rhodamine B in water.

