Adsorption Behavior and Mechanism of 2,4,6-Trinitrotoluene by Functionalized Polystyrene Nanospheres

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ABSTRACT: 3-Methactyloxylpropyltrimethoxyl silane (KH-570)-modified polystyrene (PS) nanospheres and PS nanospheres were prepared and used to absorb 2,4,6-trinitrotoluene. The absorbed amount reached 2.81 mg/g for KH-570-modified PS nanospheres at 298 K and pH 6 when the initial 2,4,6-trinitrotoluen concentration was 50 mg/L. The kinetic results showed that the pseudo-second-order model fit the two kinds of absorbents. The adsorption mechanism study revealed that the driving forces of adsorption were combined actions of Π–Π stacking interaction, hydrogen interaction, and hydrophobic interaction. The prepared nanospheres were reusable. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 128: 3720–3725, 2013

INTRODUCTION

2,4,6-Trinitrotoluene (TNT), a nitroaromatic compound, has raised health concerns because of its acute and chronic toxicity to creatures.[1] It is mainly used as an explosive in military applications and can be found in soils and ground water in the vicinity of military sites.[2] There are several method for treating wastewater contaminated by TNT, such as adsorption,[3,4] distillation,[5] biodegradation,[6] advanced oxidation such as supercritical water oxidation,[7] zero-valent iron and Fenton oxidation,[8,9] and catalytic oxidation.[10,11] However, these methods have limitations because of the complexity of byproducts from the treatment process. Adsorption is widely used but is plagued by problems such as low reusability, high cost, and a lower adsorption capacity. Hence, the development of new absorbing materials with better recyclability is technologically and commercially important.

Polystyrene (PS) microspheres are used in photonic crystals,[12] protein adsorption,[13] catalyst support,[14] templates,[15] and other applications. Silane-functionalized PS microspheres are used to improve polymer properties, such as the wetting behavior.[16,17] However, the use of PS microspheres and derivatives to absorb TNT has not been reported. In this study, PS nanospheres and 3-methactyloxylpropyltrimethoxyl silane (KH-570)-modified PS

nanospheres (KH570–PS) prepared by emulsion polymerization were used to absorb TNT in solution. The materials exhibited a high adsorption capacity and excellent reusability and have potential for industrial application.

EXPERIMENTAL

Materials

All of the chemicals used in the experiments were analytical grade. Anhydrous sodium sulfite (Na_2SO_3), sodium hydroxide (NaOH), ethanol (EtOH), acetone, KH-570, ammonium hydroxide ($NH_3 \cdot H_2O$), and tetrahydrofuran (THF) were purchased from Beijing Chemical Co., Ltd. (Beijing, China). Styrene (St) was supplied by ShanTou XiLong Chemical Co., Ltd. (Shantou, China) and was extracted with 5% NaOH to remove the polymerization inhibitor. Potassium persulfate was also provided by ShanTou XiLong Chemical Co. $Al_2(SO_4)_3$ and sodium dodecyl sulfate were obtained from Beijing YiLi Chemical Reagent Co., Ltd. (Beijing, China). Tetraethyl orthosilicate was purchased from Tianjin Yongda Chemical Reagent Co., Ltd. (Tianjin, China).

Characterization

The concentration of TNT was determined on a spectrophotometer (722-S, Yuguang Instrument Co., Ltd, Shanghai, China)

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Table I. Ratios of KH570 to St

	KH570-PS(1)	KH570-PS(2)	KH570-PS(3)	KH570-PS(4)
Volume of KH570 (mL)	1	2	3	4
Weight of St (g)	10	10	10	10

(GB/T 13905-92). The structures of PS and KH570-PS were analyzed by Fourier transform infrared (FTIR) spectroscopy (PerkinElmer spectrum 100, Waltham, Massachusetts, USA), and the samples were pressed into KBr pellets. Field emission scanning electron microscopy patterns were acquired from a field emission scanning electron microscope (LEO-1530, Krefeld, Germany) operating at 5 kV.

Synthesis of the PS Nanospheres by Emulsion Polymerization
Emulsion polymerization was performed in an oil batch reactor. A 250-mL, three-necked, round-bottom flask was equipped with a polytetrafluoroethylene-bladed paddle stirrer and a water-cooled reflux condenser. In a typical experiment, 100 mL of distilled water and 0.2 g of sodium dodecyl sulfate were added to the 250-mL flask, and the oil bath was set at 80°C. The solution was stirred for 30 min at this temperature, and then, 10 g of St and 0.1 g of potassium persulfate as the initiator were added to the solution. Polymerization was performed at this temperature for 24 h under stirring, and a white emulsion was formed. Afterward, the emulsion was put into a 250-mL beaker, to which 1.0 g of $Al_2(SO_4)_3$ was added. After 15 min, water was extracted with a vacuum filtration machine. The product was washed by distilled water and EtOH several times and dried at 50°C for 5 h before it was ground into powder.

Synthesis of the KH570–PS Nanospheres by Emulsion Polymerization
The synthesis of KH570–PS nanospheres was similar to that of the PS nanospheres. After the polymerization of St for 5 h, KH570 was added dropwise into the emulsion, and then, the polymerization was continued for another 19 h. The prepared KH570–PS nanospheres with different ratios of KH570 to St were assigned as KH570–PS(1), KH570–PS(2), KH570–PS(3), and KH570–PS(4), respectively; this is summarized in Table I.

Synthesis of the SiO$_2$ Microspheres
50 mL of EtOH, 5 mL of tetraethyl orthosilicate and 1 mL of $NH_3.H_2O$ were stirred magnetically at room temperature for 48 h. Then, the resulting solution was dried at room temperature. The transparent solid was obtained and grinded into powders.

Preparation of the TNT Solution
TNT (50 mg) was added to deionized water and stirred at 70°C for 4 h, and then, the solution was cooled with deionized water and transferred to a 1000-mL volumetric flask. The final volume of TNT solution was 1000 mL.

Adsorption of TNT by the PS and KH570–PS Nanospheres
This study was performed in batch experiments in a water bath shaker (SHA-BA, Jintan, China).

Determination of the Optimum Adsorbent Weight. Amounts of 0.2, 0.4, 0.6, 0.8, and 1.0 g of the PS or KH570–PS nanospheres were introduced into individual 150-mL conical flasks,

into each of which 50 mL of the TNT solution with an initial concentration of 50 mg/L at pH 6 was added. The conical flasks were placed in a shaker and agitated for 13 h at 298 K. The resulting TNT solution was obtained after the PS nanospheres were removed by filtration. The removal efficiency (E; %) was calculated according to eq. (1):

$$E\% = \frac{C_0 - C_t}{C_0} \times 100 \qquad (1)$$

where C_0 (mg/L) is the initial concentration of TNT, C_t (mg/L) is the concentration of TNT after adsorption, and E (%) is the removal efficiency rendered by the PS or KH570–PS nanospheres.

Kinetic Adsorption Curves. An amount of 0.8 g of PS or KH570–PS nanospheres was introduced into a 150-mL conical flask, into which 50 mL of the 50 mg/L TNT solution was added. The conical flask was shaken for different time periods at 298 K. Different TNT concentrations were determined at different time periods. The absorbed amount was calculated according to eq. (2):

$$Q_t = \frac{V(C_0 - C_t)}{m}, \qquad (2)$$

where Q_t is the adsorbed amount (mg/g), V is the volume of the TNT solution (L), and m is the weight of the PS nanospheres (g).

Reusability
After the adsorption of TNT, the PS nanospheres were filtered from TNT solution and were then added to a mixture of EtOH and HCl at pH 2 and stirred for 7 h at room temperature. After they were dried at 318 K, these nanospheres were used to absorb TNT again. To test the reusability of the PS nanospheres,
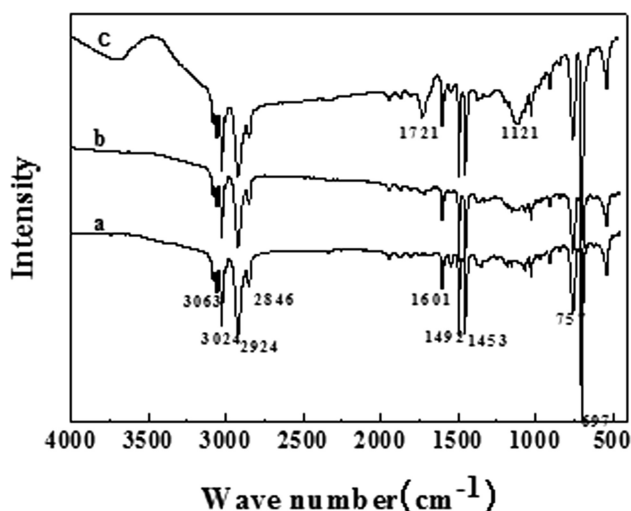

Figure 1. FTIR of (a) PS, (b) KH570–PS(1), and (c) KH570–PS(2).

(a)   (b)
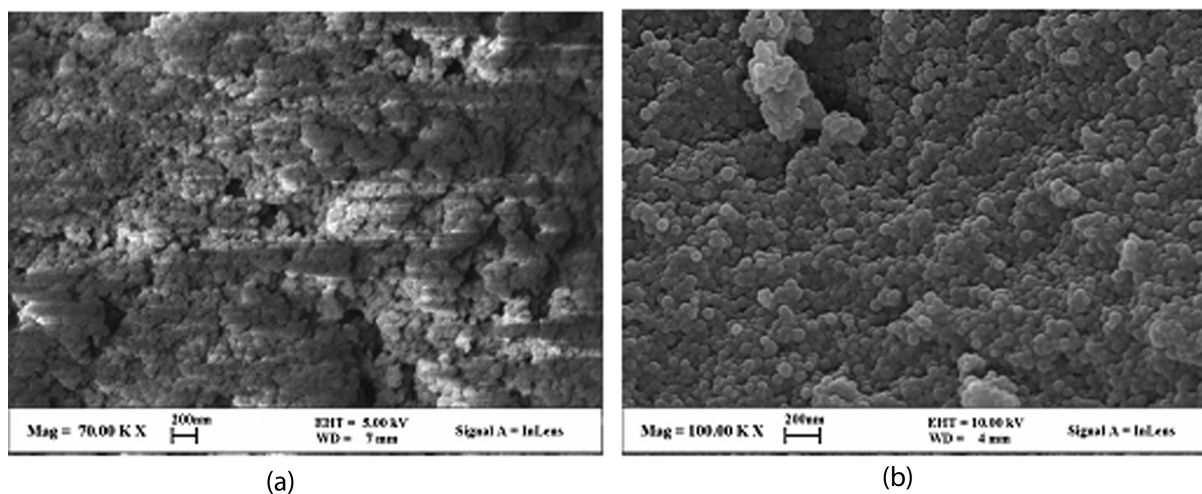
Figure 2. Morphology of the PS and KH570–PS(2) nanospheres.

the adsorption–desorption procedure was repeated seven times with the same materials, and the E (%) value for each adsorption–desorption cycle was determined according to eq. (1).

RESULTS AND DISCUSSION

Characterization of the PS and KH570–PS Nanospheres

FTIR Analysis. The structures of the KH570–PS nanospheres with different KH-570 contents were characterized by FTIR spectroscopy (Figure 1). When the content of KH-570 was 0 mL/10 g of St (PS), the peaks at 3063 and 3024 cm^{-1} corresponded to the stretching bands of C—H on the benzene ring. The peaks at 2924 and 2846 cm^{-1} were the stretching bands of saturated —CH$_2$— and —CH—, and the peaks at 1453–1601 cm^{-1} were associated with the vibration bands of the benzene ring. The characteristic absorbance bands of PS appeared at 757 and 698 cm^{-1}; these were the out-of-plane C—H bending vibrations of the monosubstituted benzene ring.[18] When the content of KH-570 was 1 mL, a weak peak at 1721 cm^{-1} referred to the stretching band of O═C of KH-570. The results indicate a large

amount of absorbed TNT on the PS nanospheres. When the content of KH-570 was 2 mL, the peak at 1121 cm^{-1} was associated with the Si—O—Si. The peak at 1721 cm^{-1} became strong because of the large content of KH-570. The existence of the benzene ring and O═C indicated that TNT could interact with the PS and KH570–PS nanospheres.

Morphology of the PS and KH570–PS Nanospheres. The scanning electron microscopy images of the PS and PS–KH-570(2) nanospheres are depicted in Figure 2. The diameter of the nanospheres was about 40 nm. The smaller diameter indicated a lager specific surface area, which contributed to the large amount of adsorption of TNT.

Determination of the Optimized Adsorption Parameter

Effect of the Absorbency Dose on the Adsorption Capacity. An increase in E (%) with the adsorbent mass (Figure 3) was observed when the mass of the adsorbent increased from 0.2 to 0.8 g, no matter what kind of adsorbent was used. A larger adsorbent weight meant a bigger overall surface area on
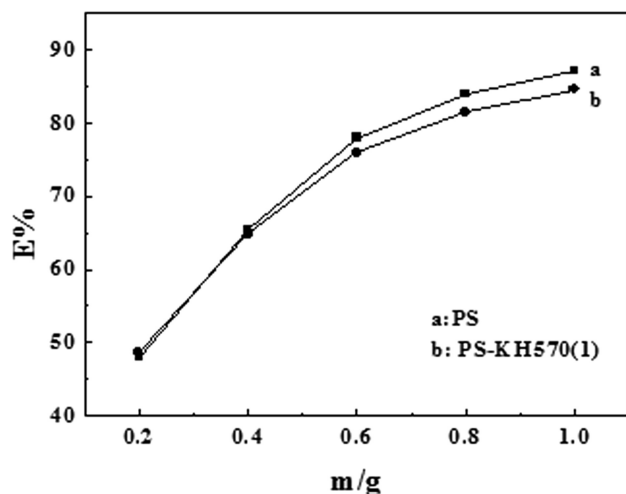

Figure 3. Effects of the adsorbent dosage on the adsorption capacity at a temperature of 298 K and at pH 6 ($C_0 = 50$ mg/L).
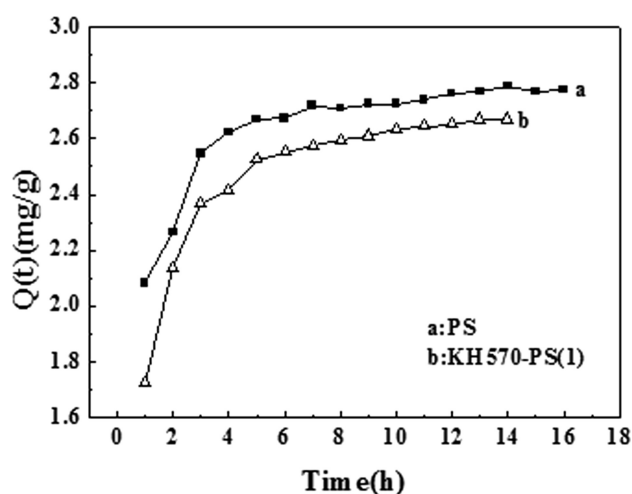

Figure 4. Variation of the absorbed TNT amount [$Q(t)$] with the adsorption time at a temperature of 298 K and at pH 6 ($C_0 = 50$ mg/L).
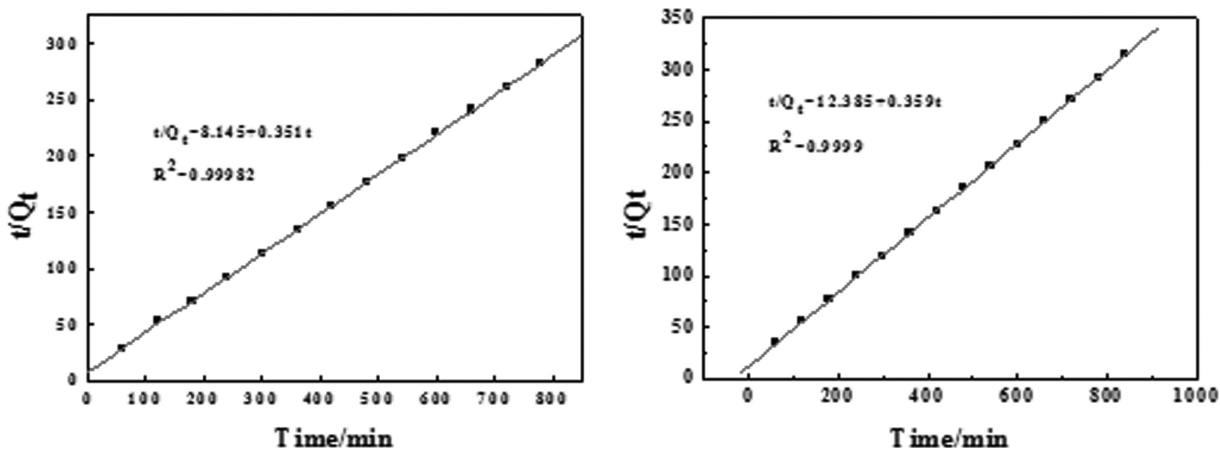
Figure 5. Pseudo-second-order kinetic curves of the PS and KH570–PS(2) nanospheres. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the PS or KH570–PS nanospheres available to interact with the TNT molecules; this led to increase in E. However, the increase was not obvious when the mass of the adsorbent increased from 0.8 to 1.0 g. This results may have due to the fact that with the increase in adsorbent mass, the nanospheres tended to aggregate with each other, and then, the effective overall surface area used to interact with TNT did not increase. An amount of 0.8 g was chosen to be the optimal weight in subsequent experiments because of a higher E and acceptable adsorption capacity.

Kinetic Adsorption Curve of TNT on the PS and KH570–PS(1) Nanospheres. The kinetic adsorption curve in Figure 4 indicates that the adsorption of TNT by the PS and KH570–PS(1) nanospheres reached equilibrium after 10 h. Afterward, the absorbed amount only changed slightly. Hence, to make sure the adsorption was completed, a time of 15 h was chosen in this study.

Adsorption Kinetic Study
Lagergren's equation is one of the most widely used rate equations for describing the adsorption of an adsorbate from the liquid phase.[19] The linear form of the pseudo-first-order rate expression of Lagergren's equation is given as follows:

Figure 6. Variation of E with different KH-570 contents.

$$\log(q_e - q_t) = \log q_e - \frac{k_f}{2.303}t \qquad (3)$$

where k_f is the rate constant of pseudo-first-order adsorption (L/min) and q_e and q_t (mg/g) are the amounts of adsorbate (TNT) adsorbed per gram of PS or KH570–PS at equilibrium and at any time t, respectively.

The pseudo-second-order kinetics can be expressed in a linear form as follows:[20]

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

where k_s is the rate constant of pseudo-second-order adsorption (g mg^{-1}/min). The plot of t/q_t versus t is shown in Figure 5.

The correlation coefficient (R) values for the pseudo-second-order model are much higher than those of the pseudo-first-order model. The R^2 values for PS and KH570–PS(2) were 0.99982 and 0.9999, respectively; this suggested that the adsorbent systems could be well described by the pseudo-second-order kinetic model.

Effect of the KH-570 Content on Adsorption
Figure 6 shows the variation of E with increasing amount of KH-570. Amounts of 0.8 g of adsorbent and 50 mL of 50 mg/L TNT solution were used in this part of the study. E decreased first and then increased to a certain degree before it leveled off as the amount of KH-570 increased. E of PS was higher than E of KH570–PS(1); this could be explained by the fact that the benzene ring of PS could make contact with the benzene ring of the TNT, and this directly resulted in Π–Π stacking
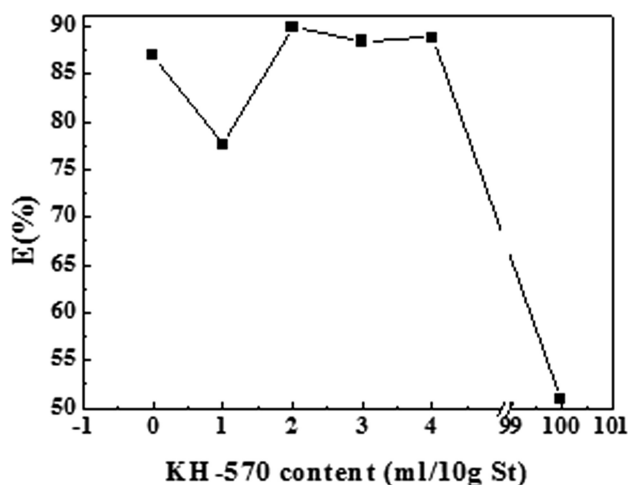
Table II. Effect of the Media on E

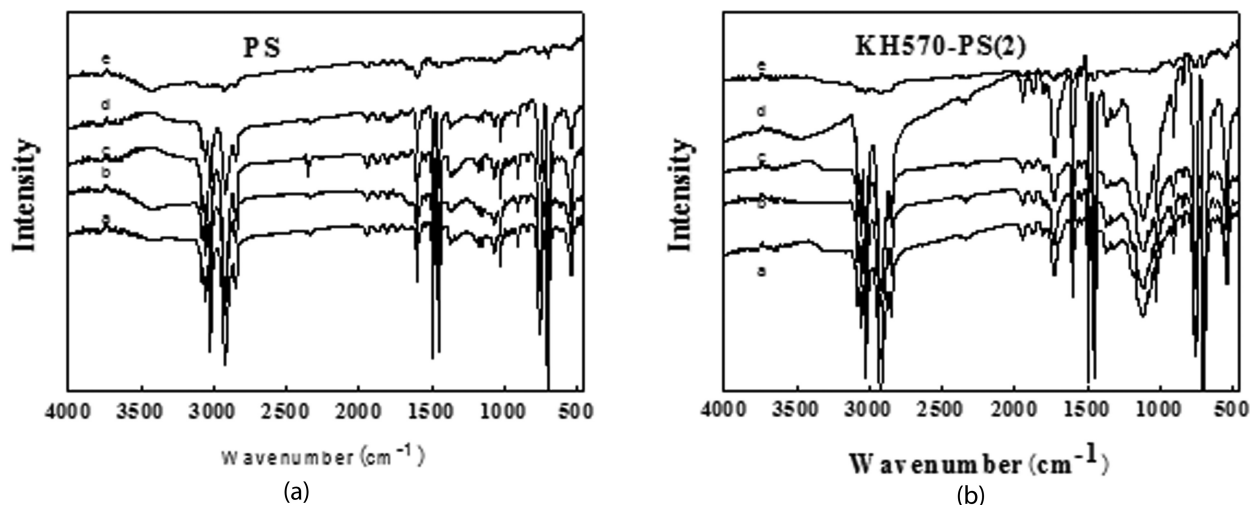|	E (%)			
	H_2O		Acetone/ H_2O = 1/1	
PS	80.4	40.5	17.6	—
KH570–PS(2)	84.5	46.6	27.0	—

Figure 7. FTIR spectra of the PS and KH570–PS(2) nanospheres before (a) adsorption and after adsorption of TNT in (b) H_2O, (c) EtOH/H_2O, (d) acetone/H_2O, and (e) THF/H_2O.

interactions.[21] The KH570–PS(1) nanospheres aggregated together during the process of drying, and this resulted in a lower absorbed amount. When the KH-570 content was 2 mL/10 g of St, E was the highest. E of KH570–PS(2) was the highest, and the adsorption capacity was 2.81 mg/g. With increasing KH-570 content, more and more Si—OH, O=C groups existed on the KH570–PS nanospheres. —OH and O=C were considered to be electron donors.[21] In addition, because of the presence of the electron-withdrawing NO_2 groups on the TNT molecules, the TNT molecules were characterized as highly electron deficient Π-electron systems.[22] So electron donor–acceptor interaction between the KH570–PS nanospheres and TNT were produced. However, with increasing KH-570 content, there was more and more KH-570 on the PS nanospheres; this hindered the Π–Π stacking interactions between PS and TNT.[23] Thus, E decreased slightly. When the adsorbent was replaced by SiO_2, E decreased sharply because there was no Π–Π stacking interactions between SiO_2 and TNT. The results prove that the Π–Π stacking interactions played an important role in the interactions of the adsorbents with TNT. To clarify this inference, a further experiment was carried out to determine the adsorption mechanism.

Effect of Different Media on Adsorption

The adsorption mechanism of the PS and KH570–PS nanospheres was further studied in an aqueous medium. Table II indicates that in the H_2O medium, both the PS and KH570–PS nanospheres possessed the strongest adsorption interaction toward TNT. We speculated that the driving force of adsorption in the aqueous medium were Π–Π stacking interactions, hydrophobic interactions, and electron donor–acceptor interactions between the groups of —OH, O=C, and TNT. In the media of H_2O/EtOH and acetone/H_2O, the adsorption capacity was lower than that in aqueous solution; this may have been due to the fact that the interaction of —OH in the EtOH molecules and O=C in the acetone molecules with TNT decreased, and the hydrophobic effect also decreased. Thus, the adsorption amount of TNT on the PS or KH570–PS nanospheres decreased. In the

medium of THF/H_2O, both PS and KH570–PS showed no adsorption capacity toward TNT. This phenomenon may be explained by the fact that TNT was soluble in THF and had weak interactions with PS and KH570–PS; this resulted in a small adsorption capacity toward TNT. The characteristic peaks (Figure 7) on both PS and KH570–PS were restricted because of the dense stacking of PS molecule chains originating from the Π–Π stacking interactions. As discussed previously, the rank of interaction forces between KH570–PS and TNT in order of importance could be described as follows: Hydrophobic interactions > Electron donor–acceptor interactions > Π–Π Stacking interactions.

Reusability

The adsorption–desorption cycle (Figure 8) was repeated seven times on the same materials, and E was 90% in the first cycle, decreased to 84% in the second cycle, and then increased to 89% in subsequent cycles. The results shown in Figure 8 are better than those reported in the literature.[24,25] After several
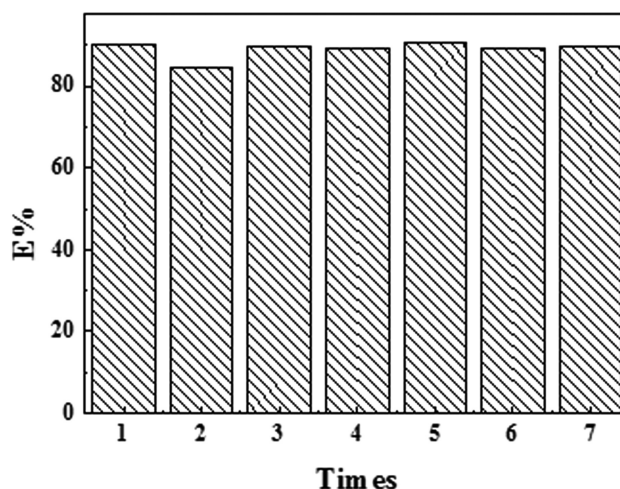

Figure 8. Reusability of the PS nanospheres.

adsorption–desorption processes, there was only slight variation in E; this suggested that the adsorption materials were reusable.

CONCLUSIONS

PS and KH570–PS nanospheres prepared by emulsion polymerization were used as adsorbents for TNT in aqueous solution. The adsorption results show that Π–Π stacking interactions between the PS and TNT molecules contributed to the high adsorption. The highest adsorption amount under the optimized conditions for KH570–PS(2) reached 2.81 mg/g, and the corresponding TNT removal efficiency was 90% when C_0 of TNT was 50 mg/L at 298 K. The nanospheres could be reused at least seven times without suffering an appreciable loss in their adsorption capability. This study indicated that PS or KH570–PS can be used to functionalize some adsorbents, such as active carbon, minerals, and so on, in actual field application to improve the adsorption capacity and reusability of polymers. More applicable possibilities will be explored in our laboratory.

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