Synthesis of Positively Charged Polystyrene Microspheres for the Removal of Congo Red, Phosphate, and Chromium(VI)

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Supporting Information

ABSTRACT: Uniform positively charged polystyrene microspheres were synthesized and further examined as a new sorbent for water remediation. The structures of the resulting sorbent were characterized by field-emission scanning electron microscopy, Fourier transform infrared spectroscopy, and 1H nuclear magnetic resonance spectroscopy. The adsorption performance of the sorbent was evaluated using three typical pollutants, namely, Congo red, phosphate, and Cr(VI). The adsorption isotherms were fitted by the Langmuir and Freundlich models, while the adsorption kinetics was analyzed by the pseudo-first-order, pseudo-second-order, and intraparticle diffusion equations. The thermodynamic parameters of the adsorption process including changes of enthalpy, entropy and Gibbs free energy, and binding constant were obtained by isothermal titration calorimetry measurements. The effects of solution pH and competitive ions on the adsorption process were investigated. The adsorption isotherms could be better fitted by the Langmuir model, yielding maximum adsorption capacities of 18, 6.2, and 1.1 mg g⁻¹ for the adsorption of Congo red, Cr(VI), and phosphate, respectively. The adsorption kinetics could be best described by the pseudo-second-order equation. The spent sorbent was regenerated by washing with 1 M KOH and showed outstanding long-term cyclic performance. The findings suggested that the positive charges at the surface of polystyrene microspheres could serve as effective sites for the immobilization of anionic pollutants in solutions owing to the electrostatic attraction.

1. INTRODUCTION

Accompanying with industrialization and urbanization, various pollutants are entering into water sources, giving rise to detrimental impacts on human health and ecological systems. Congo red (CR), Cr(VI), and phosphate are anionic pollutants in water.¹⁻³ CR, a typical synthetic dye, is always found in effluents from many industries such as printing, textile, paper, plastics, and so forth. The presence of CR in water is highly visible and significantly increases chemical and biochemical oxygen demands.⁴⁻⁶ Being one of the notorious pollutants, a trace of Cr(VI) is generally present in surface and ground waters while high-concentration Cr(VI) can be found in effluents originated from industrial processes such as electroplating, mining, and petroleum refining processes.⁷ Cr(VI) is highly toxic, mutagenic, and carcinogenic to living organisms.⁸⁻¹⁰ Phosphate is one of the essential nutrients for plant growth.¹¹ However, excess phosphate in water can stimulate the growth of organisms and algae, leading to the death of aquatic life in water bodies, which is the so-called eutrophication.¹²⁻¹⁴ Because of the abovementioned harmful impacts, it is of great significance to remove CR, Cr(VI), and phosphate from water sources.

To this end, various physical, chemical, and biological methods have been explored in different conditions, such as (bio)sorption,¹⁵ membrane filtration,¹⁶ precipitation,¹⁷ chemical reduction/oxidation,¹⁸ and microbial remediation.¹⁹ Among these approaches, sorption has been considered as one of the most promising methods for water remediation because of its high efficiency, simplicity of design, and ease of operation and maintenance.²⁰ In a typical sorption process, the pollutant is separated from the solution by immobilizing to the surface of the sorbent. The performance of the sorbent plays a decisive role in the efficiency of the sorption process. Activated carbon has been widely used as a sorbent to remove contaminants from water because of its low cost. However, activated carbon always takes long contact time, which inhibits the practical applications. Thus, studies have been

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devoted to exploring new sorbents for water purification. So far, numerous sorbents, such as carbons,22−25 oxides,26−31 and polymers,32−35 have been reported. Unfortunately, most of these reported sorbents suffer some drawbacks, such as unsatisfactory regeneration and cycling ability. As a result, high-performance sorbents are desirable but unfortunately still lacking. Recently, authors’ group has reported an approach to prepare sulfonated polystyrene (PS) nanospheres which showed outstanding ability to extract heavy metal ions from protein solutions owing to the strong interaction between negatively charged SO3− groups and positively charged metal ions.36 Encouraged by this outcome, herein, the authors synthesized monodispersed positively charged PS microspheres to sequestrate CR, Cr(VI), and phosphate. A prominent advantage of these functionalized PS microspheres lies in the positive charge, which serve as effective sites for the immobilization of CR, Cr(VI), and phosphate in solutions. The central objective of this work is to reveal the adsorption characteristics of the adsorption processes. The adsorption isotherms, thermodynamics, kinetics, regeneration, and cyclic performance of the sorbent were investigated in detail. In addition, the effects of solution pH and competitive ions were also investigated.

2. RESULTS AND DISCUSSION

2.1. Material Synthesis and Characterization. The synthesis procedure of positively charged PS−N+ microspheres is illustrated in Scheme 1. It consists of four steps. In step I, PS microspheres are synthesized via a typical radical polymerization process, in which azobisisobutyronitrile (AIBN) and polyvinyl pyrrolidone (PVP) are used as an initiator and surfactant, respectively. The PS powder is purely white as seen from the digital photo. Field-emission scanning electron microscopy (FESEM) images shown in Figure S4 reveal that the resulting PS microspheres are monodisperse and possess a uniform diameter of ca. 1.4 um. In step II, nitro groups are grafted into the benzene rings of the PS via the nitration reaction. The color of the resulting PS−NO2 powder turns into slight yellow. However, PS−NO2 has no distinct morphological change as shown in Figure S5. The energy-dispersive X-ray (EDX) mapping images reveal the distribution of carbon, oxygen, and nitrogen. The latter two elements are ascribed to the nitro groups, manifesting the success of the nitration reaction. In step III, the nitro groups are reduced into amino groups. During the reduction process, NaBH4 and (NH4)2SO4 are served as a reducing agent and catalyst, respectively. The PS−NH2 powder is of a salmon-like color and composed of uniform microspheres (see Figure S6). Carbon, oxygen, and nitrogen elements are noted from the EDX mapping images. Further analyses indicate that the content of oxygen in PS−NH2 is significantly reduced relative to that in PS−NO2. In step IV, the positively charged groups are introduced via a quaternization reaction in which glycidyl trimethyl ammonium chloride (GTAC) is used as a quaternization reagent, while HClO4 is used to control the pH of the solution. The resulting PS−N+ powder is yellowish. FESEM images, shown in Figure 1, reveal that PS−N+ is still monodisperse and well preserves a uniform spherical structure, manifesting that the aforementioned reactions only take place at the surface of the microspheres.

The structures of the samples were studied by Fourier transform infrared spectroscopy (FTIR) as shown in Figure 2. A comparative inspection could reveal that a distinct adsorption peak at 870 cm−1 is noted from the spectra of
the PS−NO₂, PS−NH₂, and PS−N⁺ samples, which can be ascribed to the stretching vibration of C−N bonds. Two peaks located at 1300 and 1550 cm⁻¹ are also noted from the spectra of the PS−NO₂, PS−NH₂, and PS−N⁺ samples, which could be assigned to the N−O stretching vibration. This result suggests that the PS−NH₂ and PS−N⁺ samples still contain some nitro groups owing to the incomplete reduction, which is consistent with the EDX results. The spectra in the range of 3200−3800 cm⁻¹ also well illustrate the variations of the functional groups. For the PS and PS−NO₂ samples, no peak is observed in this range. In contrast, the PS−NH₂ sample exhibits a broad peak centered around 3500 cm⁻¹ which is the characteristic of NH₂ groups. This peak is significantly depresses as evidenced from the spectrum of the PS−N⁺ sample because of the quaternization reaction. To further investigate the structures of the samples, ¹H nuclear magnetic resonance (NMR) spectra of the samples are recorded (see Figure S7). It can be seen that the spectrum of the PS is different from those of the PS−NO₂, PS−NH₂, and PS−N⁺ samples, which is attributed to the grafting of functional groups in the benzene rings. However, the differences in the spectra of the PS−NO₂, PS−NH₂, and PS−N⁺ are limited. This could be explained from the fact that the number of the substituted groups is low because the modifications occur only at the surface of the microspheres.

The powered samples were dispersed in distilled water by ultrasonication to form stable suspensions with a concentration of 10 mg L⁻¹. The conductivity of the suspension was recorded at room temperature as shown in Figure 3. For reference, the conductivity of distilled water is determined to be 1.5 μS cm⁻¹.

The PS−N⁺ suspension exhibits the largest conductivity of 5.1 μS cm⁻¹, which is 3.4, 2.4, 2.04, and 1.34 times those of distilled water, PS, PS−NO₂, and PS−NH₂, respectively. This is exactly attributed to the positive charges at the surface of the PS−N⁺ microspheres.

2.2. Adsorption Isotherms and Thermodynamics. It has been demonstrated that positively charged groups are successfully grafted into the benzene rings and that the resulting PS−N⁺ well maintains a monodispersed spherical structure. Such structural features render it as a promising sorbent for water purification. As a proof of concept, the adsorption performance of PS−N⁺ was evaluated by three typical pollutants, namely, CR, phosphate, and Cr(VI). The adsorption characteristics of PS−N⁺ toward these three pollutants were studied in detail. First of all, the adsorption performance of the four samples was compared as shown in Figure S8. It shows that PS−N⁺ possesses the largest adsorption capacities of the three pollutants, indicating that the positively charged groups in the PS−N⁺ microspheres play an essential role in immobilizing the pollutants. The adsorption isotherms of PS−N⁺ were recorded, as shown in Figure 4. It shows that the adsorption uptake initially increases with increasing equilibrium concentrations and then reaches a plateau stage at high concentrations. To determine the theoretical maximum adsorption capacity, the adsorption isotherms were analyzed by Langmuir and Freundlich models as expressed by eqs 1 and 2, respectively.

\[ q_e = \frac{q_{\text{max}} b C_e}{1 + b C_e} \]  (1)

\[ q_e = K C_e^{1/n} \]  (2)

where \( q_{\text{max}} \) (mg g⁻¹) is the maximum adsorption capacity, \( b \) (L mg⁻¹) is the Langmuir adsorption constant, and \( k \) (mg⁻¹ Lⁿ g⁻¹) and \( n \) are the Freundlich constants associated with adsorption capacity and adsorption intensity, respectively. The resulting fitting curves are displayed in Figure S9. The corresponding fitting parameters are listed in Table S1. Modeling results indicate that, compared with the Freundlich model, the Langmuir model is more applicable for the description of the adsorption data. PS−N⁺ has theoretical maximum adsorption capacities of 18, 6.2, and 1.1 mg g⁻¹ for the adsorption of CR, Cr(VI), and phosphate, respectively. The maximum adsorption capacities are well correlated with the molecular weight of the substrates, indicating that the major adsorption sites are the positively charged groups. It is worth noting that the adsorption of CR shows the largest adsorption constant \( b \) value because each CR molecule has two negative charges arisen from two SO₄⁻ groups while Cr(VI) and phosphate in the forms of HCrO₄⁻ and H₂PO₄⁻, respectively, have only one negative charge, leading to the strongest electrostatic interaction between PS−N⁺ and CR. It should be pointed out that the maximum capacity is smaller than those of the sorbents reported in the literature.³⁷−⁴⁰ This could be because of the limited number of the positive charges in the surface of PS−N⁺.

To gain in-depth understanding of the adsorption process, isothermal titration calorimetry (ITC) measurements were performed. Figure 5 displays the thermograms. The resulting parameters including changes of enthalpy (\( \Delta H \)), entropy (\( \Delta S \)), Gibbs free energy (\( \Delta G \)), binding constant (\( K_b \)), and the number of binding sites (\( N \)) are summarized in Table S2. For
the thermogram of CR (Figure 5a), clear thermonegative peaks are noted for the initial injections and gradually changed to thermopositive. In contrast, for the thermograms of phosphate (Figure 5b) and Cr(VI) (Figure 5c), only thermonegative peaks appear during the whole titration process. The \( \Delta G \) values of the processes are negative, indicative of that the processes are thermodynamically favorable. The \( \Delta S \) values of the processes are positive, suggesting that the binding of the sorbates to the PS\textsuperscript{−}N\textsuperscript{+} increases the structural disorder of the systems. The \( \Delta H \) values of the adsorption of phosphate (\(-4.7\) kcal mol\(^{-1}\)) and Cr(VI) (\(-3.71\) kcal mol\(^{-1}\)) are negative while that of CR (\(3.08\) kcal mol\(^{-1}\)) is positive. These results reveal that the spontaneous binding of CR to PS\textsuperscript{−}N\textsuperscript{+} is mainly driven by \( \Delta S \) of the process. In contrast, both \( \Delta S \) and \( \Delta H \) play a role in the adsorption of Cr(VI) and phosphate. Similar to the parameter \( b \) in the Langmuir model, the \( K_b \) value is closely related to the adsorption intensity. The adsorption of CR shows the smallest \( K_b \) value, indicating the strongest binding strength, which is attributed to the two negative charges of CR molecules.

### 2.3. Adsorption Kinetics

The adsorption kinetics was studied. The concentrations of the sorbates are monitored as a function of contact time as shown in Figure 6. To investigate the kinetics of the process, three kinetic models including the pseudo-first-order,\(^{41}\) pseudo-second-order,\(^{42}\) and intraparticle diffusion\(^{43}\) equations were employed to analyze the data. The fitting curves are shown in Figure S10 and the resulting parameters are listed in Table S3. The experimental data are best fitted by the pseudo-second-order equation. On the basis of the pseudo-second-order equation, the equilibrium adsorption uptakes of CR, Cr(VI), and phosphate are determined to be 8.89, 2.27, and 0.3 mg g\(^{-1}\), corresponding to rate constants of 51.1, 0.406, and 1.59 min\(^{-1}\), respectively. The largest equilibrium adsorption uptake of CR is attributed to its large molecular weight while the remarkable rate constant could be explained from the two negative charges per molecule.

### 2.4. Effects of Solution pH

It is well known that Cr(VI) and phosphate can form various species in different solution pHs (see Figure S11). For Cr(VI), there are following equilibrium reactions in solutions\(^{11,44}\)

\[
H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^- \tag{3}
\]
Taking Cr(VI) as an example, the effects of solution pH in the adsorption process were studied. The adsorption isotherms were recorded at pHs of 3, 4.8, 6.6, and 9 as shown in Figure 7a. It shows that the adsorption uptake decreases with increasing solution pHs. The adsorption isotherms were further fitted by the Langmuir model (see Figure S12) and the resulting modeling results are listed in Table S4. The maximum theoretical adsorption capacities of Cr(VI) were determined to be 7.1, 6.2, 6.1, and 4.6 mg g⁻¹ at solution pHs of 3, 4.8, 6.6, and 9, respectively. The maximum adsorption capacity decreases with increasing pH. This could be related to the formation of CrO₄²⁻ in high-solution pHs, whose adsorption over PS−N⁺ could involve more sites. The effects of solution pH in the adsorption kinetics were also explored. Figure 7b shows the variations of Cr(VI) concentration at different solution pHs. The concentration of Cr(VI) rapidly decreases and reaches to an equilibrium state within 20 min, indicating the fast adsorption kinetics. The kinetic data were well fitted by the pseudo-second-order equation as shown in Figure S13, and the resulting parameters are listed in Table S5. The equilibrium adsorption uptakes of Cr(VI) were 2.3, 2.2, 1.7, and 1.4 mg g⁻¹, corresponding to rate constants of 0.24, 0.4, 1.1, and 1.86 min⁻¹, at pHs of 3, 4.8, 6.6 and 9, respectively. Interestingly, at high pHs, adsorption of Cr(VI) showed lower equilibrium uptakes but larger rate constant values. This could also be explained from the presence of CrO₄²⁻ in high-solution pHs. The adsorption of this species involves more binding sites and stronger binding strength with the PS−N⁺ sorbent.

2.5. Effects of Competitive Ions. The effects of competitive negative nitrate ions in the adsorption process were also investigated. Figure 8a comparatively shows the isotherms of the adsorption of CR with and without nitrate ions. It can be seen that in the presence of 0.01 M NO₃⁻, the adsorption uptakes are lower than those obtained in the absence of 0.01 M NO₃⁻. Based on the Langmuir model, the maximum adsorption capacity of CR in the presence of 0.01 M NO₃⁻ was determined to be 17.1 mg g⁻¹, which is slightly smaller than that of 18 for the single adsorption of CR.
8b shows the effects of NO$_3^-$ in the adsorption kinetics. Further fitting analyses based on the pseudo-second-order equation indicate that with the addition of 0.01 M NO$_3^-$ in the pollutant solution, the equilibrium adsorption uptake decreases from 8.9 to 8.6 mg g$^{-1}$ while the rate constant decreases from 51.1 to 3.64 min$^{-1}$. These findings suggest that the presence of NO$_3^-$ shows limited effects in the adsorption kinetics.

2.6. Regeneration and Recyclability. To study the regeneration and recyclability of the sorbent, cyclic adsorption–desorption tests were further conducted. CR- and Cr(VI)-saturated PS–N$^+$ microspheres were regenerated by washing with 1 M KOH. It was found that the desorption process was also fast and could be completed in several minutes. This adsorption–desorption process was repeated eight times and the adsorption uptakes were recorded as a function of cycle number as shown in Figure 9. It shows that the adsorption uptakes of CR and Cr(VI) are quite stable and possess outstanding long-term cyclic performance. The morphology of the pollutant-saturated PS–N$^+$ microspheres was further observed by FESEM as shown in Figures S14–S16. It can be seen that the spent sorbents well preserve the spherical structure. Elemental analyses indicate that additional sulfur, chromium, and phosphorus elements are noted from the spent adsorbents after the adsorption of CR, Cr(VI), and phosphate, respectively.

3. CONCLUSIONS

Monodispersed positively charged PS microspheres were fabricated for the removal of CR, phosphate, and Cr(VI). The adsorption isotherms were better fitted by the Langmuir model, yielding maximum adsorption capacities of 18, 6.2, and 1.1 mg g$^{-1}$ for the adsorption of CR, Cr(VI), and phosphate, respectively. The adsorption kinetics was best described by the pseudo-second-order equation, resulting in rate constants of 51.1, 0.406, and 1.59 min$^{-1}$ for the adsorption of CR, Cr(VI), and phosphate, respectively. ITC results indicated that the adsorption of CR to PS–N$^+$ was mainly driven by the entropy change while the changes of both entropy and enthalpy played a role in the adsorption of Cr(VI) and phosphate. At high-solution pHs, the PS–N$^+$ microspheres showed low adsorption uptakes but large adsorption rate constants, which could be explained from the formation of CrO$_4^{2-}$. The presence of competitive NO$_3^-$ ions had limited influence on the adsorption uptakes of CR but significantly decreased the rate constants. The spent sorbent could be facilely regenerated by washing with 1 M KOH and showed outstanding long-term cyclic performance.

4. EXPERIMENTAL SECTION

4.1. Materials. Sodium hydroxide (≥96.0%), potassium peroxysulfate (≥99.5%), perchloric acid aqueous solution (72 wt %), and anhydrous ethanol (≥99.7%) were purchased from the Nanjing chemical reagent Co. Ltd., China. Sulfuric acid (98.0%), nitric acid (≥68.0%), sodium dodecyl sulfate (≥99.0%), potassium dichromate (≥99.9%), ammonium sulfate (≥99%), sodium borohydride (≥98%), acetic acid (≥99.7%), and CR (≥95%) were purchased from the Damao chemical reagent co. Ltd. Tianjin, China. Potassium dihydrogen phosphate (≥99.5%), l-aminomony potassium tartrate (≥99%), ammonium molybdate (≥99%), polyvinyl pyrrolidone (PVP-30 ≥95%), and AIBN (≥99%) were purchased from the Kemiou chemical reagent Co. Ltd. Tianjin, China. GTAC aqueous solution (80 wt %) was purchased from the Tokyo Chemical Industry Co., Ltd.

4.2. Synthesis of PS Microspheres. PVP (2 g) was dissolved into 200 mL of ethanol. The resulting solution was poured into a three-necked flask and heated to 75 °C under a nitrogen atmosphere. 50 mL of styrene and 0.4 g of AIBN were added under continuous stirring. The mixture was refluxed at 75 °C for 24 h. After cooling to room temperature, the product was thoroughly washed with ethanol and dried at 50 °C using a vacuum oven for 24 h.

4.3. Synthesis of PS–NO$_2$ Microspheres. Concentrated sulfuric acid and nitric acid were mixed with a mass ratio of 3:2. A 3 g of PS microspheres was dispersed in 120 mL of the mixed acid by ultrasonication. The nitration process was conducted at 50 °C for 4 h. After cooling to room temperature, the mixture was transferred into 500 mL of distilled water, separated by filtration, and thoroughly washed with distilled water. The product was dried at 50 °C for 24 h. For convenience, the resulting product was denoted as PS–NO$_2$.

4.4. Synthesis of PS–NH$_2$ Microspheres. PS–NO$_2$ (3 g) was dispersed into 80 mL of ethanol by ultrasonication to form a stable suspension. 1 g of NaBH$_4$ and 0.3 g of (NH$_4$)$_2$SO$_4$ were dissolved into 80 mL of ethanol. The resulting solution was slowly introduced into the suspension under stirring. The reduction process was conducted at 60 °C for 48 h. During the reaction, 1 g of NaBH$_4$ was added at a time interval of 10 h. After cooling to room temperature, the product was thoroughly washed with distilled water and ethanol, and dried at 50 °C for 24 h. For convenience, the resulting product was denoted as PS–NH$_2$.

4.5. Synthesis of Positively Charged PS–N$^+$ Microspheres. PS–NH$_2$ microspheres (2 g) were dispersed into 120 mL of distilled water by ultrasonication. 0.5 mL of HClO$_4$ solution (10 wt %) and 2 mL of GTAC solution (80 wt %) were added. The reaction was conducted at 95 °C for 48 h. During the reaction, 0.5 mL of HClO$_4$ solution and 2 mL of GTAC solution were added with time intervals of 3 and 8 h, respectively. After cooling to room temperature, the product was thoroughly washed with distilled water and ethanol, and dried at 50 °C for 24 h. For convenience, the resulting product was denoted as PS–N$^+$.

4.6. Material Characterization. The morphology of the samples was observed by FESEM (JSM-7600F, JEOL). An EDX analyzer equipped in FESEM was used to analyze the elemental composition of the samples. The structures of the samples were analyzed by $^1$H NMR (JOEL, JNM-ECA 600 MHz) and FTIR (AV360). The conductivity of the suspension was measured by a conductivity analyzer (DDS-11A) at room temperature.

4.7. Batch Adsorption Tests. To study the adsorption kinetics, 100 mg of PS–N$^+$ was added into 30 mL of CR solution (initial concentration = 30 mg L$^{-1}$), while 150 mg of PS–N$^+$ was separately added into 12 mL of phosphate solution (initial concentration = 10 mg L$^{-1}$) and 25 mL of dichromate solution (initial concentration = 10 mg L$^{-1}$). The mixture was agitated at 180 rpm using a mechanical shaker at 25 °C. At given time intervals, 0.5 mL of aliquot was sampled and filtered through a membrane filter (pore diameter = 220 nm) to remove the sorbent. The concentration of the pollutant was determined using a UV–visible spectrophotometer (North point Rayleigh UV-1801). The concentrations of the pollutants
are well correlated with the intensity of the maximum adsorption peak ($\lambda_{\text{max}}$). The $\lambda_{\text{max}}$ value of CR solution is located at 497 nm as shown in Figure S1. Notably, the $\lambda_{\text{max}}$ values of dichromate solutions are dependent on solution pH. The $\lambda_{\text{max}}$ values of the dichromate solutions are determined to be 257 and 273 nm at pHs of 3 and 9, respectively (see Figure S2). The measurement of phosphate concentration is relatively complicated. The details of the experimental procedures are listed as follows: 50 mL of 5 M H$_2$SO$_4$, 5 mL of L-antimony potassium tartrate solution (0.55 wt %), 15 mL of ammonium molybdate solution (8 wt %), and 30 mL of 0.2 M ascorbic acid solution were mixed. 0.5 mL of the mixed solution was added into 2 mL of the phosphate solution. After shaking, the solution was transferred for analysis. The concentration of phosphate was determined from eq 6
\[
q_t = \frac{(C_0 - C_t)V}{W}
\]
where $C_0$ and $C_t$ (mg L$^{-1}$) are the initial and constant concentrations in the liquid phase, respectively, $V$ (L) is the solution volume, and $W$ (g) is the sorbent weight. To obtain the equilibrium adsorption capacity $q_e$ (mg g$^{-1}$), 10 mg of PS–N$^+$ powder was separately introduced into CR, phosphate, and dichromate solutions with volumes of 7, 2, and 4 mL, respectively, with predetermined initial concentrations. The sorbent was dispersed in the pollution solution for at least 24 h to achieve an equilibrium state of adsorption. To study the regeneration and recyclability of the PS–N$^+$ sorbent, cyclic adsorption–desorption tests were conducted. A 100 mg of PS–N$^+$ was separately added into 20 mL of CR solution with a concentration of 50 mg L$^{-1}$ and 10 mL of dichromate solution with a concentration of 30 mg L$^{-1}$ under continuous magnetic stirring. The adsorption process was conducted at 25 °C for at least 12 h. Subsequently, pollutant-saturated PS–N$^+$ was regenerated by immersing into 1 M KOH. The regenerated PS–N$^+$ was collected by centrifugation and washed with water. The sorbed sorbent was employed again to remove pollutants from the solutions. This adsorption–desorption process was repeated eight times. The adsorption uptake was recorded as a function of cycle numbers.

4.8 ITC Tests. ITC (PEAQ-ITC, Malvern) was employed to measure the heat exchange during the adsorption process. Typically, a suspension of PS–N$^+$ with a concentration of 5 mg L$^{-1}$ was added into the cell. 0.4 μL of 1 mM pollutant solution was injected into the cell using a syringe within 4 s under stirring (700 rpm). Subsequently, 18 drops of the adsorbate solution with a volume of 0.2 μL were injected with a time interval of 150 s. The titration process was conducted at 25 °C.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00318.

UV-spectra and the corresponding calibrated curves of CR, Cr(VI), and phosphate, FESEM, EDX, $^1$H NMR spectra, modeling results on the isotherms and kinetics, and distribution of Cr(VI) and phosphate in solutions (PDF)

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Notes

The authors declare no competing financial interest.

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