Nitrate Adsorption Using Poly(dimethyl diallyl ammonium chloride)/Polyacrylamide Hydrogel

Yian Zheng[†,‡] **and Aiqin Wang***[,†]

Center of Eco-materials and Green Chemistry, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China, and Graduate University of the Chinese Academy of Sciences, Beijing 100049, China

In this study, poly(dimethyl diallyl ammonium chloride)/polyacrylamide (PDMDAAC/PAM), a hydrogel containing quaternary ammonium groups, was prepared and used as the adsorbent to remove the nitrate anion from aqueous solution. The effects of operating conditions, such as PDMDAAC content, contact time, pH, initial nitrate concentration, temperature, ion strength, and the presence of the competitive ion phosphate on the adsorption capacities were examined. The Langmuir, Freundlich, and Redlich−Peterson isotherms were used to describe the adsorption experimental data. The results indicate that the adsorption equilibrium can be achieved within 60 min, and the hydrogel has an increasing adsorption capacity with increasing PDMDAAC content up to 50 % (by weight). As-prepared hydrogel shows an appreciable adsorption capacity within the pH range of 5 to 9, and the calculated maximum adsorption capacity is found to be (1.1 to 1.4) $\text{mmol}\cdot\text{g}^{-1}$. The hydrogel with higher PDMDAAC content is sensitive to the changes in the ion strength and competitive anion concentration. Effective desorption of nitrate is achieved using strong acid or base as the desorbing agent. It is proposed that two mechanisms are responsible for the higher adsorption capacity: one is swelling, and the other is electrostatic attraction.

Introduction

Nitrate is one of the most common groundwater contaminants in rural areas and can create serious problems, such as eutrophication and outbreaks of infectious disease, when released into the environment.[1] Nitrate may reduce to nitrosamines in the stomach which is suspected to cause gastric cancer.[2] In addition, nitrate can be reduced to nitrite inside the stomach of fetuses after digestion of nitrate by the mother. The nitrite reacts with the hemoglobin in blood and results in a bluish color of the infant’s skin, the so-called methemoglobinemia or blue baby syndrome.[3−5] Nitrate pollution is caused by the extensive use of nitrogen fertilizers, crop irrigation with domestic wastewater, and use of manure. To remove nitrate, several technologies have been tested, such as constructed wetlands,[6] ultrafiltration,[7] ion exchange,[8] electrodialysis,[9,10] hybrid denitrification filters,[11] and adsorption.[12−14] Among these technologies, adsorption has received much attention and is considered to be a robust and effective technique used in water and wastewater treatments due to its economical advantages, low energy input, and easy operation.[15,16]

Adsorption is the process of collecting soluble substances from water thanks to the surface properties of the adsorbent material. The success of an adsorption technology depends on the choice of an appropriate adsorbent.[17] Materials used as the adsorbents for nitrate removal include polypropylene-*g*-*N*,*N*-dimethylaminoethyl methacrylate,[18] poly(dimethylaminoethyl methacrylate/2-hydroxyethyl methacrylate),[19] functionalized mesoporous silica,[20] sepiolite,[14] bentonite,[21] slag,[14] activated carbon,[14] red mud,[22] agricultural waste,[23] M^{II}-Al-CO_3 layered double hydroxide,[24] and chitosan beads,[25] etc. Hydrogels are cross-linked polymeric networks and have shown faster adsorption rates and higher adsorption capacities for cationic pollutants, such as heavy metals,[26,27] dyes,[28,29] and ammonium.[30−32]

Dimethyl diallyl ammonium chloride (DMDAAC) is a water-soluble quaternary ammonium compound that can be polymerized to its corresponding polymer, PDMDAAC (poly(dimethyl diallyl ammonium chloride)), in aqueous solution through free-radical polymerization. PDMDAAC has captured much scientific attention due to its highly hydrophilic charged quaternary ammonium group which can afford the polymer with high water solubility and strong electrolytic solution properties that are exploited in water treatment, paper manufacturing, the mining industry, and biological fields.[33] In general, PDMDAAC can be regarded as a linear polymer to interpenetrate with vinyl monomers to form special semi-interpenetrating networks.[34] Consequently, in this study a series of cationic hydrogels based on DMDAAC and acrylamide (AM) were prepared, and the potential of as-prepared hydrogels for nitrate removal was evaluated.

Experimental Section

Materials. Acrylamide (AM, chemically pure, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), ammonium persulfate (APS, analytical grade, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), *N*,*N*′-methylene-bisacrylamide (MBA, chemically pure, Shanghai Yuanfan additives plant, Shanghai, China), and dimethyl diallyl ammonium chloride (DMDAAC, 60 % solution in water, Luyue Chemical Co., Ltd., Shandong, China) were used as received without further purification.

A 100 mg $\text{N}\cdot\text{L}^{-1}$ stock standard solution of nitrate was prepared by dissolving an appropriate amount of potassium nitrate (KNO_3) in 1000 mL of distilled water. The working solutions containing different concentrations of nitrate were

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* Corresponding author. E-mail: aqwang@licp.cas.cn. Tel.: 86 931 4968118. Fax: 86 931 8277088.
[†] Chinese Academy of Sciences.
[‡] Graduate University of the Chinese Academy of Sciences.

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prepared by stepwise dilution of the stock solutions. The initial pH value was adjusted by addition of (0.1 and 1.0) mol·L^{-1} NaOH or HCl solution to a designed value (Mettler Toledo pH-meter). Other reagents used were all analytical grade, and all solutions were prepared with distilled water.

Preparation of PDMDAAC. In a 250 mL three-necked flask, 150 g of 60 % DMDAAC aqueous solution was heated to (60 to 70) °C, while 5 mL of solution containing 0.5 g of APS was added. The mixture was stirred under a nitrogen atmosphere for 2 h, and the resulting polymer was washed with acetone and absolute ethanol several times to remove the impurities present. The white precipitate was dried at 60 °C in a vacuum oven.

Preparation of PDMDAAC/PAM (Polyacrylamide). A series of cationic hydrogels were prepared by aqueous solution polymerization. A certain amount of PDMDAAC was added into a 250 mL four-neck flask equipped with a stirrer, a condenser, a thermometer, and a nitrogen line until it was dissolved. Then, a weighed amount of AM and 50 mg of MBA (0.5 % (by weight) relative to the monomers) were added to the above solution. After removing oxygen by bubbling with pure nitrogen for 20 min, a 2 mL solution containing 0.2 g of APS (2 % (by weight) relative to the monomers) was introduced, and afterward the mixture was heated and kept at 70 °C for 3 h to complete the polymerization reaction. When the reaction was finished, the resulting product was cooled to room temperature and washed with distilled water. The swollen product was dehydrated with methanol and dried at 70 °C to a constant weight. The hydrogels were milled, and all samples used for the adsorption test were passed through (40 to 80) mesh stainless screens.

Adsorption Experiments. Nitrate adsorption experiments were performed in a series of Erlenmeyer flasks mounted on a temperature-regulated orbital shaker THZ-98A. An amount of 0.05 g of hydrogel was added to 25 mL of KNO_3 solution and shaken for 60 min. The hydrogel was separated from the nitrate solution by direct filtration with a 100-mesh stainless screen, and the filtrate was collected for further analysis. The concentration of nitrate was determined using a UV−vis spectrophotometer (210 nm for nitrate). The amount of nitrate adsorbed per unit mass of adsorbent, q_e (mmol·g^{-1}), was calculated by the following equation

$$q_e = \frac{C_0V_1 - C_eV_2}{m \cdot 14} \tag{1}$$

where C_0 is the initial nitrate concentration (mg N·L^{-1}); C_e is the equilibrium nitrate concentration (mg N·L^{-1}); m is the mass of adsorbent used (mg); and V_1 and V_2 are the volumes of nitrate solution before and after the adsorption (mL). All analyses were performed in triplicate, and the relative standard deviation was 5 %.

For the adsorption kinetic studies, a series of solutions containing 100 mg N·L^{-1} nitrate were allowed to contact with 0.05 g hydrogels with different amounts of PDMDAAC. At different intervals [(1, 5, 10, 30, 60, and 90) min], the hydrogels were separated by direct filtration, and the filtrates were analyzed for residual nitrate concentration. The effects of pH on nitrate adsorption onto these hydrogels were studied at pH 2, 3, 5, 7, 9, 11, and 12 for an initial nitrate concentration of 100 mg N·L^{-1} and contact time of 60 min. During this process, the equilibrium pH values after the adsorption were also measured. To investigate the adsorption isotherms, a series of nitrate solutions with different concentrations [(40 to 160) mg N·L^{-1}] were kept in contact with 0.05 g hydrogels for 60 min at pH 6 to 7. The temperature effect on adsorption for determination of temperature dependence was studied for five temperatures: (30, 35, 40, 45, and 50) °C. In addition, the effects of ion strength prepared from analytical grade NaCl and coexisting competitive phosphate prepared from analytical grade KH_2PO_4 on the adsorption capacity were investigated.

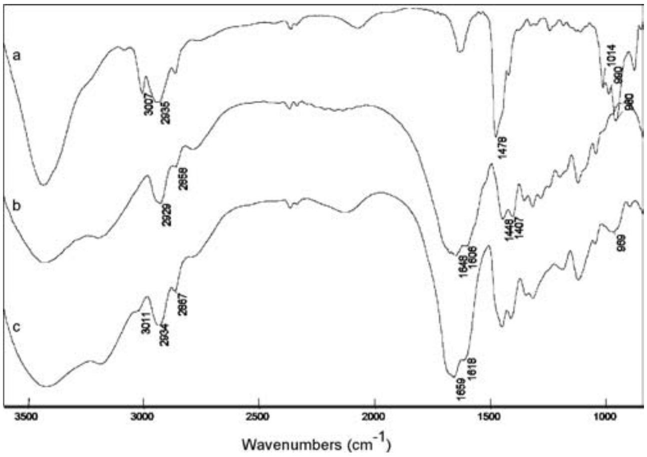

Figure 1. FTIR spectra of (a) PDMDAAC, (b) PAM, and (c) PDMDAAC/PAM with 50 % (by weight) PDMDAAC.

Desorption and Reusability. A series of 0.05 g hydrogels were contacted separately with 25 mL of 100 mg N·L^{-1} nitrate solution for 60 min and separated by direct filtration. Then, these nitrate-loaded hydrogels were put into 25 mL of solution with different pH values and agitated for 30 min at 30 °C/120 rpm. The quantity of desorbed nitrate was determined by the amount of nitrate in solution after the desorption experiment. The desorption ratio is determined as the ratio of the desorbed nitrate amount to that adsorbed. After desorption, the recovered hydrogel was washed with distilled water several times for another adsorption. Then, the reusability of the as-prepared hydrogel for nitrate adsorption was evaluated.

Characterization. FTIR was recorded on a Thermo Nicolet NEXUS TM spectrophotometer using KBr pellets in the range of 400 cm^{-1} to 4000 cm^{-1}. The Zeta potential of the adsorbent was measured using a Malvern Zetasizer Nano-ZS.

Results and Discussion

FTIR Analysis. The FTIR spectra of PDMDAAC, PAM, and PDMDAAC/PAM (50 % (by weight) PDMDAAC) are shown in Figure 1. The characteristic absorption bands of PDMDAAC around (3007 and 1478) cm^{-1} correspond to $-CH_3$ stretching and bending vibrations, respectively.[35] The presence of the absorption band at 3011 cm^{-1} in the cationic hydrogel validates the presence of this group in the adsorbent. On the other hand, the PDMDAAC spectrum shows a distinctive absorption band at about 1000 cm^{-1}, attributed to the presence of the quaternary amine group which can be observed in the spectrum of the cationic hydrogel. The PAM spectrum shows characteristic absorption bands at (1648 and 1606) cm^{-1} for C═O stretching and N−H deformation vibrations, and these bands are observed in the cationic hydrogel. All the information suggests that the PDMDAAC/PAM cationic hydrogel is formed.

Effect of PDMDAAC Content on Adsorption Capacity. The effects of PDMDAAC content on the adsorption capacity are shown in Figure 2. It is found that the adsorption capacity is (0.11, 0.32, 0.44, 0.48, and 0.16) mmol·g^{-1} for hydrogels with (0, 10, 25, 50, and 75) % (by weight) PDMDAAC, respectively.

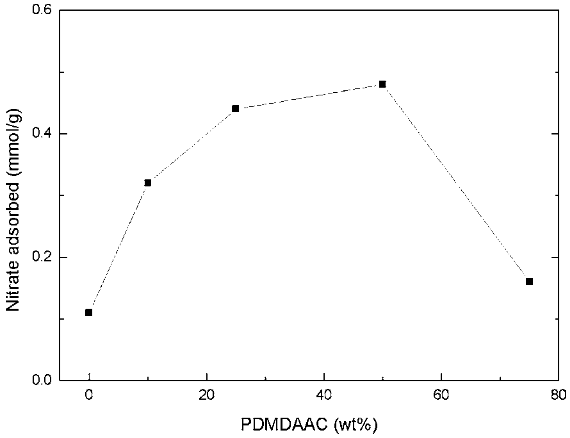

Figure 2. Adsorption capacity as a function of PDMDAAC content in the hydrogel. Adsorption conditions: $C_0 = 100$ mg N·L^{-1}, $t = 60$ min, $m/V = 2$ g·L^{-1}, $T = 30$ °C, natural pH.

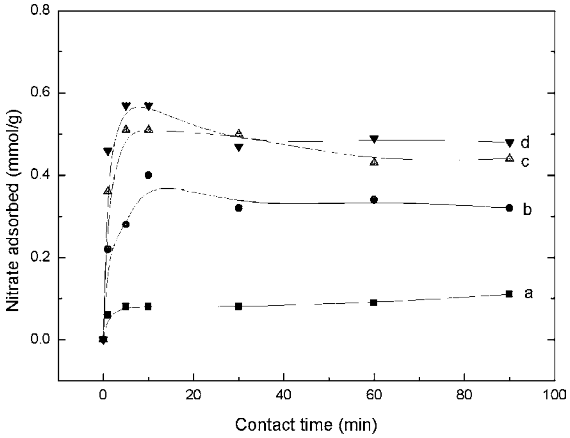

Figure 3. Adsorption kinetics of PDMDAAC/PAM with different amounts of PDMDAAC. Adsorption conditions: $C_0 = 100$ mg N·L^{-1}, $m/V = 2$ g·L^{-1}, $T = 30$ °C, natural pH. a, 0 % (by weight) PDMDAAC; b, 10 % (by weight) PDMDAAC; c, 25 % (by weight) PDMDAAC; d, 50 % (by weight) PDMDAAC.

That is, the adsorption capacity increases first with increasing PDMDAAC content until 50 % (by weight) beyond which a sudden decrease in the quantity of nitrate adsorption is found. During the preparation process, the hydrogel with higher PDMDAAC content got softer, and when 75 % (by weight) PDMDAAC was introduced into the hydrogel, the resulting product was in a form of a viscous liquid in which much cationic PDMDAAC may be dissolved in the solution during the post-treatment process, and consequently, the adsorption capacity for nitrate decreased.

Effect of Contact Time on Adsorption Capacity. The variation of nitrate adsorption as a function of contact time is shown in Figure 3. Preliminary adsorption tests show that the adsorption equilibrium can be achieved within 10 min for PAM, while for PDMDAAC/PAM, the adsorption capacity is shown to reach its highest within (5 to 10) min and then decrease until the adsorption equilibrium is obtained at the contact time of 60 min.

As-prepared cationic hydrogel can interact strongly with anionic species due to the swollen character and existence of positive charges within the polymeric networks. This nature makes possible the occurrence of two different mechanisms of nitrate removal: (i) adsorption by swelling and (ii) electrostatic interaction. The swollen polymeric networks can diminish the diffusion limitation during the adsorption, shortening the adsorption time to reach adsorption equilibrium. For the tests thereafter, stirring was continued for 60 min before aliquots were withdrawn and analyzed.

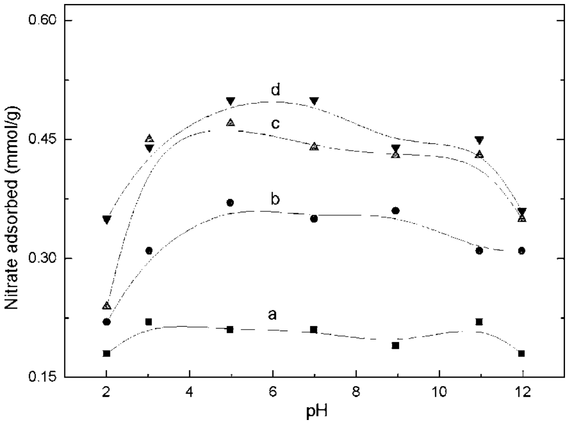

Figure 4. Adsorption capacity as a function of pH. Adsorption conditions: $C_0 = 100$ mg N·L^{-1}, $t = 60$ min, $m/V = 2$ g·L^{-1}, $T = 30$ °C. a, 0 % (by weight) PDMDAAC; b, 10 % (by weight) PDMDAAC; c, 25 % (by weight) PDMDAAC; d, 50 % (by weight) PDMDAAC.

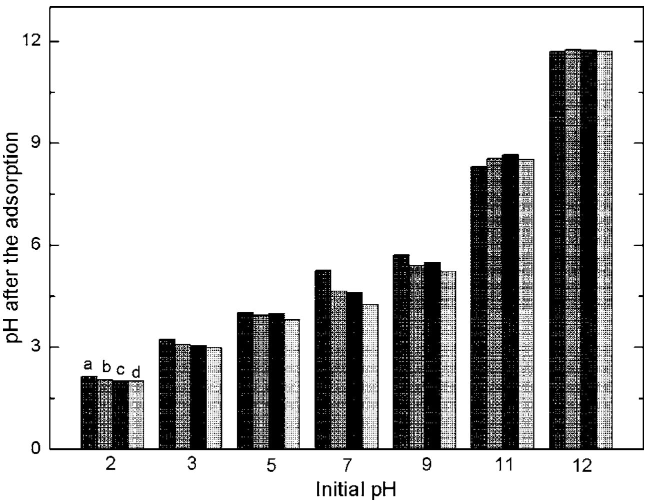

Figure 5. Relationship between equilibrium pH and initial pH values for nitrate adsorption. a, 0 % (by weight) PDMDAAC; b, 10 % (by weight) PDMDAAC; c, 25 % (by weight) PDMDAAC; d, 50 % (by weight) PDMDAAC.

Effect of pH Values on Adsorption Capacity. In general, the adsorption capacity of an ionic adsorbent is mainly governed by the number of charged groups on its backbone that are highly dependent on pH of a solution. To determine the effects of pH values on nitrate removal, a series of experiments were carried out at different pH values of 2 to 12, as shown in Figure 4. It is clear that the hydrogel with higher PDMDAAC content shows higher pH sensitivity, and at pH 5 these hydrogels [(25 and 50) % (by weight) PDMDAAC] give the highest adsorption capacities for nitrate. In all cases, the adsorption capacity is lower in strong acid (pH ≤ 3) or basic (pH ≥ 11) conditions. At lower pH or higher pH values, a large number of anions coexist with nitrate in the solution, such as Cl^- or OH^-, and as a consequence the competition between these ions would lower the adsorption capacity for nitrate. Nevertheless, the adsorption capacity is comparably high within the pH range of 5 to 9. After the adsorption, the equilibrium pH values are determined to be 3.8 to 5.7 when the initial pH value increases from 5 to 9, as shown in Figure 5. It seems that actually the equilibrium pH value serves as an important role during the whole adsorption

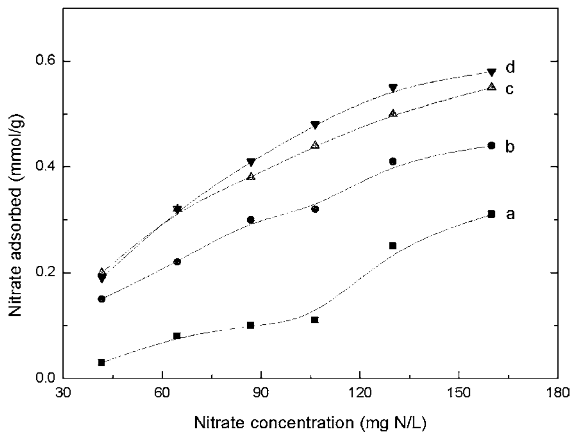

Figure 6. Adsorption isotherms of PDMDAAC/PAM with different amounts of PDMDAAC. Adsorption conditions: $t = 60$ min, $m/V = 2$ g·L^{-1}, $T = 30$ °C, natural pH. a, 0 % (by weight) PDMDAAC; b, 10 % (by weight) PDMDAAC; c, 25 % (by weight) PDMDAAC; d, 50 % (by weight) PDMDAAC.

process, which makes the occurrence of an approximate platform for the adsorption capacity within the pH range of 5 to 9.

Effect of Nitrate Concentration on Adsorption Capacity. As shown in Figure 6, the adsorption capacity for nitrate increases with increasing initial nitrate concentration. This is because more nitrate ions are available at higher initial concentration of nitrate, and higher nitrate concentration provides higher driving force for the anion from the solution to the polymeric network.

The fitting of adsorption isotherm equations to experimental data is often an important aspect of data analysis. In this study, three typical isotherms are used for fitting the experimental data

$$\text{Langmuir equation:} \quad q_e = \frac{q_m b C_e}{1 + bC_e} \tag{2}$$

$$\text{Freundlich equation:} \quad q_e = K C_e^{1/n} \tag{3}$$

$$\text{Redlich–Peterson equation:} \quad q_e = K_r C_e / (1 + a C_e^{\,b}) \tag{4}$$

where q_e is the equilibrium adsorption capacity of nitrate onto the adsorbent (mmol·g^{-1}); C_e is the equilibrium nitrate concentration (mmol·L^{-1}); and the other parameters are different isotherm constants. Due to the inherent bias resulting from linearization, alternative isotherm parameter sets can be determined by nonlinear regression. The nonlinear regression approach provides a mathematically rigorous method for determining isotherm parameters using the original form of the isotherm equation.

The estimated model parameters with the coefficient of determination (R^2) are summarized in Table 1. During the data regression analysis, it is found that the adsorption capacity for nitrate using PAM as the adsorbent cannot be described by the Langmuir model. For other hydrogels, the suitability of isotherms for fitting the experimental data is in the following order: Redlich–Peterson > Langmuir > Freundlich. However, the Redlich–Peterson isotherm should be subjected under the constraints $0 < b < 1$.[36] Considering these cases, it can be concluded that for PAM the adsorption data are well described by the Freundlich model, while for hydrogels with PDMDAAC, the Langmuir model can give better regression results. Gener-

Table 1. Estimated Isotherm Parameters for Nitrate Adsorption

PDMDAAC	Langmuir			Freundlich			Redlich–Peterson			
	q_m	b		K	n		a	b	K_r	
(%, by weight)	(mmol·g^{-1})	(L·mmol^{-1})	R^2	(L·g^{-1})		R^2	(L·mmol^{-1})		(L·g^{-1})	R^2
0	/	/	/	0.0057 ± 0.00258	0.6024 ± 0.0726	0.9798	21.32 ± 4.78	−1.753 ± 0.939	0.03652 ± 0.0248	0.9833
10	1.287 ± 0.325	0.0485 ± 0.0170	0.9793	0.0732 ± 0.0111	1.315 ± 0.126	0.9732	0.00087 ± 0.00480	2.441 ± 0.116	0.05231 ± 0.00617	0.9826
25	1.098 ± 0.0967	0.0938 ± 0.0140	0.9915	0.1236 ± 0.0135	1.572 ± 0.132	0.9786	0.02036 ± 0.0292	1.492 ± 0.493	0.08641 ± 0.0103	0.9941
50	1.408 ± 0.290	0.068 ± 0.0214	0.9754	0.1129 ± 0.0203	1.417 ± 0.175	0.9567	0.00012 ± 0.0003	3.363 ± 0.943	0.07354 ± 0.00292	0.9955

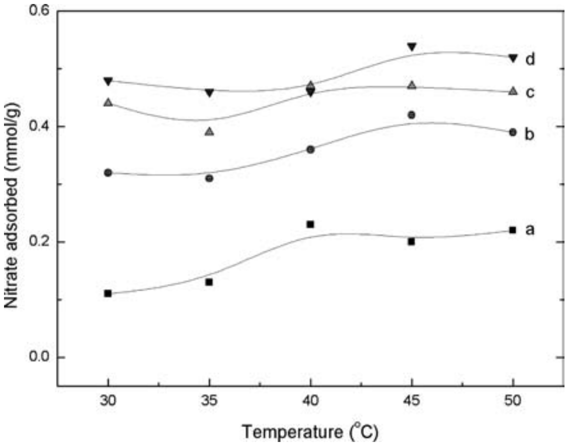

Figure 7. Effect of temperature on the adsorption capacity. Adsorption conditions: $C_0 = 100$ mg N·L^{-1}, $t = 60$ min, $m/V = 2$ g·L^{-1}, natural pH. a, 0 % (by weight) PDMDAAC; b, 10 % (by weight) PDMDAAC; c, 25 % (by weight) PDMDAAC; d, 50 % (by weight) PDMDAAC.

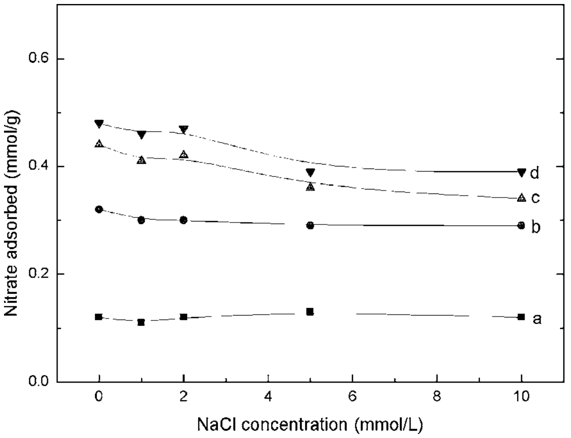

Figure 8. Effect of ion strength on the adsorption capacity. Adsorption conditions: $C_0 = 100$ mg N·L^{-1}, $t = 60$ min, $m/V = 2$ g·L^{-1}, $T = 30$ °C, natural pH. a, 0 % (by weight) PDMDAAC; b, 10 % (by weight) PDMDAAC; c, 25 % (by weight) PDMDAAC; d, 50 % (by weight) PDMDAAC.

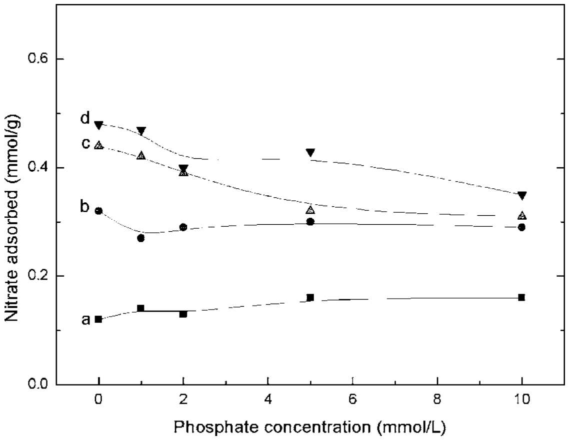

Figure 9. Effect of competitive phosphate ion on the adsorption capacity. Adsorption conditions: $C_0 = 100$ mg N·L^{-1}, $t = 60$ min, $m/V = 2$ g·L^{-1}, $T = 30$ °C, natural pH. a, 0 % (by weight) PDMDAAC; b, 10 % (by weight) PDMDAAC; c, 25 % (by weight) PDMDAAC; d, 50 % (by weight) PDMDAAC.

ally, at high adsorbate concentrations, the Langmuir isotherm can predict a constant monolayer adsorption capacity, as defined by q_m, which provides one of the most useful parameters in the literature for comparing adsorbent capacities. In this study, the monolayer adsorption capacity for nitrate is within the range of (1.1 to 1.4) mmol·g^{-1}, i.e., (68.2 to 86.8) mg·g^{-1} for cationic hydrogels, comparable with other reported adsorbents, such as Mg3P10-500 of 45.48 mg·g^{-1} and Zn3P10-500 of 34.34 mg·g^{-1}[24] and chitosan beads of 104.0 mg·g^{-1}.[25] For the Freundlich model, the K value is related to the adsorption capacity of an adsorbent, and the higher values for K indicate higher affinity of hydrogel for nitrate. It is observed from Table 1 that the hydrogels with PDMDAAC possess a higher adsorption capacity for nitrate. In addition, values of the empirical parameter $1/n$ in the range $0.1 < 1/n < 1$ indicate favorable adsorption. It can then be deduced that except for PAM the hydrogels with cationic PDMDAAC show a favorable adsorption for anionic nitrate.

Effect of Other Parameters on Adsorption Capacity. In this section, the effects of temperature, ion strength, and coexisting nutrient on the adsorption capacity are investigated, as shown in Figures 7 to 9. It seems that the adsorption capacity for nitrate is slightly higher at elevated temperature (> 40 °C). Though the adsorption capacity for nitrate changes obviously for hydrogel without PDMDAAC, the differences in adsorption capacity are not significant for hydrogels with PDMDAAC.

As shown in Figure 8, the hydrogel adsorbent with higher PDMDAAC content has higher sensitivity for changes in the ion strength. NaCl (2 mmol·L^{-1}) has no considerable effect on the adsorption capacity of as-prepared hydrogel adsorbent for nitrate, while at higher NaCl concentration (> 2 mmol·L^{-1}), an appreciable decrease in the adsorption capacity is observed for hydrogel adsorbents with higher PDMDAAC content. Generally, when the electrostatic interaction is attractive, an increase of ion strength will diminish the adsorption capacity, which is ascribed to the screening effect of the surface charge by the salt addition.[37] In this study, the electrostatic attraction between the adsorbent and adsorbate is responsible for the adsorption, and thus the screening effect of the surface charge would result in a decrease in the adsorption capacity.

Nitrate and phosphate are recognized as the two important nutrients involved in the eutrophication of water bodies. A competitive adsorption was conducted to observe the adsorption capacity of as-prepared hydrogel for nitrate in the presence of phosphate (Figure 9). It is found that hydrogels with fewer or without PDMDAAC have almost no response to the changes in the competitive phosphate concentration. However, the adsorption capacity of hydrogels with higher PDMDAAC shows a decreasing tendency with increasing phosphate concentration. In spite of the negative effects of ion strength and competitive anion, cationic hydrogel has good adsorption capacity for nitrate, and 0.39 mmol·g^{-1} and 0.35 mmol·g^{-1} can be achieved at higher-concentration saline and competitive ion solutions (10 mmol·L^{-1}), enabling it as a potentially feasible absorbent for nitrate removal from complex environments.

Adsorption Mechanism. As mentioned above, the adsorption mechanism of nitrate onto cationic hydrogel is proposed as follows: when as-prepared hydrogel is immersed into the nitrate solution, water molecules penetrate primarily into the hydrogel because of its hydrophilic networks, resulting in a dimensional increase of the polymeric network. During the swelling process, some nitrate ions take advantage of this opportunity to enter into the polymeric networks. In addition, a large number of positively charged adsorption sites at the hydrogel interior can attract and then trap many negatively charged nitrate ions. That is, during the whole adsorption process, two adsorption mechanisms occur: adsorption by swelling and by electrostatic interaction. The zeta potential and conductivity of these hydro-

Table 2. Zeta Potentials and Conductivities of the Hydrogels

PDMDAAC (%, by weight)	0	10	25	50
zeta potential (mV)	1.45	25.7	30.6	32.2
conductivity ($mS \cdot cm^{-1}$)	0.015	0.051	0.203	0.704

gels are listed in Table 2. As expected, increasing the PDMDAAC content in the hydrogel, the zeta potential and conductivity are observed to increase, testifying that electrostatic attraction plays an important role during the whole adsorption process, consistent with the presumption. Figure 10 shows the FTIR spectra of cationic hydrogel before and after the adsorption for nitrate. Compared with the spectrum before the adsorption, the spectrum after the adsorption shows an absorption band at 1382 cm^{-1} characteristic for nitrate, and no other differences in the spectrum are found, confirming also the presence of electrostatic attraction between the adsorbent and adsorbate.

Desorption and Reusability. A good adsorbent, in addition to its high adsorption capacity, must also exhibit a good regeneration ability for multiple uses. In this work, desorption of nitrate from the cationic hydrogel was studied using a series of solutions with different pH values as the eluents, as shown in Figure 11. In a stronger acid or basic media (pH $\leq$ 3 or pH $\geq$ 12), the nitrate ions adsorbed by the sample are desorbed efficiently (desorption ratio > 80 %). Desorption studies are helpful in elucidating the adsorption mechanism of an adsorption process. In this study, the strong acid or strong base can desorb the nitrate ion from the adsorbent, meaning that the electrostatic attraction is present between the adsorbent and adsorbate.[30] In addition, partial nitrate ions can be desorbed at the neutral condition (pH 5 to 7), arising from the adsorption by swelling. Subsequently, the reusability of PDMDAAC/PAM for nitrate adsorption was evaluated using 0.1 $mol \cdot L^{-1}$ NaOH as the desorbing agent. The results indicate that after five cycles of the adsorption−desorption process no obvious loss in adsorption capacity is observed, revealing a good reusability of the as-prepared hydrogel for nitrate adsorption.

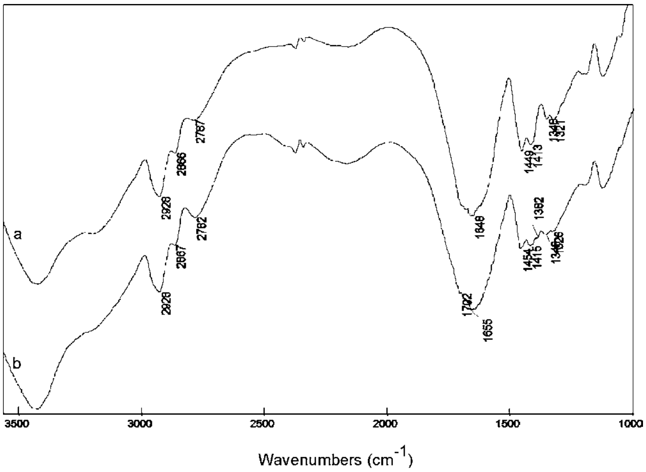

Figure 10. FTIR spectra of PDMDAAC/PAM (25 % (by weight) PDMDAAC) before (a) and after (b) the adsorption.

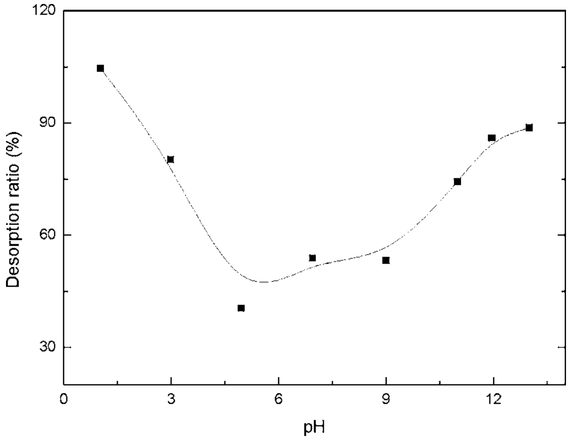

Figure 11. Desorption ratio at different pH values. Adsorption conditions: $C_0 = 100$ mg $N \cdot L^{-1}$, $t = 60$ min, $m/V = 2$ $g \cdot L^{-1}$, $T = 30$ °C. Desorption conditions: $t = 30$ min, $m/V = 2$ $g \cdot L^{-1}$, $T = 30$ °C.

Conclusions

In this study, a cationic hydrogel PDMDAAC/PAM was obtained and proved for its potential for nitrate removal on a laboratory scale. The adsorption capacity increases with increasing PDMDAAC content until 50 % (by weight) beyond which a sudden decrease is observed. After the initial increase, the adsorption capacity is shown to decrease, and at 60 min, the adsorption process reaches its equilibrium. As-prepared hydrogel had comparably high adsorption capacity within the pH range of 5 to 9, and the monolayer adsorption capacity is found to be (1.1 to 1.4) $mmol \cdot g^{-1}$. Higher temperature favors the adsorption for nitrate. The presence of ion strength and competitive phosphate ions can produce some negative effects on the adsorption capacity of hydrogels with higher PDMDAAC, but 0.39 $mmol \cdot g^{-1}$ and 0.35 $mmol \cdot g^{-1}$ can still be obtained at 10 $mmol \cdot L^{-1}$ saline and competitive ion. During the whole adsorption process, adsorption by swelling and adsorption by electrostatic interaction are considered to be the two main adsorption mechanisms, which are well testified by the zeta potential, FTIR spectra before and after the adsorption, and desorption studies. There are no doubts that as-prepared cationic hydrogel is promising in nitrate removal from aqueous solutions.

Literature Cited

(1) Ahlgren, S.; Baky, A.; Bernesson, S.; Norberg, A.; Norén, O.; Hansson, P.-A. Ammonium nitrate fertiliser production based on biomass-environmental effects from a life cycle perspective. *Bioresour. Technol.* **2008**, *99*, 8034–8041.

(2) Galvez, J. M.; Gomez, M. A.; Hontoria, E.; Gonzalez-Lopez, J. Influence of hydraulic loading and air flowrate on urban wastewater nitrogen removal with a submerged fixed-film reactor. *J. Hazard. Mater.* **2003**, *101*, 219–229.

(3) Shrimali, M.; Singh, K. P. New methods of nitrate removal from water. *Environ. Pollut.* **2001**, *112*, 351–359.

(4) Ghafari, S.; Hasan, M.; Aroua, M. K. Bio-electrochemical removal of nitrate from water and wastewater-A review. *Bioresour. Technol.* **2008**, *99*, 3965–3974.

(5) Fewtrell, L. Drinking-water nitrate, methemoglobinemia, and global burden of disease: a discussion. *Environ. Health Perspect.* **2004**, *112*, 1371–1374.

(6) Bastviken, S. K.; Weisner, S. E. B.; Thiere, G.; Svensson, J. M.; Ehde, P. M.; Tonderski, K. S. Effects of vegetation and hydraulic load on seasonal nitrate removal in treatment wetlands. *Ecol. Eng.* **2009**, *35*, 946–952.

(7) Zhu, X.; Choo, K.-H.; Park, J.-M. Nitrate removal from contaminated water using polyelectrolyte-enhanced ultrafiltration. *Desalination* **2006**, *193*, 350–360.

(8) Matos, C. T.; Sequeira, A. M.; Velizarov, S.; Crespo, J. G.; Reis, M. A. M. Nitrate removal in a closed marine system through the ion exchange membrane bioreactor. *J. Hazard. Mater.* **2009**, *166*, 428–434.

(9) Sahli, M. A. M.; Annouar, S.; Mountadar, M.; Soufiane, A.; Elmidaoui, A. Nitrate removal of brackish underground water by chemical adsorption and by electrodialysis. *Desalination* **2008**, *227*, 327–333.

(10) Banasiak, L. J.; Schäfer, A. I. Removal of boron, fluoride and nitrate by electrodialysis in the presence of organic matter. *J. Membr. Sci.* **2009**, *334*, 101–109.

(11) Park, J. B. K.; Craggs, R. J.; Sukias, J. P. S. Removal of nitrate and phosphorus from hydroponic wastewater using a hybrid denitrification filter (HDF). *Bioresour. Technol.* **2009**, *100*, 3175–3179.

(12) Saad, R.; Belkacemi, K.; Hamoudi, S. Adsorption of phosphate and nitrate anions on ammonium-functionalized MCM-48: Effects of experimental conditions. *J. Colloid Interface Sci.* **2007**, *311*, 375–381.

(13) Chatterjee, S.; HanWoo, S. The removal of nitrate from aqueous solutions by chitosan hydrogel beads. *J. Hazard. Mater.* **2009**, *164*, 1012–1018.

(14) Öztürk, N.; Bektaş, T. E. Nitrate removal from aqueous solution by adsorption onto various materials. *J. Hazard. Mater* **2004**, *B112*, 155–162.

(15) Zanota, M. L.; Heymans, N.; Gilles, F.; Su, B. L.; Frre, M.; Weireld, G. D. Adsorption isotherms of pure gas and binary mixtures of air compounds on faujasite zeolite adsorbents: Effect of compensation cation. *J. Chem. Eng. Data* **2010**, *55*, 448–458.

(16) Başçetin, E.; Atun, G. Adsorptive removal of strontium by binary mineral mixtures of montmorillonite and zeolite. *J. Chem. Eng. Data* **2010**, *55*, 783–788.

(17) Onyango, M. S.; Kuchar, D.; Kubota, M.; Matsuda, H. Adsorptive removal of phosphate ions from aqueous solution using synthetic zeolite. *Ind. Eng. Chem. Res.* **2007**, *46*, 894–900.

(18) Taleb, M. F. A.; Mahmoud, G. A.; Elsigeny, S. M.; Hegazy, E.-S. A. Adsorption and desorption of phosphate and nitrate ions using quaternary (polypropylene-*g-N*, *N*-dimethylamino ethylmethacrylate) graft copolymer. *J. Hazard. Mater.* **2008**, *159*, 372–379.

(19) Tian, Y. Characterization of nitrate ions adsorption and diffusion in P(DMAEMA/HEMA) hydrogels. *Chin. Chem. Lett.* **2008**, *19*, 1111–1114.

(20) Hamoudi, S.; Saad, R.; Belkacemi, K. Adsorptive removal of phosphate and nitrate anions from aqueous solutions using ammonium-functionalized mesoporous silica. *Ind. Eng. Chem. Res.* **2007**, *46*, 8806–8812.

(21) Mena-Duran, C. J.; Kou, M. R. S.; Lopez, T.; Azamar-Barrios, J. A.; Aguilar, D. H.; Domínguez, M. I.; Odriozola, J. A.; Quintana, P. Nitrate removal using natural clays modified by acid thermoactivation. *Appl. Surf. Sci.* **2007**, *253*, 5762–5766.

(22) Cengeloglu, Y.; Tor, A.; Ersoz, M.; Arslan, G. Removal of nitrate from aqueous solution by using red mud. *Sep. Purif. Technol.* **2006**, *51*, 374–378.

(23) Mishra, P. C.; Patel, R. K. Use of agricultural waste for the removal of nitrate-nitrogen from aqueous medium. *J. Environ. Manage.* **2009**, *90*, 519–522.

(24) Hosni, K.; Srasra, E. Nitrate adsorption from aqueous solution by M^{II}-Al-CO_3 layered double hydroxide1. *Inorg. Mater.* **2008**, *44*, 742–749.

(25) Chatterjee, S.; Lee, D. S.; Lee, M. W.; Woo, S. H. Nitrate removal from aqueous solutions by cross-linked chitosan beads conditioned with sodium bisulfate. *J. Hazard. Mater.* **2009**, *166*, 508–513.

(26) Kaşgöz, H.; Durmuş, A.; Kaşgöz, A. Enhanced swelling and adsorption properties of AAm-AMPSNa/clay hydrogel nanocomposites for heavy metal ion removal. *Polym. Adv. Technol.* **2008**, *19*, 213–220.

(27) Wang, X.; Zheng, Y.; Wang, A. Fast removal of copper ions from aqueous solution by chitosan-*g*-poly(acrylic acid)/attapulgite composites. *J. Hazard. Mater.* **2009**, *168*, 970–977.

(28) Wang, L.; Zhang, J.; Wang, A. Removal of methylene blue from aqueous solution using chitosan-*g*-poly(acrylic acid)/montmorillonite superadsorbent nanocomposite. *Colloids Surf., A* **2008**, *322*, 47–53.

(29) Karada, E.; Üzüm, Ö. B.; Saraydin, D. Swelling equilibria and dye adsorption studies of chemically crosslinked superabsorbent acrylamide/maleic acid hydrogels. *Eur. Polym. J.* **2002**, *38*, 2133–2141.

(30) Zheng, Y.; Zhang, J.; Wang, A. Fast removal of ammonium-nitrogen from aqueous solution using chitosan-*g*-poly (acrylic acid)/attapulgite composite. *Chem. Eng. J.* **2009**, *155*, 215–222.

(31) Zheng, Y.; Wang, A. Evaluation of ammonium removal using a chitosan-*g*-poly (acrylic acid)/rectorite hydrogel composite. *J. Hazard. Mater.* **2009**, *171*, 671–677.

(32) Zheng, Y.; Wang, A. Enhanced adsorption of ammonium using hydrogel composites based on chitosan and halloysite. *J. Macromol. Sci., Part A: Pure Appl. Chem.* **2010**, *47*, 33–38.

(33) Ren, J.; Ha, H. Study on interpenetrating polymer network hydrogel of diallyldimethylammonium chloride with kappa-carrageenan by UV irradiation. *Eur. Polym. J.* **2001**, *37*, 2413–2417.

(34) Zheng, L.; Xu, S.; Peng, Y.; Wang, J.; Peng, G. Preparation and swelling behavior of amphoteric superabsorbent composite with semi-IPN composed of poly(acrylic acid)/Ca-bentonite/poly(dimethyldiallylammonium chloride). *Polym. Adv. Technol.* **2007**, *18*, 194–199.

(35) Radian, A.; Mishael, Y. G. Characterizing and designing polycation-clay nanocomposites as a basis for imazapyr controlled release formulations. *Environ. Sci. Technol.* **2008**, *42*, 1511–1516.

(36) Kumar, K. V.; Porkodi, K. Comments on “adsorption of 4-chlorophenol from aqueous solutions by xad-4 resin: Isotherm, kinetic, and thermodynamic analysis”. *J. Hazard. Mater.* **2007**, *143*, 598–599.

(37) Lópes-Ramón, V.; Moreno-Castilla, C.; Rivera-Utrilla, J.; Radovic, L. R. Ionic strength effects in aqueous phase adsorption of metal ions on activated carbons. *Carbon* **2003**, *41*, 2020–2022.

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