

Rapid Removal of Cr(VI) Ions from Aqueous Solutions by the Macroporous Poly(*N*, *N'*-dimethylamino ethyl methacrylate) Hydrogels

Weixia Zhu, Hang Song, Kaifeng Du, Hao Zeng, Shun Yao

Department of Pharmaceutical & Biological Engineering, School of Chemical Engineering, Sichuan University, Chengdu 610065, People's Republic of China

Correspondence to: S. Yao (E-mail: youngsun9802@163.com)

ABSTRACT: To improve the adsorption ability of hexavalent chromium [Cr(VI)], the macroporous poly(*N*, *N'*-dimethylamino ethyl methacrylate) [poly(DMAEMA)] hydrogels were successfully fabricated by free-radical copolymerization in ethanol/water mixture using *N*, *N'*-dimethylamino ethyl methacrylate (DMAEMA) as the monomer, *N*, *N'*-methylenebisacrylamide (MBAA) as the cross-linker, and Na₂SO₄ solution as the porogen. The effects of various parameters, such as the concentration of Na₂SO₄ solutions, the dosage of MBAA, pH values, adsorption kinetic, and isotherm curves, were all investigated through systematic experiments. Scanning electron microscope (SEM) was employed to characterize the various pore structures. The experimental results showed that the influence of Na₂SO₄ solution to the pore morphology in the matrix was significant. The poly(DMAEMA) hydrogels can effectively adsorb Cr(VI) ions in aqueous media, and the macroporous structures could obviously improve the response rate and adsorption capacity. These results prove that the macroporous poly(DMAEMA) gels can be treated as a potential material for environmental pollution control. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: macroporous poly(DMAEMA); free-radical copolymerization; hexavalent chromium; Na₂SO₄ porogen

Received 22 February 2012; accepted 26 July 2012; published online

DOI: 10.1002/app.38409

INTRODUCTION

In recent years, the environmental pollution by heavy metals is increasingly severe along with the rapid development of industry. Various diseases can be caused because of their bioaccumulation and persistence in the food chain, especially chromium (Cr).¹ In the aquatic environment, chromium usually exists in trivalent [Cr(III)] and hexavalent [Cr(VI)] states, but the toxicity of Cr(VI) is almost 100 times than that of Cr(III).² Hexavalent chromium is easily absorbed by human body and can cause allergy, acute toxicity, carcinogenicity and so on.³ So the disposal of wastewaters with Cr(VI) is of great urgency. There are several techniques employed to remove Cr(VI) from the aqueous phase, such as chemical reduction, precipitation, ion-exchange, and sorption.⁴ At present, among all of these techniques, sorption has gained noticeable interest because of low cost and easy operation. Different kinds of adsorbents such as activated carbon, chitosan, zeolite, silica, and their derivatives⁵ have been widely researched, and the obvious advantage of adsorption amount promotes polymer-based adsorbents as potential substitutes of conventional adsorbents.⁶ However, poly(*N*, *N'*-dimethylamino ethyl methacrylate) [poly(DMAEMA)] hydrogel, as a new cationic polymer, has been scarcely any directly applied to adsorb Cr(VI).

Poly(DMAEMA) hydrogel, possessing of tertiary amino groups, is obtained by cationic polymerization which is a type of chain growth polymerization. In this polymerization, the cationic initiator transfers charge to the monomer which becomes reactive and then goes on to react similarly with other monomers to form a polymer.⁷ This kind of hydrogel has attracted considerable attention owing to its thermosensitivity and pH-sensitivity, but conventional hydrogels are limited by its slow swelling and deswelling rate in many applications. So many researchers have contributed to solve the problem with new modified hydrogels.^{8,9} Cheng et al. used 2-(dimethylamino)ethyl methacrylate modified with 1-bromoalkanes as the adsorbent for Cr(VI) and showed clearly that diffusion of Cr(VI) ion into the pores of the adsorbent controlled the adsorption rate.¹⁰ At present, some methods including preparation of comb-like hydrogels¹¹ and porous gels,^{12–14} have been used to improve the response rate. The results indicated that pore structures could efficiently improve the flaw of the slow swelling and deswelling rate. Inspired by this, macroporous poly(DMAEMA) hydrogels were prepared for improving the adsorption capacities of heavy metal ions.

Previously, it has been reported by us that Na₂SO₄ was employed as a solid template in the fabrication of macroporous

Table I. The Effect of MBAA on Swelling Ratio and the Amount of Cr(VI) Adsorbed

Code	DMAEMA mol/L	MBAA mol/L	Swelling ratio Times	Amount of Cr(VI) adsorbed mg/g
Poly 1	1	0.025	100.11	79.67
Poly 2	1	0.050	45.37	73.25
Poly 3	1	0.075	25.06	43.54
Poly 4	1	0.100	15.47	24.36

poly(GMA-EDMA) monolith.¹⁵ In this study, Na₂SO₄ was first used as liquid-solid porogen to synthesize the macroporous poly(DMAEMA), and the latter was also adopted to absorb Cr(VI) for the first time. The specific purposes of the study were to: (1) observe the influence of the liquid-solid porogen (Na₂SO₄) in the forming process of macropores to the morphology of the gel; (2) evaluate the feasibility of using poly(DMAEMA) to remove Cr(VI) from aqueous solution; (3) investigate the influence of amount of Na₂SO₄ to response rate and amount of Cr(VI) adsorption on the poly(DMAEMA).

MATERIALS AND METHODS

Materials

N, *N*'-Dimethylamino ethyl methacrylate (DMAEMA) monomer, *N*, *N*'-methylenebisacrylamide (MBAA) cross-linker, and azodiisobutyronitrile (ABN) initiator were purchased from Puguang industrial (Shanghai, China). K₂CrO₄ was obtained from Jingqiu chemistry factory (Beijing, China). Na₂SO₄ was provided by Hangjia Bio-Pharm (Sichuan, China). 1,5-Diphenylcarbazine was purchased from Kelong chemical reagent factory (Sichuan, China).

Preparation of Conventional and Macroporous Hydrogels

Poly(DMAEMA) hydrogels were prepared according to previous reports.^{14,16} The recipes of DMAEMA monomer and MBAA cross-linker were given in Table I. For each polymerization, solid Na₂SO₄ was dissolved with 18 mL distilled water to obtain a series of Na₂SO₄ solution with the mass concentration (0–12 wt %), and mixed with ethanol solution including DMAEMA, MBAA, and ABN. Then, the mixtures were poured into 6-mm tubes after being magnetically stirred in nitrogen atmosphere for 10 min, which were rapidly sealed and submerged in a thermostatic water bath for 3 h at 70°C. Finally, after rapid cooling to room temperature, the poly(DMAEMA) hydrogels were taken out and cut into cylinders with the diameter of 6 mm and the thickness of 3 mm for later evaluation. The gels prepared with 0, 4, 8, and 12 wt % Na₂SO₄ solution were marked as NP 0, NP 4, NP 8, and NP 12, respectively.

Morphology of the Hydrogels

The morphology of the gels was observed by the scanning electron microscope (SEM) (JEM-100CX-II, JEOL, Japan). First, the hydrogels swelled to equilibrium in distilled water at room temperature, and then were exchanged by ethanol with different concentrations to obtain dried gels. Finally, the samples were sputter-coated with gold and observed by SEM.

Static Adsorption of Cr(VI) Onto Hydrogels

A certain amount of K₂CrO₄ was diluted with redistilled water to 1 g/L as the stock Cr(VI) solution. pH value was adjusted by 1 mol/L HCl or 1 mol/L NaOH monitored by a pH meter (Shanghai Yulong Instrument CO., China). The concentration of Cr(VI) was determined by UV-Vis spectrophotometer (TU1810SPC, Puxitongyong Instrument CO., China) at 540 nm in the present of 1,5-diphenylcarbazine.

Measurement of Kinetic Adsorption Curve. Briefly as follows, 0.02 g of the conventional and macroporous hydrogels were subsequently added into the conical flasks containing 50 mL Cr(VI) solution with an initial concentration (*C*₀) of 150 mg/L and an initial pH value of 2. The conical flasks were placed in a shaking bed at 40°C. In every interval, 0.2 mL of the supernatant was periodically collected, and the concentration of samples (*C*_{*t*}, mg/L) was determined as described in "Static Adsorption of Cr(VI) Onto Hydrogels" section. The adsorption amounts (*Q*, mg/g) of the gels for the Cr(VI) were calculated according to eq. (1).

$$Q = \frac{V \times (C_0 - C_t)}{m} \quad (1)$$

where *V* (mL) and *m* (g) stand for the solution volume and the mass of the adsorbent, respectively.

The adsorption data were correlated with the adsorption kinetic models¹⁷:

Pseudo-first order kinetic model:

$$\log(Q_e - Q_t) = \log Q_e - \frac{K_1}{2.303} t \quad (2)$$

Pseudo-second order kinetic model:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{1}{Q_e} t \quad (3)$$

where *Q_e* and *Q_t* are the adsorption amounts of Cr(VI) for the gels at equilibrium (*e*) and other time (*t*), respectively, and *K*₁ (1/min) and *K*₂ (min g/mg) are the adsorption rate constants for each model.

Measurement of Adsorption Isotherm. In the procedure, 0.02 g of the conventional and macroporous hydrogels were subsequently placed into the conical flasks containing 50 mL of Cr(VI) solution with an initial pH value of 2 and different initial concentrations (*C*₀)(25–225 mg/L). The conical flasks were placed at 40°C for 4 h to reach equilibrium in a shaking bed. The Langmuir and Freundlich isotherm were used to fit the equilibrium data by using the following equations¹⁸:

Langmuir adsorption model:

$$\frac{C_e}{Q_e} = \frac{1}{K_1 Q_{\max}} + \frac{C_e}{Q_{\max}} \quad (4)$$

Freundlich adsorption model:

$$\log Q_e = \log KF + \frac{1}{n} \log C_e \quad (5)$$

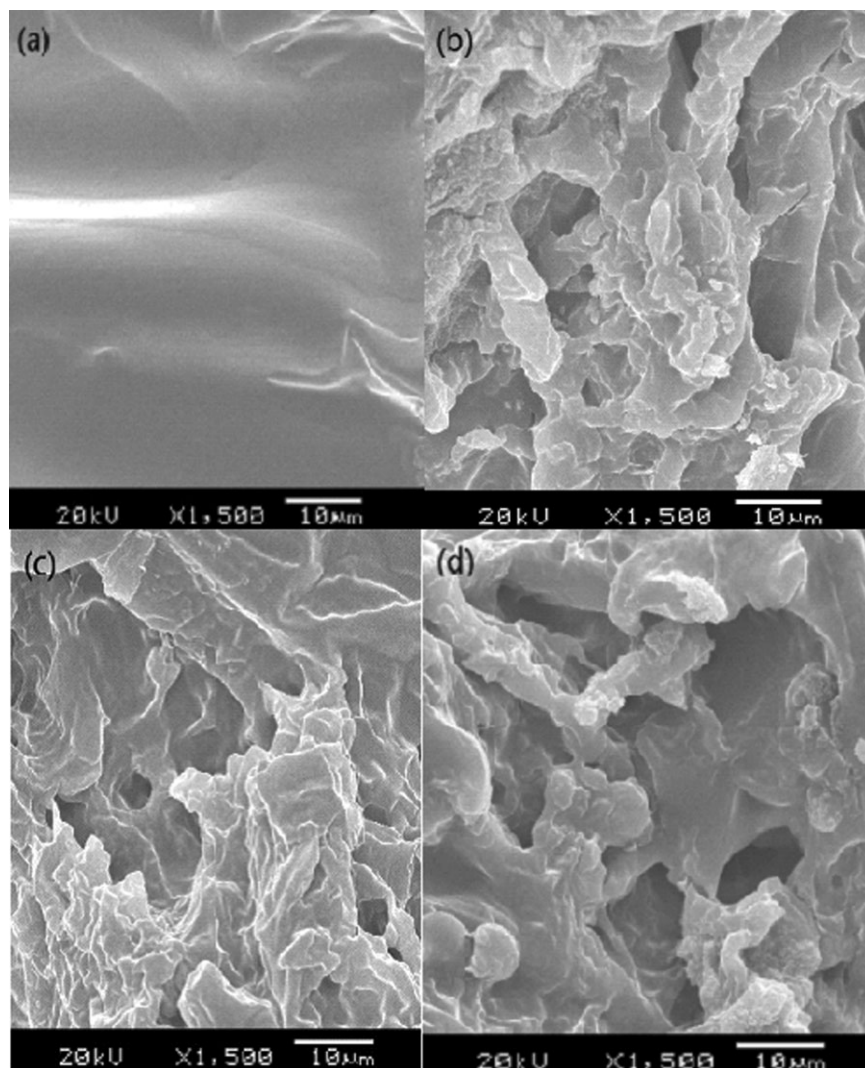


Figure 1. SEM images of the different hydrogels: (a) NP 0; (b) NP 4; (c) NP 8; and (d) NP 12.

where Q_{max} and Q_e (mg/g) are the adsorption capacity when the surface is completely covered with Cr(VI) ions and the adsorption amounts of Cr(VI) for the gels at equilibrium, respectively; C_e is the equilibrium concentration (mg/L); K_L , K_F , and n are three isotherm constants, respectively.

R_L is a dimensionless separation factor, which can be expressed by the following equation²:

$$R_L = \frac{1}{1 + K_L C_0} \quad (6)$$

where C_0 is the initial concentration of Cr(VI).

The valuable parameter R_L can be used to estimate the feasibility of the sorption process. The process is: (1) irreversible, when $R_L = 0$; (2) favorable, when $0 < R_L < 1$; (3) linear, when $R_L = 1$; (4) unfavorable, when $R_L > 1$.

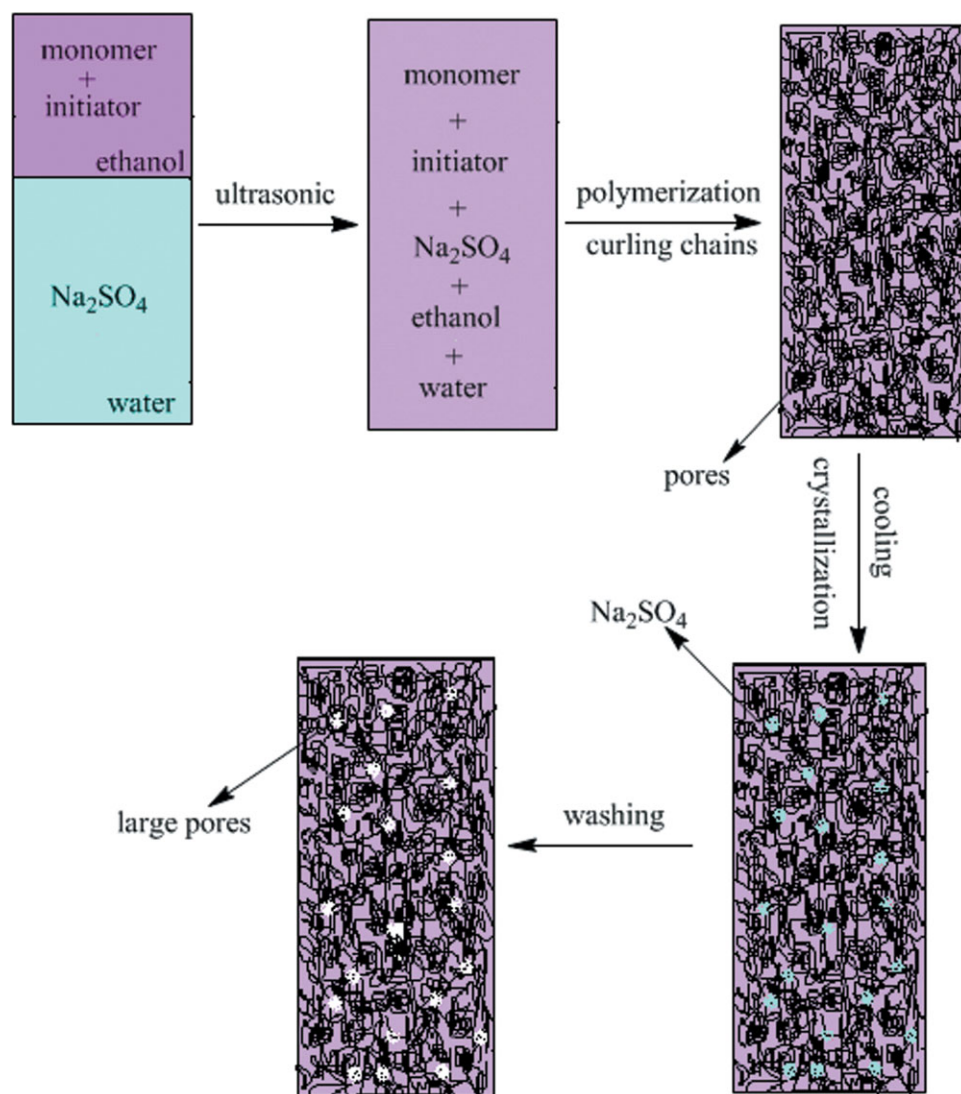
Effect of Initial pH. The effect of pH on sorption was studied by adding 0.02 g of the conventional and macroporous hydro-

gels into the labeled conical flask containing 50 mL of Cr(VI) solution with an initial concentration (C_0) of 150 mg/L and an initial pH (0.5–10). And then the conical flasks were placed at 40°C for 4 h to reach equilibrium in a shaking bed. When pH value was varied, the other conditions were kept constant.

Static Desorption of Cr(VI) From the Hydrogels

First, the sorbents contacted with 150 mg/L of Cr(VI) solution at pH 2.0 for 4 h to reach equilibrium. The adsorption amount of Cr(VI) Q_a was calculated by eq. (1). And then the sorbents were filtered and immersed in 10 mL of NaOH solution (pH = 10) or redistilled water for 20 h at room temperature. Finally, the Cr(VI) concentrations in the eluent were analyzed, and the desorption amount of Cr(VI) denoted by Q_d (mg/g). The desorption ratio was defined by the following equation:

$$\text{Desorption} = \frac{Q_d}{Q_a} \quad (7)$$



Scheme 1. Schematic illustration of the preparation of porous hydrogels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

Characterization of the Hydrogels

The solvent exchange was adopted to solve the problem that the structure collapses during the drying process of gel. Compared with the frozen-dry, this method could effectively avoid the pores left in the hydrogels after the ice crystals were sublimated.²⁰ Different morphology of the conventional poly(DMAEMA) gels and porous poly(DMAEMA) were observed by SEM [Figure 1(a–d)]. It was obvious that the surface morphology of the conventional poly(DMAEMA) gels was dense and smooth, but the topographies of the porous gels were rugged and rough. What's more, the volume of the pores got larger with the increasing concentration of Na₂SO₄. The reason was that Na₂SO₄ in the reaction medium could make the poly(DMAEMA) chains curl and arouse phase separation during the polymerization, and then porous structures formed.^{13,21} In addition, some large pores could be observed in Figure 1(b–d), which may be brought by the appearance of

Na₂SO₄ crystals during the cooling process. Schematic illustration of the preparation of porous hydrogels was shown in Scheme 1.

Effect of MBAA Cross-Linker

The effects of MBAA on swelling ratio and adsorption amount of Cr(VI) were shown in Table I. The results indicated that the swelling ratio and adsorption amount of Cr(VI) decreased significantly, with the increasing dosage of MBAA. This may be the reason that the DMAEMA monomer coagulates to form tighter internal structure in the high concentration of cross-linker,¹⁶ and this close inner structure made the hydrophilicity lower. This was unfavorable to the protonation of tertiary amino groups of poly(DMAEMA) and the adsorption sites of Cr(VI). But if the dosage of cross-linker was too low, the hydrogel would be too sticky to be handled easily. Considering the mechanical strength and adsorption amounts of Cr(VI), poly 2 was chosen for the following experiments.

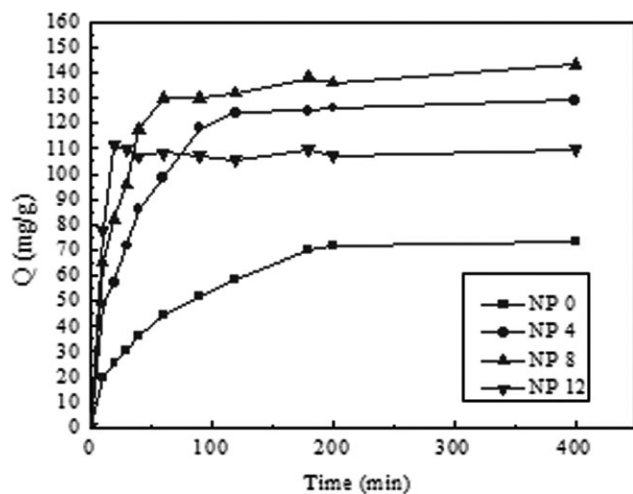


Figure 2. Kinetic adsorption curve of Cr(VI) onto four types of gels. Initial concentration of Cr(VI): 150 mg/L; dried gels: 0.02 g; temperature: 40°C; pH = 2.

Adsorption Kinetics of Cr(VI)

The influence of contact time to reach saturated adsorption is of great importance. Figure 2 shows the effect of contact time to amount of Cr(VI) adsorbed onto four types of adsorbents. It was found that the amount of the porogen Na₂SO₄ had significant effect on the adsorption behaviors between Cr(VI) and the sorbents. For Cr(VI) ions, all of the macroporous hydrogels were better than the conventional gels about both adsorption rate and adsorption amount. What's more, as the amount of the porogen increased, the adsorption rate of Cr(VI) increased. The similar Cr(VI) adsorption amounts were achieved in 200 min, 30 min, 20 min, 10 min on NP 0, NP 4, NP 8, NP 12, respectively. Compared with that of NP 12, the Cr(VI) adsorption rate on NP 0 increases 20 times. As mentioned above, Na₂SO₄ in the solution could make the poly(DMAEMA) chains curl to form porous structures. And that the volume of the pores was proportional to the concentration of Na₂SO₄. These pores could afford the channels for Cr(VI) ions, and then accelerate Cr(VI) ions into the interior of the gels. But it was also found that the adsorption amounts of Cr(VI) increased at first and then decreased with the increasing amount of Na₂SO₄. This phenomenon was probably because the increased surface area caused by the pore structure was beneficial for the adsorption amounts. But researches^{13,15} showed that the pore structure can

Table II. Kinetic Parameters for the Adsorption of Cr(VI) onto Four Types of Gels

Absorbent	Pseudo-first order		Pseudo-second order	
	K_1 (1/min)	R^2	K_2 (min g/mg)	R^2
NP 0	0.018	0.963	0.00027	0.994
NP 4	0.018	0.938	0.00034	0.998
NP 8	0.013	0.834	0.00051	0.999
NP 12	-	-	0.0075	0.997

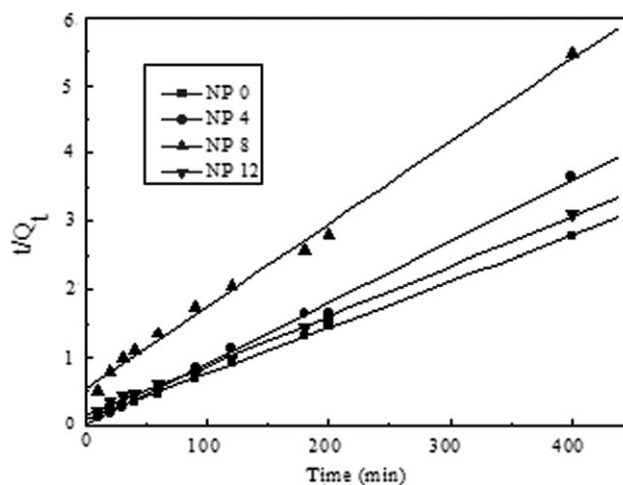


Figure 3. Pseudo-second order model for Cr(VI) adsorption onto four types of gels. Initial concentration of Cr(VI): 150 mg/L; dried gels: 0.02 g; temperature: 40°C; pH = 2.

decrease the mechanical strength of the substrate. After a period of time, the hyperosmotic pressure of the K₂CrO₄ solution tended to collapse the gel,⁸ and then some channels disappeared and the adsorption amounts decreased.

The experimental data were fitted with the models according to eqs. (2) and (3), and the adsorption kinetic parameters were summarized in Table II. It was found that the pseudo-second order model was more suitable for Cr(VI) adsorption onto poly(DMAEMA) compared with the pseudo-first order kinetic model. The pseudo-second order model for adsorption of Cr(VI) onto hydrogels was shown in Figure 3. The result showed that all correlation coefficients of the gels were over 0.99, and the adsorption data fit the pseudo-second order model very well, which has been widely applied to study the adsorption of heavy metals in recent years.

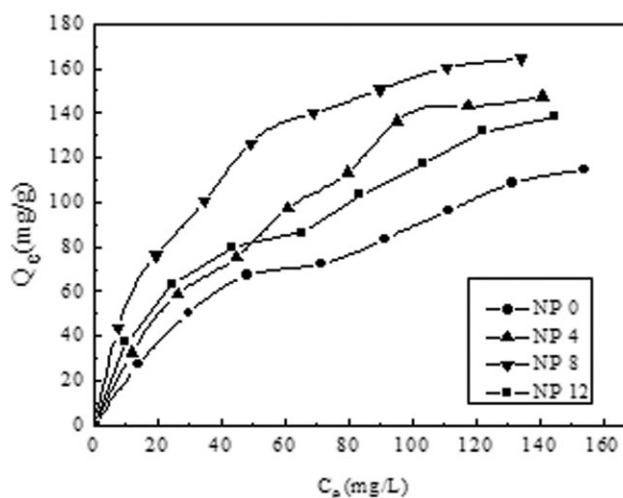


Figure 4. Adsorption isotherms of Cr(VI) onto four types of gels. Initial concentration of Cr(VI): 25–225 mg/L; dried gels: 0.02 g; temperature: 40°C; pH = 2.

Table III. Isotherm Parameters for the Adsorption of Cr(VI) onto Four Types of Gels

Absorbent	Langmuir isotherm			Freundlich isotherm			
	K_L	Q_{\max} (mg/g)	R^2	R_L	K_F (mg/g)	n	R^2
NP 0	0.013	165.29	0.974	0.339	7.017	1.803	0.978
NP 4	0.013	224.3	0.974	0.339	7.92	1.668	0.980
NP 8	0.033	200.4	0.998	0.168	19.85	2.250	0.966
NP 12	0.019	180.18	0.966	0.260	13.097	2.127	0.988

Adsorption Isotherm of Cr(VI)

Figure 4 shows the results of Cr(VI) adsorption equilibrium on four types of gels. It was found that the adsorption capacity of NP 8 was better than that of the others, up to 169.96 mg Cr(VI)/g of sorbents when the initial concentration of Cr(VI) was 225 mg/L, whereas it was only 43.63 mg/g at the initial concentration of 25 mg/L. These results indicated that the uptake of Cr(VI) was closely interrelated with the concentration. VEERA M.¹⁹ summarized the maximum adsorption capacity of kinds of different sorbents, which ranged from 3.3 to 241 mg/g. The value of this research was above the counter level compared with those reported values.

To obtain some further insight into the adsorption behavior and sorption mechanism, the adsorption data were fitted with the linear Langmuir and Freundlich isotherm models. The results were shown in Table III. The values of correlation coefficient R^2 were above 0.966, which indicated that both Langmuir and Freundlich were well-fitting with the experiment data, and the adsorption of Cr(VI) onto these gels strongly followed monolayer adsorption. The adsorption between the Cr(VI) anion and the cationic poly(DMAEMA) was a site-specific electrostatic interaction. In addition, the values of R_L at different gels were found in the range of 0 and 1, which indicated the favorable adsorption of Cr(VI) onto gels.

Effect of Initial pH Value on Adsorption Process

It is well known that Cr(VI) is in different forms at various pH values. H_2CrO_4 is the primary form at $pH < 1.0$;

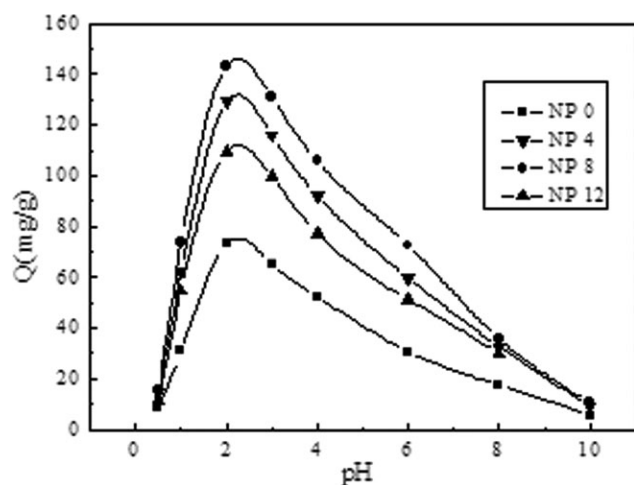


Figure 5. Effect of pH for Cr(VI) adsorption onto four types of gels. Initial concentration of Cr(VI): 150 mg/L; dried gels: 0.02 g; temperature: 40°C.

$HCrO_4^-$ and $Cr_2O_7^{2-}$ exist mainly at $1.0 < pH < 6.0$; and CrO_4^{2-} predominates at $pH > 6.0$. The forms of Cr(VI) determine the valence state, which is closely interrelated with the electrostatic interaction between the poly(DMAEMA) and Cr(VI), and then affect the uptake of Cr(VI) onto the sorbents.

The effect of pH value for Cr(VI) adsorption onto four types of gels was shown in Figure 5. With the increasing pHs, the adsorption amount of Cr(VI) increased in the pH range of 0.5–2, but decreased in the pH range of 2–10. It was found that the uptake of Cr(VI) could be effectively influenced by various pHs. For example, Cr(VI) uptake on the NP 8 was only 10.5 mg/g at $pH = 10$, but it was up to 143 mg/g at $pH = 2$. In addition, the sorbents could be used in a wide pH range, and the optimal pH is between 2 and 2.5, according to our study. These results were attributed mainly to electrostatic attraction between the sorbents and Cr(VI).¹ When the pH was less than 1.0, Cr(VI) was mainly in the form of H_2CrO_7 , which was unfavorably adsorbed onto the cationic polyelectrolyte; however, OH^- would compete with CrO_4^{2-} in the adsorption and deprotonation process occurs at pH above 6.0, which resulted in the decrease of the Cr(VI) adsorption amounts. The feature of sorbents provided a meaningful method for desorption Cr(VI) from the poly(DMAEMA).

In addition, pH values had an important effect on the morphology of the sorbents. In this experiment, the volume of the sorbents obviously shrank in acid Cr(VI) solution and swollen in basic solution. This phenomenon was opposite with that of sorbents in the aqueous solution which swollen in acid solution and shrank in basic solution.⁸ This opposite behavior was possibly caused by the poly(DMAEMA) curling when the electrostatic interaction between the cationic polyelectrolyte and Cr(VI) anion happened. What's more, after interacting with Cr(VI), the electrostatically repulsive property of poly(DMAEMA) decreased.

Table IV. The Rate of Desorption of Cr(VI) from the Sorbents by Different Eluents

Gels	Eluents	
	Distilled water	NaOH solution (pH = 10)
NP 0	75.3%	97.5%
NP 8	73.8%	95.3%

Static Desorption Studies

The desorption studies are very important for the economic benefit and resource utilization. Considering the foregoing experiment, NP 0 and NP 8 were chosen for the static desorption experiments. The results were shown in Table IV. The desorption rates of Cr(VI) from the NP 0 and NP 8 were quite similar, so the comparative data did not appear in this article. It was evidently found that the efficiency of Cr(VI) desorption by NaOH was clearly higher than that by distilled water. This result was in accord with the effect of pH as mentioned above. In addition, when the eluent was NaOH, the desorption efficiency from NP 0 was up to 97.5%, which was a little higher than 95.3% from NP 8. This may be because minority complicated pore structure was disadvantageous for Cr(VI) desorption.

CONCLUSIONS

The characteristics of the macroporous/conventional gels for Cr(VI) adsorption were studied systematically. On the basis of this study, the viability of directly using poly(DMAEMA) gels as the Cr(VI) adsorbent was confirmed, and the response rate and adsorption amount of hexavalent chromium on the poly(DMAEMA) gels could be effectively improved by the introduction of the pores. In comparison with conventional poly-(DMAEMA), the Cr(VI) adsorption rate of NP 8 increased 10 times and the adsorption amount was raised to 143 mg/g. The adsorption kinetics followed the pseudo-second order model. The adsorption isotherm indicated the adsorption of Cr(VI) onto these gels strongly follows site-specific monolayer adsorption. The desorption rate was still up to 95.3% after adding NaOH solution (pH = 10) in high absorbability for Cr(VI) ions. Thus, it can be concluded that macroporous poly (DMAEMA) is a potential useful sorbent for Cr(VI) ions, and the porous structure has facilitated its extensive application on the Cr(VI) wastewater treatment.

REFERENCES

1. Qiu, J.; Wang, Z.; Li, H.; Xu, L.; Peng, J.; Zhai, M.; Yang, C.; Li, J.; Wei, G. *J. Hazard. Mater.* **2009**, *166*, 270.
2. Selvi, K.; Pattabhi, S.; Kadirvelu, K. *Bioresour. Technol.* **2001**, *80*, 87.
3. Mohan, D.; Singh, K. P.; Singh, V. K. *J. Hazard. Mater.* **2006**, *135*, 280.
4. Zhao, L.; Sun, J.; Zhao, Y.; Xu, L.; Zhai, M. *Chem. Eng. J.* **2011**, *170*, 162.
5. Liu, M.; Liu, H.; Bai, L.; Liu, Y.; Cheng, J.; Yang, G. *J. Mater. Sci.* **2011**, *46*, 4820.
6. Marambio, O. G.; Pizarro, G. C.; Jeria, O. M.; Geckeler, K. E. *J. Appl. Polym. Sci.* **2009**, *113*, 1792.
7. Mark, H. F.; Bikales, N.; Overberger, C. G.; Menges, G.; Kroschwitz, J. *Encyclopedia of Polymer Science and Engineering*; John Wiley and Sons Inc.: New York, **1987**.
8. Tokuyama, H.; Ishihara, N. *React. Funct. Polym.* **2010**, *70*, 610.
9. Chen, J.; Eblevins, W.; Park, H.; Park, K. *J. Control. Release* **2000**, *64*, 39.
10. Cheng, Q.; Li, C.; Xu, L.; Li, J.; Zhai, M. *Chem. Eng. J.* **2011**, *173*, 42.
11. Kim, J. H.; Lee, S. B.; Kim, S. J.; Lee, Y. M. *Polym. Commun.* **2002**, *43*, 7549.
12. Ma, G.; Su, Z.; Omi, S.; Sundberg, D.; Stubbs, J. *J. Colloid Interf. Sci.* **2003**, *266*, 282.
13. Cheng, S.; Zhang, J.; Zhuo R. *J. Biol. Mater.* **2003**, *67*, 96.
14. Zhang, J.; Keller, Thomas F.; Bhat, R.; Garipcan, B.; Jandt, Klaus D. *Acta Biomater.* **2010**, *6*, 3890.
15. Du, K.; Yang, D.; Sun, Y. *J. Chromatogr. A* **2007**, *1163*, 212.
16. Hu, L.; Chu, L.; Yang, M.; Wang, H.; Niu, C. *J. Colloid Interf. Sci.* **2007**, *311*, 110.
17. Oshannessy, D. J.; Winzor, D. *J. Anal. Biochem.* **1996**, *236*, 275.
18. Choia, H.; Jungb, W.; Choa, J.; Ryua, B.; Yangc, J.; Baek, K. *J. Hazard. Mater.* **2009**, *166*, 642.
19. Boddu, V. M.; Abburi, K.; Talbott, J. L.; Smith, E. D. *Environ. Sci. Technol.* **2003**, *37*, 4449.
20. Zhao, Q.; Sun, J.; Lin, Y.; Zhou, Q. *React. Funct. Polym.* **2010**, *70*, 602.
21. Okay, O. *Prog. Polym. Sci.* **2000**, *25*, 711.