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Study on Adsorption Characteristics of Cr(VI) on Poly(*N,N'*-dimethylamino ethyl methacrylate) Hydrogels

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Poly(*N,N'*-dimethylamino ethyl methacrylate) [poly(DMAEMA)] hydrogel was synthesized and the adsorption characteristics of Cr(VI) ions on it were evaluated. A series of static adsorption experiments with Cr(VI) were carried out at different mass of cross-linker, temperature, pH and concentration of Cr(VI). It was found that the optimum pH was 2 and the maximum adsorption amount of Cr(VI) were up to 116 mg/g. The results of the adsorption kinetics and isotherms indicated the adsorption date were well fitted with the preudo-second order model and Langmuir model, respectively. The desorption experiments showed that more than 97.4 % Cr(VI) can be desorbed by NaOH (pH = 10). The present study proved that the poly(DMAEMA) gel was an excellent potential Cr(VI) adsorbent.

Key Words: Poly(N,N'-dimethylamino ethyl methacrylate), Cr(VI), Static adsorption, Desorption.

INTRODUCTION

Recently, the environmental pollution caused by heavy metal ions has become a significant issue owing to the factors of the whole ecosystem and economy. Among the heavy metal contaminations, chromium is one of major pollutants in industrial wastewater[1,2], which mainly comes from electroplating, tanning, steel fabrication, *etc*. It could bring risks to human health when its concentration is more than 0.1 g/L, such as severe burn, acute toxicity, carcinogenicity *etc.*[3,4]. Chromium frequently exists in both of trivalent [Cr(III)] and hexavalent [Cr(VI)] states in the aquatic environment, but the toxicity of Cr(VI) is almost 100 times than that of Cr(III)[5-7]. So dispose of Cr(VI) ion from wastewaters is of great urgency. Various techniques have been developed and employed to remove Cr(VI) from the aqueous phase, such as chemical reduction, precipitation, ion-exchange and (bio)sorption[8]. Among them, adsorption has been paid much more attention because of the low cost and no secondary pollution and different adsorbents including activated carbon, chitosan, zeolite, sillca and their derivatives, have been studied[2,5,8]. However, the adsorption capacity for Cr(VI) of these adsorbents is unsatisfactory, *e.g.* 20 mg/g for activated carbon, 39.7 mg/g for sawdust and 27.2 mg/g for chitosan[9]. In comparison, the adsorption amount of the polymer gels are much more, such as 147.5 mg/g for poly[2-(methacryloyloxy)ethyl]dimethyl-hexaneammo-nium bromide(PMHDAB) and 137.7 mg/g for poly(GMA-EGDMA) derivatives[1,10]. With the low cost, no secondary pollution and high efficiency advantages, the polymer gels are believed to be a kind of potential ideal adsorbent for Cr(VI).

Poly(*N,N'*-dimethylamino ethyl methacrylate)(poly (DMAEMA)) hydrogels, as a kind of temperature- and pH-sensitive polymers, have been applied in many fields, such as gene carriers[11,12], drug release[13], protein purification[14], adsorption of organic wastes[15] and pollutant treatment for metal ions[11,16]. Cheng *et al.*[1] has reported 2-(dimethylamino) ethyl methacrylate modified with 1-bromoalkanes as the adsorbent for Cr(VI) and acquired good results. However, poly(DMAEMA) gels with tertiary amino groups have been scarcely any directly applied to adsorb Cr(VI) as cationic polymer, which is easy to obtain and operate.

In this work, poly(*N,N'*-dimethylamino ethyl methacrylate) [poly(DMAEMA)] was synthesized directly by atom transfer radical polymerization. The characteristics of Cr(VI) ions onto this polymer were investigated in a wide range of conditions, such as treatment time, the amount of cross-linker, initial pH value and Cr(VI) concentration, and the different desorption conditions were also studied. Finally, the adsorption data were fitted with the kinetic and isotherm models to obtain some insight into the adsorption behaviour and related mechanism.

EXPERIMENTAL

N,N'-dimethylamino ethyl methacrylate (DMAEMA) monomer, *N,N'*-methylenebisacrylamide (MBAA) cross-linker and ammonium persulfate (APS) initiator were purchased from Puguang Industrial Co. Ltd., (Shanghai, China). K_2CrO_4 was purchased from Jingqiu Chemistry Factory. (Beijing, China). 1,5-Diphenylcarbazide was purchased from Kelong Chemical Reagent Factory. (Chengdu, China).

Preparation of hydrogels: Poly(DMAEMA) hydrogels were prepared according to the previous report[17]. Firstly, DMAEMA monomer and MBAA cross-linker were dissolved in 2 mL ethanol, and mixed with 18 mL distilled water containing ammonium persulfate initiator. The recipes of DMAEMA monomer and MBAA cross-linker were given in Table-1. Then, the mixtures were magnetically stirred in nitrogen atmosphere for 10 min at room temperature and poured into 6 mm tubes. The tubes were rapidly sealed and submerged in a thermostatic water bath for 3 h at 70 ºC. Finally, the tubes were immediately cooled 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.

Static adsorption of Cr(VI) onto hydrogels: A certain amount of K_2CrO_4 was diluted with distilled water to 1 g/L as the stock Cr(VI) solution. pH was adjusted by 1 mol/L HCl or 1 mol/L NaOH with a pH meter (Shanghai Yulong Instrument CO. Ltd., China). The concentration of Cr(VI) was determined by UV-VIS spectrophotometer (TU1810SPC, Puxi, China), the absorbance (Abs) of Cr(VI) solution was measured at 540 nm in the presence of 1,5-diphenylcarbazide.

In brief, the gels were added into the conical flasks containing 50 mL of Cr(VI) solutions with different initial concentrations (C_0) (25-225 mg/L) and initial pH values (0.5-10). The conical flasks were placed in a shaking bed at different temperature (25-70 ºC). 0.2 mL of the supernatant was periodically collected, and the concentrations of samples (C_t, mg/L) were determined as described above. The adsorption amounts (Q, mg/g) of the gel for the Cr(VI) were calculated according to the eqn. (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 absorbent, respectively.

Models for adsorption kinetics and isotherm: The adsorption kinetic data were correlated with the adsorption kinetic model[18]:

Pseudo-second order kinetic model:

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

where, Q_e and Q_t (mg/g) are the adsorption amounts of Cr(VI) for the gels at equilibrium and time t, respectively and K_2 (min g/mg) are the adsorption rate constant for the model.

The Langmuir isotherm was used to fit the equilibrium data by the following equation[2]:

Langmuir adsorption model:

$$\frac{C_e}{Q_e} = \frac{1}{K_l Q_{max}} + \frac{C_e}{Q_{max}} \quad (3)$$

where, Q_{max} and Q_e 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 is the isotherm constant.

R_L[5] is a dimensionless separation factor, which can be expressed by the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

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 $R_L = 0$; 2) Favourable $0 < R_L < 1$;
3) Linear $R_L = 1$; 4) Unfaborable $R_L > 1$.

Static desorption of Cr(VI) from the hydrogel: Firstly, the sorbents contacted with 150 mg/L of Cr(VI) solution at pH 2.0 for 4 h to reach equilibrium. The adsorption amounts of Cr(VI) Q_a were calculated by eqn. (1). And then the sorbents were filtered and immersed in a 50 mL conical flask which contained 10 mL of NaOH solution (pH = 10) or distilled water for 20 h at room temperature. Finally, the Cr(VI) concentrations in the eluents were analyzed, and Q_d (mg/g) denoted the desorption amount of Cr(VI). The rate of desorption was defined by the following equation:

$$\text{Desorption} = \frac{Q_d}{Q_a} \quad (6)$$

RESULTS AND DISCUSSION

Effect of MBAA cross-linker on adsorption process: The effects of MBAA on swelling ratio and adsorption amount of Cr(VI) are shown in Table-1. The results indicated that the swelling ratios and adsorption amount of Cr(VI) decreased clearly, with the increasing of MBAA dosage. This may be the reason that the DMAEMA monomer coagulates to form tighter internal structure due to the higher concentration of cross-linker[17] and this close inner structure makes the lowering of hydrophilicity. It is unfavourable to the protonation of tertiary amino groups of poly(DMAEMA), so the adsorption sites of Cr(VI) reduce. But if the dosage of cross-linker is too low, the hydrogel will be too sticky to be handled easily. Considering the mechanical strength and adsorption amount of Cr(VI), poly 2 was chosen for the present experiments.

TABLE-1
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

Adsorption kinetics of Cr(VI): The influence of contact time to reach saturated adsorption is of great importance and Fig. 1 shows the effect of contact time to amount of Cr(VI) adsorbed onto the poly 2. At the beginning of adsorption, the uptake of Cr(VI) increased quickly, after 200 min, the adsorption curve turns horizontal gradually. The result suggested that the process of Cr(VI) adsorption onto the poly(DMAEMA) includes two stages. At the first stage, the adsorption of Cr(VI) occurred on the surface of the gel and the uptake rate was rather high and at the second stage, the uptake took place into the inner surface of the porous gel *via* the diffusion of metal

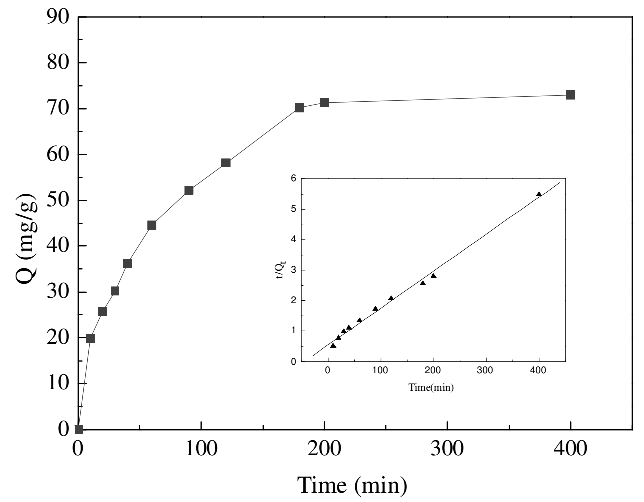


Fig. 1. Kinetic adsorption curve of Cr(VI) onto the poly 2. Initial concentration of Cr(VI): 150 mg/L; dried gels: 0.02 g; temperature: 40 ºC; pH = 2

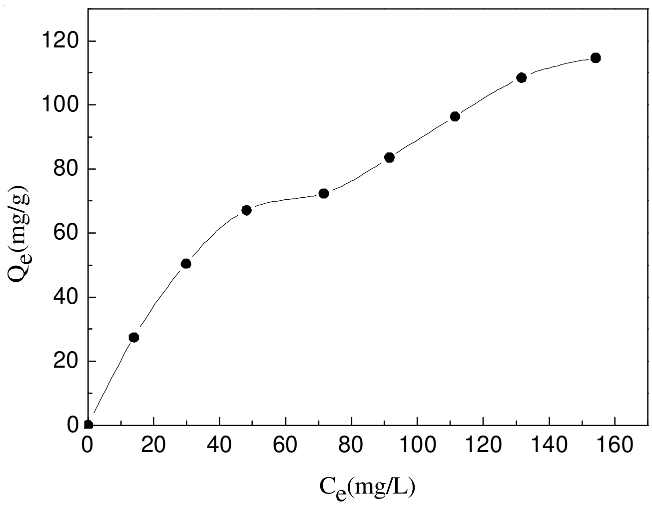


Fig. 2. Adsorption isotherms of Cr(VI) onto four types of gels. Initial concentration of Cr(VI): 25-225 mg/L; dried gels: 0.02 g; temperature: 40 ºC; pH = 2

ions into the polymer matrix and the process proceeded slowly[1,19].

The kinetic study of Cr(VI) adsorption onto the gels is significant, because the kinetic curve is related to the physical and/or chemical characteristics of the adsorbent and the mechanism of adsorption[20]. The experimental data were fitted with the models according to eqn. (2) and the adsorption kinetic parameters are summarized in Table-2. It is found that the preudo-second order model is well suited for Cr(VI) adsorption onto poly(DMAEMA). The result is consistent with the previous study[2].

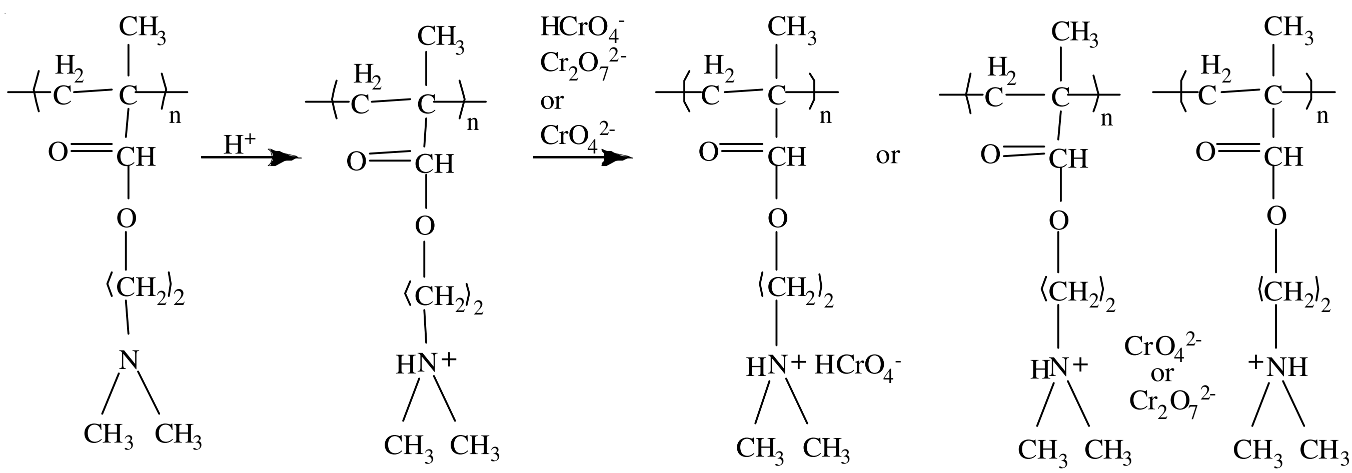
Adsorption isotherm of Cr(VI): Fig. 2 shows the results of adsorption equilibrium of Cr(VI) onto the gels. The effect of the initial concentration of Cr(VI) is studied in the range 25-225 mg/L at 40 ºC and pH 2. The result showed that the equilibrium adsorption capacities increase with the increase of initial concentrations of metal ions and the amount of the Cr(VI) adsorption is up to 116 mg/g with the initial concentration of Cr(VI) 225 mg/L. This performance is better than many other materials summarized by Boddu *et al.*[9].

The adsorption data were fitted with the linear Langmuir isotherm model to obtain some insight into the adsorption behaviour and the sorption mechanism. The results were shown in Table-2. The value of R^2 (0.974) indicated the adsorption between the gels and Cr(VI) fitted well with the Langmuir model and the adsorption of Cr(VI) onto the gel strongly followed site-specific monolayer adsorption. The process of Cr(VI) adsoption onto the poly(DMAEMA) was shown in **Scheme-I**. In addition, the value of R_L (0.013) indicated the favourable adsorption of Cr(VI) onto the gel.

Effect of initial pH on the adsorption process: The effect of pH on the adsorption process was shown in Fig. 3. It is obviously found that pH is closely related with the adsorption amounts of Cr(VI). With the enhancement of pH values, the

TABLE-2
KINETIC PARAMETERS FOR THE ADSORPTION OF Cr(VI) ONTO THE GEL

Poly2	Pseudo-first order		Pseudo-second order			Langmuir isotherm		
	K_1 (1/min)	R^2	K_2(min g/mg)	R^2	K_L	Qmax(mg/g)	R^2	R_L
	0.018	0.963	0.00027	0.994	0.013	165.29	0.974	0.339



Scheme-I: The process of the Cr(VI) adsorption onto poly(DMAEMA)

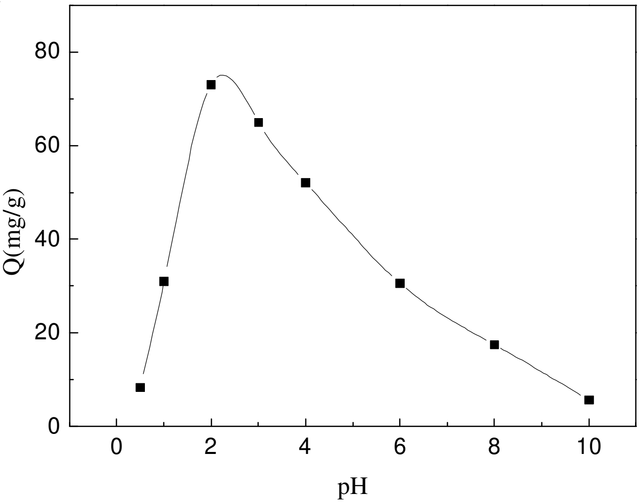


Fig. 3. Effect of pH for Cr(VI) adsorption onto the gel; Initial concentration of Cr(VI): 150 mg/L; dried gels: 0.02 g; temperature: 40 ºC

adsorption amounts increased from pH 0.5 to 2 and decreased from pH 2 to 10. The sorbent can be used in a rather wide pH range and the optimum pH value is between 2 and 2.5. The effect of pH might work with two factors: (a) pH can influence the protonation of poly(DMAEMA), which is important for the Cr(VI) adsorption. As mentioned above, the adsorption between the sorbents and Cr(VI) is mainly attributed to electrostatic attraction. So the low pH is beneficial for adsorption process. (b) pH value determines the states of Cr(VI), which is crucial to the Cr(VI) adsorption. It is well known that Cr(VI) is present in different forms at various pHs, which is H_2CrO_4 (pH < 1.0); $HCrO_4^-$ and $Cr_2O_7^{2-}$ (1.0 < pH < 6.0); CrO_4^{2-} (pH > 6.0). When the pH is less than 1.0, Cr(VI) is mainly in the form of H_2CrO_7, which is unfavourably adsorbed onto the cationic polyelectrolyte. However, OH^- is in competition with CrO_4^{2-} and deprotonation processes take place in the adsorbent at pH above 6.0, which lead to the decrease of the Cr(VI) adsorption amounts.

Effect of temperature on the adsorption process: Fig. 4 showed the effect of temperature on the adsorption process. It was found that the optimum temperature was 40 ºC. The high temperature can accelerate Cr(VI) ion contacting with the sorbent. However, as mentioned above, the Cr(VI) ion adsorption onto the gel is closely related to the protonation/ deprotonation of tertiary amino groups and the protonation process is exothermic[11]. So the increasing temperature is unfavourable to the uptake of Cr(VI). There exists an equilibrium at 40 ºC.

Static desorption studies: The desorption studies are important for the economic benefit and resource utilization. It has been confirmed that pH and the temperature can affect the Cr(VI) adsorption. Considering the economic benefit, the room temperature is adopted.

The results of Cr(VI) desorption from the gel was shown in Table-3. It is evidently found that the efficiency of Cr(VI) desorption by NaOH eluent, which is up to 97.5 %, is clearly higher than, which in the desorption by distilled water. The results proved that the poly(DMAEMA) gel is a kind of potential renewable material for treating Cr(VI) wastewater.

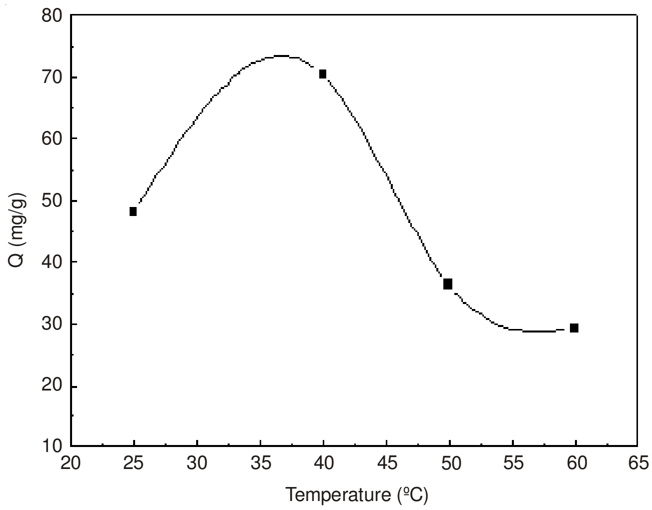


Fig. 4. Effect of temperature for Cr(VI) adsorption onto the gel. Initial concentration of Cr(VI): 150 mg/L; dried gels: 0.02 g; pH = 2

TABLE-3
RATE OF DESORPTION OF Cr(VI) FROM THE SORBENTS BY DIFFERENT ELUENTS

Poly 2	Eluents	
	Distilled water	NaOH solution (pH = 10)
	75.3 %	97.5 %

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