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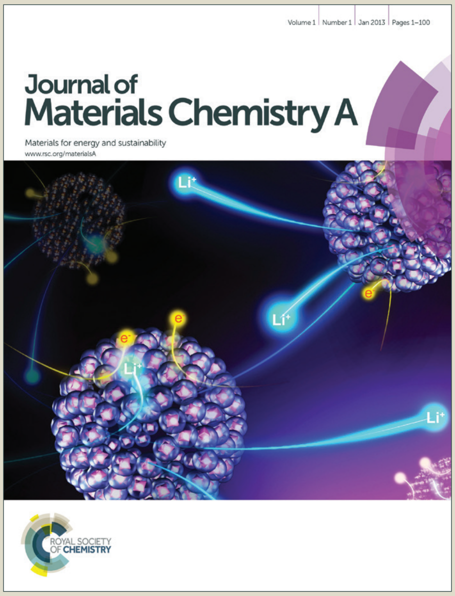
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PAPER

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Preparation and Adsorption Characteristic of Imprinted Polymer for Selective Removal of Cr(VI) Ions from Aqueous Solutions

Zhongqi Ren*, Delong Kong, Keyuan Wang, Weidong Zhang*

To achieve a fast adsorption rate and a high adsorption capacity in the selective adsorption of Cr(VI) from wastewater, a novel Cr(VI) ion imprinted polymer (Cr(VI)-IIP) was synthesized by bulk polymerization with ethyleneglycol dimethacrylate (EGDMA) as a crosslinking agent, azodiisobutyronitrile (AIBN) as an initiator, and acetone as a solvent. Eight functional monomers, including acidic, basic and neutral agents, were investigated in the synthesis of Cr(VI)-IIPs. The prepared Cr(VI)-IIP with 4-vinyl pyridine (4-VP) as functional monomer provided the highest adsorption capacity, which was characterized by the Fourier infrared spectroscopy, Zeta potential, BET and scanning electron microscopy. The influences of functional monomer amount, crosslinking agent, initiator, solvent, pH in aqueous solution, initial Cr(VI) concentration, and etc. on adsorption performance were studied. The adsorption process of Cr(VI)-IIP followed pseudo-second-order kinetic model and Langmuir adsorption isotherm model. The electrostatic interactions between Cr(VI) anion and the protonated N atoms of functional pyridine groups on prepared IIPs could enhance the adsorption capacity and adsorption rate. Under the optimal operating condition, the maximum adsorption capacity of prepared Cr(VI)-IIP with 4-VP was up to 338.73 mg/g, and the adsorption equilibrium was reached within 3 mins. The prepared Cr(VI)-IIPs also showed good selectivity, reusability and stability. The selectivity coefficient was up to 189.05 and 96.56 for Cr(VI)/Cu(II) and Cr(VI)/Cr(III), respectively.

1 Introduction

Chromium plays an essential role in our life and health as carbon, nitrogen, iron.[1] However, the excessive discharges of untreated industrial effluents containing Chromium from factories, such as electroplating, textile, steel works, wood preservation and artificial fertilizers, result in environmental pollution and ecological destruction.[2] There are several valence states of Chromium, such as +6, +3 and 0 valences. Chromium mainly exists in two oxidation states,[3] Cr(III) and Cr(VI), which are stable in aqueous environments. Relative to Cr(III), Cr(VI) is more toxic because of its strong oxidation property, which may trigger vomiting, gastric ulceration, lung cancer, and liver damage to human beings.[4] US EPA (U.S. Environmental Protection Agency) regulated that the concentration of Cr(VI) discharged to surface water must be lower than 0.05 mg/L, and the maximum contaminant level of total chromium is 0.10 mg/L.[5]

There are many methods to remove Cr(VI) from industrial wastewater, including precipitation by chemical or electrochemical reduction, ion exchange resin, membrane separation, adsorption, and etc. Among them, adsorption process is the most popular method to remove Cr(VI) from aqueous solution because of its high efficiency, low-cost, easy operation, and stable regeneration ability. Many types of materials had been reported as adsorbents for the removal of Cr(VI), including activated carbon,[6] chitosan,[7] fly ash,[8] saw dust,[9] magnetic nanocomposites,[10,11] wool and other low cost adsorbents.[12-14] Especially, Guo and Wei et al. have developed many high redox potential magnetic nanoadsorbents for the removal of Cr(VI), including magnetic carbon nanocomposite fabrics[15], magnetic graphene nanocomposites[16], magnetic polyaniline polymer nanocomposites[17], magnetic carbon nanocomposites[18] and carbon-encapsulated magnetic nanoparticles[19], which showed a good adsorption ability and efficiency for Cr(VI) removal. Although these adsorbents have good adsorption performance, their selectivity of adsorption is relatively poor. For a adsorption process, Cr(VI) and other ions, such as Cr(III), Cu(II), Pb(II), Ni(II), and Zn(II),[8] would be adsorbed together, which would inevitably require complex separation procedure and high operation cost for further disposal. It is necessary to find more efficient adsorbents with

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Electronic supplementary information (ESI) available: Effect of amount of acetone on the adsorption; Plots for pseudo-first-order kinetic (a) and pseudo-second-order kinetic (b) models; Simulation for adsorption of Cr(VI)-IIP using Langmuir model (a) and Freundlich model (b); Stability of Cr(VI)-IIPs

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high adsorption capacity and fast adsorption rate for the removal of Cr(VI) from wastewater.

Molecular imprinted technique (MIT) is a polymerizing technique to produce molecular recognition materials with high selectivity and affinity based on the template of particular target molecule.[20] Wulff et al.[21] completed the first covalent imprinted experiment in 1973, which made a breakthrough in MIT process. In 1994, the non-covalent interactions were first used for the synthesis of theophylline molecularly imprinted polymer by Mosbach.[22] Then, MIT got a rapid development.

Ion imprinted technology is an important branch of MIT. In the preparation of ion imprinted polymers (IIP), one target ion was picked as the template to form a pre-polymer with functional monomers through electrostatic interaction or coordination bond, then polymerization was conducted with crosslinking agent, and rigid polymers with specific recognition sites were obtained after the template ion was removed.[23] Nishide et al [24] first reported several metal ion imprinted polymers could be used as templates, i.e. Cu(II), Zn(II), Co(II), Ni(II), Hg(II) and Cd(II). However, their adsorption rate and capacity should be improved for industrial applications.

Currently, many applications of ion imprinted polymers (IIPs) for Cr(VI) removal have been reported. Pakade et al.[25] synthesized ion-imprinted polymers for the selective removal of Cr(VI) from other metal ions. Their adsorption capacity was 37.58 mg/g, and the selectivity for other ions was unsatisfied. Bayramoglu et al[26] prepared a high-performance Cr(VI) ion imprinted polymer, but the maximum adsorption capacity of IIPs was only about 170 mg/g, meanwhile the adsorption rate was low. Li et al[27] prepared IIP-PEI/SiO_2 for the adsorption of Cr(VI) by surface imprinting. The adsorption equilibrium time was 2h, and the selectivity coefficient for PO_4^{3-} was only 12.23.

The objective of this work is to prepare a novel kind of Cr(VI)-imprinted polymer with large adsorption capacity and high adsorption rate. In this paper, Cr(VI)-imprinted polymer was synthesized by bulk polymerization, and eight functional monomers was investigated. The effects of parameters on the adsorption performance, such as functional monomer, crosslinking agent, initiator, solvent, initial pH in the aqueous solution, initial concentration of Cr(VI), selectivity, stability and reusability, etc. were studied. The adsorption isotherm and kinetic models were also discussed.

2 Materials and method

2.1 Materials and apparatus

Ethyleneglycol dimethacrylate (EGDMA), 4-vinyl pyridine (4-VP, Alfa-L13316), 2-vinylpyridine (2-VP), N-Vinyl-2-pyrrolidone (NVP), 1-vinylimidazole (1-VI), N,N-diethyl aminoethyl methacrylamide (DEAEM), methacrylic acid (MAA), acrylamide (AM) and 2-hydroxyethyl methacrylate (2-HEMA) were analytical grade reagents from Sinopharm Chemical Reagent Beijing Co., Ltd. Polymerization inhibitors, azodiisobutyronitrile (AIBN), were from Tianjin Jinke chemical reagent plant. 1,5-diphenylcarbazide and all other chemicals were analytical reagents and purchased from Beijing chemical factory. The Cr(VI) aqueous solution was prepared by dissolving potassium dichromate in deionized water. Copper(II) aqueous solutions were prepared by cupric chloride ($CuCl_2·2H_2O$). Deionized water was used to prepare all solutions. The polymer morphology was evaluated by SEM using a JSM-300LV microscope (JEOL, Tokyo, Japan). Zetasizer Nano-Zeta potential analyzer (Malvern Instrument Company, UK) was employed to obtain its zeta potential curve. STA449 thermogravimetric analyzer (TGA, Netzsch Company, German) was used to determine its thermo-stability. UV-Vis spectrophotometer (UV-1800, Shimadzu Corporation) was used to monitor the Cr(VI) concentration in aqueous solutions. A pH-meter (Denver UB-7) was used to adjust the acidity of aqueous solutions.

2.2 Synthesis of Cr(VI)-imprinted polymer

Synthesis procedure: A certain amount of functional monomers were dissolved into 10mL of acetone, and 1.0mL of 5,000mg/L Cr(VI) anions solution was added dropwise into this solution with continuous stirring at room temperature for 1h. Then, the solution was slowly transferred drop by drop into a conical flask containing a mixture of 50mg AIBN and 6mmol EGDMA. After 15mins, the mixture was purged with nitrogen for 10mins to remove dissolved oxygen, and transferred into sampling bottles and sealed. These bottles were kept at 60°C for 24h.

Elution procedure: The resulting polymer was crushed, ground in a mortar and subsequently sieved. In order to remove the Cr(VI) ions confined in the selective cavity of the polymer, successive washings with 0.1 mol/L NaOH aqueous solution were performed and simultaneously monitored by UV. After complete extraction, the polymer was exhaustively washed with deionized water and dried at 50 °C.

2.3 Adsorption experimental procedures

Batch adsorption experiments were carried out by mixing 0.1g Cr(VI)-IIP particles into 100mL Cr(VI) solution, whose pH was adjusted by HCl and NaOH, and magnetically stirred throughout the adsorption process at 25°C. The concentration of Cr(VI) was determined by Diphenylcarbazide-spectrophotometry method.[28]

The adsorption capacity of Cr(VI)-IIPs was calculated by the following equation,

$$Q = \frac{(C_0 - C_f)V}{m} \tag{1}$$

where Q represents the adsorption capacity of polymers, mg/g. C_0 and C_f are the initial and final concentrations of metal ion in aqueous solution, mg/L, respectively. V is the volume of aqueous solution, L. m is the weight of the polymers added into the solution, g.

The selectivity experiments were conducted in a batch system by putting 0.1g Cr(VI)-IIPs into 100.0mL aqueous solution containing 200.0mg/L of Cr(VI)/Cu(II) or Cr(VI)/Cr(III), stirred magnetically during the adsorption at pH 2.0 at 25°C. The distribution ratio, the selectivity factor and the relative selectivity factor were calculated using the following equations,

$$K_d = \frac{C_0 - C_f}{C_f}(V / m) \tag{2}$$

$$k = \frac{K_d(\mathrm{Cr(VI)})}{K_d(\mathrm{M})} \tag{3}$$

$$k' = \frac{k_{\mathrm{imprinted}}}{k_{\mathrm{non\text{-}imprinted}}} \tag{4}$$

where K_d is distribution ratio, M represents other competitive metal ions, k and k' are selectivity factor and relative selectivity factor, respectively.

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3 Results and discussion

3.1 Effect of functional monomer

Functional monomers play an important role in the adsorption performance of IIPs. The selected functional monomer should have interaction with template molecule and good polymerization performance with crosslinking agent. For the preparation of metal ion imprinted polymers, the selected functional monomer should have the unsaturated double bond for the polymerization.[13] Usually, for non-covalent ion imprinted polymer, the functional monomers could be divided into three categories: acidic, basic and neutral agents.[29] In this work, in order to get a Cr(VI)-IIPs with high adsorption capacity and fast adsorption rate, eight monomers, including 4-vinylpyridine (4-VP), 2-vinylpyridine (2-VP), N-Vinyl-2-pyrrolidone (NVP), 1-vinylimidazole (1-VI), N,N-diethyl aminoethyl methacrylamide (DEAEM), methacrylic acid (MAA), acrylamide (AM), and 2-hydroxyethyl methacrylate (2-HEMA), were studied for the synthesis Cr(VI)-IIPs. As shown in Fig. 1, among these monomers, the first five were basic agents, the sixth one was acidic agent, and the other two were neutral agents. Species and amount of other components of the synthesis process were listed in Table 1 (IIP1).

Table 1 Synthesis conditions of Cr(VI)-IIPs

	Template		Functional monomer	Crosslinking agent	Initiator	Solvent
	Concentration of Cr(VI)×10^{-3}/(mg/L)	Volume of Cr(VI)/(mL)	/mmol	EDGMA/mmol	AIBN/mg	Acetone/mL
IIP1	5.0	1.0	~	6.0	50.0	10.0
IIP2	5.0	1.0	12.0	~	50.0	10.0
IIP3	5.0	1.0	12.0	6.0	50.0	~
IIP4	5.0	1.0	12.0	6.0	~	10.0
IIP5	5.0	1.0	12.0	6.0	50.0	10.0

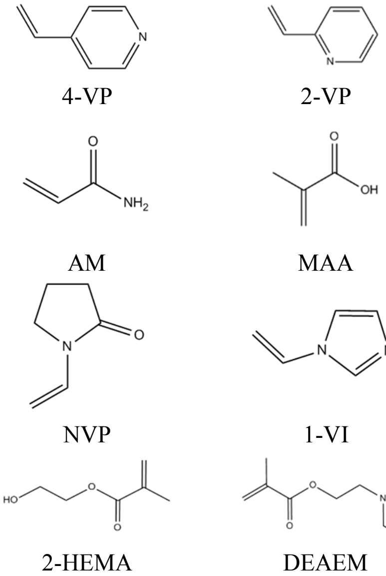

Fig. 1 Molecular formula of functional monomers

The adsorption experiments were conducted at 25°C and aqueous solution pH of 2.5. The initial Cr(VI) concentration was 200.0 mg/L. As shown in Fig. 2, for all prepared Cr(VI)-IIPs with selected functional monomers, the adsorption equilibrium were reached within 3 mins. But the adsorption characteristics of these prepared adsorbents were significant different. Adsorption capacity of polymers synthesized by MAA、AM and 2-HEMA were evidently lower than others, only 2.0 mg/g to 4.0 mg/g. It maybe because Cr(VI) in aqueous solution was acidic. For acidic functional monomer of MAA and neutral functional monomers of AM and 2-HEMA, the stable polymerization complex could not formed between template and functional monomer, and the prepared polymers had few specific Cr(VI) binding cavities. On the contrary, for the weak basic functional monomers of 4-VP, 2-VP, NVP, 1-VI and DEAEM, the polymerization complex had more stable structures, and the specific binding cavities could remain in the prepared IIPs, then the adsorption capacity was higher. The Cr(VI)-IIPs synthesized with 4-VP had the highest adsorption capacity among them. The formations of Cr(VI)-IIP with 4-VP and non-imprinted polymer (NIP) were determined by FTIR spectroscopy. The IR spectra showed that both IIP and NIP had a similar backbone as shown in Fig. 3. The Cr(VI)-IIP with 4-VP has the characteristic stretching vibration band at 3400-3500 cm^{-1} for -OH belongs to crosslinking agent, EGDMA , stretching vibration band at 2937.0 cm^{-1} for C-H, and at 1726.0 cm^{-1} for C=O, also belongs to EGDMA. The peak at 1600.0 cm^{-1} represents the 4-VP functional groups. A new band was observed at 1363.4 cm^{-1} which could be assigned to the characteristic stretching vibration of the pyridine group after the complexation of Cr(VI) anions.

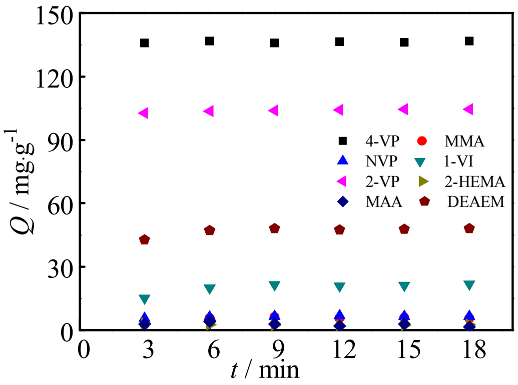

Fig. 2 Effect of functional monomers on the adsorption (Sample volume: 100mL, Cr(VI) concentration: 200 mg/L, pH=2.5, T=25°C)

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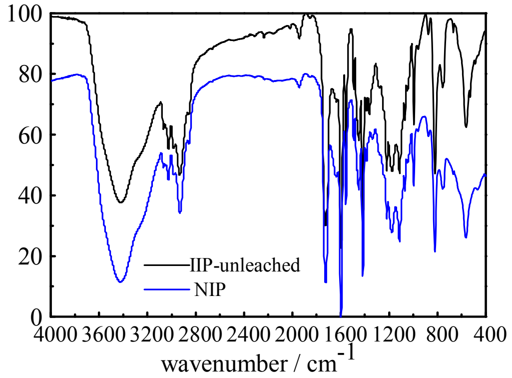

Fig. 3 FTIR curves of Cr(VI)-IIP (unleached) and NIP

The amount of functional monomer also has important influence on the adsorption performance of prepared Cr(VI)-IIPs. The effect of the amount of 4-VP was investigated. The synthesis conditions were listed in Table 1 (IIP1). The adsorption experiments were conducted in aqueous solution with the pH of 2.5 at 25°C, the initial Cr(VI) concentration was 200.0 mg/L. As can be seen in Fig. 4, the adsorption capacity of Cr(VI) increased with the increase of additional amount of 4-VP. It was mainly because more binding cavities could be formed in the prepared polymer with the increase of additional amount of 4-VP. The adsorption capacity reached its maximum value at the amount of 12.0mmol of 4-VP. Then adsorption capacity decreased when additional amount exceeded 12.0mmol.

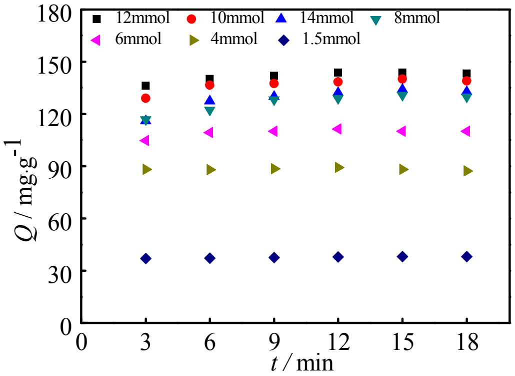

Fig. 4 Effect of the amount of 4-VP on the adsorption (Sample volume: 100mL, Cr(VI) concentration: 200 mg/L, pH=2.5, *T*=25°C)

3.2 Effect of crosslinking agent amount

The function of crosslinking agent is to fix the structure of prepolymer formed by functional monomers and template ions, then the polymers would possess certain rigidity, which would protect the binding cavities of Cr(VI) from being destroyed after crosslinking. In many literatures regarding IIPs, EGDMA was used as crosslinking agent. In this work, EGDMA is also used as crosslinking agent. As the amount of crosslinking agent would affect the number and distribution of bonding sites in the prepared polymer, the effect of EGDMA amount on the performance of prepared IIPs was investigated in this section. The synthesis conditions were listed in Table 1 (IIP2). The adsorption experiments were conducted in aqueous solution with the pH of 2.5 at 25°C. The initial Cr(VI) concentration was 200.0 mg/L. When the additional amount of EGDMA was lower than 1.0mmol, the prepared complex was gel formation and could not form polymer. When the additional amount of EGDMA was higher than 1.0 mmol, the adsorption capacity of prepared Cr(VI)-IIPs increased with the increase of additional amount of EGDMA, and reached a maximum value at 2.0 mmol, then decreased as shown in Fig. 5.

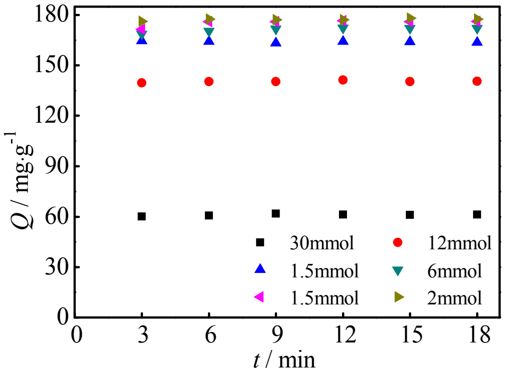

Fig. 5 Effect of the amount of EGDMA on the adsorption (Sample volume: 100mL, Cr(VI) concentration: 200 mg/L, pH=2.5, *T*=25°C)

The adsorption equilibrium was reached within 3 mins. When the additional amount of EGDMA was lower than 2.0 mmol, the crosslinking degree was lower, the prepared IIPs was not very stable, which would result in the loss of functional monomer (4-VP) and bonding sites of polymer in elution procedure. When the additional amount of EGDMA was higher than 2.0 mmol, the crosslinking degree is higher, some template ions (Cr(VI)) were embedded in polymer, which would result in the loss of bonding sites, then the adsorption capacity decreased.

3.3 Effect of solvent

Solvent plays an important role in non-covalent imprinted polymerization. The solvent should have good solubility for functional monomer and template ions, and it could affect the morphology of polymer and the bonding strength between functional monomers and ions. Also, the solvent could avoid side reaction resulted from local high temperature by the heat accumulation in polymerization. In this study, isopropyl alcohol, acetone and two mixtures (isopropyl alcohol/water (9:1, v:v), acetone/water (9:1, v:v)) were used to investigate the influence of solvent on polymerization. Synthesis conditions are listed in Table 1 (IIP3). The adsorption experiments were conducted in aqueous solution with the pH of 2.5 at 25°C. The initial Cr(VI) concentration was 200.0 mg/L. As shown in Fig. 6, the adsorption capacity of prepared Cr(VI)-IIPs with acetone as solvent was the highest, followed by the mixture of acetone/water and isopropyl alcohol. The Cr(VI)-IIP synthesized with isopropyl alcohol/water had the lowest adsorption capacity. It is mainly because of the polarity of solvent. When the polarity of solvent was strong, hydrogen bonds were easy to form between solvent molecules, which would weaken the interaction between template ion and functional monomer, then the adsorption capacity of prepared polymer decreased. The effects of additional amount of solvent on the polymer were conducted. The synthesis conditions were listed in Table 1 (IIP3). The adsorption experiments were conducted in aqueous solution with the pH of 2.5 at 25°C. The initial Cr(VI) concentration was 200.0 mg/L. The results (see

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Fig.S1 in the ESI) showed that the influences of the additional amount of solvent on the adsorption capacity of Cr(VI)-IIPs were slight. The additional amount of solvent mainly affected the hardness of prepared polymer.

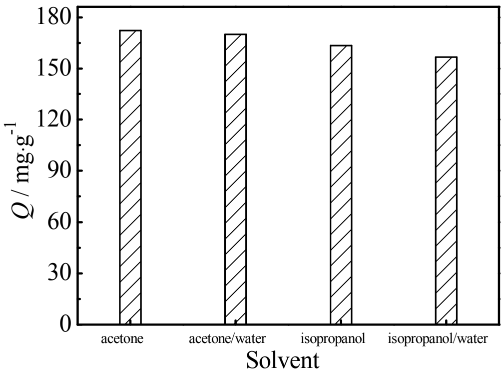


Fig. 6 Effect of solvents on the adsorption (Sample volume: 100mL, Cr(VI) concentration: 200 mg/L, pH=2.5, T=25°C)

3.4. Effect of initiator

In this work, Cr(VI)-IIPs was prepared by a free radical polymerization introduced by heating. Azodiisobutyronitrile (AIBN) was selected as initiator, as it only produced one kind free radical with less side reaction and a stable property. The effects of additional amount of AIBN on IIPs were studied. The synthesis conditions were listed in Table 1 (IIP4). The adsorption experiments were conducted in aqueous solution with pH of 2.5 at 25°C. The initial Cr(VI) concentration was 200.0 mg/L. As can be seen in Fig. 7, the additional amount of AIBN slightly influences the adsorption capacity of prepared Cr(VI)-IIPs. It is shown that small amount of initiator was enough for the polymerization.

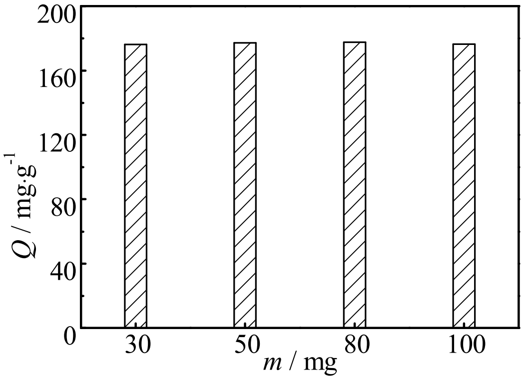


Fig. 7 Effect of amount of AIBN on the adsorption (Sample volume: 100mL, Cr(VI) concentration: 200 mg/L, pH=2.5, T=25°C)

3.5. Characterization of Cr(VI)-IIPs particles

Zeta Potential Curve: The zeta potential curves of Cr(VI)-IIPs was given in Fig. 8. The zeta potential of Cr(VI)-IIP particles is highly sensitive to the pH of solution. In the case of pH < 5.5, the zeta potential of IIPs is positive, it is mainly caused by the protonation of N atoms in the pyridine groups of Cr(VI)-IIPs. In the case of pH > 5.5, the zeta potential of Cr(VI)-IIP particles is negative. When the pH lower than 2.5, then zeta potential of Cr(VI)-IIP particles increases with the increase of pH. However, when pH > 2.5, the zeta potential of Cr(VI)-IIP particles decreases with the increase of pH.

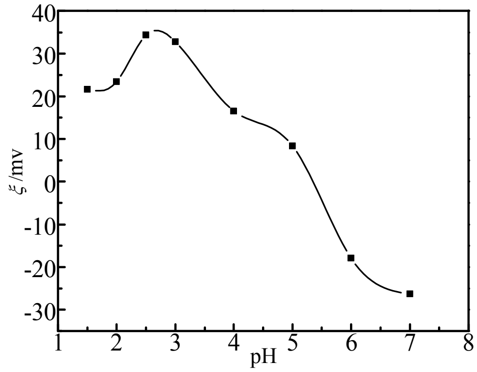
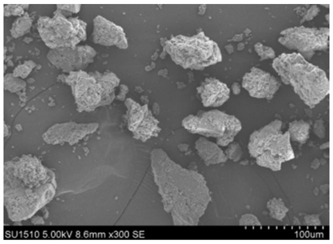
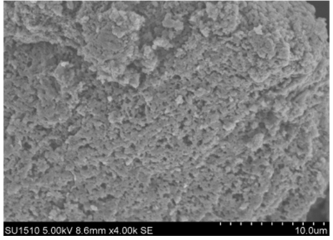


Fig. 8 Zeta potential curves of Cr(VI)-IIPs particles

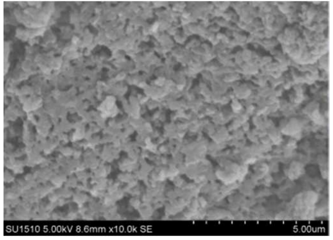
Surface morphology and porous structure of the IIPs: The surface structures were determined by BET. The porosity of the prepared materials is revealed by N_2 adsorption isotherms. The surface area of Cr(VI)-IIPs was 17.602 m^2/g. The pore volume and average pore diameter were 0.196 cc/g and 33.71nm, respectively. The surface morphology of Cr(VI)-IIP particles is obtained by SEM. As shown in Fig. 9, the particles of IIPs have irregular shape and rough surface. The surface of IIPs was exhibited with some degree of porous surface that will benefit adsorption process. It is showed that the prepared Cr(VI)-ion imprinted polymers was mesoporous material with large specific surface area.



A. The images were amplified in 300×



B. The images were amplified in 4000×



C. The images were amplified in 10000×

Fig. 9 SEM images of the Cr(VI)-IIPs(A, B, C)

The thermal stability of prepared Cr(VI)-IIP was determined by thermal gravity analysis method. The results were shown in

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Fig. 10. When the temperature ranges from 52°C to 100°C, the weight loss of the polymer was observed due to the loss of physisorbed water. When temperature was in the range of 300°C to 400°C, the weight loss of polymer was obvious and fast. When the temperature was over 450°C, the weight loss of polymer was above 95%. The results showed that the operation temperature of prepared Cr(VI)-IIPs should be kept less than 300°C.

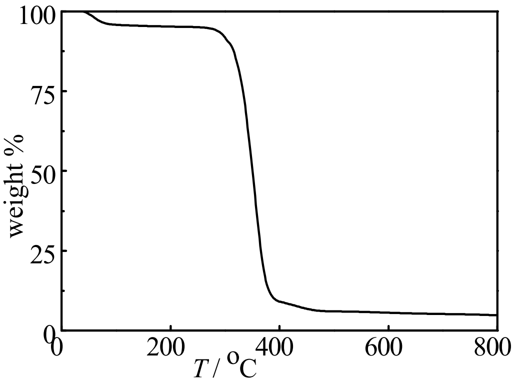

Fig. 10 TGA curves of Cr(VI)-IIP

3.6. Effect of pH

The pH in aqueous solution would affect the ion valences of chromium and the number of protonated nitrogen in bonding sites of IIPs. It has significant effect on the adsorption performance. Usually, in aqueous solutions, chromium ion mainly exists in the form of soluble oxides, including $Cr_2O_7^{2-}$, $HCrO_4^-$, CrO_4^{2-} and H_2CrO_4. The actual form depends on the pH and total concentration of chromium in the solution.[30,31] When pH is below 1.0, the dominant form is H_2CrO_4 throughout the concentration range; when pH is above 7.0, only CrO_4^{2-} ions exists in the aqueous solution; when pH is between 1.0 and 6.0, $HCrO_4^-$ and $Cr_2O_7^{2-}$ are both existing; when the concentration of chromium in solution is above 1000.0 mg/L, the dominant form is $Cr_2O_7^{2-}$.

The influences of pH in aqueous solution were investigated. The synthesis conditions in this section and later adsorption experiments were all the same as listed in Table 1 (IIP5). The adsorption experiments were conducted at 25°C. The initial Cr(VI) concentration was 200.0 mg/L. The adsorption capacity of prepared Cr(VI)-IIPs increased with the increase of pH in aqueous solution, and reached a maximum value of 179.89 mg/g at the pH of 2.0, then decreased as shown in Fig. 11. Adsorption of chromium with Cr(VI)-IIPs was mainly caused by the electrostatic interactions between the protonated N atoms of functional pyridine groups on the prepared IIPs and chromium anionic species.[26,32] At lower pH, the number of protonated N atoms increased with the increase of pH, the dominant species in solution was H_2CrO_4 and $H_2Cr_2O_7$, chromium anionic species of CrO_4^- and $Cr_2O_7^{2-}$ were reduced, the electrostatic interactions were weak, then the adsorption capacity was lower. At higher pH, the number of protonated N atoms in the polymer molecule decreased with the increase of pH, and electrostatic interaction between N atoms and Cr(VI) was weakened, which led to the decrease of adsorption capacity of Cr(VI).

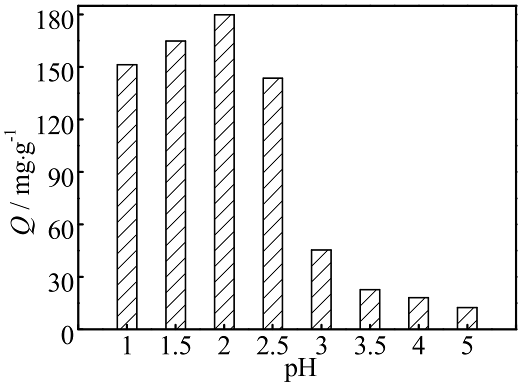

Fig. 11 Effect of pH in aqueous solution on the adsorption (Sample volume: 100mL, Cr(VI) concentration: 200 mg/L, *T*=25°C)

3.7. Effect of initial concentration of Cr(VI)

Initial concentration of Cr(VI) in aqueous solution would affect the mass transfer driving force in adsorption process. As shown in Fig. 12, the influences of initial concentration of Cr(VI) on the adsorption were conducted at the pH of 2.0 and the temperature of 25°C. The adsorption capacity of Cr(VI)-IIPs increased with the increase of initial concentration of Cr(VI), and the plateau values were obtained at Cr(VI) concentration of 600.0 mg/L, the maximum adsorption capacity was up to 338.73 mg/g. Compared with other adsorbents reported in literatures as listed in Table 2, the prepared Cr(VI)-IIPs in this work had the highest adsorption capacity. It was mainly because the prepared Cr(VI)-IIPs with 4-VP had more specific binding cavities in polymer and stronger electrostatic interactions between polymer surface group and Cr(VI) anion.

Table 2 Comparison of different adsorbents' performance

Adsorbent	equilibrium time	q_{max} (mg/g)	Ref.
IIP chitosan	24h	50.96	[33]
Chitosan based on perlite	300min	153.8	[34]
Aniline formaldehyde based silica gel	90min	65.00	[35]
GMA-amino functionalized	30min	109.72	[36]
Poly(ethylene terephthalate) fiber	150min	81.0	[31]
functionalized pyridine copolymers	120min	94.34	[32]
Black carbon	4h	21.34	[37]
Poly(EGMA-co-VI)	20min	108.68	[38]
Cr(VI)-IIPs (4-VP/HEMA)	40min	172.12	[26]
Cr(VI)-IIPs(4-VP/DEAEM)	5min	286.56	[39]
Cr(VI)-IIPs (this study)	3min	338.73	this work

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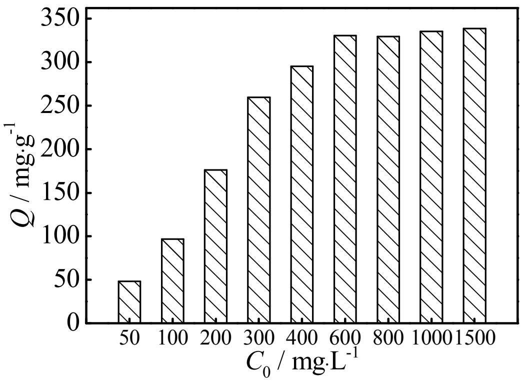

Fig. 12 Effect of initial concentration of Cr(VI) on the adsorption (Sample volume: 100mL, pH=2.0, *T*=25°C)

3.8. Studies on adsorption kinetics

In order to study the kinetics of adsorption, the adsorption rate was investigated at the pH of 2.0, the temperature of 25°C and the initial Cr(VI) concentration of 200.0 mg/L. As can be seen in Fig. 13, the adsorption equilibrium could be reached within 3min. Compared with other adsorbents reported in literatures as listed in Table 2, the adsorption rate of Cr(VI)-IIPs was the fastest. It was mainly because of the stronger electrostatic interactions between protonated N atoms and Cr(VI) anion.

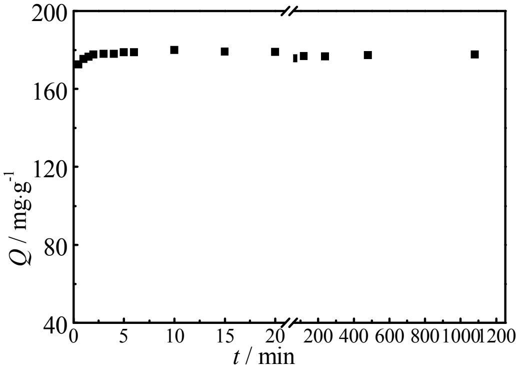

Fig. 13 The various of adsorption capacity with time (Sample volume: 100mL, Cr(VI) concentration: 200 mg/L, *T*=25°C)

Pseudo-first-order and pseudo-second-order models were used to evaluate the adsorption kinetics of Cr(VI)-IIPs. Both models were expressed as following equations,[40,41]

Pseudo-first-order model: $$\log(q_{e1} - q_{t_1}) = \log q_{e1} - (\frac{k_1}{2.303})t \quad (5)$$

Pseudo-second-order model: $$\frac{t}{q_{t_2}} = \frac{1}{k_2 q_{e2}^{\ 2}} + \frac{t}{q_{e2}} \quad (6)$$

where q_{e1}, q_{e2} are the experimental amount of Cr(VI) adsorbed at equilibrium state, mg/g; q_{t1}、q_{t2} are the amount of Cr(VI) adsorbed at time *t*, mg/g; k_1、k_2 are the adsorption rate constant of the pseudo-first-order and pseudo-second-order adsorption, l/min. The subscripts, 1 and 2 refer to the order in kinetics equations. The curves of adsorption kinetics were obtained (see Fig.S2 in the ESI) and parameters of two kinetic models were given in Table 3. The correlation coefficient (R^2) for the pseudo-first-order equation was 0.9021, and corresponding theoretical value of q_{e1} was lower than the experimental value significantly. The experimental data can be well fitted into the pseudo-second-order equation with correlation coefficients R^2 of 0.999997, and the calculated value of q_e (179.57 mg/g) was very close to the experimental result (179.84 mg/g). The results showed that the adsorption mechanism of prepared Cr(VI)-IIPs can be considered as a pseudo-second-order adsorption process.

Table 3 Parameters for kinetic adsorption model

q_{exp} / mg/g	q_e / mg/g	k_1	R^2	Ref
pseudo-first-order kinetic models				
179.84	6.64	0.4014	0.9021	this work
		0.408		[26]
pseudo-second-order kinetic models				
179.84	179.57	0.24	0.9999	this work
		0.172		[26]

3.9. Adsorption thermodynamic studies

Langmuir and Freundlich isotherm model were used to analyze the adsorption thermodynamic properties. The expression of both models were as following,

Langmuir: $$C_e / Q_e = C_e / Q_{\max} + 1/(Q_{\max} \cdot b) \quad (7)$$

Freundlich: $$\ln Q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \quad (8)$$

where Q_e、C_e are the experimental amount of Cr(VI) adsorbed by the IIP and Cr(VI) concentration at equilibrium state, mg/g; Q_{max} is the maximum amount of adsorption, mg/g; *b* represents the constant in Langmuir adsorption model, L/mg; K_F and *n* are both constants in Freundlich adsorption model. The curves of adsorption thermodynamics were obtained (see Fig.S3 in the ESI) and parameters of two models were given in Table 4. The results showed that Langmuir model was more appropriate than Freundlich model. The maximum amount of adsorption Q_{max} (344.83mg/g) was very close to the experiment amount Q_{exp} (338.73 mg/g). This indicated that the adsorption of Cr(VI) with prepared Cr(VI)-IIPs was a monolayer adsorption.[28]

Table 4 The comparison of Langmuir and Freundlich isotherm model constants

Langmuir			
Q_{exp} / mg/g	Q_{max} / mg/g	*b*	R^2
338.73	344.83	0.064	0.9998
Freundlich			
K_F	*n*	R^2	
60.78	3.49	0.7384	

3.10. Selectivity studies

The selectivities of prepared Cr(VI)-IIPs were studied with Cu(II) and Cr(III) as competitive ions in adsorption process. The concentrations of Cr(VI) ,Cu(II), Cr(III) were all 200 mg/L. 0.1g Cr(VI)-IIP particles were added into 100.0mL solution at 25°C and pH of 2.0. The results were listed in Table 5.

Table 5 The selectivity coefficient for Cr(VI)/Cu(II) and Cr(VI)/Cr(III)

	Q / mg/g	K_d / L/g	*k*
Cr(VI)	159.12	7.285	189.05
Cu(II)	8.12	0.039	

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Cr(VI)	166.93	7.761	95.56
Cr(III)	13.56	0.081	

The imprinted polymer particles had a high adsorption capacity and selectivity to Cr(VI) in both Cr(VI)/Cu(II) and Cr(VI)/Cr(III) aqueous solution, and the selectivity coefficients, *k,* were up to 189.05 and 95.56, respectively. These results showed that the imprinted bonding sites of Cr(VI)-IIPs could enhance the interaction between polymer and target ions.

3.11. Reusability and stability

Reusability of absorbent is very important for its industrial application. The elute solution was 0.1M NaOH solution. 0.1g Cr(VI)-IIPs with saturation adsorption of Cr(VI) were eluted several times in a bottle containing 100mL elute solution under stirring. When the Cr(VI) couldn't be detected, the regeneration of Cr(VI)-IIPs was finished. In order to investigate the reusability of the Cr(VI)-IIPs, adsorption-desorption cycle was repeated five times, the results were shown in Fig. 14. The variances of adsorption capacity of Cr(VI)-IIPs were very small. Stability of the prepared Cr(VI)-IIPs was also investigated. Cr(VI)-IIP was stored at dryer. No change had been detected on the adsorption capacities of the IIP after 60 days (see Fig.S4 in the ESI). It showed that the IIPs had a good stability. It showed that Cr(VI)-IIPs had good stability and regeneration ability.

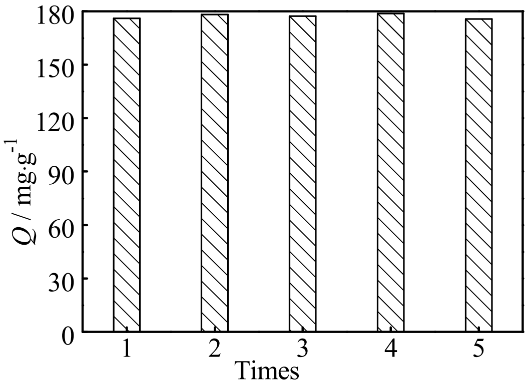

Fig. 14 Reusability of Cr(VI)-IIPs

Conclusions

In this paper, a novel Cr(VI)-IIPs was synthesized by bulk polymerization with EGDMA as crosslinking agent, AIBN as initiator, and acetone as solvent. The basic functional monomer was better than acid and neutral agents, and 4-VP was the best one. The additional amounts of functional monomer and crosslinking agent had significant influences on the adsorption performance of IIPs, while the influences of initiator and solvent were slight. The prepared Cr(VI)-IIP was characterized by the Fourier infrared spectroscopy, Zeta potential, BET and scanning electron microscopy. The adsorption of chromium with Cr(VI)-IIPs was mainly caused by the electrostatic interactions between the protonated N atoms of functional pyridine groups on the prepared IIPs and chromium anionic species. The kinetic and thermodynamic results showed that the adsorption of Cr(VI)-IIPs was a monolayer adsorption process, the adsorption mechanism of prepared Cr(VI)-IIPs was following the pseudo-second-order adsorption process, and the adsorption isotherm was more appropriate with Langmuir model. The adsorption capacity of prepared Cr(VI)-IIPs depended on the pH in aqueous solution, which could affect the ion valences of chromium and the interaction between polymer and Cr(VI) anions. The initial concentration of Cr(VI) would affect the adsorption by the mass transfer driving force. Under the optimal condition, the maximum adsorption capacity of Cr(VI) was up to 338.73 mg/g, this is much higher than that of other adsorbents reported in literatures. And the adsorption rate was also faster than others. The prepared Cr(VI)-IIPs had good selectivity for Cr(VI)/Cu(II) and Cr(VI)/Cr(III), the selectivity coefficients were up to 189.05 and 96.56, respectively. Also the prepared polymer had good reusability and stability. In summary, a new synthesized adsorbent demonstrated a high adsorption capacity and a fast adsorption rate in selective separation of Cr(VI), and it had good potential application in related wastewater treatment, rapid detection, sensor, and trace material removal.

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