Polym. Bull. (2010) 64:351–362
DOI 10.1007/s00289-009-0146-8

ORIGINAL PAPER

Synthesis of cross-linked graft copolymer from [2-(methacryloyloxy)ethyl] trimethylammonium chloride and poly(vinyl alcohol) for removing chromium(VI) from aqueous solution

Pranesh Chowdhury · P. Mondal · K. Roy

Received: 2 April 2009 / Revised: 25 July 2009 / Accepted: 27 July 2009 /

Abstract A novel graft copolymer of [2-(methacryloyloxy)ethyl] trimethylammonium chloride onto poly(vinyl alcohol) has been synthesized and it is cross-linked by glutaraldehyde for the investigation of its efficiency in removing Cr(VI) from aqueous solution. The chemical nature of the ion-exchange resin has been elucidated with the help of chemical test, Fourier transform infrared, thermo gravimetric analysis and DTA. Particle size, surface area, ion-exchange capacity, optimum pH, reaction time and temperature for Cr(VI) extraction were determined. Chromium(VI) adsorption kinetics, isotherm and thermodynamics have been studied. A plausible mechanism for chromium ion-exchange has been suggested.

Keywords Graft copolymer · Cross-linking · Chromium(VI) · Adsorption · Ion-exchange

List of symbols

PMETAC	Poly[2-(methacryloyloxy)ethyl] trimethylammonium chloride
PVA	Poly(vinyl alcohol)
X-PMETAC-g-PVA	Cross-linked graft copolymer of METAC from PVA
PMETAC-g-PVA	Uncross-linked graft copolymer of METAC from PVA
Sorbate	Chromium(VI) ion
Sorbent	Cross-linked graft copolymer
R^2	Correlation coefficient
q_t	Adsorption capacity at time 't' (mg g^{-1})
q_e	Adsorption capacity at equilibrium (mg g^{-1})
q_m	Langmuir constant related to mono-layer capacity (mg g^{-1})
K_a	Langmuir constant (L mg^{-1})

P. Chowdhury (✉) · P. Mondal · K. Roy
Department of Chemistry, Visva-Bharati University, Santiniketan 731235, India
e-mail: pranesh_02@yahoo.co.in

n	Freundlich constant (dimensionless)
K_F	Freundlich constant (mg g^{-1})
a	Temkin constant
b	Temkin constant
x	Dimensionless constant in Toth isotherm
b_T	Toth isotherm constant (mg L^{-1})

Introduction

Chromium exists in water mainly as +3 and +6 oxidation states. Chromium(III) is non-toxic and essential to mammals [1]. Chromium(VI) on the other hand is a powerful human carcinogenic and toxic to many plants, aquatic animals and bacteria [1]. Therefore, the concentration of Cr(VI) has to be decreased to permissible levels [1] which is less than 0.05 mg L^{-1}. Several industries such as paints, leather tanning, chrome plating, fertilizer, textile and photography discharge Cr(VI)-contaminated effluent to surface water [1, 2]. Most industries discharge wastewater containing Cr(VI) after reduction to Cr(III) followed by precipitation as chromic hydroxide into the surface. The major drawbacks [2, 3] of this treatment is lengthy process, significant sludge production and high cost of chemicals. Several methods [3, 4] such as reverse osmosis, ion-exchange, foam flotation, electrolysis, solvent extraction, magnetic separation, liquid membrane isolation and surface adsorption has been reported for removal of Cr(VI). A varieties of adsorbent materials studied for Cr(VI) removals, which include bio-sorbents [5], natural materials [6] and polymeric sorbent [7]. Polymeric materials such as polyacrylamide grafted sawdust [2], quaternized polyvinyl pyridine coated silica gel [8], polyaniline [3, 4] based composites [9] and polyacrylonitrile fiber [10] has been reported to be good polymeric adsorbent for Cr(VI). Rivas et al. [11] copolymerized METAC with acrylic acid and then cross-linked the polymer by *N*,*N*-methylene bisacrylamide to obtained ion specific resin. The polymer uptakes Cr(III) and Cr(VI) through cation and anion exchange mechanism, respectively. The low Cr(VI) adsorption capacity, slow uptake and poor thermal stability make the polymer inferior. The incorporation of PVA through grafting and cross-linking by glutaraldehyde may increase the hydro-gel character and crosslink density of the reported polymer. Better hydro-gel character and higher crosslink density of PMETAC may upgrades the polymer towards Cr(VI) adsorption capacity.

In the present work, a new procedure for extracting Cr(VI) by X-METAC-g-PVA (cross-linked graft copolymer of METAC from PVA) has been developed. Under the sorption condition, kinetic and thermodynamic parameters are evaluated. Different adsorption isotherm have been studied and possible mechanism of Cr(VI) ion binding has been discussed.

Materials and methods

Materials

Poly vinyl alcohol (Burgoyne, Burbidges and co. Bombay, India), [2-(methacryloyloxy)ethyl] trimethylammonium chloride (Aldrich, USA), glutaraldehyde (SD Fine-Chem Ltd, Mumbai, India), Potassium peroxo-disulfate (E. Merck, Bombay, India) were used as received. Potassium dichromate (Pfizer Ltd, Mumbai, India) was used for the preparation of stock solution of Cr(VI) (250 mg L^{-1}). All the working solutions were prepared by proper dilution of stock solution with distilled water. 1,5-Diphenyl carbazide was used for the colorimetric estimation of Cr(VI) was of analytical grade(Merck, Mumbai, India). Methylene blue strain (Merck, Mumbai, India) was used to determine specific surface area of X-PMETAC-g-PVA particle.

Instruments

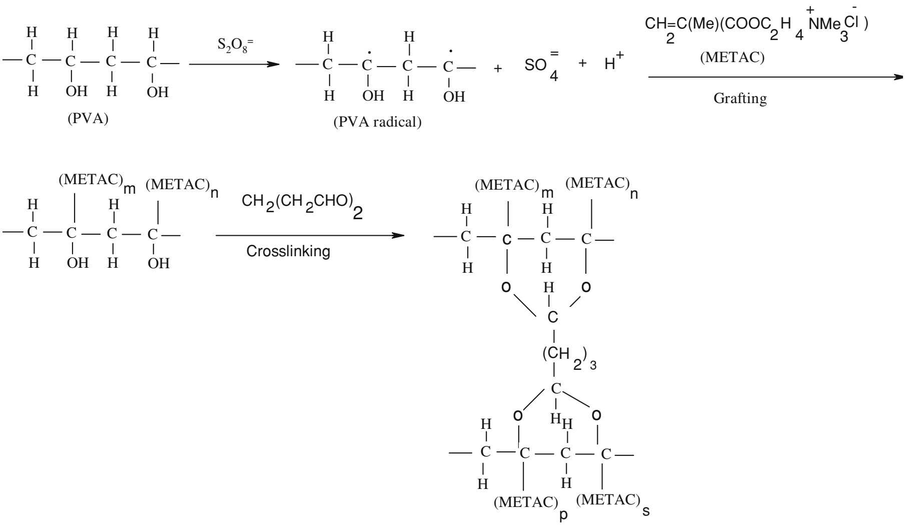
UV–VIS–NIR spectrometer was used for the analysis of Cr(VI) from aqueous solution. Thermal analysis was conducted using Pyris Diamond TG/DTA, (Perkin Elmer) in air at a rate of 10 °C/min. An Elico made pH meter (model L1120) was used for pH measurement. The Fourier transform infrared (FTIR) spectrum was recorded using KBr pellets by Shimadzu-8400S model. Scanning electronic microscope (SEM) of the polymer was conducted by JEOL JSM 6700F FESEM.

Synthesis of crossed-linked graft copolymer

Grafting copolymerization (Scheme 1) was carried out in a two necked round bottomed flask at 70 °C. PVA (1 g) was dissolved in 100 mL distilled water and a definite amount of METAC (1.25 mL), 1.2 N H_2SO_4 (1.0 mL) and potassium peroxo-disulfate (0.25 g) were then added and stirred. Nitrogen atmosphere was maintained through the reaction period. After 2 h, the polymer was precipitated by the addition of non-solvent acetone. The homo-polymers PVA and PMETAC were removed from the graft copolymer through repeated washing with warm water. The purified grafted polymer was dissolved in 100 mL hot water and glutaraldehyde (0.78 g) was then mixed to crosslink the grafted product (Scheme 1). After an hour, the precipitated polymer was separated by filtration and washed several times by hot distilled water.

Study of adsorption kinetics

Batch adsorption tests were carried out by mechanical agitation (agitation speed: 90–100 rpm) at temperature from 8 to 45 °C. To determine the amount of Cr(VI) adsorption, 0.103 g sorbent, PMETAC was taken in a 100 mL beaker with 25 mL sorbate solution. The concentration of Cr(VI) in aqueous solution was kept to 4–70 mg L^{-1}. The pH of the solution was maintained to 5.76. One milliliter of sample solution was withdrawn each time from the reaction mixture by a syringe at



Scheme 1 Synthesis of cross-linked METAC-graft-PVA

a gap of fixed interval and analyzed. Amount of Cr(VI) adsorbed was calculated using the relationship [3]:

$$q_t = (W_i - W_t)/M \quad (1)$$

Here q_t is the amount of Cr(VI) adsorbed per unit mass of adsorbent (mg/g) at time 't'. W_i and W_t are the initial and residual amount (mg) of Cr(VI), respectively, in solution. M is the mass (g) of the adsorbent added.

Study of adsorption isotherm

An aliquot (25 mL) of sorbate (concentration: 4–70 mg L^{-1}, pH 5.76) was taken with 0.103 g sorbent into 10 separate 100 mL container and agitated with a speed of 100 rpm for 1 h and filtered. The filtrates were analyzed for residual chromium by standard method. The amount of Cr(VI) adsorbed per unit mass of the adsorbent at equilibrium was calculated using Eq. 1.

Thermodynamic study

The thermodynamic parameters, free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were calculated to evaluate the thermodynamic feasibility and confirm the nature of the adsorption process. Based on the available literature [3, 4] (Eqs. 2, 3), the Langmuir constant K_a was used for the determination of thermodynamic parameters. The value of ΔH^0 and ΔS^0 were calculated from the slope and intercept of the plot of $\ln K_a$ versus $1/T$.

$$\ln K_a = \left[\left(\Delta S^0 / R \right) - \left(\Delta H^0 / RT \right) \right] \tag{2}$$

$$\Delta G^0 = \left[\Delta H^0 - T\Delta S^0 \right] \tag{3}$$

Results and discussion

Physico-chemical characteristics

The FTIR spectrum of the synthesized cross-linked graft copolymer exhibits several peaks at 2,929, 1,724 and 1,130 cm^{-1}, which corresponds to stretching of N$^+$–C, >C=O and C–O-C (ether) linkage, respectively [12]. These bonds are the characteristic structural features of cross-linked graft copolymer of METAC from PVA (Scheme 1). The traces of thermo gravimetric analysis (TGA) of the samples (X-PMETAC-g-PVA and chromium loaded X-PMETAC-g-PVA) are shown in Fig. 1. The traces indicate that the mass loss of both the samples occurs mainly through three stages (30–250, 250–300 and 300–500 °C). First stage weight loss (for both the samples) starts at 30 °C and continued up to 250 °C. The initial weight loss (28–29%) may be attributed to loss of moisture. The second stage weight loss from 250 to 300 °C (3% for chromium loaded X-PMETAC-g-PVA and 11% for X-PMETAC-g-PVA) is probably due to loss of HCl. The low chlorine content of chromium loaded polymer indicates that chloride ion is probably replaced by the chromate ion during adsorption process. The third step (330–500 °C) weight loss (55% for X-PMETAC-g-PVA and 63% for chromium loaded X-PMETAC-g-PVA) indicates the oxidative degradation of the polymer. TGA shows that X-PMETAC-g-PVA and chromium loaded X-PMETAC-g-PVA is stable up to 250 and 300 °C, respectively. Integral procedure decomposition temperature (IPDT) [13] values (330 °C for X-PMETAC-g-PVA and 387 °C for chromium impregnated X-PMETAC-g-PVA) and activation energies (0.011 kJ mol^{-1} for X-PMETAC-g-PVA and 0.671 kJ mol^{-1} for chromium loaded X-PMETAC-g-PVA) confirm the better thermal stability of chromium loaded X-PMETAC-g-PVA. DTA traces (Fig. 2) show three endothermic peaks at 60, 300 and 440 °C for X-PMETAC-g-PVA and 70, 330 and 470 °C for chromium loaded X-PMETAC-g-PVA. The first endothermic peak (for both the sample) is due to evaluation of moisture. The second peak in both cases indicates of decomposition of polymer. While the third peaks are responsible for the decomposition of impurities present in the polymer. The irregular surface morphology is found for chromium loaded X-PMETAC-g-PVA as evident from the SEM photograph (Fig. 3). Some other physicochemical parameters are shown Table 1. The surface area, zero point charge, molecular weight and cross-linking density are much improved in the case of X-PMETAC-g-PVA (cross-linked by glutaraldehyde) compared to ungrafted PMETAC. Grafting with PVA (degree of grafting 1.22) and cross-linking by glutaraldehyde is probably responsible for this improvement. The prepared cross-linked graft copolymer is insoluble in the common organic and inorganic solvents.

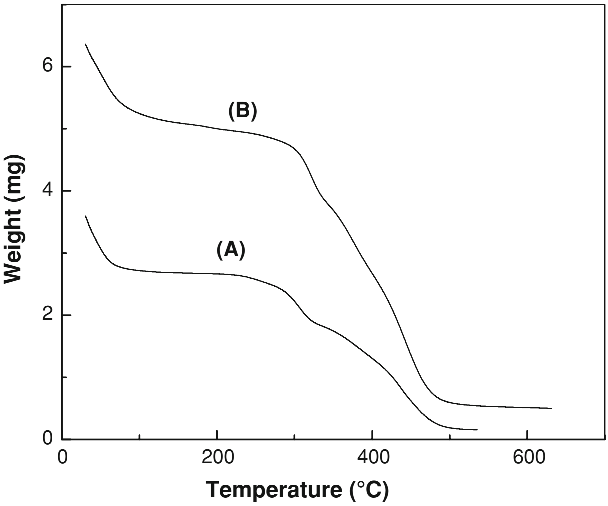


Fig. 1 TGA curve for (**a**) X-PMETAC-g-PVA and (**b**) Cr(VI) loaded X-PMETAC-g-PVA

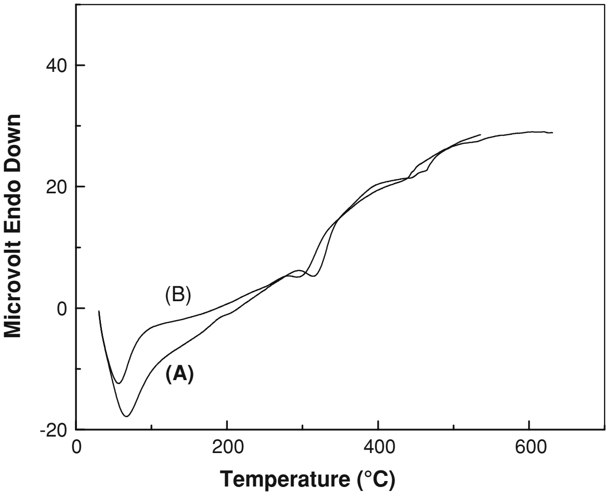


Fig. 2 DTA curve for (**a**) X-PMETAC-g-PVA and (**b**) Cr(VI) loaded X-PMETAC-g-PVA

Effect of pH on Cr(VI) adsorption and adsorption mechanism

The results of Cr(VI) adsorption with increasing pH from 1 to 8 are shown in Fig. 4. It was found that the adsorption capacity was increased with the increase of pH from 1 to 3 and then decreased gradually up to pH 8. The initial increase is probably due to autoionisation ($2H_2CrO_4 = Cr_2O_7^{=} + 2H^+ + H_2O$) at relatively higher pH of the solution. The ionic species are trapped by the polymer through ionic interaction (Scheme 2). The gradual decrease (beyond pH 3) may be explained by the gradual conversion of dichromate ion to chromate ion. Chromate

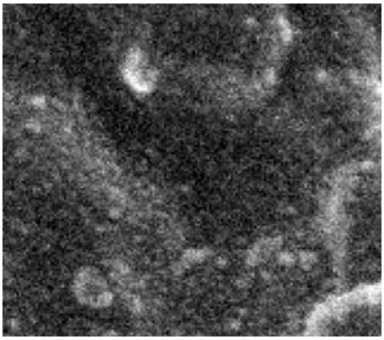


Fig. 3 SEM photograph of Cr(VI) loaded X-PMETAC-g-PVA

Table 1 Some physicochemical characteristics of X-PMETAC-g-PVA

Parameters	Value	Method
Bulk density (g/ml)	1.33	Specific gravity [3, 4]
Particle size (mm)	0.22–0.24	Set of sieves [3, 4]
Surface area (m^2/g)	9.47	Methylene blue [3, 4]
pH (Zero point charge)	8.0	Chromate titration [3, 4]
Degree of grafting	1.22	Gravimetry [13]
Molecular weight between two consecutive cross-linked of X-PMETAC-g-PVA (M_c)	547.78	Flory–Rehner equation [15]
Cross-linking density (ρ)	0.3966	Flory–Rehner equation [15]
Ion-exchange capacity (meq Cl^-/g)	1.175	Chloride titration [3, 4]

being a monomeric form lacks the proper size to fit in the polymer sites. The sorption of Cr(VI) probably took place through ion-exchange process (Scheme 2), particularly at pH less than 8 and sorbate dose within 100 mg L^{-1}. The presence of exchangeable chloride (ion-exchange capacity 1.175 meq Cl^-/g) favors the ion-exchange mechanism. The release of chloride ion in the aqueous media is tested by chemical test [3, 4].

Effect of sorbate dose

The effect of sorbate dose on adsorption capacity was studied within the range 4–70 mg L^{-1} Cr(VI), keeping the other conditions (pH 5.76, sorbent dose 4.12 g L^{-1}, time 1 h) fixed. It was found that adsorption capacity of the prepared adsorbent was increased with the increase of sorbate level. The adsorption capacity was 3.07, 4.27 and 4.77 (mg g^{-1}) at 8, 27 and 45 °C, respectively, at 70 mg L^{-1} of Cr(VI). These value increases further with the increase of sorbate dose beyond 70 mg L^{-1}. The adsorption capacity of the ungrafted crosslink PMETAC anion-exchanger lays in the range [11] 1.0–1.4 mg g^{-1} in the similar conditions. The higher adsorption capacity may be attributed to the cross-linking of grafted polymer.

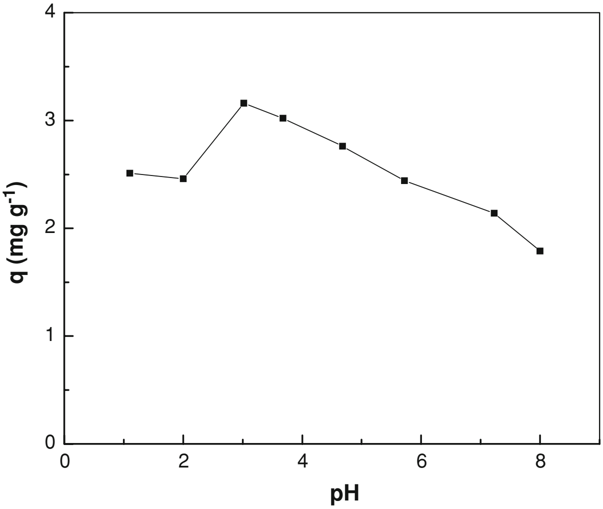
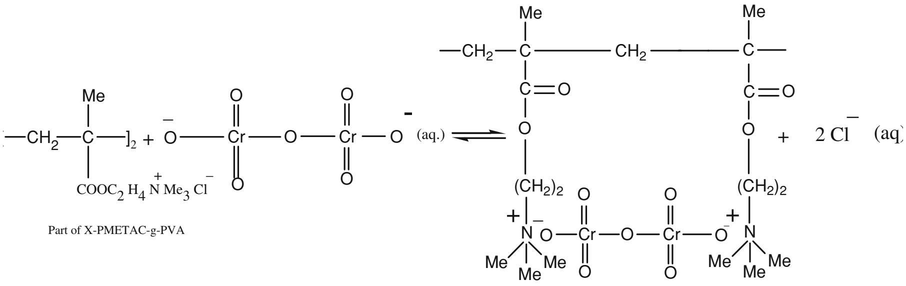


Fig. 4 Variation of adsorption capacity with pH (sorbent dose 4.12 g L^{-1}, sorbate 45 mg L^{-1}, temperature 27 °C, time 1 h)



Scheme 2 Sorption of Cr(VI) through ion-exchange process

Effect of contact time: kinetic analysis and transport mechanism

Figure 5 shows that the amount of Cr(VI) adsorbed (q_t, mg g^{-1}) at different contact time. Almost 90% adsorption took place within 1 h and the time required to reach the equilibrium is 1.5 h. The initial rapid adsorption probably due to the availability of the positive charged surface of the sorbent (PH_{zpc} 8.0). The late slow adsorption may be due to electrostatic hindrance between adsorbed negative charged sorbate species and available anionic sorbate in solution, and the slow pore diffusion of the solute into the bulk of the sorbent. The similar type results were observed by Ghosh et al. [6]. The contact time required for maximum Cr(VI) adsorption was found to be nearly 1.5 h. This equilibrium time is much less than commercially available exchangers [14] such as Amberlites (IRA-400, IR-410 and XAD-16). The time dependent data are used to fit the various kinetic models by regression plots [3, 4]. The models used for fitting the data are first order, pseudo first order, second order,

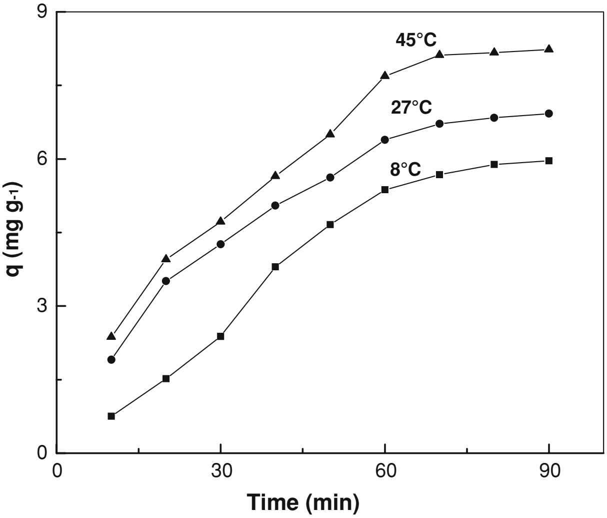


Fig. 5 Variation of adsorption capacity with time and temperature (pH 5.76, sorbent dose 4.12 g L^{-1}, sorbate dose 52 mg L^{-1})

pseudo second order, simple Elovich model, Weber-Morich equation and G. E. Byod equation. The present kinetic data could be best described by pseudo second order equation.

Adsorption isotherm

Four isotherm (Langmuir, Freundlich, Temkin and Dubinin–Radhushkevick) were used for fitting the experimental data (Fig. 6) obtained at temperature 8, 27 and 45 °C (pH 5.76, time 1 h). The isotherm data has been analyzed using the linear equation of the models (Table 2). Among the isotherm studied, the order of fitting the experimental data are Freundlich > Langmuir > Temkin. The parameter q_m (Langmuir constant) is the measure of theoretically possible maximum adsorption capacity under the experimental conditions. The value of q_m increases with the increase of temperature from 8 to 45 °C.

Effect of temperature and thermodynamics parameters

The effect of temperature of Cr(VI) adsorption is shown in Figs. 4 and 5, and the adsorption capacity increases with the increase of temperature up to 45 °C. The adsorption and desorption probably occurs through ion-exchange process (Scheme 2). Initial increase of temperature favors the adsorption process, while increase of temperature above 45 °C accelerates the desorption process. The values of thermodynamic parameters are given in Table 3. The negative value of ΔG^0 confirms the spontaneity and feasibility of the sorption process. The positive ΔH^0 indicates the endothermic nature of the adsorption process and positive ΔS^0 value signifies that the ion-exchange process is involved during adsorption (Scheme 2).

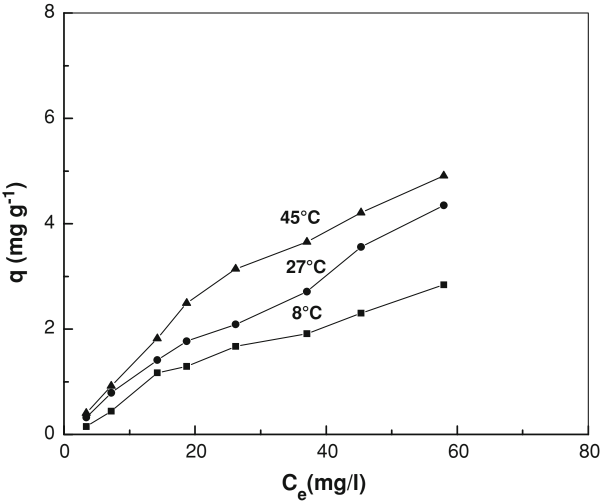


Fig. 6 Adsorption isotherm at different temperature (pH 5.76, sorbate dose 4.12 g L^{-1}, time 1 h)

Table 2 Isotherm models and related statistical parameters

	Statistical parameter	8 °C	27 °C	45 °C
1. Langmuir model	R^2	0.8900	0.9054	0.8999
$C_e/q_e = 1/K_a\ q_m + C_e/q_m$	q_m	5.28	6.69	9.16
	K_a	1.77×10^{-2}	2.09×10^{-2}	2.39×10^{-2}
2. Fruendlich model	R^2	0.9825	0.9704	0.9557
$\log q_e = \log K_F + (1/n) \log C_e$	N	1.60	1.32	1.61
	K_F	0.21	1.32	1.61
3. Temkin model	R^2	0.9418	0.9050	0.9836
$q_e = a + 2.303 \log C_e$	A	1.99	3.76	2.85
	B	1.14	1.92	1.96
4. Dubinin–Radushkevick model	R^2	0.8144	0.8202	0.9585
$\ln q_e = \ln q_m - K_{DR}\ \varepsilon^2$	q'_m	2.65	3.59	4.62
$\varepsilon = RT \ln(1 + 1/C_e)$	K_{DR}	63.26	31.02	19.38
	E_{DR}	0.089	0.13	0.16

Table 3 Calculated Langmuir constants and thermodynamic parameters for Cr(VI) adsorption at pH 5.76

T (K)	K_a (L mg^{-1})	K_a (L mg^{-1} mol^{-1})	ΔG^0 (KJ mol^{-1})	ΔH^0 (KJ mol^{-1})	ΔS^0 (KJ mol^{-1})
281	1.77×10^{-2}	3.4×10^{-4}	−18.61	+5.12	+0.048
300	2.09×10^{-2}	4.02×10^{-4}	−19.52		
318	2.39×10^{-2}	4.6×10^{-4}	−20.38		

Desorption study

Regeneration of Cr(VI) loaded exchanger (1.56 mg g^{-1}) was carried out by a batch method at 25 ± 2 °C. Chromium(VI) loaded adsorbent (0.105 g) was equilibrated with 20 mL 1 M NaOH solution for 1 h. After filtration, 1 mL filtrate was analyzed. The percentage of regeneration (desorption) of Cr(VI) was found to be 82.67. The desorption using 1 M NaCl, $NaNO_3$, Na_2SO_4, CH_3COONa and $NaClO_4$ as eluents were not satisfactory (below 82.67%).

Conclusion

The synthesized resin acts as anion exchanger with higher adsorption capacity and lower equilibrium time compared to ungrafted one. It has good chemical and thermal stability. The proposed method is highly efficient, cost effective, simple and rapid. The adsorption and desorption of chromium ion took place mainly by ion-exchange process. The adsorption process follows the pseudo second order kinetic and Langmuir adsorption isotherm. The optimum pH, time and temperature for Cr(VI) adsorption using X-PMETAC-g-PVA are 5.75, 60 min and 45 °C, respectively.

Acknowledgment The authors gratefully acknowledge the financial supports provided by the UGC (NO.F-32-305/2006/SR) dated 26.02.2007.

References

1. Sidiauskiene D, Klimaviciute R, Zemaitis A (2008) Adsorption of hexavalent chromium on cationic starches with different degree of cross-linking. J Appl Polym Sci 107:3469–3475
2. Unnithan MR, Anirudhan TS (2001) The kinetic and thermodynamic of sorption of Cr(VI) onto the iron(III) complex of a carboxylated polyacrylamide grafted sawdust. Ind Eng Chem Res 40: 2693–2701
3. Chowdhury P, Roy K, Mondal P (2008) HCl doped polyaniline: an adsorbent for the treatment of Cr(VI) contaminated wastewater. J Polym Mat 25:589–600
4. Chowdhury P, Roy K, Mondal P (2009) Studies on adsorption and desorption of Cr(VI) onto chemically synthesized hydrochloric acid doped polyaniline surface. Open J Macromol 3:6–12
5. Ahalya N, Kanamdi RD, Ramachandra TV (2005) Bio-sorption of Cr(VI) from aqueous solutions by the husk of Bengal Gram. Electrochem J Biotechnol 8:258–264
6. Debhnath S, Ghosh UC (2008) Kinetic, isotherm and thermodynamics for Cr(III) and Cr(VI) adsorption from aqueous solutions by crystalline hydrous titanium oxide. J Chem Thermodym 40:67–77
7. Bajpai SK, Johnson S (2006) Poly(acrylamide-co-mallic acid) hydro-gel for removal of Cr(VI) from aqueous solutions, Part-I: synthesis and swelling characteristic. J Polym Sci 100:2759–2769
8. Gang D, Banerjee SK, Clevenger TE (2001) Chromium(VI) removal by modified poly vinyl pyridine coated silica gel. Pract Periodic Hazard Toxic Radioactive Waste Manage 4(B):105–110
9. Konar RR, Kumar PA, Chakraborty S, Ray M (2007) Hexavalent chromium removal from wastewater using aniline formaldehyde condensate coated silica gel. J Hazard Mat 143:24–32
10. Deng S, Bai R (2004) Removal of trivalent and hexavalent chromium with aminated polyacrylonitrile fiber-performance and mechanism. Water Res 38:2426–4229
11. Rivas BL, Maturana HA, Peric IM, Villegas S (1999) Metal ion extraction behavior of poly [2(methacryloyloxy)ethyl) trimethylammonium chloride-co-acrylic acid] resin. Polym Bull 43: 277–283
12. Dyer JR (1991) Application of absorption spectroscopy of organic compounds. Prentice Hall of India Private Limited, New Delhi, pp 30–40

13. Chowdhury P, Ali A (2008) Vanadium(V) initiated graft co-polymerisation of vinyl monomers onto poly(vinyl alcohol). J Ind Chem Soc 85:600–606
14. Sadikin AN, Muis ZA, Saha B (2007) Removal of Chromium(VI) with aliquat-336 impregnated in amberlite XAD-16. I. Batch mode sorption studies. J Technologi 46(F):1–10
15. Flory P, Renher R (1943) Determination of molecular weight of polymer between two consecutive cross-linked. J Chem Phys 11:521–526