Synthesis of a quaternary amine anion exchange resin and study its adsorption behaviour for chromate oxyanions

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Abstract

Glycidyl methacrylate/*N,N'*-methylene bis-acrylamide (GMA/MBA) was prepared and allowed to react with tetraethylenepentamine (TEP) to give glycidyl methacrylate amine resin (RPA) followed by treatment with glycidyl trimethylammonium chloride (GTA) to give glycidyl methacrylate resin bearing quaternary ammonium chloride moieties (RQA). Zeta potential measurements showed that RQA particles are positively charged over pH 2–10 indicating the strong basic nature of the quaternary amine sites. The effect of pH on the recovery of chromate by RPA and RQA was examined. The results indicated that RQA is an efficient sorbent for chromate from both acidic and basic media. The repeated use of RQA was tested through stripping the adsorbed chromate using a mixture of 0.05 NaOH and 2 M NaCl in the case of the uptake from acidic media and using 2 M NaCl solution in the case of alkaline solutions.
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1. Introduction

Chromium compounds are extensively used in electroplating, anodizing operations in the surface finishing industry, corrosion control, oxidation, leather industry and various other industrial applications [1–5]. The effluents from these industries contain Cr(III) and Cr(VI) with the latter the most toxic form. The discharge of Cr(VI) into surface water is regulated to below 0.05 mg/L while total Cr (including Cr(III), Cr(VI) and other forms) is regulated to below 2 mg/L [6]. Cr(III) is not a significant groundwater contaminant whereas Cr(VI) is approximately 100 times more toxic than Cr(III) [1].

Precipitation, solvent extraction and adsorption are the most commonly methods used for the treatment of Cr(VI) containing wastewater. Precipitation requires Cr(VI) to be reduced to Cr(III) prior to chemical precipitation in order to form the poorly soluble chromium (III) hydroxide. Solvent extraction is a convenient technique for the removal of chromate from aqueous solutions [1,7]. The small but finite aqueous solubility of extractants, diluents and modifiers is a major disadvantage of solvent extraction. The loss of organics by evaporation and entrainment is also a potential problem. Adsorption has been approved as a reliable technique used in treatment of wastewater. Various adsorbents have been investigated towards the removal of chromium from solutions, e.g. clays and activated carbons [8], organo-clays [9–12], biomass [13–15], biopolymers [16–18], agriculture products [19]. Ion exchange resins have been also widely used in recovery and pre-concentration of metal ions [20–22]. Kabay et al. [1] used impregnated resins to remove Cr(VI) and obtained a maximum uptake of 10.32 mg/g resin. Gode and Pehlivan [23] studied the removal of Cr(III) from aqueous solutions using two commercial ion-exchange resins. Adsorption capacities up to 0.341 mmol Cr(III)/g were reported. Spinelli et al. [17] used quaternary chitosan salt for removing of Cr(VI) and uptake capacity of 1.31 mmol/g was reached.

In this paper, pentamine and quaternary ammonium chloride moieties were immobilized on glycidyl methacrylate/*N,N'*-methylene bis-acrylamide resin (GMA/MBA) to give amino (RPA) and quaternary amine (RQA) resins, respectively. The adsorption behaviour of chromate oxyanions by the two resins was studied in the pH range of 2–10. The influence of counter ions on the uptake of chromate by resin RQA was examined. Breakthrough curves of the uptake of chromate by resin RQA

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at acidic and basic conditions were obtained. The availability of resin RQA for repeated use was also studied.

2. Experimental

Glycidyl methacrylate (GMA), *N,N'*-methylene bis-acrylamide (MBA), benzoyl peroxide (Bz_2O_2), triethylenepentamine (TEP) and glycidyl trimethylammonium chloride (GTA) were Aldrich products. Diphenylcarbazide (DPC) was Hanna product, Italy. All other chemicals were of analytical grade and were used as received. Potassium dichromate ($K_2Cr_2O_7$) was used as a source of Cr(VI). Table 1 presents the materials used and their chemical formulae.

2.1. Preparation of resin

The GMA/MBA was prepared through the polymerization of GMA in the presence of MBA as a cross-linking agent at ratio 9.9:0.1 (w/w), respectively. A 0.1 g Bz_2O_2 (initiator) was added to the mixture of GMA/MBA with stirring. One milliliters of isopropyl alcohol and 12.6 mL of cyclohexane were mixed and then added to the former solution. All the contents were poured into a flask containing 73 mL (1%) polyvinyl alcohol and heated on a water bath at 75–80 °C with continuous stirring for 3 h. A heavy white precipitate was formed, filtered off then washed repeatedly with methanol to remove the unreacted materials then dried in air.

Four grams of GMA/MBA previously prepared was suspended in 40 mL of DMF. Ten milliliters of TEP was added then the contents of the flask were heated in oil bath for 48 h. The product was subsequently washed with distilled water, methanol, then acetone and dried in air and was referred by RPA.

The concentration of amino group of resin RPA was estimated using the volumetric method. Forty milliliters of 0.05 N HCl solution was added to 0.1 g resin and conditioned for 15 h on a shaker. The residual concentration of HCl was measured through the titration against 0.05 N NaOH solution and phenolphthalein as indicator. The number of moles of HCl interacted by the amino groups and consequently the amino group concentration (in mmol/g of resin) was calculated.

Four grams of RPA was suspended in 50 mL of DMF/water mixture (1:1, v/v). To this mixture, 6 mL of GTA was added and heated at 60 °C for 24 h. The product was washed with distilled water, methanol, acetone and dried in air and was referred by RQA.

The quaternary amine sites of resin RQA was determined using Bench Conductivity Meter, model EC215 (Hanna Instruments) [17]. A 0.1 g of resin was suspended in 200 mL of distilled water. Silver nitrate solution (0.01 M) was added dropwise to the suspension of the resin with continuous stirring and the conductivity was recorded.

2.2. Electrokinetic measurements

The zeta potential measurements were performed for resins RPA and RQA. A 0.01 g of resin was mixed with 50 mL of 0.01 M KCl. The suspension was then adjusted to the specified pH and kept stirring for 15 min. After conditioning, the suspension was left for another 15 min for settling before measurements, which were performed using zeta sizer 2000 (Malvern Instruments Ltd., London, UK).

2.3. Adsorption studies using batch method

Preliminary experiments were carried out to verify the equilibrium time for the uptake of chromate on resins RPA and RQA and was estimated to be 1 h (data are not given). Uptake experiments of chromate by the resins were carried out at pH range of 2–10 by placing 0.1 g portions of dried resin in a series of flasks containing 100 mL metal ions at initial concentration of 100 mg/L. The pH was adjusted using 1 M HCl or NaOH and the contents of the flasks were equilibrated for 1 h at 30 °C. The concentration of Cr(VI) was determined using Bench Photometer, model C200 (Hanna Instruments) and diphenylcarbazide (DPC), Hanna product, as complexing agent for Cr(VI). Fifty microliters of Cr(VI) solution were placed in the cell of the instrument using a micropipette. The volume of the solution was completed to 10 mL using bi-distilled water and the instrument was readjusted to zero reading at 540 nm. The quantity of one kit of DPC was added to the cell contents where a red-orange colour was produced. After waiting for 6 min, the reading of the meter was recorded at 540 nm. Each data point was taken as the average of three measurements.

The effect of initial concentration of chromate on the resin uptake was carried out at pH 3 and 8 and at 30, 40 and 50 °C. A quantity of 0.1 g portions of dried resin were placed in a series of flasks containing 100 mL of chromate anions at the desired concentration. The contents of the flasks were equilibrated on a shaker for 1 h in a water thermostat at the desired temperature then the residual concentration of chromate anions in each flask was determined.

The effect of counter ion on the uptake of chromate by RQA was carried out at pH 8 and 30 °C. The effect of NaCl, $NaNO_3$ and Na_2SO_4 were tested as counter ions at different concentrations. The adsorption experiments were performed by placing

Table 1
Materials used and their chemical formulae

Chemical name	Formula
Glycidyl methacrylate (GMA)	$CH_3-CH-\overset{\overset{O}{\|\|}}{C}-O-CH_2-CH-CH_2$ with CH_2 and O
N,N'-methylene bis-acrylamide (MBA)	$CH_2=CH-CH-NH-CH_2-NH-\overset{O}{C}-CH=CH_2$
Benzoyl peroxide (Bz_2O_2)	$PhC-O-O-CPh$ (with two O)
Tetraethylenepentamine (TEP)	H_2N-CH_2-NH-NH-NH-NH_2
Glycidyl trimethylammonium chloride (GTA)	O with $\overset{+}{N}Cl$, Me, Me, Me

0.1 portions of resin RQA in a series of flasks. In each flask 100 mL (100 mg/L) was added while keeping the ionic strength at the desired concentration using NaCl, NaNO$_3$ or Na$_2$SO$_4$. After equilibration for 1 h, the residual concentration of chromate anions in each flask was determined.

2.4. Uptake experiments using column

Recovery of chromate using resins was studied at pH 3 and 8. The column (diameter = 0.5 cm and length = 10 cm) was packed with 0.4 g resin (bed volume 1.0 cm^3) and solution of chromate (1 mg/L) was passed through the column at flow rate of 3 mL/min. Ten milliliters were collected at time intervals where the residual concentration of Cr(VI) was determined. This process continuous until the residual and initial concentrations of chromate become identical.

2.5. Resin regeneration

Elution experiments were performed by placing resin RQA in a glass column then loaded to saturation with chromate solution (100 mg/L) at pH 3 or 8. The resin loaded by chromate was then subjected to elution using a mixture of 2 M NaCl and 0.5 M NaOH for experiments carried out at pH 3 and using 2 M NaCl for experiments performed at pH 8. The concentration of the released metal ions at 10 mL intervals of the down-flow was determined. The elution process continued till the down-flow becomes free of metal ions. The resin was prepared for the next loading cycle by washing the resin carefully by flowing distilled water through the column. The loading/elution/washing processes were repeated for three cycles.

3. Results and discussions

3.1. Synthesis of resin

Scheme 1 shows the synthetic routes of resins RPA and RQA. As shown in Routes (I) and (II), primary (–NH$_2$) and secondary (–NH–) amine sites of TEP may interact with the epoxy groups of GMA resin giving resin RPA containing secondary (–NH–) and tertiary ($\equiv$N) amine sites, respectively. Formation of resin RQA requires the presence of a replaceable H-atom attached to the nitrogen site. So, RQA may be obtained from the interaction of GTA with secondary amine sites or any residual primary amine sites (RPA) (Route (II)). In case of interaction of GMA with a primary amine site (–NH–) of TEP, the produced resin (RPA) would have no replaceable H-atom to interact with (GTA), Route (I). In such case, resin RQA would not form.

The amine active sites of RPA determined using HCl was found to be 8.1 mmol/g resin. Fig. 1 shows the titration of a suspension of RQA against 0.01 M AgNO$_3$. The end point was detected at 75 mL AgNO$_3$. At the end point, the concentration of quaternary ammonium sites was calculated to be 7.5 mmol/g resin. This indicates that most (and not all) of amino sites of RPA have been transformed to quaternary amine sites in RQA. The slightly lower value of concentration of quaternary amine sites of RQA compared to the amine active sites of RPA may be
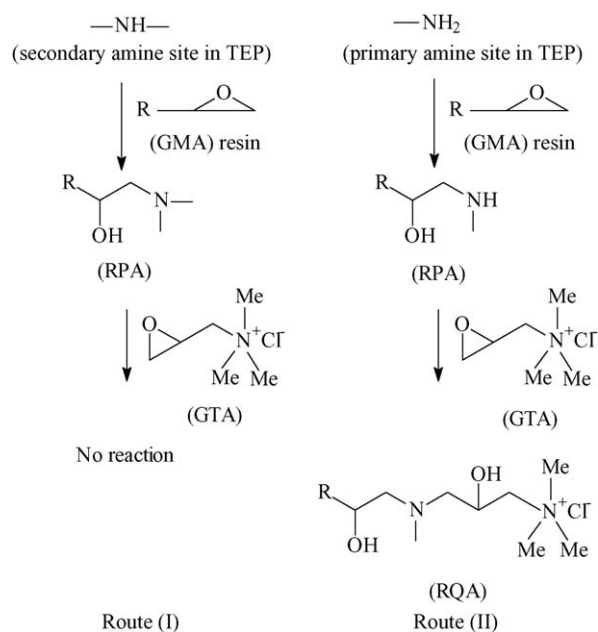
Scheme 1.

attributed to that not all amine sites are amenable to react with GTA since such interaction requires presence of replaceable H-atom on RPA.

3.2. Adsorption studies using batch method

Fig. 2 shows the uptake of chromate by RPA and RQA at different pH values and 30 °C. Resin RPA showed high uptake values at acidic media and the uptake was dramatically decreased in basic conditions. Chromate ions may exist in the aqueous phase in different ionic forms, with total chromate concentrations and pH dictating which particular chromate species will predominate. It has been reported that HCrO$_4^-$, CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$ are the predominant species at pH < 6.5 while CrO$_4^{2-}$
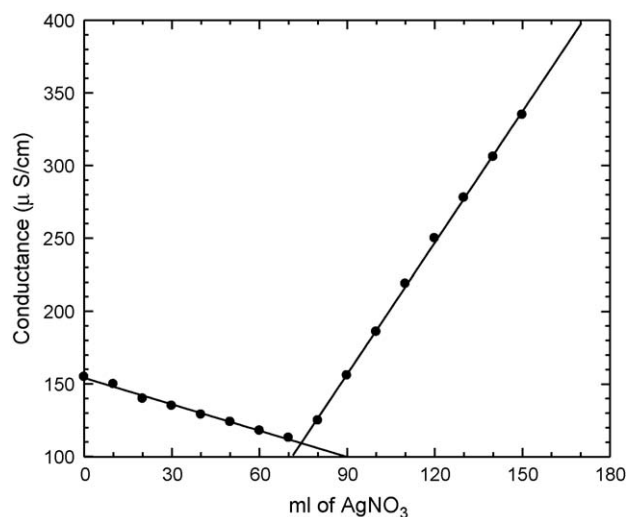

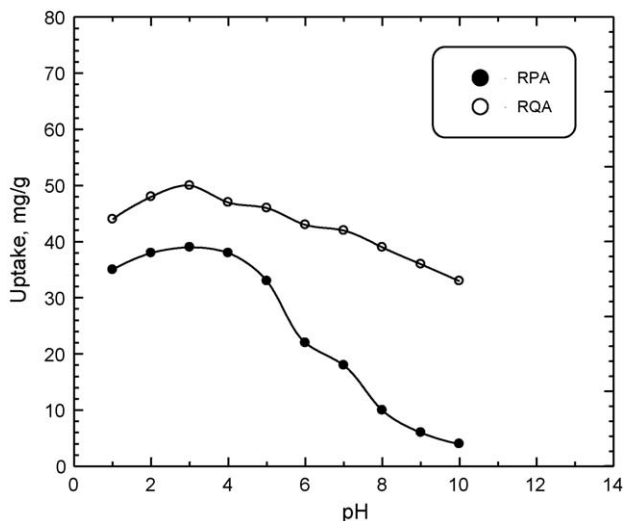Fig. 1. Change in conductance during titration of suspension of resin (RQA) with added 0.01 M AgNO$_3$ solution.

Fig. 2. Effect of pH on the uptake of chromate anions from initial concentration of 120 mg/L by resins RPA and RQA at 30 °C.

Fig. 3. Change of zeta potential of particles of resin RQA as a function of pH.

is the dominant species at pH > 7.5 [20–22]. The uptake of chromate by resin is considered as competition between different chromate species. At pH < 7, the uptake of chromate by RPA may undergo through the protonated amino active sites as follows:

$$R\text{-}N + HCl \leftrightarrow RNH^+Cl^- \tag{1}$$

$$2RNH^+Cl^- + Cr_2O_7^{2-} \leftrightarrow (2RNH^+)Cr_2O_7^{2-} + 2Cl^- \tag{2}$$

$$RNH^+Cl^- + HCrO_4^- \leftrightarrow RNH^+HCrO_4^- + Cl^- \tag{3}$$

$$2RNH^+Cl^- + CrO_4^{2-} \leftrightarrow (2RNH^+)Cr_2O_7^{2-} + 2Cl^- \tag{4}$$

At pH > 7.5, the amino groups become deprotonated, i.e. no Cl$^-$ ions would be available on the resin to be exchanged with chromate species and consequently the uptake by resin RPA was decreased sharply. On the other hand, resin RQA showed uptake at both acidic and basic conditions with slightly improved capacities in the case of the former. In acidic media, the uptake of chromate on RQA may follow the above mentioned reaction steps (2)–(4). In basic media, CrO$_4^{2-}$ is the predominant species and its uptake by RQA may be represented as:

$$2RN^+Cl^- + CrO_4^{2-} \leftrightarrow (2RN^+)CrO_4^{2-} + 2Cl^- \tag{5}$$

The inflection of the curves of both RPA and RQA below pH 3 indicates the higher uptake capacity of chromate in the indicated region. The maximum peak may refer to the preferential adsorption of HCrO$_4^-$ species and/or competitive adsorption as the acidity decreases due to the increase of the concentration of chloride ions. The formation of HCrO$_4^-$ diminishes at either lower or higher pH values and consequently the uptake decreases. The ability of RQA to adsorb chromate from both acidic and basic media may be attributed to the strong basic nature of the quaternary amine moiety. The highly ionized quaternary amine moiety thus permitting the existence of the positively charged sites ($\equiv$N$^+$) necessary for interaction with chromate anions.
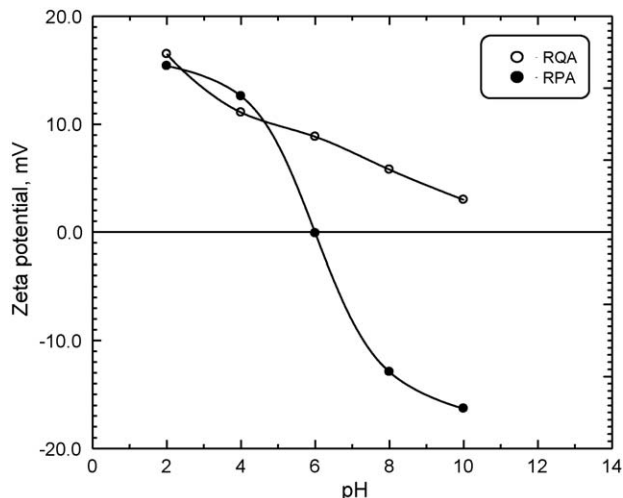
Fig. 3 shows the change in zeta potential of RPA and RQA as a function of pH. Clearly, the point of zero charge (pzc) of RPA is located at pH 6 while RQA is positively charged over pH 2–10. This indicated the higher dissociation of the quaternary amine moiety immobilized on resin RQA in both acidic and alkaline media. Thus, resin RQA may be considered as a strong anionic resin to be used effectively to remove anions from their solutions in the pH range of 2–10.

Fig. 4 shows the variation of the uptake of chromate on RQA with the change in the initial concentration of chromate at pH 3 and 8 and at 30 °C. In all experiments, the equilibrating time was kept at 1 h. In Fig. 4, the maximum uptake values of chromate are 48 and 40 mg/g at pH 3 and 8, respectively. These values correspond to 0.96 and 0.80 mmol/g of chromate adsorbed on RQA at pH 3 and 8, respectively. Comparing these values with the concentration of quaternary ammonium sites of RQA (7.5 mmol/g), a percent of 12.8 and 10.6% surface active sites
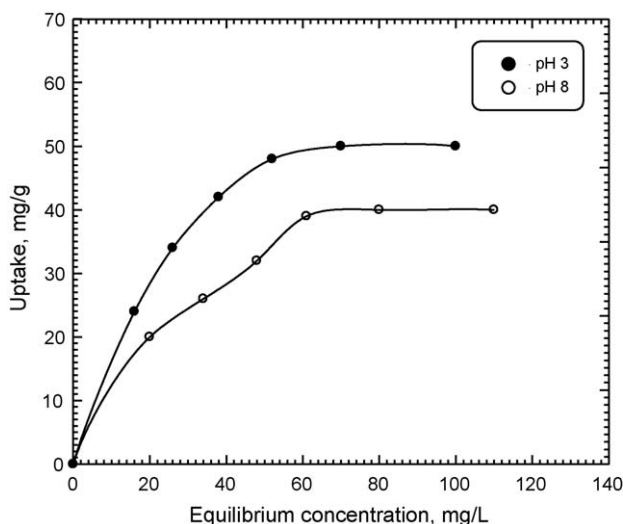

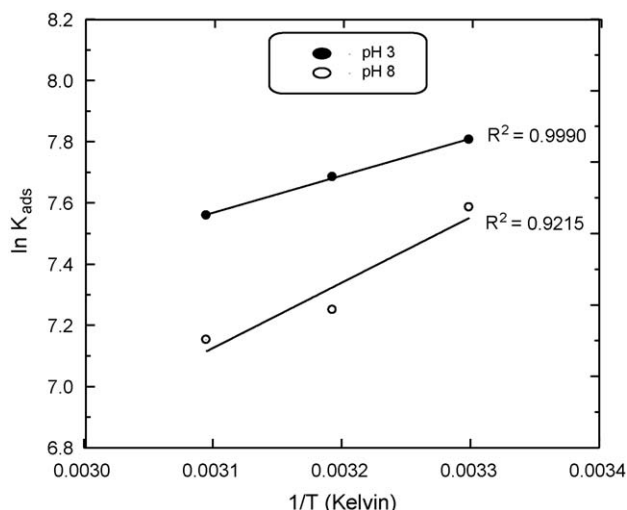Fig. 4. Adsorption isotherms of chromate anions by resin RQA at pH 3 and 8 and 30 °C.

Fig. 5. Van't Hoff plots for the adsorption of chromate anions by resin RQA.

Fig. 6. Effect of counter ions on the uptake of chromate anions at initial chromate concentration of 100 mg/L by resin RQA.

participate in the anion exchange process with chromate at pH 3 and 8, respectively. This ratio is in accordance with the findings of other investigators who reported chromate occupation ratio of 10–20% of the total ion-exchange sites [21].

The effect of temperature on the adsorption capacity of chromate on resin RQA was carried out at 30, 40 and 50 °C. At both pH 3 and 8, the adsorption capacity was found to decrease with the increase of temperature (data are not shown). The adsorption data were analyzed according to Langmuir adsorption isotherm to get the values of Langmuir constant (K_{ads}) at each temperature [24,25]. Thermodynamic parameters were calculated from Van't Hoff equation:

$$\ln K_{ads} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \qquad (6)$$

where ΔH° and ΔS° are enthalpy and entropy changes, R is the universal gas constant (8.314 J/mol K) and T is the absolute temperature (in K). Plotting $\ln K_{ads}$ against $1/T$ gives a straight line with slope and intercept equal to $-\Delta H^\circ/R$ and $\Delta S^\circ/R$, respectively. The values of ΔH° and ΔS° were calculated from Fig. 5 and were used to calculate the Gibbs free energy of adsorption (ΔG°) using relation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (7)$$

The values of ΔG° were found to be −19.68 and −19.03 kJ/mol for pH 3 and 8, respectively. The obtained negative values of ΔG° implies a spontaneous and a physical adsorption process. This supports the operating adsorption mechanism as anion exchange in both acidic and basic media.

Fig. 6 shows the effect of counter ions on the uptake of chromate ($C_o = 100$ mg/L) on RQA at pH 8 and at 30 °C. Obviously, the uptake of chromate decreased with 13.5 and 25% in presence of 0.1 M Na_2SO_4 or 0.1 M $NaNO_3$, respectively. Meanwhile, the uptake of chromate was greatly affected in presence of NaCl and almost depressed at 0.1 M NaCl. This indicates strong competition between Cl^- and chromate anions for the interaction with RQA active sites. Consequently, NaCl was used as an eluent for regeneration of RQA resin for the repeated use.
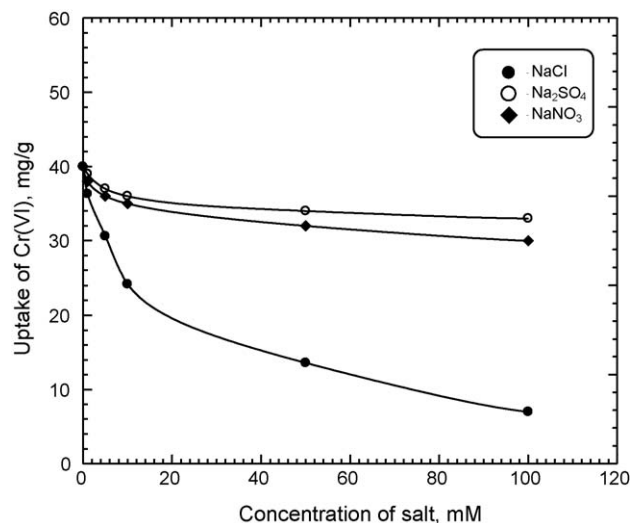
3.3. Adsorption studies using column

Fig. 7 shows the breakthrough curves of chromate at pH 3 and 8 using 0.4 g resin RQA packed in a plastic column (diameter 0.5 cm, height 10 cm, bed volume 1.0 cm^3). In both cases, chromate (1.0 mg/L) broke through after 15 h, equivalent to 900 bed volumes. At the break through point, up to 2700 mL solution was completely free of chromate.

3.4. Resin regeneration

Fig. 8 shows the elution of chromate from resin RQA at pH 3 (using a mixture of 2 M NaCl and 0.05 M NaOH) and at pH 8 (using 2 M NaCl). The concentration of chromate in the down flow was gradually decreased with the increase of volume of NaCl flowing through the column. Complete elution was achieved for solutions of pH 3 and 8 using 100 mL eluent. The mechanism of elution of chromate in acidic media could be
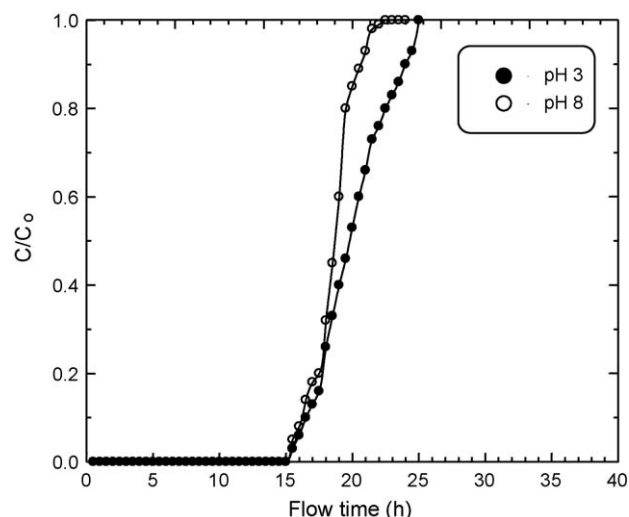

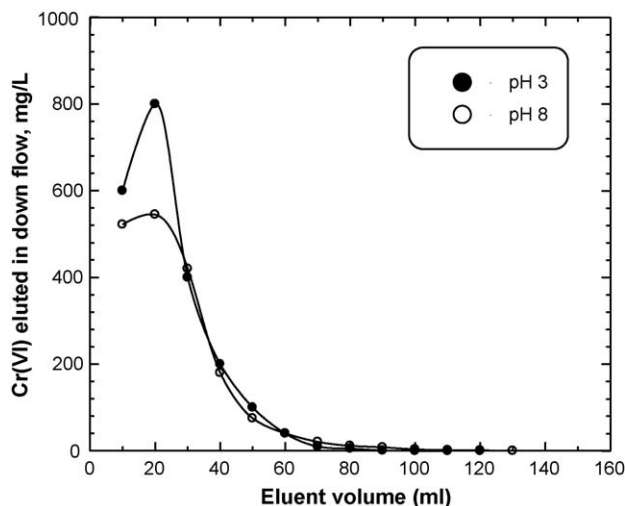Fig. 7. Uptake of chromate anions by resin RQA at pH 3 and 8 using column.

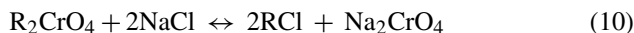Fig. 8. Elution of chromate anions from resin RQA at pH 3 and 8.

represented as follows [21]:

(a) Deprotonation of exchange-phase $HCrO_4^-$ and $Cr_2O_7^{2-}$:

$$2RHCrO_4 + 2NaOH \leftrightarrow R_2CrO_4 + Na_2CrO_4 + 2H_2O \quad (8)$$

$$R_2Cr_2O_7 + 2NaOH \leftrightarrow R_2CrO_4 + Na_2CrO_4 + H_2O \quad (9)$$

Alkali addition is required for the deprotonation of the chromate species.

(b) Removal of exchange-phase CrO_4^{2-} with brine:

$$R_2CrO_4 + 2NaCl \leftrightarrow 2RCl + Na_2CrO_4 \quad (10)$$

The desorption ratio (%) of chromate from resin was calculated using the relation [24,25]:

$$\text{Desorption ratio}(\%)$$
$$= \frac{\text{Amount of metal ion desorbed to the elution medium}}{\text{Amount of metal ion sorbed on the resin}}$$
$$\times 100 \quad (11)$$

The process of loading/elution was repeated for three successive cycles and the resin showed constancy in the uptake capacity with a standard deviation of ±0.1.

4. Conclusions

Quaternary ammonium moieties were immobilized on glycidyl methacrylate/N,N'-methylene bis-acrylamide resin. Zeta potential measurements showed that the resin obtained (RQA) is positively charged over pH 2–10 indicating the strong basic nature of the quaternary ammonium active sites. The resin RQA showed good affinity to adsorb chromate anions from both acidic and basic media. Regeneration of the resin was achieved using 2 M NaCl or a mixture of 0.05 NaOH and 2 M NaCl.

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