

Application of superporous magnetic cationic cryogels for persistent chromate (toxic chromate and dichromate) uptake from aqueous environments

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ABSTRACT: Poly((3-Acrylamidopropyl)trimethylammonium chloride) (p(APTMACl)) cryogels were prepared with cryopolymerization technique and employed for the removal of toxic chromate and dichromate anions from aqueous media. The maximum adsorption capacities of 94 mg/g and 135 mg/g for chromate and dichromate anions, respectively, were determined with the application of the Langmuir isotherm. These values are very close to the experimental values of about 77 and 128 mg/g from 100 mL, 100 ppm chromate, and dichromate solutions using 0.03 g cryogel. The removal efficiency of chromate and dichromate anions were increased with the increase in the amount of cryogel and the removal percentage of chromate and dichromate toxic anions were estimated as 99.21 and 93.61%, respectively, for 0.15 g of p(APTMACl) cryogels used in 100 mL, 100 ppm chromate, and dichromate solutions. Furthermore, magnetic p(APTMACl) cryogels were also prepared and used in the removal of chromate and dichromate, and the maximum adsorption capacities were 30 mg/g and 40 mg/g, respectively. Additionally, the adsorption of these anions were investigated from different media such as drinking water, tap water, seawater, and creek water; and the maximum adsorption amounts in drinking water were 65.5 ± 15 , and 125.5 ± 11 mg/g for chromate and dichromate anions, respectively. The reusability of p(APTMACl) cryogels for the removal of chromate and dichromate anions was also investigated, and it was found that the adsorption capacity for chromate anions decreased to 71.23 ± 4.3 from 97.37 ± 4.5 mg/g, whereas the adsorption capacity of dichromate anions only decreased to 123.69 ± 3.5 mg/g from 129.9 ± 7 mg/g at the end of five adsorption-desorption cycles. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2016, 133, 43438.

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INTRODUCTION

Toxic contamination of water sources has been a long-standing environmental problem that will probably attract more serious attention in the near future due to the gradual decrease in permanent water resources and the ever-increasing demands caused by improvements in quality of life. Among the many toxic contaminants, chromium is known for its troublesome pollutant nature, and exists in two stable forms as chromium (VI) and chromium (III).^{1,2} Although trivalent chromium (III) is essential for organisms, hexavalent chromium (VI) is a highly toxic agent that acts as carcinogen, mutagen, and teratogen in biological systems.^{3,4} For this reason, the maximum concentration

level of chromium (VI) in water is set under 3 $\mu\text{g/L}$ by regulations.⁵ Accordingly, many studies on the removal of chromium from aquatic environments, including one of our earlier reports,⁶ necessitate the use of different techniques, such as chemical reduction, precipitation, and adsorption.^{7,8}

In this work, cryogels with superporous structures were used in the removal of chromate and dichromate from aqueous media. As the cryogels are synthesized with a frozen solvent (water), icy media allow formation of interconnected pores sizes between a few tens of micrometers and a few hundreds of micrometers, with pore wall thicknesses providing better elasticity in comparison to conventional hydrogels.^{9–12} Cryogels' structural

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flexibility, high mechanical strength and fast responsiveness are their most important advantages,¹³ making them intriguing materials for many applications, such as template for metal nanoparticles,^{14,15} bioreactor,¹⁶ column materials,^{17,18} cell-scaffolds,¹⁹ biosensor,^{20,21} and absorbents for environmental application.^{22–24} Therefore, herein p(APTMACl) cryogel possessing cationic quaternary ammonium salts were prepared by cryopolymerization technique and characterized by using FTIR, TGA, and SEM. Additionally, the prepared cryogels were made magnetic field responsive by *in situ* preparation of magnetic metal nanoparticles within them. Finally, the prepared p(APTMACl) and magnetic p(APTMACl) cryogels were used in the removal of chromate and dichromate from aqueous media. Potassium chromate (K_2CrO_4) and potassium dichromate ($K_2Cr_2O_7$) were used as the sources of chromate and dichromate anions, respectively. Various parameters affecting the removal of chromate and dichromate anions, such as the amount of adsorbent (cryogels), the initial concentration of chromate and dichromate, and reusability of p(APTMACl) cryogels were also investigated. Furthermore, the suitability of Langmuir and Freundlich isotherms for the adsorption of chromate and dichromate were examined.

EXPERIMENTAL

Materials

Cationic (3-Acrylamidopropyl)trimethylammonium chloride (APTMACl) (75% in H_2O , Aldrich) as a monomer, *N*, *N*-methylenebisacrylamide (MBA) (99%, Sigma Aldrich) as a cross-linker, *N*, *N*, *N*, *N*-tetramethylethylenediamine (TEMED) (99%, Merck) as a catalyst and potassium persulfate (KPS) (99%, Sigma Aldrich) as an initiator were used for the synthesis of p(APTMACl) cryogels. Potassium chromate (K_2CrO_4) (99%, Sigma Aldrich), and potassium dichromate ($K_2Cr_2O_7$) (99.5%, Sigma Aldrich) were used as anion sources. $FeCl_2 \cdot 4H_2O$ (99%, Fluka) and $FeCl_3 \cdot 6H_2O$ (99%, Acros) as magnetic metal nanoparticle ion sources in pure ethanol (99.9%, Sigma) and sodium hydroxide (NaOH) (99%, Sigma Aldrich) as a precipitation agent were used for synthesis of magnetic p(APTMACl) cryogels. Finally, hydrochloric acid (HCl, 36–38%, Sigma Aldrich) was used for the preparation HCl solution to be used in reusability studies of p(APTMACl) cryogels.

Preparation and Characterization of p(APTMACl) and Magnetic p(APTMACl) Cryogels

The cryogels were synthesized by a cryopolymerization technique.^{9,14,15} In short, 0.832 g (10.4 w/v %) APTMACl and 0.0842 g MBA (18 mol % of APTMACl) were dissolved in 5.5 mL DI water and to this solution 50 μ L TEMED was added and vortexed. In a separate vial, 0.0083 g KPS (1 mol % of APTMACl) initiator dissolved in 1 mL chilled DI water was added and cooled in an ice-bath at $0 \pm 2^\circ C$. The initiator was added into the monomer solution and quickly placed in plastic straws (~8 mm in diameter). The straws were placed in a freezer at $-18^\circ C$ for 16 h to complete cryopolymerization. Thereafter, the prepared cryogels, which were cut into identical cylindrical shapes, were washed with 500 ml DI water three times and dried in an oven at $50^\circ C$ for adsorption studies. The FTIR (Nicolet iS10, Thermo) and TGA

(TG/DTA 6300, SEIKO, Japan) devices were used for the characterization of the p(APTMACl) cryogels.

In situ preparation of magnetic ferrites was performed by using the previously reported method.^{25,26} Accordingly, a cleaned and known amount of dried cryogel was placed in $[FeCl_4]^{2-}$ and $[FeCl_5]^{2-}$ solution in ethanol medium (Fe(II):Fe(III) mole ratio was 1:2) for 2 h for metal salt loading. After that, the mixture of ferric and ferrous ion-loaded cryogels was washed 2 times with pure ethanol to remove unbound metal salts. After that, the removal of unbound metal salts, the metal salt-loaded p(APTMACl) cryogels were transferred into 0.75M NaOH solution and the precipitation reaction continued for 3 h in a beaker at 300 rpm mixing rate with magnetic stirrer at room temperature. Finally, the cryogels were washed with DI water, and dried in an oven at $50^\circ C$ for the adsorption studies.

Removal of CrO_4^{2-} and $Cr_2O_7^{2-}$ Anions from Aqueous Media

The adsorption experiments were performed in a beaker in batch type studies. The 100 ppm 100 mL chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) anion solutions were used with 0.03 g dried p(APTMACl) cryogel dose. The adsorption experiments lasted for 180 min. During the adsorption, 0.5 ml samples were taken from the anion solution at 0, 5, 15, 30, 60, 120, and 180 min, and were diluted 10 times before measuring the amounts with atomic absorption spectrometer (AAS, Thermo iCE 3000) measurements.

The effects of the various parameters such as the concentrations of the anions and the amounts of the p(APTMACl) were investigated. The concentrations of the anion solutions were 50, 100, 150, 200, and 250 ppm with 100 mL volume of CrO_4^{2-} and $Cr_2O_7^{2-}$ anions and a constant amount of cryogel (0.03 g). Additionally, the effect of the amount of cryogels was examined by using 0.03, 0.05, 0.1, and 0.15 g of cryogel at constant concentration of 100 ppm 100 mL of CrO_4^{2-} and $Cr_2O_7^{2-}$ anions.

The removal of CrO_4^{2-} and $Cr_2O_7^{2-}$ anions from media such as drinking water (commercially available, ERIKLI), tap water, seawater (Dardanelles from Canakkale province, Turkey) and a local creek water (Saricay) was examined. A certain amount of p(APTMACl) cryogels (0.05 g) was placed in 100 ppm 100 mL CrO_4^{2-} and $Cr_2O_7^{2-}$ anion solution prepared in the above-mentioned waters separately, and the maximum adsorption amounts of toxic anions were determined after 180 min via AAS measurements.

Reusability Studies

The reusability studies for p(APTMACl) cryogels in the removal of toxic CrO_4^{2-} and $Cr_2O_7^{2-}$ anions were carried out by using 100 ppm 100 mL CrO_4^{2-} and $Cr_2O_7^{2-}$ solution with 0.05 g p(APTMACl) cryogels. The reusability of p(APTMACl) cryogels was investigated by repeating adsorption-desorption cycles five times. The cryogels adsorbed the toxic anions (CrO_4^{2-} and $Cr_2O_7^{2-}$) from their aqueous solution in about 180 min and were washed with DI water and placed into a 100 mL 5M HCl solution about 180 min for the desorption step. In each adsorption and desorption cycle, 0.5 mL samples were taken and diluted 10 times with DI water and the amount of toxic anions was determined via AAS measurements. In each cycle, e.g., after desorption; the cryogels were placed into a beaker with DI water

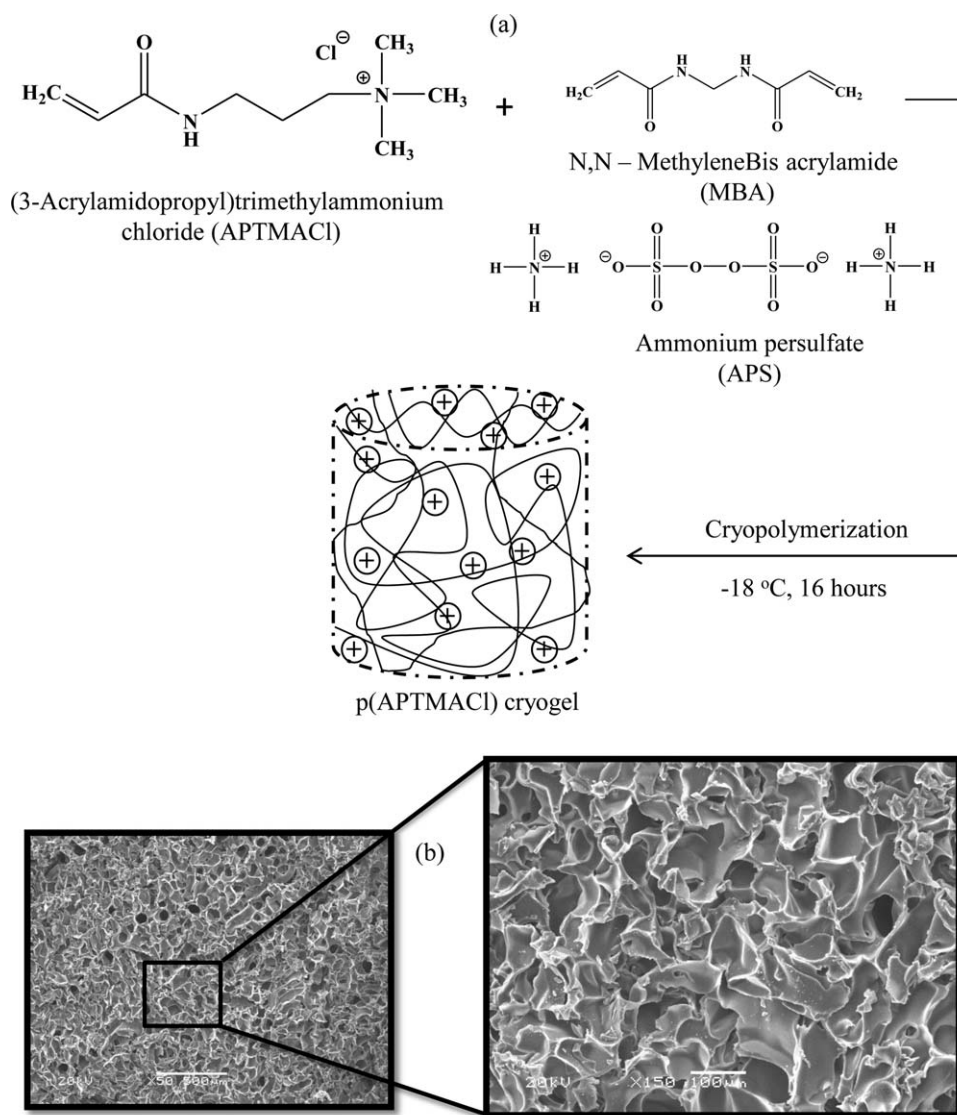


Figure 1. (a) Schematic presentation of synthesis of p(APTMACl) cryogel, (b) and its SEM images.

for about 60 min for washing, and then placed into the toxic anion solutions. These cycles continued five times repetitively, and each experiment was repeated three times.

RESULTS AND DISCUSSION

Synthesis and Characterization of p(APTMACl) and Magnetic p(APTMACl) Cryogels

The p(APTMACl) cryogels were synthesized with a cryopolymerization technique. The schematic presentation of the synthesis of p(APTMACl) cryogel is illustrated in Figure 1(a). The characterization of p(APTMACl) cryogels was performed by scanning electron microscopy (SEM, JSM-5600, JEOL) and is presented in Figure 1(b). As can be seen, the pore sizes of p(APTMACl) cryogels range between 10 and 100 μm and are macroporous (>50nm) or superporous. The FTIR spectrum of p(APTMACl) cryogel is illustrated in Figure 2(a) and the functional groups are in accordance with the structure of conventional p(APTMACl) hydrogels that were reported in earlier investigations.^{6,27,31} The N-H stretch-

ing modes of amide groups of APTMACl were observed at 3354 and 3247 cm^{-1} , respectively. Additionally, C-H stretching of $-\text{CH}_3$ at 2942 cm^{-1} , the quaternized amine at 1640 cm^{-1} , N-H bending at 1540 cm^{-1} , C-H bending vibrations at 1480 cm^{-1} , and C-N-C stretching peaks at 1091 cm^{-1} were observed.

The magnetic ferrite or metal nanoparticles with magnetic properties were prepared inside the cryogels.^{18,19} The positively charged polymers, such as with modification such as p(4-VP)³² simultaneously p(APTMACl), can be loaded with metal salts only from their ethanol solutions, not from aqueous solutions, due to the charge-charge repulsion between the quaternary amine of p(APTMACl) and metal ions in aqueous medium. It is known that the chloride salts of transition metals are soluble in molecular form in ethanol.²⁷ And these molecularly dissolved metal salts complexes with cationic part of p(APTMACl) cryogels where there are Cl^- anions because of the quaternary ammonium chloride salt in the chemical structure as shown in Figure 1(a), and these dissolved metal salts are introduced into

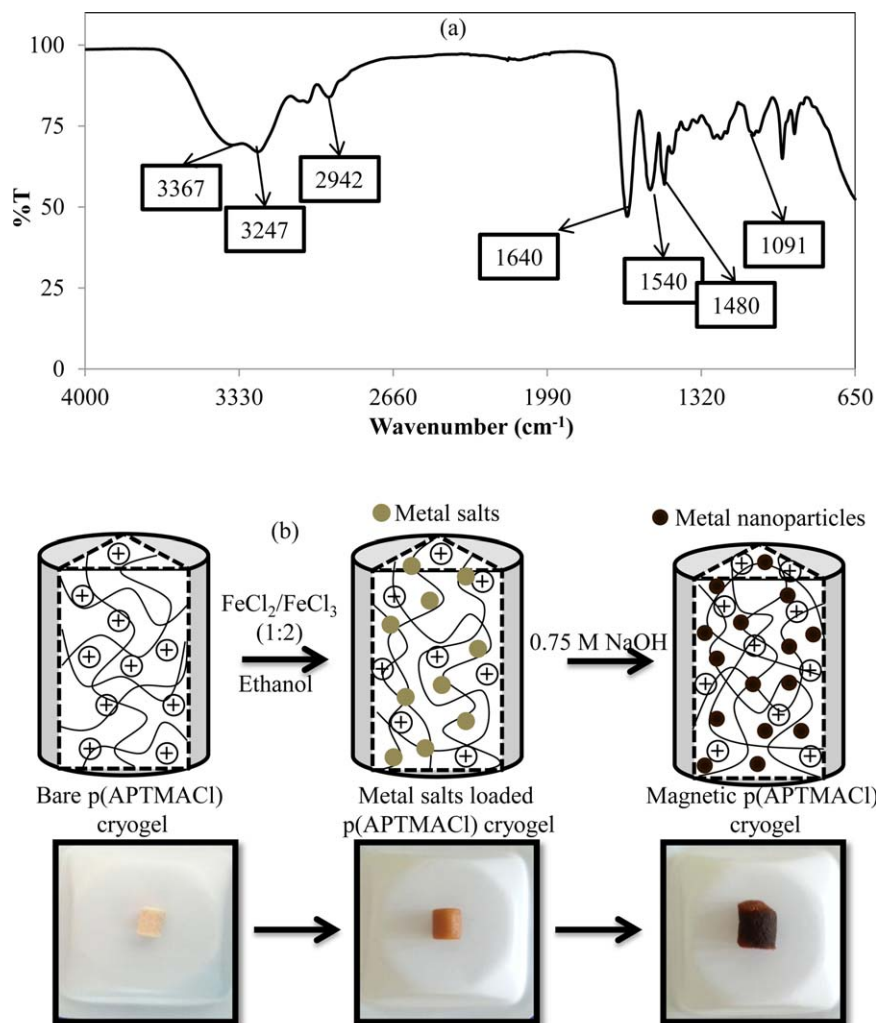


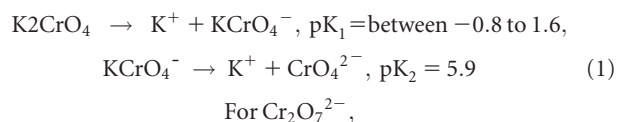
Figure 2. (a) The FTIR spectrum of p(APTMACI) cryogels, (b) preparation of magnetic p(APTMACI) cryogels, and the digital images of bare, metal salt-loaded and magnetic p(APTMACI) cryogels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cationic cryogels as tetrachloride and/or pentachloride coordination forms.³³ The magnetic p(APTMACI) cryogel composites were prepared by loading a mixture of FeCl₂ and FeCl₃ in 1:2 mole ratio from the corresponding salts in ethanol solution. It was assumed that these metal salts are loaded as [FeCl₄]²⁻ and [FeCl₅]²⁻ within cationic structures.^{14,25,26} The iron salt-loaded p(APTMACI) cryogel was then precipitated by treatment with 100 mL 0.75M NaOH solution in water. Accordingly, the schematic presentation of the magnetic p(APTMACI) cryogel preparation is illustrated in Figure 2(b) with the corresponding digital camera images. It is obvious from the color change that the bare p(APTMACI) cryogels changed from cream color to dark brown due to the formation of magnetic particles within p(APTMACI) cryogels.

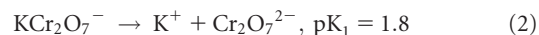
Adsorption Studies with p(APTMACI) Cryogels for the Removal of CrO₄²⁻ and Cr₂O₇²⁻ Toxic Anions from Aquatic Media

The removal of CrO₄²⁻ and Cr₂O₇²⁻ anions was carried out from aqueous media at room temperature. K₂CrO₄ and K₂Cr₂O₇ were used as the sources of CrO₄²⁻ and Cr₂O₇²⁻ anions,

respectively. As the oxidation number of the CrO₄²⁻ depends strongly on the medium pH, the corresponding values of pK_a for CrO₄²⁻ are given below;



For Cr₂O₇²⁻,



As can be seen, these ionization steps are substantially affected by the change in pH of the medium. In Figure 3(a), the maximum adsorption amount (mg/g) of CrO₄²⁻ and Cr₂O₇²⁻ anions by p(APTMACI) cryogels is presented from their aqueous solutions using 100 mL of 100 ppm CrO₄²⁻ solutions with 0.03 g cryogel as adsorbent dosage. A certain amount of cryogel was placed in a beaker containing 100 mL 100 ppm CrO₄²⁻ and Cr₂O₇²⁻ solution, and 0.5 mL samples were taken from the anion solution at certain time intervals: 0, 5, 15, 30, 60, 120, and 180 min and after dilution ten-fold with DI water, the amounts of CrO₄²⁻ anions were determined via AAS measurements. The p(APTMACI) cryogels could adsorb 76.8 ± 6.3 and 128.1 ± 8.9 mg/g of CrO₄²⁻ and Cr₂O₇²⁻

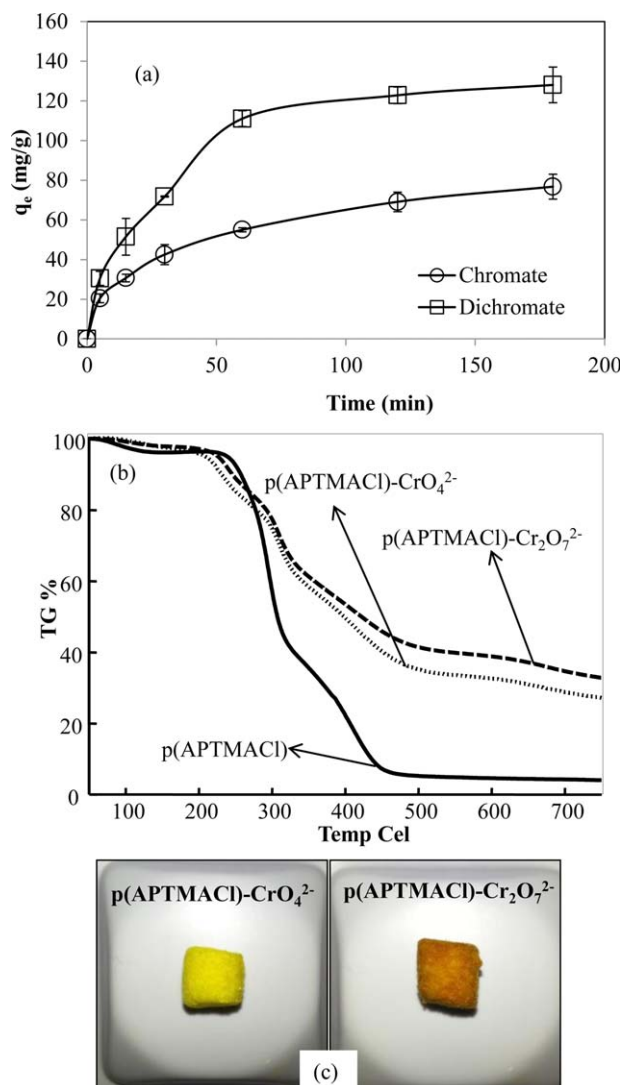


Figure 3. (a) The chromate and dichromate anion adsorption isotherms of p(APTMACl) [0.03 g cryogel, 100 mL, 100 ppm chromate and dichromate solution], (b) TGA thermograms of p(APTMACl), chromate, and dichromate anion-adsorbed p(APTMACl) cryogels, and (c) digital camera images of chromate and dichromate-adsorbed p(APTMACl) cryogels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

anions from their aqueous solutions, respectively and the corresponding values are presented in Supporting Information Table I. These values are much higher than the ones reported in the literature for the cationic structure on the different materials such as silica and Fe-(OH)_x-polymerin complex.^{34–37} Additionally, the thermal behaviors of p(APTMACl), p(APTMACl)-CrO₄²⁻ and p(APTMACl)-Cr₂O₇²⁻ are given in Figure 3(b). The thermal stability of p(APTMACl), p(APTMACl)-CrO₄²⁻ and p(APTMACl)-Cr₂O₇²⁻ cryogels were determined using a thermogravimetric analyzer (TGA, SII TG/DTA 6300) by heating about 3–5 mg samples up to 750 °C at 10 °C/min heating rate under N₂ flow of 20 mL/min. The corresponding thermograms are also presented in Figure 3(b) comparing the thermal behavior of the p(APTMACl), p(APTMACl)-CrO₄²⁻, and p(APTMACl)-Cr₂O₇²⁻ cryogels. The

degradation temperature range and the amount of degradation are given in Supporting Table 2 for p(APTMACl), p(APTMACl)-CrO₄²⁻ and p(APTMACl)-Cr₂O₇²⁻. The bare p(APTMACl) cryogels degraded in four steps. The first step of thermal degradation of bare p(APTMACl) cryogel was observed between 50 °C and 122 °C with 3.4% weight loss. The second step was seen between 230 °C and 324 °C with 58.2% weight loss, and the third step was between 325 °C to 446 °C with 92.2% weight loss. Finally, the last step was between 450 °C to 750 °C with 95.9% weight loss. On the other hand, p(APTMACl)-CrO₄²⁻ and p(APTMACl)-Cr₂O₇²⁻ showed similar behavior for all temperatures on thermograms. Both of them showed similar degradation characteristics to bare p(APTMACl) cryogels with smaller degradation steps and the temperature intervals were approximately between 50–122 °C, 209–288 °C, 290–325 °C, 330–473 °C, and 475–750 °C for the degradation steps, respectively. Their degradation percentages are presented in Supporting Information Table II. The first degradation step, 50–122 °C could be due to the loss of water from all samples. As can be seen, the weight losses for p(APTMACl)-CrO₄²⁻ and p(APTMACl)-Cr₂O₇²⁻ materials is much less than for bare p(APTMACl) cryogels, as an indication of greater thermal stability of the metal ion-adsorbed cryogels. This can be expected as the cryogel chains are also connected via electrostatic interaction with negatively charged metal salts and positively charged p(APTMACl) cryogel networks. Up to heating to 750 °C, the weight losses of p(APTMACl), p(APTMACl)-CrO₄²⁻ and p(APTMACl)-Cr₂O₇²⁻ were estimated at about 96, 73, and 67%, respectively, again as an indication of the increased thermal stability of p(APTMACl) cryogels with metal binding. The digital camera images of CrO₄²⁻ and Cr₂O₇²⁻ anions adsorbed by p(APTMACl) cryogels are shown in Figure 3(c). It is clear that the color of p(APTMACl)-CrO₄²⁻ was yellow, and p(APTMACl)-Cr₂O₇²⁻ was orange, different to bare p(APTMACl) which is shown in Figure 2(b) with a light reddish color, a lighter shade of the color of the APTMACl monomer itself.

The effects of the amount of cryogels on the removal of CrO₄²⁻ and Cr₂O₇²⁻ anions were also investigated and the corresponding adsorption amounts versus time graphs are illustrated in Figure 4. Different amounts of p(APTMACl) cryogels, 0.03, 0.05, 0.1, and 0.15 g, were placed in 100 mL solution of 100 ppm CrO₄²⁻ and Cr₂O₇²⁻ solution separately. The adsorbed amounts as a function of time was graphed after removing 0.5 mL samples from the solutions and completing AAS measurements. It is obvious from Figure 4(a) that the removal efficiency of CrO₄²⁻ anions increased with the increase in the amounts of p(APTMACl) cryogel. The removal percentage of CrO₄²⁻ reached a maximum value of 70.9% with 0.05 g cryogels after 120 min. A further increase in the amount of cryogels slightly increased the removal efficiency and facilitated the further removal of CrO₄²⁻. The removal efficiency of CrO₄²⁻ was estimated as 91.9% and 99.2% for 120 min of treatment with 0.1 g and 0.15 g of cryogels, respectively. Additionally, the removal efficiency of Cr₂O₇²⁻ is shown in Figure 4(b). The removal efficiency of Cr₂O₇²⁻ by p(APTMACl) cryogel showed similar behavior to CrO₄²⁻ removal, as the increase in the amount of cryogel slightly increased the removal efficiency to 62.8%, 85.2%, 93.1% and 93.6% for 0.03, 0.05, 0.1, and 0.15 g of p(APTMACl) cryogels, respectively. Although, the adsorption

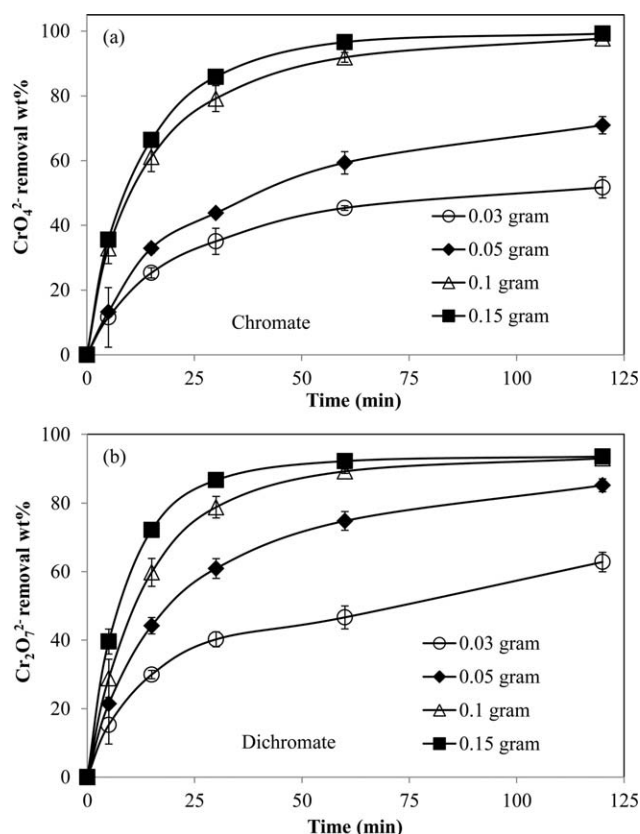


Figure 4. The effect of amount of p(APTMACI) cryogel on the (a) CrO_4^{2-} and (b) $\text{Cr}_2\text{O}_7^{2-}$ anion removal. [100 mL, 100 ppm CrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$ solution].

amount of toxic CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ anions increased with the increase in the amount of p(APTMACI) cryogels, all the functional groups on the cryogel network, which were responsible for the adsorption, were not completely fully engaged. This is based on the weight of used cryogels and theoretical calculations that suggest ~ 1.5 moles of cationic monomer/charges are used for 1.0 mole of $\text{Cr}_2\text{O}_7^{2-}$ anions. This can be explained by sufficient use of all functional groups in p(APTMACI) cryogel network due to the crosslinking density. Accordingly, when the cryogels swell, initially the functional groups on the surface layer were filled with the toxic anions, with time the inner layers of functional groups towards the center of the cryogels became available for adsorption after all the functional groups on the surfaces were filled. This process continued until all the functional groups were filled with toxic anions and an equilibrium was then reached between the adsorbed and desorbed metal ions on and from the surfaces of p(APTMACI) cryogel network. Furthermore, the effect of the concentration of toxic CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ solutions on the adsorption process was investigated and the results are illustrated in Supporting Figure 1. Accordingly, the effect of initial concentration on the adsorption of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ were observed. A certain amount of p(APTMACI) cryogels (0.05 g) were placed in 100 mL of 50, 100, 150, 200, and 250 ppm CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ solution separately and the maximum amounts of adsorbed toxic CrO_4^{2-} anions were determined after 120 min for each

solution. As can be seen in Supporting Information Figure 1(a,b), the maximum amount of adsorbed CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ anions clearly increased with the increase in the initial toxic anion concentrations. The increase in the amount of the adsorbed CrO_4^{2-} was 35.11, 53.18, 63.86, 77.65, and 89.68 mg/g, and $\text{Cr}_2\text{O}_7^{2-}$ was 32.11, 65.06, 90.86, 105.80, and 131.24 mg/g, respectively, with the increase in the initial adsorption solution concentrations in the order of 50, 100, 150, 200, and 250 ppm with 100 mL volume. As can be seen, adsorption amounts of both anions (CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$) almost linearly increased with the increase in the initial concentrations with pretty good correlation coefficients ($R^2 = 0.98$ for both metallic oxy anions) suggesting the coverage of p(APTMACI) cryogels with the increase in the amounts of chromates in the solutions.

Application of Langmuir and Freundlich Equations for CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ Anion Adsorption by p(APTMACI) Cryogels

To determine interactions between the cryogel and chromate ions, the adsorption isotherms of Langmuir and Freundlich were applied to relate the adsorbate concentration and the adsorbed amounts at the interface. The Langmuir (eq. (3)) and Freundlich (eq. (4)) equations were applied to determine and define the nature of adsorption of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ anions by p(APTMACI) cryogels:

$$C_e/q_e = (C_e/q_m) + 1/q_m K_L \quad (3)$$

where, C_e (mg/L) is the equilibrium concentration of anions in solution, q_e (mg/g) is the adsorption capacity at the equilibrium, q_m (mg/g) is the maximum adsorption of the anions and K_L (L/mg) is the Langmuir adsorption equilibrium constant. The Langmuir isotherms for the adsorption of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ are illustrated in Figure 5(a,b), respectively. Additionally, their corresponding values are presented in Table I. Q_m (mg/g) was ~ 94 and 135 mg/g for CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ respectively.

$$\text{Log } q_e = \text{log } K_F + 1/n \text{log } C_e \quad (4)$$

where, C_e is the equilibrium concentration of anions (mg/L), q_e is the amount of the adsorbed anions per gram of adsorbent (mg/g), K_F and n are physical constants of the Freundlich adsorption isotherm. In other words, K_F and n are indicators of the adsorption capacity and the adsorption intensity, respectively. Accordingly, the application of the Freundlich isotherm for the adsorption of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ anions is given in Figure 5(c,d), respectively, and their corresponding values are presented in Table I.

The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, without any interaction between adsorbed molecules.^{28–30} Figure 6(a,b) illustrates the linear plot of specific adsorptions C_e/q_e against the equilibrium concentrations C_e for CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ ions, respectively; the Langmuir constants q_m (mg/g) and K_L (L/mg) can be determined from the slope and intercept of the plot and are presented in Table I. The Freundlich isotherm²⁸ is an empirical equation used to describe heterogeneous systems, and applied to CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ ion adsorption by p(APTMACI) cryogels. The values of K_F and n are

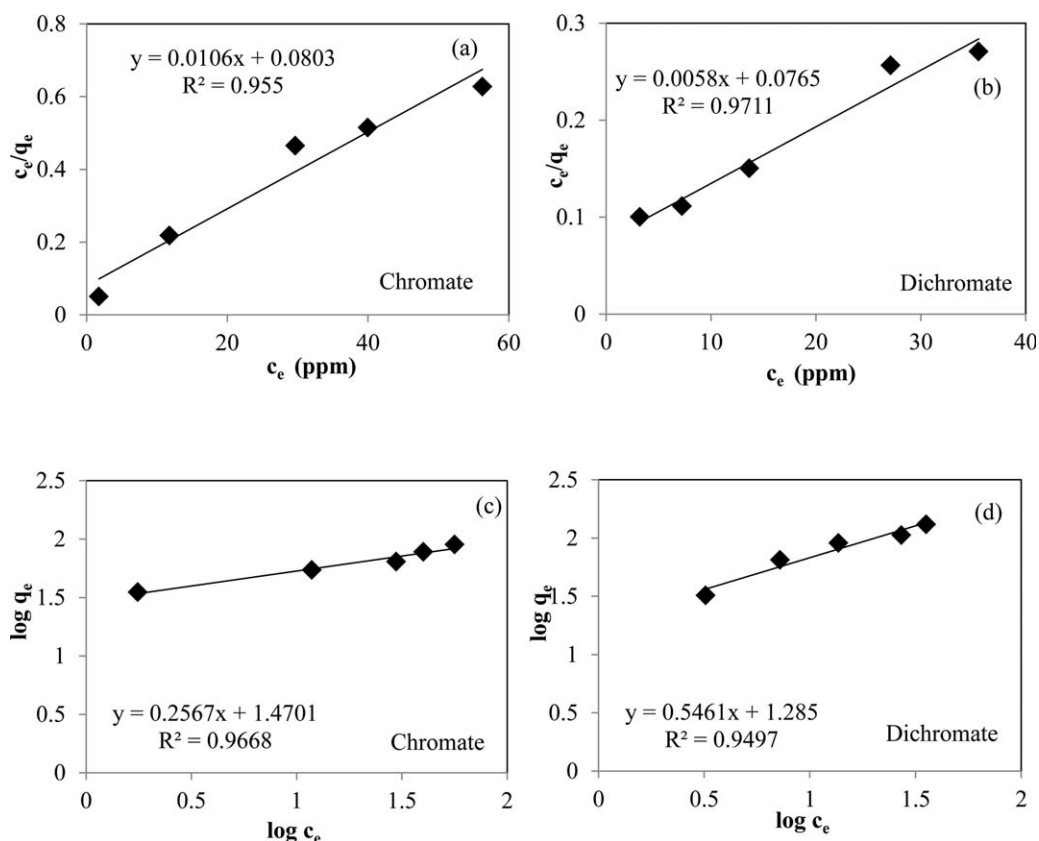


Figure 5. The application of Langmuir (a) and (b), and Freundlich (c) and (d) isotherms to the adsorption of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ anions with p(APTMACl) cryogels.

calculated from the intercept and slope of the plot as shown in Figure 6(c,d), respectively; $n > 1$ indicates the favorability of adsorption.²⁸ As both plots demonstrated good linearity ($r^2 > 0.95$), the adsorption process can be represented by both of the isotherms. The values of the correlation coefficients point to the favorable nature of adsorption of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ ions into p(APTMACl) cryogels.

The CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ Anion Adsorption Properties of mag-p(APTMACl) Cryogels

The adsorption of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ anions from their aqueous solutions by the magnetic p(APTMACl) cryogels were also studied and results are presented in Figure 6(a). The amount of the adsorbed CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ anions were decreased greatly with respect to the bare p(APTMACl) cryogels and the corresponding values are listed in Supporting Table I. As can be seen almost 2.5- and 3-fold reduction of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ adsorption, respec-

tively, was observed and this can be attributed to the high amounts of magnetic ferrite in the p(APTMACl) cryogels. The digital camera images of the magnetic p(APTMACl) cryogels in CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ solutions are illustrated in Figure 6(b). Additionally, the thermal behavior of the magnetic p(APTMACl) and CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ adsorbed magnetic p(APTMACl) cryogels were also investigated and are illustrated in Figure 6(c). It was observed that the magnetic p(APTMACl) cryogels had four degradation steps. The first degradation step of magnetic p(APTMACl) cryogels was between 50 °C and 162 °C with 4% weight loss. Next, the second step was between 163 °C and 202 °C with 19% weight loss. The third step was observed between 210 °C and 422 °C with 50% weight loss. Finally, the fourth step was between 430 °C and 750 °C with 64% weight loss. Therefore, it is apparent that the magnetic p(APTMACl) cryogels provide earlier degradation, but less total weight loss at 750 °C compared to bare p(APTMACl) cryogels.

Table I. The Parameters for the Absorption of CrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$ by p(APTMACl) Cryogel from the Application of the Langmuir and Freundlich Isotherms

	Langmuir isotherm constants			Freundlich isotherm constants		
	K_L (L/mg)	q_m (mg/g)	r^2	K_F ($\text{g kg}^{-1} \cdot \text{gm}^{-3}$) ⁿ	n	r^2
CrO_4^{2-}	0.132	94.34	0.955	29.52	3.89	0.967
$\text{Cr}_2\text{O}_7^{2-}$	0.076	135.46	0.971	19.28	1.83	0.950

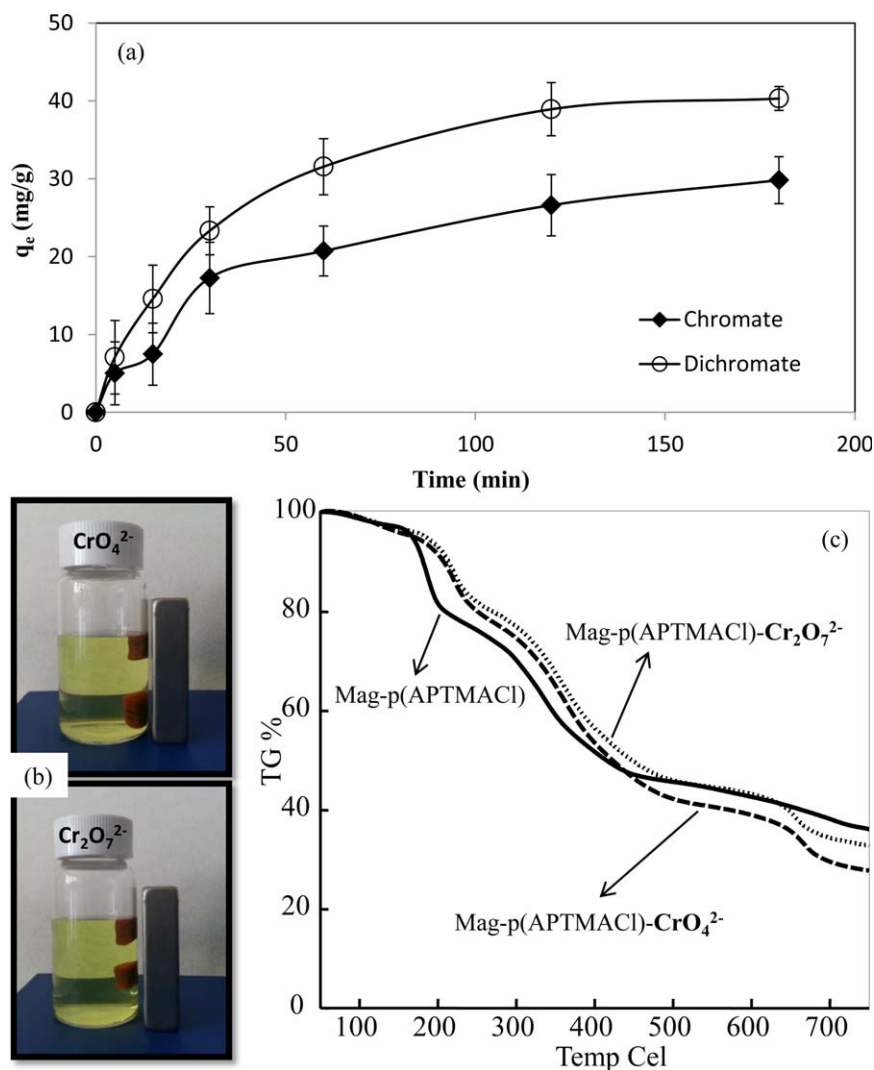


Figure 6. (a) The adsorption isotherms of magnetic p(APTMACl) for chromate, and dichromate [0.03 g cryogel, 100 mL, 100 ppm chromate, and dichromate] (b) digital camera images, and (c) TGA thermograms of chromate, and dichromate adsorbed-magnetic p(APTMACl) cryogels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ Anion Adsorption Ability of p(APTMACl) Cryogels from Different Media

It is a fact that persistent chromate anions, serious environmental pollutants, can be found in various aquatic environments such as lakes, creeks, seawater and even tap water and drinking water obtained from natural springs due to discharge of many effluents from industrial sites and factories. Therefore, the removal of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ anions from different aquatic environments has great significance. The maximum adsorption amounts of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ anions by cationic p(APTMACl) cryogels from different aqueous environments such as drinking water, tap water, sea water, and creek water were investigated and the corresponding graph is given in Figure 7(a). It obvious that the maximum adsorption amount of $\text{Cr}_2\text{O}_7^{2-}$ anions by cationic p(APTMACl) cryogels from DI water is 128.1 ± 8.9 mg/g, whereas the adsorption amounts of $\text{Cr}_2\text{O}_7^{2-}$ anions from drinking water, tap water, sea water, and creek water were determined as 125.5 ± 11 , 79.4 ± 1.5 , 26.8 ± 4.6 , and 15.4 ± 2.5 mg/g, respectively. On the other hand, the maximum adsorption amount of

CrO_4^{2-} in DI water is estimated as 76.8 ± 6.3 mg/g. The maximum adsorption amounts of CrO_4^{2-} anions adsorbed by p(APTMACl) cryogels were determined as 65.5 ± 15 , 49.4 ± 11 , 8.8 ± 1.9 , and 8.4 ± 1.3 mg/g from drinking water, tap water, seawater, and creek water. Thus, it can be inferred that p(APTMACl) cryogels are resourceful materials for the removal of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ anions from aquatic environments. The existence of various salts and anions in natural waters (spring, creek, seawater, and tap water) can hamper the adsorption capacity of p(APTMACl) cryogels for CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ anions due to competition for active sites on the cryogel network.

Reusability of p(APTMACl) Cryogels for Removal of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ Anions

The reusability of adsorbents in environmental usage determines their fate for industrial applications together with other properties, such as being environmentally friendly, long lasting shelf life, cost, and so on. Thus, the reusability of p(APTMACl) cryogels in the removal of toxic CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ anions was investigated

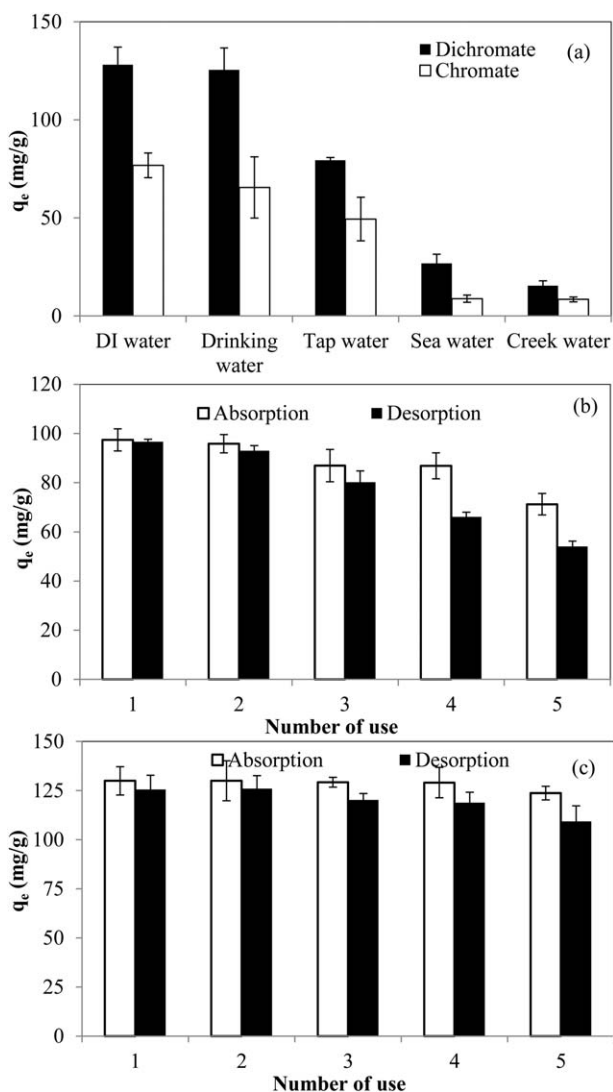


Figure 7. (a) The removal amounts of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ anions by p(APTMACl) cryogels from different aqueous environments, and the reusability of p(APTMACl) cryogels for removal of (b) CrO_4^{2-} and (c) $\text{Cr}_2\text{O}_7^{2-}$ anions. [100 mL, 100 ppm CrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$ solution, 0.05 g p(APTMACl) cryogels, elution solution is 100 mL 5M HCl].

with repeated adsorption-desorption cycles. The elution of the chromate ions was completed by the treatment of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ adsorbed p(APTMACl) cryogels with 100 mL 5M HCl. As illustrated in Figure 7(b,c) during the adsorption-desorption cycles of p(APTMACl) cryogels for CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$, the adsorption capacity decreased with the number of usages e.g., from 97.37 ± 4.5 mg/g to 71.23 ± 4.3 mg/g over 1, 2, 3, 4, and 5 times use. In correlation to this, desorption capacities were also decreased with the number of uses, from 96.64 ± 1 mg/g to 54.07 ± 2.1 mg/g and the corresponding graph is illustrated in Figure 7(b). The percentage desorption amount of CrO_4^{2-} anions from p(APTMACl) cryogels decreased from 99% to 75% with at the end of 5th usage. The reusability of p(APTMACl) cryogels in the removal of $\text{Cr}_2\text{O}_7^{2-}$ anions was also investigated, and the p(APTMACl) cryogels showed almost similar adsorption and

desorption capacities; 129.9 ± 7 mg/g adsorption capacity and 125.5 ± 6 mg/g desorption capacity for the first two cycles. However, the adsorption and desorption capacities decreased to 123.69 ± 3.5 mg/g and 109.31 ± 7.9 mg/g respectively at the end of the fifth usage and the corresponding graph is given in Figure 7(c). The percentage desorption amount of $\text{Cr}_2\text{O}_7^{2-}$ anions from p(APTMACl) cryogels were the same for the first two desorptions with 96% and at the end of 5 cycles it was decreased to 88%. So, it can be concluded that the reusability of p(APTMACl) cryogels for the removal of $\text{Cr}_2\text{O}_7^{2-}$ anions is better than that of CrO_4^{2-} anions.

CONCLUSIONS

The p(APTMACl) cryogels were prepared and used as adsorbent for toxic CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ anions. The p(APTMACl) cryogels are naturally positively charged and act as an anionic exchanger for CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ anions. The removal efficiency of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ were 99.2% and 93.6% in the presence of 0.15 g cryogel from 100 mL of 100 ppm solution. On the other hand, the adsorption speed (~ 100 min) was about three times better than that the bulk hydrogel (~ 300 min).⁶ Additionally, the application of Langmuir and Freundlich isotherms to the adsorption of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ anions was also investigated and it was found that both isotherms can be used for the process of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ adsorptions. Furthermore, the p(APTMACl) cryogels were also prepared as magnetically responsive composites, by loading $[\text{FeCl}_2]$ and $[\text{FeCl}_3]$ metal salt mixture (in 1:2 mole ratio) from their ethanol solutions and then reducing with 0.75M NaOH *in situ*. The magnetic p(APTMACl) cryogels were also used for the adsorption of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$, and the maximum amount of the adsorbed toxic anions decreased in comparison to bare p(APTMACl) cryogels from 76.8 ± 6.3 mg/g to 29.8 ± 3 mg/g and from 128.1 ± 7.2 mg/g to 40.29 ± 1.5 mg/g for CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ anions, respectively due to the existence of ferrites within the cryogel matrices. Consequently, the magnetic p(APTMACl) cryogels can be considered useful for the removal of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ anions, in spite of the reduction in their adsorption amount. Furthermore, it was demonstrated here that p(APTMACl) cryogels can even be used in removal of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ anions from natural aquatic media such as drinking, tap, sea, and creek waters. The maximum adsorption amount of 65.5 ± 15 , and 125.5 ± 11 mg/g for CrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$ anion removal efficiencies, respectively, was obtained in drinking water. Moreover, the reusability of p(APTMACl) for the removal of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ anions was investigated by repeating the adsorption-desorption cycles five times. The adsorption capacity of p(APTMACl) cryogels in the removal of CrO_4^{2-} anions decreased from 97.37 ± 4.5 mg/g to 71.23 ± 4.3 mg/g, and the removal efficiency for $\text{Cr}_2\text{O}_7^{2-}$ anions decreased from 125.5 ± 6 mg/g to 123.69 ± 3.5 mg/g at the end of the fifth usage.

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