



Research article

Removal of As(V), Cr(III) and Cr(VI) from aqueous environments by poly(acrylonitril-co-acrylamidopropyl-trimethyl ammonium chloride)-based hydrogels



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ARTICLE INFO

Article history:

Received 11 March 2015

Received in revised form

2 July 2015

Accepted 4 July 2015

Available online 15 July 2015

Keywords:

Acrylonitrile (AN)

Cationic hydrogel (APTMACI)

Toxic metal ions

Arsenic and chromium removal

ABSTRACT

Cationic poly(Acrylonitril-co-Acrylamidopropyl-trimethyl Ammonium Chloride) (p(AN-co-APTMACI)) hydrogels in bulk were synthesized by using acrylonitrile (AN) and 3-acrylamidopropyl-trimethyl ammonium chloride (APTMACI) as monomers. The prepared hydrogels were exposed to amidoximation reaction to replace hydrophobic nitrile groups with hydrophilic amidoxime groups that have metal ion binding ability. Those replacements were increased the hydrogels absorption capacity for As(V) and Cr(VI). Langmuir and Freundlich isotherms equations were utilized to obtain the best-fitted isotherm model for the absorption of the ions at different metal ion concentrations. The absorption data of As(V) ion were fitted well to Freundlich isotherm while those of Cr(VI) and Cr(III) ions were fitted well to Langmuir isotherm. The maximum absorption of poly(3-acrylamidopropyl-trimethyl ammonium chloride) (p(APTMACI)) and amid-p(AN-co-APTMACI) macro gels were 22.39 mg and 21.83 mg for As(V), and 30.65 mg and 18.16 mg for Cr(VI) ion per unit gram dried gel, respectively. Kinetically, the absorption behaviors of Cr(III) and Cr(VI) ions were fitted well to a pseudo 2nd-order kinetic model and those of As(V) ions were fitted well to a pseudo 1st order kinetic model.

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1. Introduction

Heavy metals and metalloids such as Hg(II), Pb(II), Cd(II), Cr(III), Cr(VI) and As(V) are known as a serious treat for the environment and human health with both toxic and carcinogenic effects (Barakat and Sahiner, 2008; Ozay et al., 2009, 2010; Sahiner et al., 2011a, b; Ozay et al., 2011; Hritcu et al., 2012; Denizli et al., 2004; Han et al., 2007; Ulusoy and Akkaya, 2009; Ramos et al., 2009; Guan et al., 2009). Arsenic is a trace element that occurs naturally in the Earth's crust and exists in groundwater due to natural weathering processes, as well as anthropogenic activities such as mining, coal ash disposal, pesticide application, wood preservation, energy and metallurgy. Arsenic is commonly found in two oxidation states: As(III) and As(V), while As(III) is more toxic (Manning and Goldberg, 1997; Dambies, 2004; Mohan and Pittman Jr., 2007).

Long-term exposure to arsenic can cause severe problems in living organisms (Chen et al., 2007), and also lead to diseases such as anemia and anorexia (Sarkar et al., 2010; Sahiner et al., 2011a). Chromium is also found in two forms in nature as chromium(III) and chromium(VI). Chromium(III) can be found in trace amounts in living organisms including plants and animals, while chromium(VI) is highly toxic and carcinogenic causing severe damages to biological systems (Ozay et al., 2011).

The removal of pollutants from aqueous solutions is one of the most important issues in wastewater treatment plants. As absorption processes have high impact, providing high-quality water after treatment that can be recycled, the cost of the absorbent used can be kept low and these processes are considered feasible. Therefore, the absorption processes and the study of absorption kinetics in wastewater treatment are important to provide insights into the reaction pathways of the mechanism of absorption reactions (Ho and McKay, 1999).

In recent years, chemically synthesized polymeric hydrogels with functional groups such as –OH, –COOH, –NH₂, –CONH₂ and

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SO₃H were utilized in many absorption studies (Ho and McKay, 1999; Uzum et al., 2007; Hernandez and Mijangos, 2009; Ozay et al., 2009, 2011; Sahiner et al., 2011a). Hydrogels are soft hydrophilic materials, which are considered intermediates state between liquids and solids. These properties are related to the degree of cross linker, ionic strength of the solution, temperature, pH and functional groups. Cross-linked polymers are capable of imbibing large volumes of water, which have found widespread applications in bioengineering, biomedicine, food industry, water purification, and separation processes (Uzum et al., 2007; Hernandez and Mijangos, 2009; Mostafa, 2009; Ozay et al., 2009; Sahiner et al., 2011b). Herein, acrylonitrile (AN) and 3-acrylamidopropyl-trimethyl ammonium chloride (APTMACl) monomers were used for co-polymeric hydrogel preparation as p(APTMACl-co-AN) and then amidoximated for use in the removal of ions such as As(V) and Cr(III) and Cr(VI) from aqueous solutions. The cyano groups in the acrylonitrile structure can be chemically changed by chemical modification to induce new chemical and physical properties on the polymer substrate (Pekel et al., 2004; Mostafa, 2009; Sahiner et al., 2011b). P(APTMACl) is an attractive cationic smart material possessing quaternary ammonium salt which renders a natural positive charge on the polymer chains (Sahiner and Ilgin, 2010). Therefore, p(AN-co-APTMACl) hydrogels were prepared and amidoximated for toxic metal and metalloid ions removal. In the absorption studies various parameters such as the initial metal concentrations, pH and contact time, etc. were investigated. Also, kinetic studies were completed to understand the nature of kinetics for the absorption of arsenic(V), chromium(III) and chromium(VI) ions by the prepared hydrogels. Moreover, Langmuir and Freundlich isotherms were calculated for the absorption of these metal ions by p(AN-co-APTMACl)-based hydrogels.

2. Experimental

2.1. Materials and analysis methods

3-Acrylamidopropyl-trimethyl ammonium chloride (APTMACl) (75 wt%), N,N-methylenebisacrylamide (MBA) (99%), N,N,N',N'-tetramethylethylenediamine (TEMED) (Across, 99%) were purchased from Sigma and acrylonitrile (AN) (99%) was purchased from Sigma–Aldrich, ammonium persulfate (APS) (98%), sodium hydroxide (NaOH, 99%), were purchased from Aldrich, hydroxylamine hydrochloride (NH₂OH.HCl, 98%), potassium dichromate (K₂Cr₂O₇) and chromium chloride hexahydrate (CrCl₃·6H₂O) were purchased from Merck. All reagents were of analytical grade or highest purity available and used without further purification. Stock solutions of As(V), Cr(III) and Cr(VI) were prepared by dissolving sodium arsenate heptahydrate (Na₂HAsO₄·7H₂O, Fluka Analytical). The deionized water (DI water) was 18.2 MΩ cm (Millipore Direct-Q3 UV) and was used throughout the absorption experiments. The pH measurements were performed using a Sartorius Documenter pH meter. Atomic absorption spectroscopy (AAS, Thermo scientific ice 3000 series) was used to quantify arsenic(V), chromium(III) and chromate(VI) during absorption studies.

2.2. Synthesis of p(AN-co-APTMACl)-based hydrogels

The p(AN-co-APTMACl) hydrogel was synthesized via a redox polymerization technique as shown in Fig. 1a. Briefly, 0.25 mol% of MBA was dissolved in AN monomer, and the mixture was added to APTMACl with an equal amount to AN (1:1 mol ratio) and mixed thoroughly. Thereafter, 5 μL (micro Liter) TEMED was added to the solution and finally, the initiator solution APS (1 mol% of total

monomer) in 100 μL water was added to this hydrogel precursor. After mixing carefully, the solution was injected into plastic straws with 5 mm diameter and allowed to polymerize and crosslink to complete the reaction at ambient temperature. Then, hydrogels were removed from the plastic straws, cut into 6 mm long cylinders and cleaned by placing in DI water for 72 h. The hydrogels were washed with fresh water every 8 h to remove unreacted species (monomer, polymer, cross linker, and initiator). After the cleaning procedure, hydrogels were dried in an oven at 40 °C to a constant weight and kept in sealed containers for further studies (Sahiner et al., 2011a).

An amidoximation reaction was used for conversion of hydrophobic nitrile groups in the AN structure to hydrophilic amidoxime groups as illustrated in Fig. 1b. Three fold excess amount of 10 wt% NH₂OH.HCl (based on nitrile groups) neutralized by a 1:1 mol ratio of NaOH was prepared and reacted with the polymeric bulk amid-p(AN-co-APTMACl) hydrogels under constant stirring at 150 rpm for 24 h at room temperature. The amidoximated bulk hydrogels were washed with a copious amount of DI water and were dried in an oven at 40 °C to a constant weight.

2.3. Characterization and swelling behavior of hydrogels

Determination of the thermal behavior of the cationic hydrogels was carried out by a Thermogravimetric Analyzer (SII TG/DTA 6300 model). Approximately 4–6 mg of samples were placed in ceramic crucibles and analyzed during heating up to 50–1000 °C under N₂ with 100 mL/min flow rate at 10 °C/min heating rate. The FT-IR analysis of hydrogels was completed using FT-IR (Perkin Elmer Spectrum 100 instrument) spectra of p(AN-co-APTMACl) using ATR apparatus with 4 cm⁻¹ resolution between 4000 and 650 cm⁻¹.

Swelling behaviors of hydrogels were carried out in triplicate at room temperature (%) calculated as;

$$S\% = \left(\frac{M_t - M_0}{M_0} \right) * 100 \quad (1)$$

where M_0 and M_t are the initial mass and the mass at time t , respectively. All the experiments were carried out in triplicate and the average values are reported with their standard deviations (Barakat and Sahiner, 2008). Swelling characterization was also studied as a function of pH between 2 and 12 by adjusting the pH of the solutions with 0.1 M HCl and 0.1 M NaOH. Again, hydrogels were kept for 24 h in acidic and basic solutions to determine the effect of medium pH on the swelling behavior.

2.4. Metal ion absorption studies from aqueous media

The metal and metalloid ions absorption experiments were carried out at 25 °C using different ion solutions; (As(V), Cr(III) and Cr(VI)). The effects of the selected ion concentration on the absorption performance of the prepared hydrogels were investigated by preparing 1 g/L of hydrogel solution while metal ion concentrations were ranged from 1 to 5000 mg/L for each metal ion species for 24 h. Additional experiments for the time dependent absorption were conducted with different ion concentrations at constant hydrogels amount of 0.25 g/L and mixing speed of 150 rpm. The samples were withdrawn from the medium at certain time intervals for the measurements. Finally, the metal ion absorption capacity in pH buffer solutions under experimental conditions as heavy metal concentration 10 mg/L, adsorbent dosage 1 g/L, time 24 h was measured. The amount of metal ion absorbed per unit mass of the hydrogel, q_e (mg/g) was calculated using the following equation;

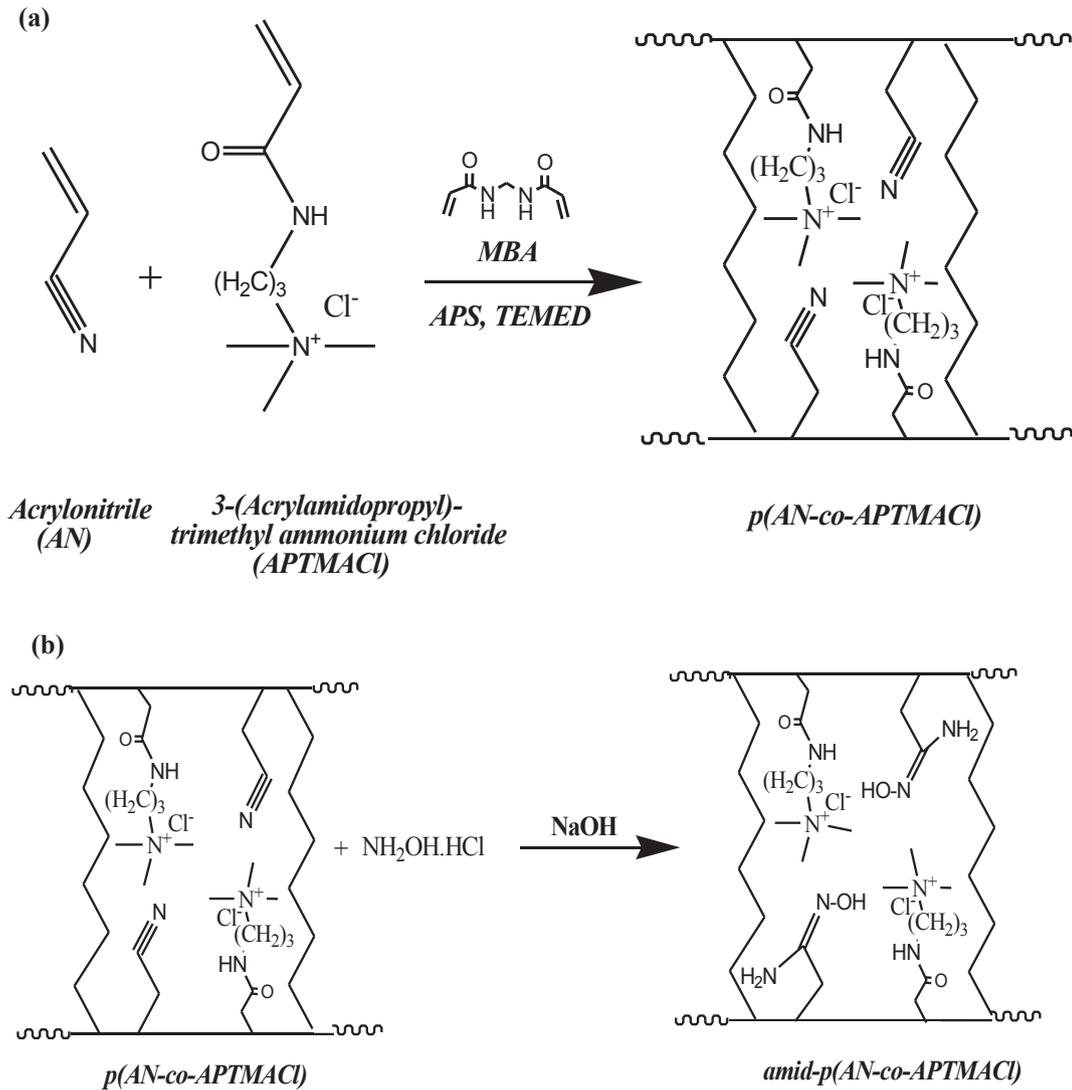


Fig. 1. (a) The chemical structure of the synthesized cationic p(AN-co-APTMACl) bulk hydrogel and (b) Schematic presentation of the amidoximation reaction mechanism of the core materials on the cationic bulk hydrogel.

$$q_e = \frac{(C_o - C_e) * V}{W} \quad (2)$$

where, C_o and C_e are the initial and equilibrium metal ion concentrations (mg/L), V is volume of metal ion solution (L) and W is the weight (g) of the hydrogels used.

The removal percentage of metal ions was calculated as follows (Bhattacharya et al., 2008);

$$\text{Removal\%} = \frac{(C_o - C_e)}{C_e} * 100 \quad (3)$$

In addition to the amount of metal ions absorbed and removal percentage Langmuir and Freundlich isotherms (Ozay et al., 2010) and reaction kinetics (Bhattacharya et al., 2008) were also investigated using the equations below;

$$\frac{C_e}{q_e} = \left(\frac{C_e}{q_{max}} \right) + \left(\frac{1}{q_{max} * K_L} \right) \quad (4)$$

where q_e is the amount of metal ions absorbed at equilibrium (mg/g), q_{max} is the maximum absorption capacity of metal ions (mg/g),

and K_L is the Langmuir absorption equilibrium constant (L/mg).

$$\log q_e = \log K_f + \left(\frac{1}{n} \right) \log C_e \quad (5)$$

where K_f and n are the physical Freundlich constants incorporating the factors affecting the absorption processes like absorption capacity and intensity of absorption. For the kinetic studies;

$$\frac{dq_t}{dt} = k_{p1} (q_e - q_t) \quad (6)$$

where q_t (mg/g) is the absorption capacities at time t (min), k_{p1} (min^{-1}) is the pseudo-first-order rate constant for the kinetic model.

$$\int_0^{q_t} \frac{dq_t}{(q_e - q_t)} = \int_0^t k_{p1} dt \quad (7)$$

Integrating Equation (7) with the boundary conditions of $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, yields

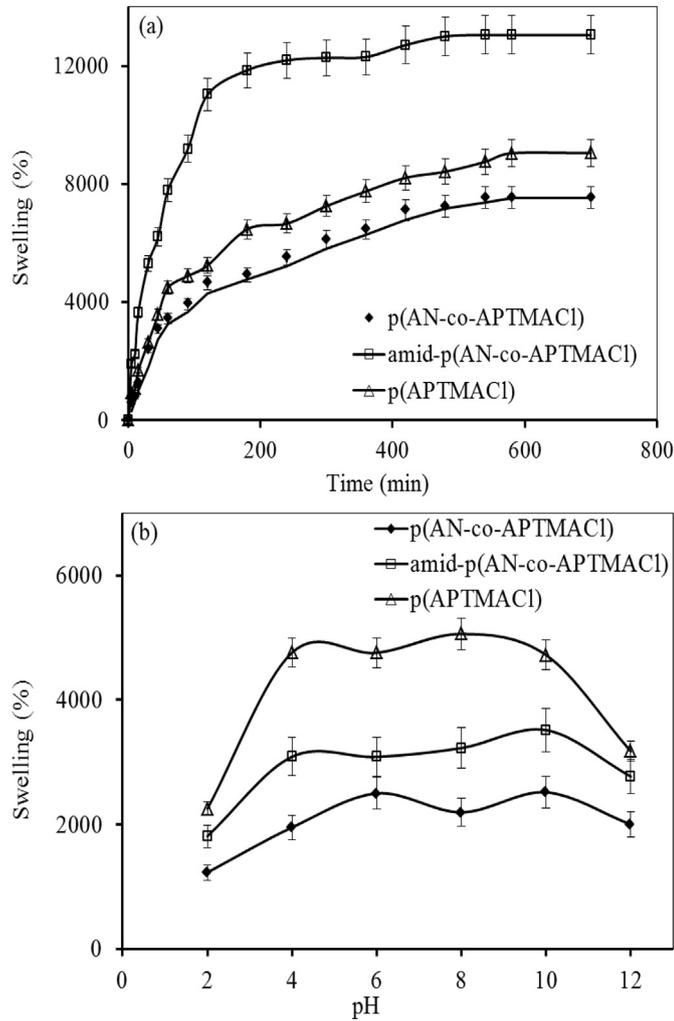


Fig. 2. (a) Percent swelling degree of the p(AN-co-APTMACI), p(APTMACI) and amid-p(AN-co-APTMACI) hydrogels with time in DI water, and (b) Swelling % of the p(AN-co-APTMACI), p(APTMACI), and amid-p(AN-co-APTMACI) hydrogels as a function of pH (pH is adjusted by the addition of 0.1 M HCl, 0.1 M NaOH).

$$q_t = R_{id}\sqrt{t} \quad (12)$$

R_{id} is the rate constant of intra-particle diffusion.

3. Results and discussion

3.1. Characterization and swelling behavior of hydrogels

Fig. 2a shows the swelling (S %) degree of p(APTMACI), before and after amidoximation of p(AN-co-APTMACI) hydrogels as a function of time. The equilibrium swelling values for p(APTMACI), p(AN-co-APTMACI) and amid-p(AN-co-APTMACI) reached their maximum values at about 10 h. Experiment results indicate that the maximum S % degree values were 9048, 7541, and 13,051% for p(APTMACI), p(AN-co-APTMACI), and amid-p(AN-co-APTMACI) hydrogels. As is known, the swelling is highly dependent on the amounts of cross linker used for pure hydrogels and in addition to

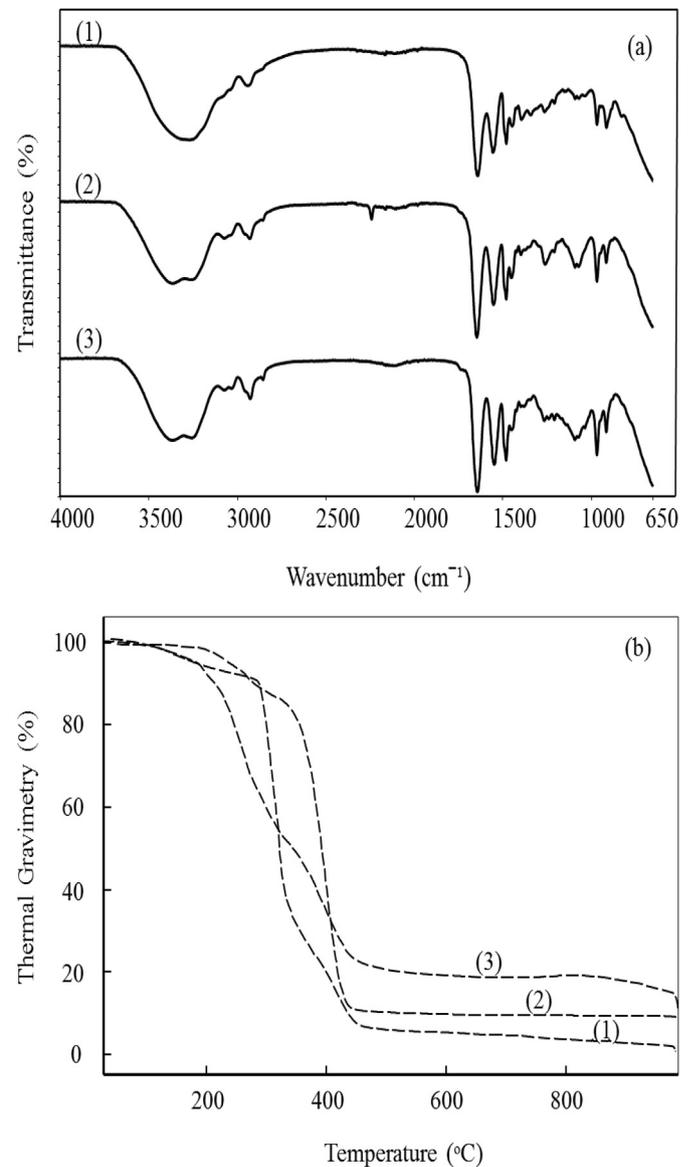


Fig. 3. (a) FT-IR spectra of (1) amid-p(AN-co-APTMACI), (2) p(AN-co-APTMACI), (3) p(APTMACI) (1:1) bulk hydrogels, and (b) the thermogravimetric analysis of (1) p(APTMACI), (2) p(AN-co-APTMACI), and (3) amid-p(AN-co-APTMACI) (1:1) bulk hydrogels.

$$\log(q_e - q_t) = \log q_e - \frac{K_{p1} t}{2.303} \quad (8)$$

Pseudo second-order rate kinetics are expressed as;

$$\frac{dq_t}{dt} = k_{p2}(q_e - q_t)^2 \quad (9)$$

Integrating Equation (9) with the boundary conditions of $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, yields

$$\int_0^{q_t} \frac{dq_t}{(q_e - q_t)^2} = \int_0^t k_{p2} dt \quad (10)$$

and

$$\frac{t}{q_t} = \frac{1}{k_{p2}q_e^2} + \frac{1}{q_e} t \quad (11)$$

k_{p2} (min⁻¹) is the pseudo-second-order rate constant for the kinetic model.

The intra-particle diffusion model can be presented as (Pekel et al., 2000);

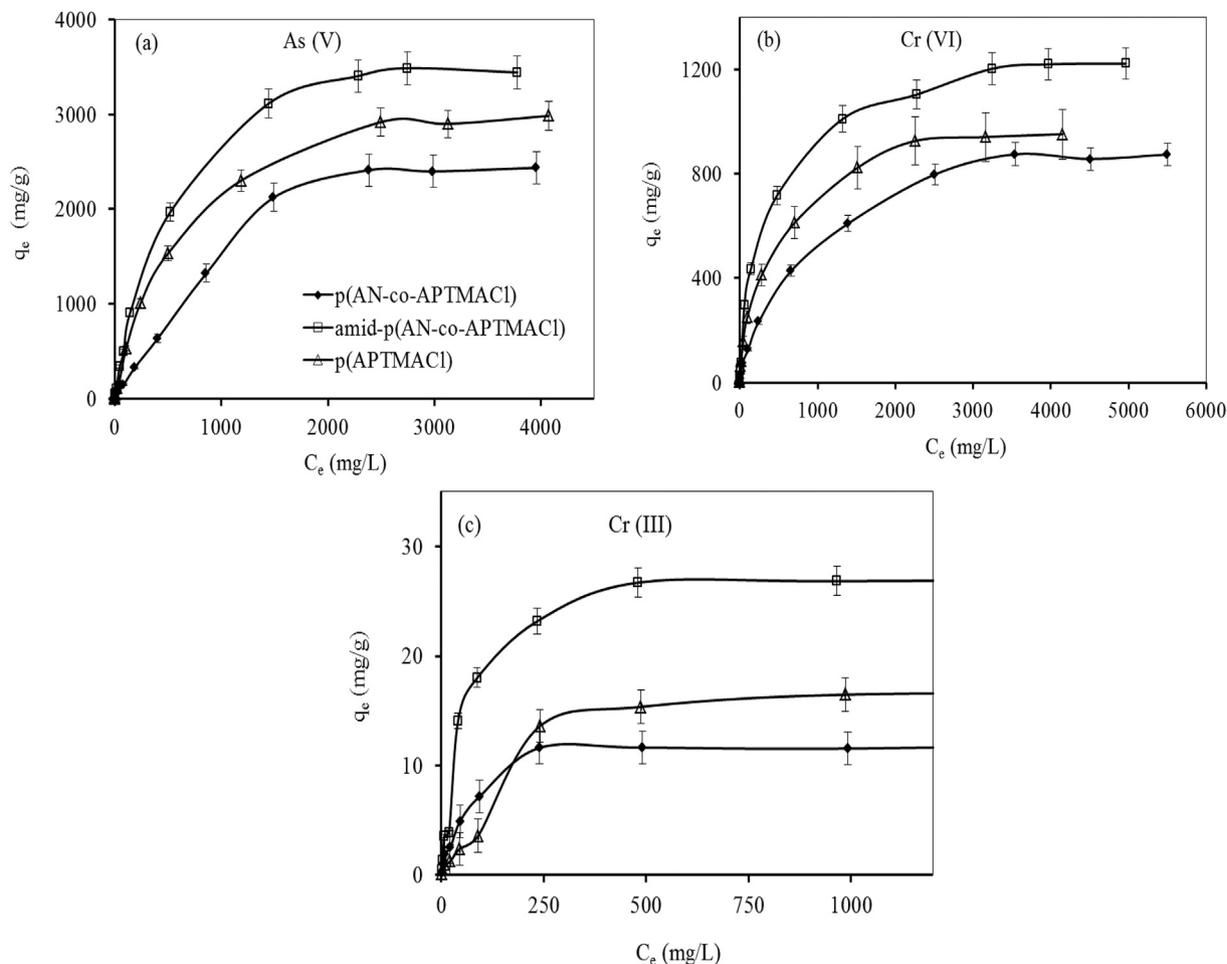


Fig. 4. The q_e vs C_e graphs of p(AN-co-APTMACl), p(APTMACl) and amid-p(AN-co-APTMACl) hydrogels (a) at different As(V) concentrations, (b) at different Cr(VI) concentrations and (c) at different Cr(III) concentrations, respectively [Heavy metal concentration: 1–5000 mg/L (50 mL), absorbent dosage: 1 g/L, time: 24 h].

cross linker is also dependent on the nature of the comonomers for copolymeric hydrogels such as p(AN-co-APTMACl). The swelling degree values for pure p(APTMACl) hydrogel were reported as 2350% (Barakat and Sahiner, 2008) and 2400% (Sahiner et al., 2006) for cationic hydrogels prepared for different purposes. The AN moieties in the copolymeric hydrogels are hydrophobic, and upon amidoximation these moieties were converted to hydrophilic amidoxime groups e.g., change in the structure of $-C\equiv N$ groups to $H_2N-C=N-OH$ groups (Pekel et al., 2000), which causes an increase in the swelling behavior of the copolymeric hydrogel. As the pH of the medium is another factor for hydrogels containing acidic and basic functional groups, we also examined the swelling of hydrogels as a function of medium pH (pH 2–12) and results are shown in Fig. 2b. In Fig. 2b, S% changed from 1230% at pH 2–2000% at pH 12 for p(AN-co-APTMACl) in accordance with the cationic nature of the hydrogel, while swelling percentage of amid-p(AN-co-APTMACl) changed from 1810% at pH 2–2767% at pH 12 because of the existence of new amidoxime functional groups. The S% values for p(APTMACl) varied between 5144% at pH 2 and 3171% at pH 12, indicating that in acidic media the basic hydrogels swell more and the swelling is reduced in basic media due to neutralization of functional groups in the basic hydrogels. The cationic nature of p(AN-co-APTMACl) hydrogel complies with high ionization at low pH values with greater swelling and in contrast at high pH values has less swelling and in between moderate swelling values (Ozay et al., 2011).

To confirm the functional groups in copolymeric hydrogels, the FT-IR spectra of hydrogels before and after amidoximation are presented in Fig. 3a. In Fig. 3a, the characteristic nitrile stretching band originating from AN groups at about 2240 cm^{-1} disappeared after the amidoximation reaction. The peaks belonging to the APTMACl monomer and cross linker at 3364 cm^{-1} , 3365 cm^{-1} and 3276 cm^{-1} for N–H stretching vibrations of the amide group, and also a broadening after the amidoximation reaction owing to the newly formed $-NH_2$ and $-OH$ groups in the amidoxime can be observed (Sahiner and Ilgin, 2010). Additionally, the peaks observed at 2941 cm^{-1} , 2929 cm^{-1} and 2926 cm^{-1} in the spectra of all the hydrogels belong to $-CH$ stretching vibrations, while the peaks at 1641 cm^{-1} , 1646 cm^{-1} and 1643 cm^{-1} in the spectrum belong to the $C=O$ stretching vibrations, and at 1479 cm^{-1} and 1480 cm^{-1} in the spectrum belong to the $C-N$ stretching vibrations, for amid-p(AN-co-APTMACl), p(AN-co-APTMACl) and p(APTMACl) hydrogels, respectively.

Fig. 3b shows thermal behavior of the cationic-based hydrogels in the pre/post-amidoximation reaction. In a previous report, the temperature dependent homopolymeric p(AN) weight loss demonstrated two step degradations at $211\text{ }^\circ\text{C}$ and $378\text{ }^\circ\text{C}$ (Sahiner et al., 2011b). However, as shown in Fig. 3b, p(AN-co-APTMACl) has three degradation steps. A total of 90% of weight was lost by $700\text{ }^\circ\text{C}$, while 9% of weight was lost up to $336\text{ }^\circ\text{C}$. The amidoximated hydrogel has three step degradations e.g., 28% of weight was lost up to heating to $265\text{ }^\circ\text{C}$, 61% of weight was lost up to heating to $388\text{ }^\circ\text{C}$,

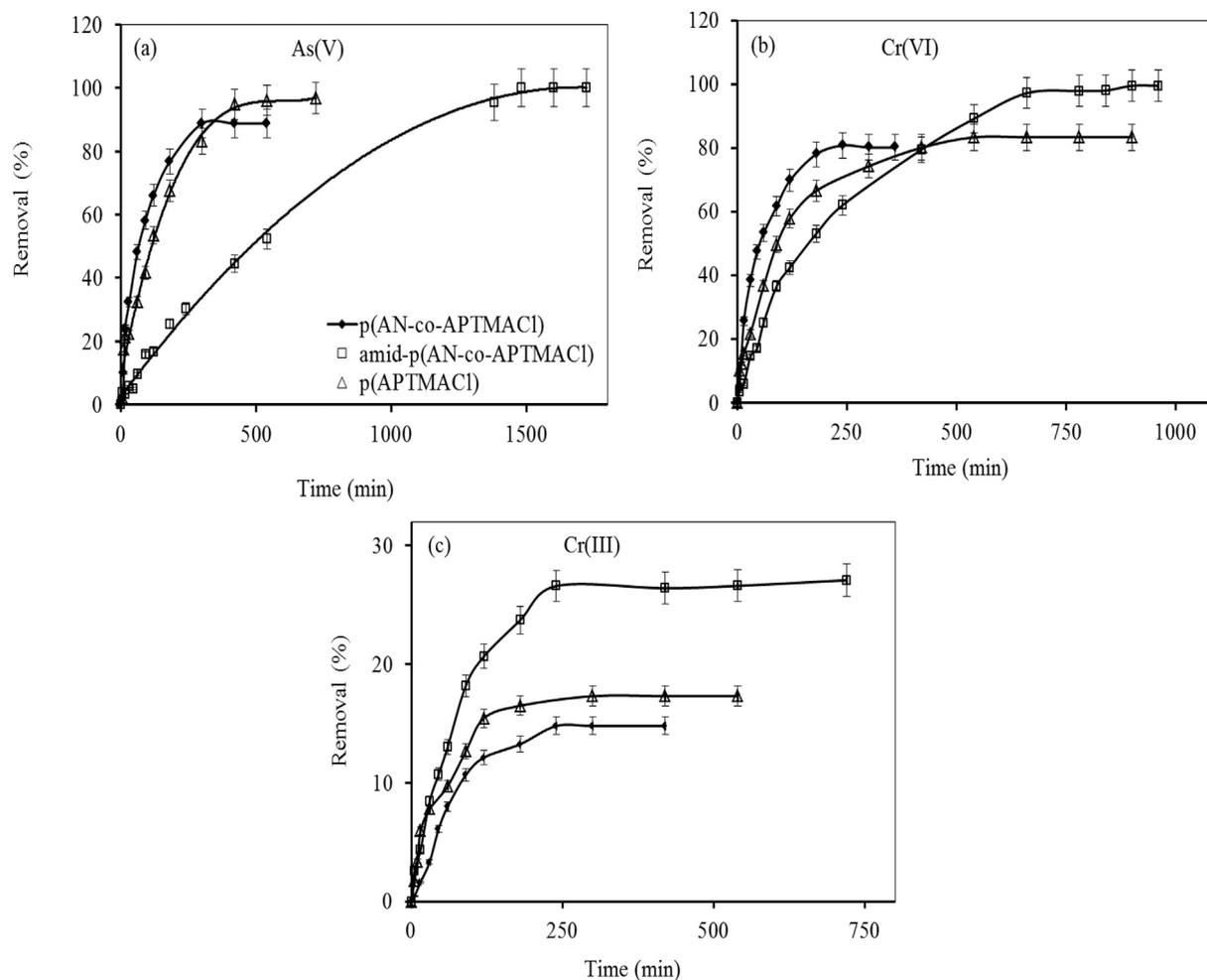


Fig. 5. The effect of contact time on (a) As(V) absorption, (b) Cr(VI) absorption, and (c) Cr(III) absorption by the p(AN-co-APTMACl) based hydrogels [Heavy metal concentration: 10 mg/L (50 mL), adsorbent dosage: 0.25 g/L].

and 80% of weight was lost at the end of heating to 700 °C. Bare p(APTMACl) also showed three step degradation similar to their corresponding copolymeric structures, and it lost a total of 95% weight up to heating to 700 °C, in accordance with the literature (Sahiner et al., 2006; Barakat and Sahiner, 2008).

3.2. Equilibrium absorption studies

The removal of As(V), Cr(III) and Cr(VI) ions were investigated in batch type absorption studies with the p(APTMACl)-based cationic hydrogels. The metal ion concentrations varied from 1 mg/L to 5000 mg/L, at adsorbent dosage 1 g/L and contact time of 24 h as shown in Fig. 4. At low metal ion/adsorbent ratios, all the metal ions were absorbed. As the metal ion/adsorbent ratio increased, the higher energy sites are saturated and absorption begins in lower energy sites, resulting in decreases in the absorption efficiency (Bhattacharya et al., 2008). It is obvious from Fig. 4 that p(AN-co-APTMACl)-based hydrogels are more effective in removing As(V) (Fig. 4a) and Cr(VI) (Fig. 4b) than Cr(III) (Fig. 4c). The maximum absorption capacity of amid-p(AN-co-APTMACl) hydrogels increased greatly for As(V) as shown in Fig. 4a, and for Cr(VI) as shown in Fig. 4b. Although Cr(III) absorption greatly increased with the amidoximation, the total amount of absorbed Cr(III) was not reached level observed for As(V) and Cr(VI). The increase in the metal ion absorption capacity of the copolymeric hydrogels can be explained by the metal ion binding ability of the newly formed

hydrophilic amidoxime groups upon conversion of hydrophobic nitrile groups to amidoxime groups by hydroxylamine hydrochloride treatment. Using 10 mg/L of the metal and the metalloid ion solutions and 1 g/L adsorbent dosage, the absorption kinetics of the mentioned ions by p(APTMACl)-based hydrogels were investigated and the results are given in Fig. 5. It is obvious that there is a fast increase in the ions removal, and then a slow-down approaching equilibrium for the studied ions. As demonstrated in Fig. 5a, b, and c, the removal percentage of the ions with time are: 100% As(V) removal in 1480 min, 27.1% Cr(III) removal in 720 min, and 99.5% Cr(VI) in 900 min for the amidoximated hydrogels providing the best absorption capacity, with the exception of the Cr(III) metal ion.

Fig. 6 indicates the removal percentage of ions by p(APTMACl)-based hydrogels over a pH range of 3–9. In those experiments 10 mg/L of the prepared ions solutions were used. As shown in the figure the removal of the ions were slightly affected by medium pH. It is well known the oxidation states of ions such As(V), Cr(III) and Cr(VI) can vary with the medium pH. As illustrated in Fig. 6a, b and c, the highest ions absorption capability were observed 99.6% for As(V) at pH 3, 96.4% for Cr(VI) at pH 9, and 21.8% for Cr(III) at pH 5 for the amidoximated hydrogels.

3.3. Absorption isotherm studies

The aim in the absorption isotherms is to relate the absorbate concentration in bulk and the absorbed amount at the interface.

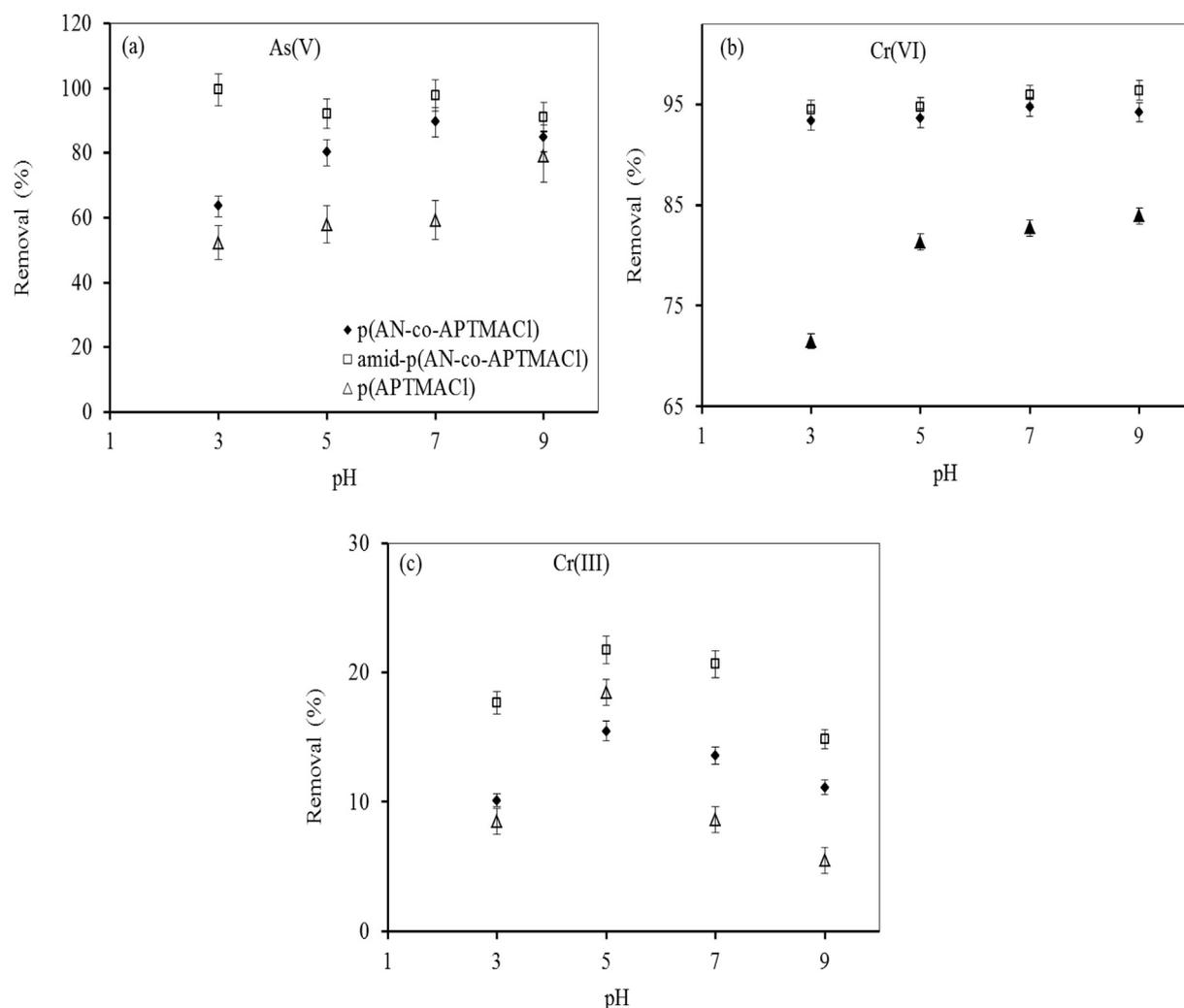


Fig. 6. Absorption of (a) As(V), (b) Cr(VI), and (c) Cr(III) into p(AN-co-APTMACl) based hydrogels as a function of solution pH [Heavy metal concentration: 10 mg/L (50 mL), absorbent dosage: 1 g/L, time: 24 h].

The corresponding isotherms were formed for As(V), Cr(III) and Cr(VI) ion absorptions by p(APTMACl)-based hydrogels by applying Langmuir and Freundlich equations (Eastoe and Dalton, 2000; Hameed et al., 2008). The Langmuir constants, q_{max} and K_L , were determined from the slope and intercept of the linear plot of specific absorptions (C_e/q_e) against the equilibrium concentrations (C_e) for As(V), Cr(VI), and Cr(III), and the data are given in Table 1. Freundlich isotherm equation, which is an empirical equation, was applied the selected ions absorption by p(APTMACl)-based

hydrogels and the values of K_f and n are calculated from the intercept and slope of the plot of $\log C_e$ against $\log q_e$. The magnitude value of the $n > 1$ indicated that the absorption was favorable (Hameed et al., 2008).

Table 1 indicates the data of Langmuir and Freundlich isotherms' constants. As easily extracted from the data, Cr(III) and Cr(VI) well agreed Langmuir while As(V) fitted Freundlich isotherms. The values of the correlation coefficients indicate the favorable nature of absorption of the ions on bare and amidoximated p(APTMACl)

Table 1

Langmuir and Freundlich isotherm data for absorption of As(V), Cr(VI) and Cr(III) by p(APTMACl), p(AN-co-APTMACl) and amid-p(AN-co-APTMACl) hydrogels.

Absorbents	Ions	Langmuir isotherm constants			Freundlich isotherm constants		
		K_L (L/mg)	q_m (mg/g)	R^2	K_f	n	R^2
p(APTMACl)	As(V)	2.09×10^{-3}	3333.3	0.9642	32.1	1.76	0.9375
p(AN-co-APTMACl)		8.12×10^{-4}	3333.3	0.8505	6.37	1.31	0.9936
Amid-p(AN-co-APTMACl)		3.41×10^{-3}	3333.3	0.9676	31.4	1.61	0.9777
p(APTMACl)	Cr(VI)	7.16×10^{-3}	833.3	0.9814	14.7	1.77	0.9024
p(AN-co-APTMACl)		5.09×10^{-3}	555.6	0.9	5.23	1.53	0.9877
Amid-p(AN-co-APTMACl)		6.83×10^{-3}	1111.1	0.9832	38.7	2.34	0.9693
p(APTMACl)	Cr(III)	2.34×10^{-3}	14.9	0.8088	0.32	4.98	0.7305
p(AN-co-APTMACl)		3.09×10^{-1}	8.56	0.9856	0.36	1.6	0.9682
Amid-p(AN-co-APTMACl)		7.78×10^{-3}	26.7	0.9754	0.98	1.78	0.9106

Table 2
Comparison of absorption capacity of some similar absorbents appeared in the literature.

Absorbents	Ions	Absorption (mg/g)	References
p(4-VP)-2-BEA-HCl	As(V)	23.26	Sahiner et al., 2011a
p(4-VP)-HCl	As(V)	22.6	Sahiner et al., 2011a
p(aniline)	Cr(VI)	4	Kumar and Chakraborty, 2009
Modified activated carbon	Cr(VI)	1.82	Choi et al., 2009
p(AMPSNa)	Cr(VI)	Did not absorb any	Ozay et al., 2011
Magnetic-p(AMPSNa)	Cr(VI)	3.94	Ozay et al., 2011
Aminated polyacrylonitrile fibers (APANFs)	Cr(VI)	32	Deng and Bai, 2004
	Cr(III)	5.8	
High iron-containing fly ash	As(V)	19.46	Li et al., 2009
Bare-p(AMPSNa-co-APTMAcI) (1:1)	Cr(III)	30.20	Ozay et al., 2011
Bare-p(AMPSNa-co-APTMAcI) (1:2)	Cr(III)	16.54	Ozay et al., 2011
Bare-p(AMPSNa-co-APTMAcI) (2:1)	Cr(III)	44.22	Ozay et al., 2011
p(AN-co-APTMAcI)	As(V)	8.87	This work
Amid-p(AN-co-APTMAcI)	As(V)	21.83	This work
p(APTMAcI)	As(V)	22.38	This work
p(AN-co-APTMAcI)	Cr(VI)	8.1	This work
Amid-p(AN-co-APTMAcI)	Cr(VI)	18.16	This work
p(APTMAcI)	Cr(VI)	30.64	This work
p(AN-co-APTMAcI)	Cr(III)	1.28	This work
Amid-p(AN-co-APTMAcI)	Cr(III)	5.9	This work
p(APTMAcI)	Cr(III)	5.59	This work

Table 3
Kinetic constants for absorption of As(V), Cr(VI), and Cr(III) by p(APTMAcI), p(AN-co-APTMAcI) and amid-p(AN-co-APTMAcI).

Absorbents	Ions	Pseudo 1st order		Pseudo 2nd order		Intra-particle diffusion	
		K_{p1} (1/min)	R^2	K_{p2} (g/(mg min))	R^2	R_{id} (mg/(g min ^{1/2}))	R^2
p(APTMAcI)	As(V)	7.14×10^{-3}	0.9807	3.82×10^{-4}	0.9665	0.6879	0.8384
p(AN-co-APTMAcI)		1.08×10^{-2}	0.9914	1.56×10^{-3}	0.971	0.4968	0.9766
Amid-p(AN-co-APTMAcI)		2.07×10^{-3}	0.9687	4.59×10^{-5}	0.7892	0.6565	0.9993
p(APTMAcI)	Cr(VI)	7.37×10^{-3}	0.9905	5.03×10^{-4}	0.9679	1.1547	0.8926
p(AN-co-APTMAcI)		1.89×10^{-2}	0.7876	3.40×10^{-3}	0.992	0.3114	0.8759
Amid-p(AN-co-APTMAcI)		5.07×10^{-3}	0.9784	2.14×10^{-4}	0.9521	0.6767	0.9758
p(APTMAcI)	Cr(III)	1.68×10^{-2}	0.9823	4.77×10^{-3}	0.9931	0.2971	0.9108
p(AN-co-APTMAcI)		1.36×10^{-2}	0.9886	1.21×10^{-2}	0.9856	0.0808	0.8984
Amid-p(AN-co-APTMAcI)		8.29×10^{-3}	0.8531	4.02×10^{-3}	0.9966	0.1603	0.7663

hydrogels. The absorption intensity given by the Freundlich coefficient, $n > 1$, is favorable for all the metal ion absorptions.

A well comparison of the data obtained during this study and those of literature are given in Table 2. It is indicated that absorption capacities of p(AN-co-APTMAcI), amid-p(AN-co-APTMAcI) and p(APTMAcI) are very well when compared those of literature (Sahiner et al., 2011a; Kumar and Chakraborty, 2009; Choi et al., 2009; Ozay et al., 2011; Deng and Bai, 2004; Li et al., 2009).

3.4. Absorption reaction models

The absorption kinetics of different heavy metal ions by cationic-based hydrogels were studied from the graphs of time versus absorbed amounts. The rate of the selected ions absorption

on p(AN-co-APTMAcI), amid-p(AN-co-APTMAcI), and p(APTMAcI) hydrogels were analyzed with three kinetic models which are pseudo 1st order, pseudo 2nd order, and intra-particle diffusion. The similarity between experimental data and the model-predicted values were denoted by the correlation coefficients (R^2) as shown in Table 3. A relatively high R^2 value proves that the model successfully defines the kinetics of metal absorption (Bhattacharya et al., 2008). The pseudo 1st and 2nd order plots of $\log(q_e - q_t)$ versus t (min) and t/q_t against t for the selected ions absorption by cationic hydrogels were plotted, and K_{p1} and q_e were determined from the slope and intercept of plot, and given in Tables 3 and 4. As comparing correlation coefficients; pseudo 1st order kinetics well represented As(V) absorption for all the hydrogels, while Cr(III), and Cr(VI) absorption were fitted well by 2nd order pseudo kinetics.

Table 4
The absorption capacity of absorption of As(V), Cr(VI), and Cr(III) by the p(APTMAcI), p(AN-co-APTMAcI) and amid-p(AN-co-APTMAcI).

Absorbents	Ions	$q_{e,exp}$ (mg/g)	Pseudo 1st order	Pseudo 2nd order
			$q_{e,cal}$ (mg/g)	$q_{e,cal}$ (mg/g)
p(APTMAcI)	As(V)	22.39	22.72	25
p(AN-co-APTMAcI)		8.88	8.26	9.7
Amid-p(AN-co-APTMAcI)		21.83	23.78	30.77
p(APTMAcI)	Cr(VI)	30.65	27.1	33.1
p(AN-co-APTMAcI)		8.01	8.1	8.69
Amid-p(AN-co-APTMAcI)		18.16	19.5	22.4
p(APTMAcI)	Cr(III)	5.59	5.44	6.03
p(AN-co-APTMAcI)		1.28	1.33	1.35
Amid-p(AN-co-APTMAcI)		5.09	3.75	5.32

Furthermore, it was observed that the intra-particle diffusion model was effective on the As(V) absorption by all the hydrogel systems as given in Table 3. Additionally, data given in Table 4, show that there were no large differences between the experimental $Q_{e,exp}$ and the calculated $Q_{e,cal}$. The correlation coefficients of As(V) absorption indicated better suitability of pseudo 1st order model. It was concluded that intra-particle diffusion was the rate-limiting step, and then the absorption process was described as being particle diffusion controlled (Pekel et al., 2000). The high magnitude of R_{id} , which was calculated from Equation (12), represented that the intra-particle diffusion model is a rate-limiting step (Sharma and Goyal, 2009). According to experimental data presented in Table 3, the intra-particle diffusion model plots did not cross the origin demonstrating that both boundary layer diffusion steps and intra-particle diffusion steps are effective in the absorption mechanism (figure not shown).

4. Conclusions

Here it was demonstrated that cationic p(APTMACI) can be copolymerized with AN to produce p(AN-co-APTMACI) and then amidoximated readily to increase the hydrophilicity and As(V), Cr(VI), Cr(III) ion binding ability of amid-p(AN-co-APTMACI) hydrogels. Therefore, the results can be summarized as:

- Hydrogels with cationic character were easily synthesized by using redox polymerization technique and applicable for the removal of toxic ions from wastewaters.
- The p(AN-co-APTMACI) hydrogels absorption capability for As(V) and Cr(VI) ions were increased by amidoximation using amid-p(AN-co-APTMACI) hydrogels due to the change of nitrile groups to more hydrophilic amidoxime groups.
- The As(V), Cr(VI), and Cr(III) absorption by amid-p(AN-co-APTMACI) is better than most of the values reported in the literature. The absorption of metal ions such as As(V), Cr(VI) and Cr(III) by p(APTMACI), p(AN-co-APTMACI) and amid-p(AN-co-APTMACI) obey both the Langmuir and Freundlich isotherms. However, the As(V) absorption data fitted the Freundlich isotherm better and the Cr(VI) and Cr(III) absorption data fit the Langmuir isotherm better. The As(V) absorption is better represented by a pseudo 1st order kinetic model, whereas the absorption of Cr(VI) and Cr(III) are better represented by pseudo 2nd order models.

Therefore, the cationic-based hydrogels of amid-p(AN-co-APTMACI) have great potential for the removal of heavy toxic metal ions such as As and Cr with different oxidation states from aquatic environments.

Acknowledgment

This work is supported by the Yuzuncu Yil University BAP with grant # 2014-ISB-MIM054.

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