

Removal of As(V), Cr(VI) and Cr(III) heavy metal ions from environmental waters using amidoxime and quaternized hydrogels

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ABSTRACT

Acrylonitrile (AN) and 1-vinyl imidazole (VI) based hydrogel was prepared in bulk (macro) dimensions via redox polymerization technique. Afterward, this hydrogel was quaternized (positively charged) and exposed to the amidoximation reaction. The prepared hydrogels (quart-p(AN-co-VI), amid-p(AN-co-VI) and p(VI)) characterized using fourier transform infrared spectroscopy (FT-IR) and thermal gravimetric analysis (TGA). Swelling experiments were performed gravimetrically at room temperature in deionized water and different pH solution. Water absorbencies of both amidoximated hydrogels and quaternized hydrogels were founded to be high. Prepared hydrogels were used to remove heavy metal ions such as arsenic(V) (As(V)), Chromium(VI) (Cr(VI)) and Chromium(III) (Cr(III)) from aqueous media. The sorption of As(V), Cr(VI) and Cr(III) metal ions by hydrogels were carried out at different initial metal ion concentrations, different pHs, different times in batch sorption experiments at 25°C. The maximum metal ion sorption capacity by all hydrogels was in the order: As(VI)>Cr(VI)>Cr(III). The maximum sorption capacity for As(VI), Cr(VI) and Cr(III) ions was found to be 598, 303.8 and 4.9 mg g⁻¹ for amid-p(AN-co-VI), respectively. As result of, amidoximated hydrogels have more sorption capacity to metal ions than quaternized hydrogels. Three different kinetic models (pseudo first order, pseudo second order and intraparticle diffusion model) were also used to investigate the sorption mechanisms. Furthermore, the Langmuir and Freundlich sorption isotherms were investigated for these metal ions. As a result of, amidoximation and quaternization of AN and VI based hydrogels have been a promising technique to increase the sorption rate and capacity of hydrogels and are thought to provide great advantages in the removal of metal ions from wastewaters. Especially, among the p(AN-co-VI) modification processes, amidoximation reaction was found to give better results than quaternization reaction. Prepared hydrogels were found to be more selective than Cr(III) versus As(V) and Cr(VI).

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1. Introduction

The hydrogels are polymeric material and they have many properties such as soft, flexible, elastic, wet structure, three-dimensional polymeric networks, indissolubility, permeability, hydrophilic/hydrophobic structure, tunable physical and chemical structure [1-3]. These properties of hydrogels provide ease of use in a lot of fields such as tissue engineering, drug release, environmental and advantageous material design, agriculture, the food industry, biotechnology and cleaning of environmental waters [4-7]. One of the most common applications in which hydrogels are used in these areas is the cleaning of environmental waters. Especially, heavy metal ions are contaminating most of the natural

resources and environmental waters. The main origins of these heavy metal ions are cosmetics, fertilizers, paint industries, metal plating, battery manufacturing and chemicals generated from other industrial waste [8,9]. Moreover, many of them are known to be toxic or carcinogenic and are not biodegradable [10]. Therefore, in recent years, for the removal of heavy metals and other hazardous materials have been developed many methods such as chemical precipitation, membrane extraction, coagulation, complexing, solvent extraction, ion change and sorption. These methods are some of the used processes, but each has its own advantages and disadvantages in its applications. Sorption is a remarkable method because of its high

efficiency, ease of handling, energy-saving and availability of different sorbents [11-13].

Many studies in which hydrogels have been used for heavy metal sorption have been widely reported in the literature. The originality of this article is to bring in a new property after the amidoximation and quaternization reactions to the synthesized hydrogel and to increase the sorption capacity of As(V), Cr(VI) and Cr(III) metal ions. For this study, acrylonitrile (AN) and 1-vinyl imidazole (VI) were chosen as monomers. Acrylonitrile-based polymers are widely used in all areas owing to ease of processing, stiffness, abrasion resistance, mechanical properties and chemical resistance [14]. Acrylonitrile is a versatile liquid and has poor hygroscopicity [15]. In addition, the cyano groups in the acrylonitrile structure provide a great advantage for any modification which may alter the chemical and physical properties of the polymer structure [16-17]. The imidazole groups in VI structure have a weak base character and they can be easily protonated in acidic solutions [18-19]. To generate a positive charge, VI structure can be quaternized by the treatment with an aqueous acid solution and exhibit reversible load changes. Therefore, VI based polymers and derivatives have attracted great interest, as they exhibit excellent properties such as easy protonation, ion exchange and complexing behaviors, catalytic, biological and physiological activities and heat resistance [18-20].

In this study, the p(AN-co-VI) hydrogel was synthesized from AN and VI monomers via redox polymerization technique. Afterward, this hydrogel was quaternized (positively charged) (quart-p(AN-co-VI)) and exposed to amidoximation reaction (amid-p(AN-co-VI)). Thus, these hydrogels became an ion exchange material which can be used to remove As(V), Cr(VI) and Cr(III) metal ions from aqueous media. Using Fourier Transform Infrared Spectroscopy (FT-IR) and Thermal Gravimetric Analysis (TGA) methods, the structural characterizations and the thermal stabilities were investigated for p(VI), quart-p(AN-co-VI) and amid-p(AN-co-VI) hydrogels. In the sorption studies, various parameters such as the initial concentration of metals, pH and contact time were investigated. Also, kinetic and isotherm studies were carried out for the sorption of As(V), Cr(VI) and Cr(III) metal ions by the quart-p(AN-co-VI), amid-p(AN-co-VI) and p(VI) hydrogels.

2. Materials and methods

2.1 Materials

1-vinyl imidazole (VI, 99%), acrylonitrile (AN, 99%) and hydrochloric acid (HCl, 37.5%) were purchased from Sigma-Aldrich, N, N'-methylene bisacrylamide (MBA, 99%) was purchased from Sigma, ammoniumpersulfate (APS, 98%) and sodium hydroxide (NaOH) were purchased from Aldrich, N, N, N', N'-tetramethylethylenediamine (TEMED) was purchased from Across, hydroxylamine hydrochloride

(NH₂OH•HCl), potassium dichromate (K₂Cr₂O₇) and chromium (III) chloride hexahydrate (CrCl₃•6H₂O) were purchased from Merck, arsenate heptahydrate (Na₂HAsO₄•7H₂O) was purchased from Fluka Analytical. All reagents were of analytical grade or highest purity available and used without further purification. The deionized water (DI water) was obtained from 18.2 MΩ.cm (Millipore Direct-Q3 UV). The pH measurements were carried out with a Sartorius Documenter pH meter. Atomic absorption spectroscopy (AAS, Thermo scientific ice 3000 series) was used to quantify the of As(V), Cr(VI) and Cr(III) metal ions during sorption studies. The instruments were calibrated by using 1000 mg L⁻¹ standard As(V), Cr(III) and Cr(VI) solution (Merck) by sequential dilutions.

2.2 Synthesis of p(AN-co-VI) hydrogel

AN and VI monomers were used to synthesis hydrogel via redox polymerization technique as shown in Figure 1a. Briefly, 2 mol% of MBA was dissolved in AN monomer and mixed (at 2500 rpm) thoroughly for one minute. Then to the AN monomer even amount (1:1 mole ratio) of the VI monomer was added to the mixture and mixed well for one minute. After then, 5 μL TEMED was added to the mixture and the initiator solution APS (1 mol% of total monomer) in 100 μL water was added to the reaction mixture. The reaction mixture was mixed carefully for approximately one minute and transferred into plastic straws with 5 mm diameter and allowed to polymerize and crosslink to complete the reaction at room temperature for approximately four hours. Then, the hydrogel was removed from the polymerization medium, cut into 6 mm long cylinders and cleaned by placing in DI water. After the cleaning procedure, the hydrogel was dried in an oven at 40°C to a constant weight and kept in sealed containers for further studies [21, 22].

2.3 Amidoximation reaction and quaternization of p(AN-co-VI) based hydrogel

To generate a positive charge, VI shell was quaternized by treating hydrogel with 0.5 M hydrochloric acid solution as a quaternization agent (Figure 1b). The quaternized p(AN-co-VI) hydrogels were washed with DI water to remove acid residues and these hydrogels were named as quart-p(AN-co-VI) hydrogels. Finally, these hydrogels were dried in an oven at 40°C to a constant weight.

Amidoximation reaction was used to convert hydrophobic nitrile groups into hydrophilic amidoxime groups of the AN structure as illustrated in Figure 1c. The 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 amid-p(AN-co-VI) hydrogels under constant stirring at 150 rpm for 24 h at room temperature. The amidoximated hydrogels were washed with a copious amount of DI water and were dried in an oven at 40°C to a constant weight.

2.4 Fourier-transform infrared spectroscopy analysis (FTIR)

Functional groups of hydrogels were analyzed by FTIR spectroscopy (Perkin Elmer, model Perkin Elmer Spectrum 100 instrument, USA) in the range of 4000–650 cm^{-1} . The hydrogel beads were ground to obtain powder and then placed on the diamond sample surface of the machine. The number of scans used was at a resolution of 4 cm^{-1} .

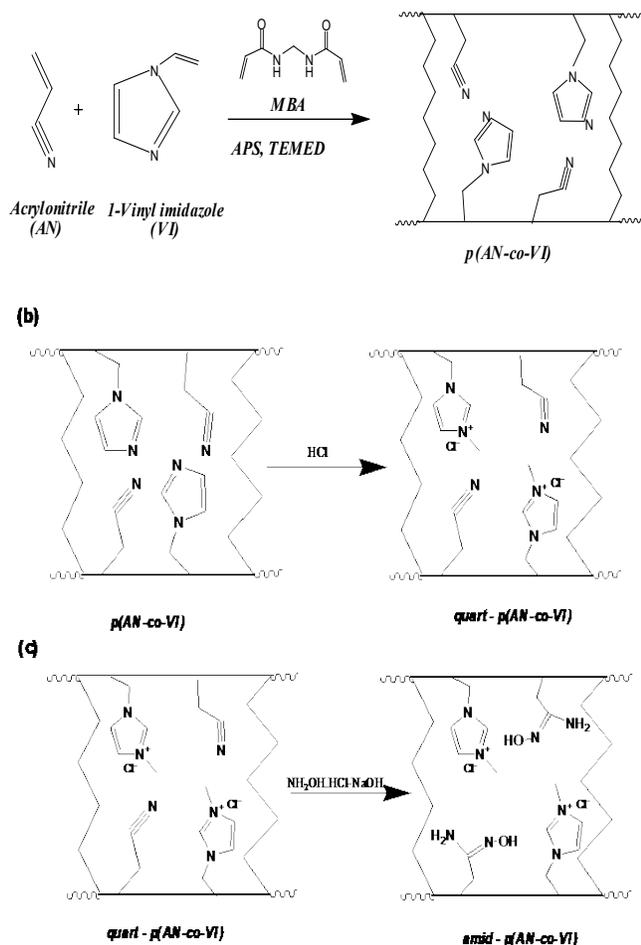


Figure 1. (a) The chemical structure of the synthesized p(AN-co-VI) hydrogel, (b) schematic presentation of the quaternization reaction mechanism on the p(AN-co-VI) hydrogel and (c) schematic presentation of the amidoximation reaction mechanism on the p(AN-co-VI) hydrogel.

2.5 Thermal gravimetric analysis (TGA)

To evaluate the thermal stability of the hydrogels, TGA analyses were performed on Thermo Gravimetric Analyzer (SII TG/DTA 6300 model, France) using between 4 and 6 mg of the hydrogel. The analysis was performed at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ under a nitrogen atmosphere and ramped up to 1000 $^{\circ}\text{C}$. As a result of the analysis, a graph of mass loss versus temperature was obtained.

2.6 Measurement of swelling in distilled water and buffer solutions

Equilibrium swelling experiments were performed in distilled water and buffer solutions at room temperature to examine the swelling ratios of quart-p(AN-co-VI), amid-p(AN-co-VI) and p(VI) hydrogels. Swelling ratios (SR) measurements for hydrogels were performed out in triplicate (%) calculated as;

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

where M_0 and M_t are the hydrogel mass (g) at beginning and at the time t , respectively. After time t , the hydrogels were removed from the DI water and blotted gently with blotting paper and weighed. All the experiments were carried out in triplicate and the average values were used with their standard deviations [23, 24]. Swelling ratio 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 ratios.

2.7 Sorption Studies

All batch sorption experiments of As(V), Cr(VI) and Cr(III) metal ions were accomplished at 25 $^{\circ}\text{C}$ for 24 h. To achieve the complete mixing of the media, the mixture was stirred at 250 rpm. In order to improve the performance of sorption conditions, metal ion concentration, media pH and time were optimized. The effect of metal ion concentration on the sorption performance was investigated ranging from 1 to 5000 mg L^{-1} for each metal ion species, at 1 g L^{-1} hydrogel concentration. The influence of pH on the sorption of metal ions was examined over the pH range of 3–9 and the pH was adjusted by using 0.1 M NaOH and 0.1 M HCl solutions. The effect of sorption time on the sorption capacity was investigated until reaching equilibrium at 10 mg L^{-1} metal ion concentration, 0.25 g L^{-1} hydrogel concentration. To determine the equilibrium concentrations of the metal ions, samples were withdrawn from the solution medium at certain time intervals and diluted with distilled water. Metal ion concentration measurements were carried out by Atomic Absorption Spectrophotometer (AAS). The equilibrium (q_e (mg g^{-1})) amounts of sorption metal ions per unit mass of the hydrogels were calculated by the following equation [25, 26];

$$q_e = \frac{(C_0 - C_e) * V}{M} \quad (2)$$

Where C_0 and C_e are the initial and equilibrium metal ion concentrations (mg L^{-1}) respectively; V is the volume of metal ion solution (L); M is the mass (g) of the hydrogels used.

The sorption percentages of metal ions were calculated by the following equation [25, 26];

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

Sorption capacities of metal ions have been evaluated from the Langmuir (Eq. 4) and Freundlich (Eq. 5) sorption isotherms by applying below equations [27, 28];

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

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

Where q_e is the amount of sorbed metal ion at equilibrium (mg g^{-1}), q_{max} is the maximum sorption capacity of metal ions (mg g^{-1}) and K_L is the Langmuir sorption equilibrium constant (L mg^{-1}). The Langmuir constants, q_{max} and K_L , were determined from the slope and intercept of the linear plot of specific sorption's (C_e/q_e) against the equilibrium concentrations (C_e) for As(V), Cr(VI) and Cr(III) metal ions. K_f and n are the physical Freundlich constants and were determined from the slope and intercept of the linear plot of $\log q_e$ versus $\log C_e$.

Experimental data generated from As(V), Cr(VI) and Cr(III) sorption tests using the hydrogels were evaluated by pseudo first kinetic, second order kinetic and intraparticle diffusion model to understand the mechanisms and dynamics of the sorption process [29-31]. Equation 6 and 7 represent the change of sorption capacity with time for first and second pseudo kinetics.

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

Where q_t (mg g^{-1}) is the sorption capacities at time t (min), k_{p1} (min^{-1}) is the pseudo first order rate constant for the kinetic model. Pseudo second order rate kinetic is expressed as;

$$\frac{dq_t}{dt} = k_{p2} (q_e - q_t)^2 \quad (7)$$

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

The intraparticle diffusion model can be presented as [32];

$$q_t = R_{id} \sqrt{t} + C \quad (8)$$

Where C is the intercept and R_{id} is the rate constant of intraparticle diffusion ($\text{mg g}^{-1} \text{h}^{-1/2}$).

3. Results and discussion

3.1 Fourier-transform infrared spectroscopy analysis (FTIR)

FTIR spectra of prepared hydrogels with their characteristic peaks were shown in Figure 2a. p(VI) hydrogel shown peaks at 3105 and 1496 cm^{-1} which assigned to C-H and C-N stretching vibration in vinyl group and crosslinker, respectively, while the peaks at 3122 cm^{-1} correspond to stretching of N-H bond. The peaks observed at approximately 1649 and 1226 cm^{-1} correspond to the vibration bands C=N and C-N, respectively. The characteristic nitrile stretching band ($\text{C} \equiv \text{N}$) of the pure AN occurs at about 2243 cm^{-1} . However, as shown in Figure 2a, this band was lost after the amidoximation reaction. In addition, in p (AN-co-VI) hydrogel, occurred both positive charges and the new $-\text{NH}_2$ and $-\text{OH}$ functional groups after quaternization and amidoximation. This formation was evidenced by the increase in the width of the N-H and $-\text{OH}$ band observed from 3724 cm^{-1} to 2600 cm^{-1} , as observed in the FT-IR spectrum of quart-p (AN-co-VI) hydrogel. In this spectrum was also clearly shown which the peaks at 1656 cm^{-1} , 1631 cm^{-1} , 1648 cm^{-1} belong to the C=O stretching vibrations for all hydrogels. Furthermore, it was determined that the C-N peak observed at about 1226 cm^{-1} and 1497 cm^{-1} decreased after the quaternization and amidoximation.

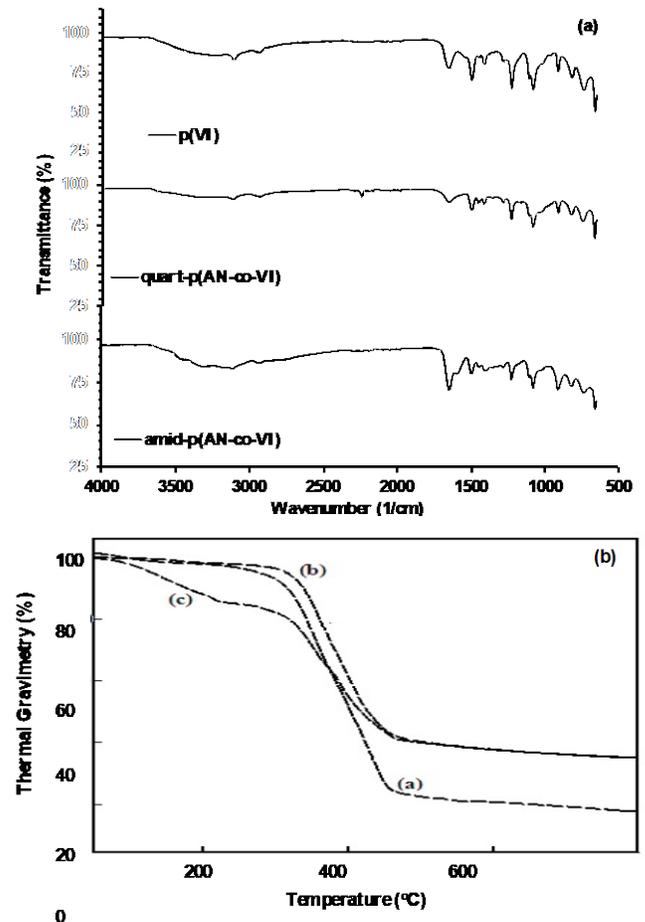


Figure 2. (a) FT-IR spectra of (a) p(VI), (b) quart-p(AN-co-VI) and (c) amid-p(AN-co-VI) (1:1) hydrogels and (b) the Thermo

Gravimetric analysis of (a) p(VI), (b) quart-p(AN-co-VI) and (c) amid-p(AN-co-VI) (1:1) hydrogels.

3.2 Thermal gravimetric analysis (TGA)

TGA/DSC analyzer was used to examine the thermal degradation behavior of p(VI), quart-p(AN-co-VI) and amid-p(AN-co-VI) hydrogels and results were presented in Figure 2b. As can be seen, mass loss of p(VI) hydrogel was nearly 78% when heated up to 542°C under argon atmosphere. And at the same time quart-p(AN-co-VI) and amid-p(AN-co-VI) hydrogels showed similar degradation temperatures with 62% and 58% mass loss, respectively. Hence, it can be said that quaternization and amidoximation reactions contributed almost 38-42% weight more degradation to the p(AN-co-VI) based hydrogel. Another prominent feature was that amid-p(AN-co-VI) hydrogel had three degradation step: the first stage was at 200°C with 11% mass loss, the second stage was in the temperature range of 200-282°C with 5% mass loss and the third step was in the temperature range of 282-525°C with 42% mass loss. The p(VI) and quart-p(AN-co-VI) hydrogels had the same thermal behavior and had two different degradation steps. The first step for p(VI) was starting at about 50 to almost 258°C with a 5% mass loss, and the other was between 258 and 542°C with 73% mass loss. The first mass loss for quart-p(AN-co-VI) was 8% in the temperature range of 50-302°C. The second step was observed in the range of 302-550°C and mass loss reached 54%. According to the data obtained, it was determined that p(AN-co-VI) hydrogel has a good resistance against increasing temperature.

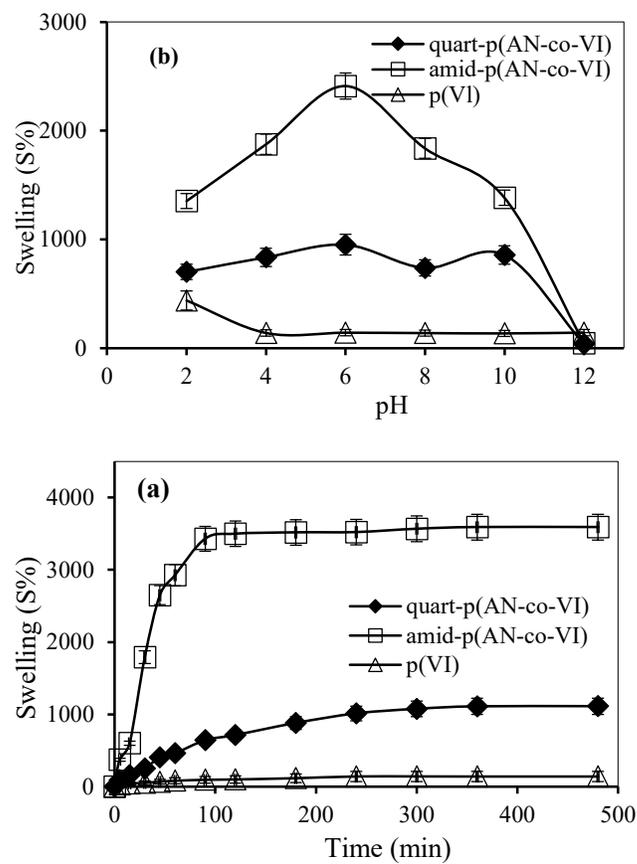


Figure 3. (a) Percent swelling degree of the p(VI), quart-p(AN-co-VI) and amid-p(AN-co-VI) hydrogels with time in DI water and (b) Percent swelling degree of the p(VI), quart-p(AN-co-VI) and amid-p(AN-co-VI) hydrogels as a function of pH (pH is adjusted by the addition of 0.1 M HCl, 0.1 M NaOH).

3.3 Measurement of swelling in distilled water and buffer solutions

The equilibrium swelling ratios (SR) of hydrogels (p(VI), quart-p(AN-co-VI) and amid-p(AN-co-VI)) were indicated in Figure 3a. The swelling rates of the hydrogels in DI water increased with increasing time and then slowed down. Figure 3a showed that the value of S% of p(VI) was 141%. On the contrary of p(VI) hydrogel, the values S% of quart-p(AN-co-VI) and amid-p(AN-co-VI) hydrogels were 1113% and 3590%, respectively. Results demonstrated that of S% values of p(AN-co-VI) based hydrogels were increased after quaternization and amidoximation reactions. Since VI is both a hydrophilic monomer and nitrogen in the imidazole structure can produce positive charges after quaternization reaction and it may cause an increase in swelling of the hydrogel. Even if AN is a hydrophobic monomer, the hydrophobic nitrile groups in the AN structure can be converted to hydrophilic amidoxime groups after the amidoximation reaction and thus the degree of swelling of the hydrogel can be increased [33]. Therefore, in this study, we aimed to increase the equilibrium swelling capacities of

hydrogels by quaternization and amidoximation reactions and to use them in heavy metal sorption.

Figure 3b indicated the pH-dependent changes in the equilibrium swelling ratio for p(VI), quart-p(AN-co-VI) and amid-p(AN-co-VI) hydrogels at room temperature in buffer solution from 2 to 12. Maximum swelling values for p(VI), quart-p(AN-co-VI) and amid-p(AN-co-VI) were obtained as 439% at pH 2, 950% at pH 6 and 2411% at pH 6, respectively. After quaternization and amidoximation reactions, the breakdown of hydrogen bonds at different pHs and the electrostatic repulsion between the polymer networks increases and then more water intake to the hydrogels is achieved [34].

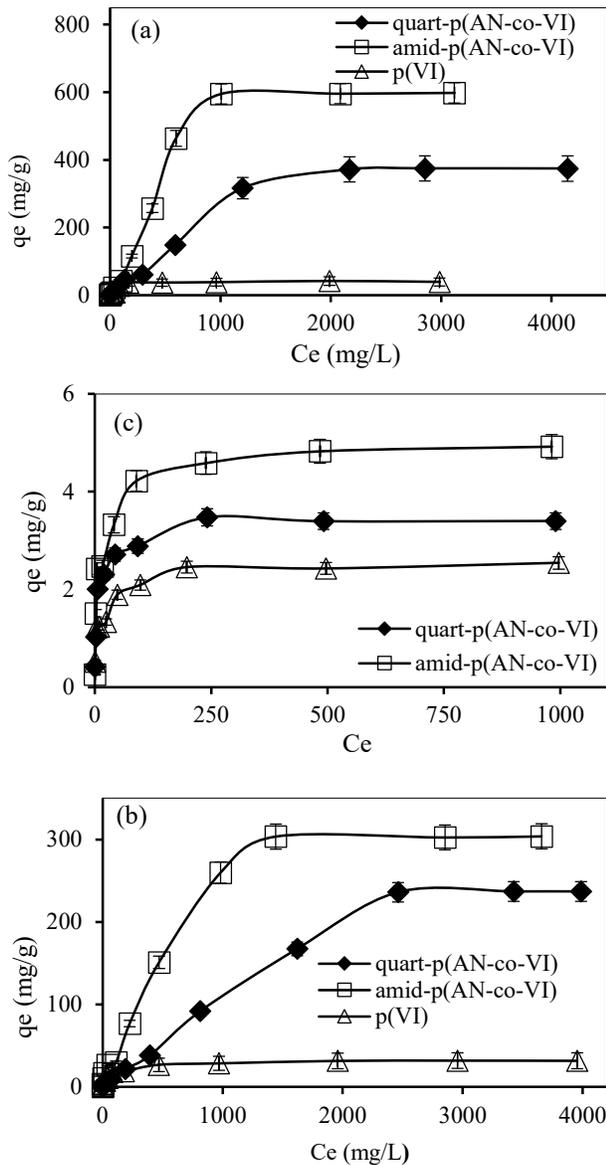
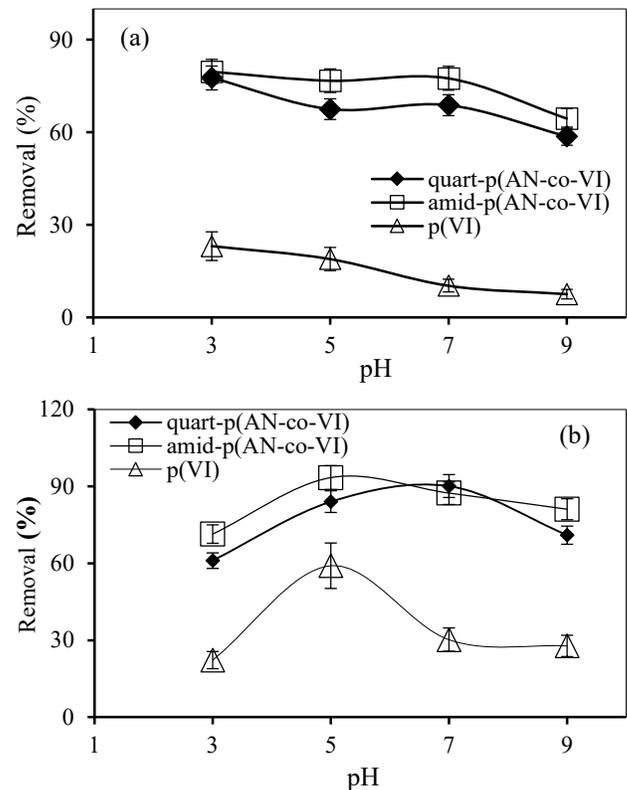


Figure 4. The q_e vs C_e graphs of p(VI), quart-p(AN-co-VI) and amid-p(AN-co-VI) hydrogels (a) at different As(V) concentrations, (b) at different Cr(VI) concentrations and (c) at different Cr(III)

concentrations, respectively [Heavy metal concentration: 1-5000 mg L⁻¹ (50 mL), sorbent dosage: 1 g L⁻¹, time: 24 h].

3.4 Equilibrium sorption studies

Single, quaternized and amidoximated hydrogels were used for the removal of some heavy metal ions such as As(V), Cr(III) and Cr(VI). The heavy metal ion concentrations were varied from 1 mg L⁻¹ to 5000 mg L⁻¹ while media temperature (°C), pH, contact time (hours) and hydrogel dosage (g L⁻¹) were set as 25, 6, 24 and 1, respectively. As shown in Figure 4(a-c), the sorption capacities to three heavy metal ions of three hydrogels gradually increased with the rise of initial concentration and then reached to maximum equilibrium sorption capacity. It was shown that the order of metal ions up taken by hydrogels was As(V)>Cr(VI)>Cr(III), while the removal capacity of the hydrogels followed the order amid-p(AN-co-VI)>quart-p(AN-co-VI)>p(VI). It was clearly seen that As(V) and Cr(VI) was considerably removed by quaternized and amidoximated hydrogels and but these hydrogels cannot removal Cr(III) ions. This data proved that positive charges in the imidazole structure were formed by the quaternization reaction and then the hydrophobic nitrile groups in the copolymer structure by the amidoximation reaction turned into hydrophilic amidoxime groups [17, 18, 33]. In addition, after the quaternization and amidoximation reactions, it was seen that the diffusion and electrostatic attraction forces increased between the functional groups and the metal ions.



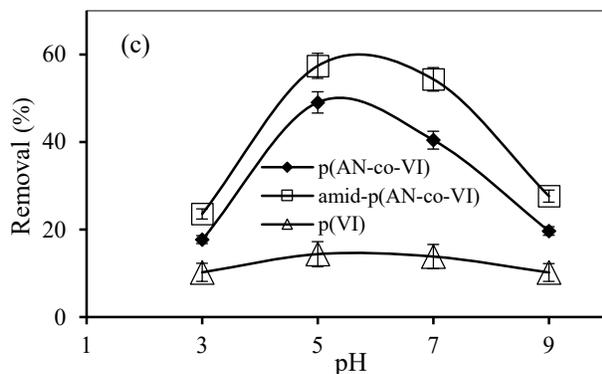


Figure 5. Sorption of (a) As(V), (b) Cr(VI) and (c) Cr(III) into p(VI), quart-p(AN-co-VI) and amid-p(AN-co-VI) hydrogels as a function of solution pH [Heavy metal concentration: 10 mg L^{-1} (50 mL), sorbent dosage: 1 g L^{-1} , time: 24 h].

The sorption amounts of p(VI), quart-p(AN-co-VI) and amid-p(AN-co-VI) hydrogels towards As(V), Cr(VI) and Cr(III) ions were measured at pHs ranging from 3 to 9 with the initial metal concentration of 10 mg L^{-1} for 24 h at room temperature and were shown in Figure 5. As illustrated in Figure 5(a-c), the highest sorption capability were observed for the amid-p(AN-co-VI) hydrogels and were determined to be 79.7% at pH 3 for As(V), 93.4% at pH 5 for Cr(VI) and 57.4% at pH 5 for Cr(III). This case may originate from that As(V) (AsO_4^{3-} , HAsO_4^{2-} , H_2AsO_4^- and H_3AsO_4), Cr(VI) ($\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- , CrO_4^{2-}) and Cr(III) (Cr^{3+} , $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_3$) ions have different oxidation steps at different pHs [35-37]. The results showed the sorption of As(V) and Cr(VI) species by synthesized hydrogels was dominant.

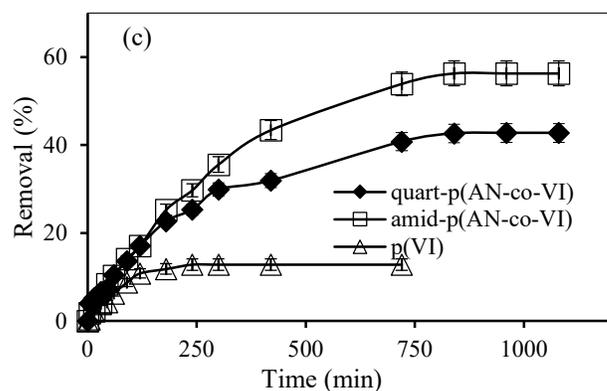
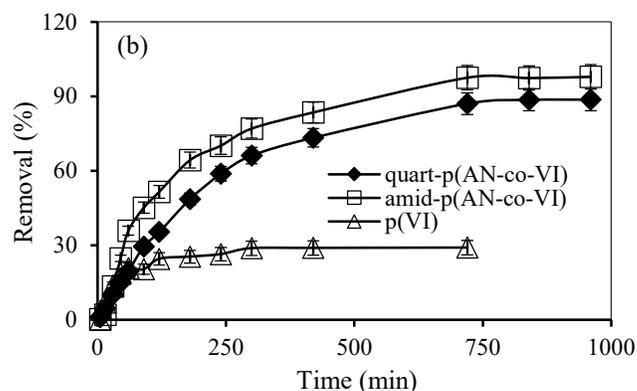
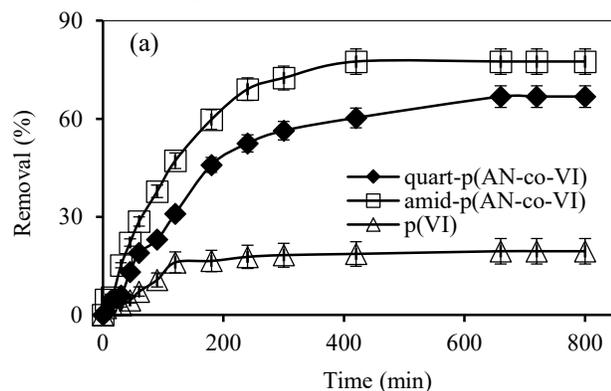


Figure 6. The effect of contact time on (a) As(V) sorption, (b) Cr(VI) sorption and (c) Cr(III) sorption by p(VI), quart-p(AN-co-VI) and amid-p(AN-co-VI) hydrogels [Heavy metal concentration: 10 mg L^{-1} (50 mL), sorbent dosage: 0.25 g L^{-1}].

Using 10 mg L^{-1} of the metal ion solutions and 1 g L^{-1} sorbent dosage, Figure 6(a-c) was shown typical results of As(V), Cr(VI) and Cr(III) sorption amounts against sorption times. For all three metal ions, it was observed that sorption equilibria were reached very quickly and lasted between 3 and 5 hours. The initial fast sorption may be due to the reaction between the metal pores with the macroscopic pore and the hydrogel outer sites. Subsequent deceleration may be due to the micropores of the crosslinked hydrogel. As shown in Figure 6(a-c), the uptake percentage of As(V), Cr(VI) and Cr(III) ions by amidoximated hydrogels was 77% in 420 min, 98% in Cr(VI) and 56% in 840 min, respectively.

3.5 Sorption isotherm studies

Langmuir and Freundlich sorption isotherms were used to evaluate the sorption behavior and were the isotherm parameters were summarized in Table 1. Based on the correlation coefficient, the sorption behavior of hydrogels was shown that was generally better fitted to the Freundlich isotherm. The Freundlich isotherm model describes the surface energies in different types of sorption sites and the Langmuir isotherm model describes monolayer sorption at the sorption site. According to experimental data, sorption of As(V), Cr(VI) and Cr(III) heavy metals were more related to multilayer sorption than monolayer sorption. Even though the

sorption capacity of the As(V) and Cr(VI) ions of amid-p(AN-co-VI) hydrogel were enhanced by modifying of p(AN-co-VI) hydrogel, there was not a significant increase in the sorption capacity of Cr(III) ion. The maximum amount of As(V), Cr(VI) and Cr(III) metal ions sorbed by amid-p(AN-co-VI) hydrogel were founded to be 833.3, 344.8 and 4.82 mg g⁻¹, respectively. The values of the Freundlich calculated sorption intensity, $n > 1$, indicated that was favorable of sorption of all the metal ions by p(VI), quart-p(AN-co-VI) and amid-p(AN-co-VI) hydrogels [27, 28].

3.6 Sorption reaction models

To determine the reaction kinetics of the sorption, we investigated three different reaction models such as first order, pseudo second order and intraparticle diffusion using equations numbered 6, 7, 8. In Table 2 was shown that the correlation coefficients of the pseudo second order kinetic

model obtained for p(VI) hydrogel were above 0.97 and that the sorption of three metal ions was generally followed the pseudo second order. In addition, the q_e values calculated from the pseudo second order were determined to be in agreement with the experimental q_e values. Table 2 and Table 3 showed that the sorption of quart-p(AN-co-VI) and amid-p(AN-co-VI) hydrogels generally followed first order kinetics and the calculated q_e values were in agreement with the experimental q_e values. It was concluded that intraparticle diffusion was the rate-limiting step and it was observed that the intra-particle diffusion model was effective on the sorption of heavy metal ions by synthesized hydrogels. Firstly, it can be assumed that the diffusion took place in the film and boundary layer around the hydrogel and then there was intraparticle diffusion into the macro and micropores of the hydrogels.

Table 1. Langmuir and Freundlich isotherm data for sorption of As(V), Cr(VI) and Cr(III) by p(VI), quart-p(AN-co-VI) and amid-p(AN-co-VI) hydrogels

Sorbents	Ions	Langmuir isotherm constants			Freundlich isotherm constants		
		K_L (L mg ⁻¹)	q_m (mg g ⁻¹)	R^2	K_f	n	R^2
p(VI)		2.15×10^{-2}	40	0.9958	2.13	2.26	0.8310
quart-p(AN-co-VI)	As(V)	1.23×10^{-3}	400	0.9046	1.39	1.43	0.9824
amid-p(AN-co-VI)		1.02×10^{-3}	833.3	0.7704	1.67	1.28	0.9733
p(VI)		2.76×10^{-3}	25.3	0.5831	1.52	2.33	0.9020
quart-p(AN-co-VI)	Cr(VI)	7.34×10^{-4}	312.5	0.5476	5.82	2.05	0.9299
amid-p(AN-co-VI)		2.73×10^{-3}	344.8	0.8654	2.54	2.02	0.9187
p(VI)		1.14×10^{-2}	2.57	0.9796	0.82	5.95	0.8651
quart-p(AN-co-VI)	Cr(III)	1.21×10^{-2}	2.33	0.8798	1.38	7.36	0.7535
amid-p(AN-co-VI)		5.29×10^{-3}	4.82	0.8780	1.16	4.42	0.8916

Table 2. Kinetic constants for sorption of As(V), Cr(VI), and Cr (III) by p (VI), quart-p(AN-co-VI) and amid-p(AN-co-VI) hydrogels

Sorbents	Ions	Pseudo first order		Pseudo second order		Intraparticle diffusion	
		K_{p1} (min ⁻¹)	R^2	K_{p2} (g mg ⁻¹ min ⁻¹)	R^2	R_{id} (mg g ⁻¹ min ^{-1/2})	R^2
p(VI)		1.08×10^{-2}	0.9494	1.62×10^{-3}	0.9741	0.1912	0.7361
quart-p(AN-co-VI)	As(V)	5.99×10^{-3}	0.9888	3.71×10^{-4}	0.9054	0.2781	0.9215
amid-p(AN-co-VI)		9.44×10^{-3}	0.9935	7.8×10^{-4}	0.9749	0.3550	0.8570
p(VI)		1.27×10^{-2}	0.9443	2.64×10^{-2}	0.9991	0.0616	0.7733
quart-p(AN-co-VI)	Cr(VI)	5.3×10^{-3}	0.9805	3.23×10^{-4}	0.8901	0.3085	0.9545
amid-p(AN-co-VI)		6.7×10^{-3}	0.9590	3.31×10^{-4}	0.6946	0.2213	0.9067
p(VI)		1.47×10^{-2}	0.9842	1.04×10^{-2}	0.9820	0.0334	0.9108
quart-p(AN-co-VI)	Cr(III)	5.8×10^{-3}	0.8966	1.01×10^{-3}	0.9792	0.1381	0.9726
amid-p(AN-co-VI)		4.1×10^{-3}	0.9797	3.38×10^{-4}	0.9608	0.2026	0.9888

Table 3. The sorption capacity of sorption of As(V), Cr(VI), and Cr(III) by the p(VI), quart-p(AN-co-VI) and amid-p(AN-co-VI) hydrogels.

Sorbents	Ions	Pseudo first order	Pseudo second order
		$q_{e,exp}$ ($mg\ g^{-1}$)	$q_{e,cal}$ ($mg\ g^{-1}$)
p(VI)		5.12	5.95
quart-p(AN-co-VI)	As(V)	5.83	8.64
amid-p(AN-co-VI)		8.07	9.77
p(VI)		3.68	1.79
quart-p(AN-co-VI)	Cr(VI)	7.83	10.6
amid-p(AN-co-VI)		6.94	9.77
p(VI)		1.17	1.3
quart-p(AN-co-VI)	Cr(III)	3.95	4.75
amid-p(AN-co-VI)		4.98	7.19

4. Conclusions

This article, it was aimed to remove heavy metal wastes such as As(V), Cr(VI) and Cr(III) which pollute the ecosystem and damage the living species. To remove these metal ions, p(VI-co-AN) based hydrogels were synthesized and their sorption properties were investigated. To change the synthesized p(VI-co-AN) hydrogel surface, it was subjected to quaternization (positively charged) and amidoximation reactions and it has been found that the hydrogel's both swelling and sorption capacity enhanced with modification. According to swelling data, the values S% of p(VI), quart-p(AN-co-VI) and amid-p(AN-co-VI) hydrogels were 141%, 1113% and 3590%, respectively. Results indicated that S% values of p(AN-co-VI) based hydrogels were raised after quaternization and amidoximation reactions. The removal of As(V), Cr(VI) and Cr(III) metal ions from aqueous solution by quart-p(AN-co-VI) and amid-p(AN-co-VI) hydrogels was found to be effective. However, the removal of As(V) and Cr(VI) by quart-p(AN-co-VI) and amid-p(AN-co-VI) hydrogels was determined to be greater than the Cr(III) removal. The maximum amount of As(V), Cr(VI) and Cr(III) sorption onto the amid-p(VI-AN) were calculated to be 598, 303.8 and 4.9 $mg\ g^{-1}$, respectively. When the isotherm models were examined, the sorption behavior of hydrogels was shown that was generally better fitted to the Freundlich isotherm. The reaction kinetics of the sorption were determined using first order, pseudo second order and intraparticle diffusion models. In addition, q_e values calculated with experimental q_e values were found to be compatible. Based on these results, we believe that p(VI-co-AN) based hydrogels can be used as an effective sorbent for the removal of heavy metal residues that threaten the ecosystem and the living.

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