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Removal of Cu(II), Ni(II) and Zn(II) from aqueous solutions using poly(2-acrylamido-2-methyl-1-propanesulfonic acid) gel: sorption kinetics and characterization

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ABSTRACT

Removal of Cu(II), Ni(II) and Zn(II) ions from aqueous solutions was studied by using poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) gel. The gel was prepared by free radical polymerization at 60°C for 24 h in the presence of the ammonium peroxodisulfate and N,N′-methylenebis(acrylamide) as the initiator and the cross-linker, respectively. The effect of initial metal ion concentration (25–100 mg/L) on the removal efficiency and the sorption process were investigated by batch method. At initial concentration of 25 mg/L, the removal efficiencies were found to be higher and too close to each other (95%–95.5%), whereas lower removal efficiencies (65.8%–72.0%) were determined at an initial concentration of 100 mg/L, for all the metal ions investigated. Sorption data of Cu(II), Zn(II), and Ni(II) ions on the gel showed good fit to the pseudo-second order type kinetics. PAMPS exhibited slightly higher selectivity for the sorption of Zn(II) from ternary solutions at higher concentrations. Characterizations of the poly(2-acrylamido-2-methyl-1-propanesulfonic acid) gel before and after the sorption process were carried out by Fourier transform infrared (FTIR) spectroscopy, thermal gravimetric analysis (TGA), environmental scanning electron microscopy (ESEM), and zeta (ζ) potential measurements. PAMPS gel was found to be charged negatively at pH values between 3 and 9.

Keywords: Sulfonic acid; Sorption; Gel; Heavy metal ions

1. Introduction

Toxic heavy metal ions, such as Cr, Pb, Zn, Cu, Ni, Cd, and Co, cause many environmental problems due to their increasing discharge to environment day by day [1]. High solubility of heavy metal ions in aqueous solutions creates risk for living organisms [2,3] and also their presence in food chain may result in excess accumulations in human body [2] since biodegradation of heavy metal ions is not possible in contrast to organic contaminants [4,5]. Therefore, it is vitally important to treat metal-contaminated wastewaters before their discharge process [2]. Nickel is one of the heavy metal ions, which can be found in water as a result of wastewater discharge from electroplating, steel manufacturing, pulp processing, leather tanning, mining, and metallurgical processes [1]. Nickel exposure above critical level can cause gastrointestinal distress [1,5], neurological effects [1], skin dermatitis [5], and lung and kidney problems [5]. Copper and zinc also take place among the most toxic pollutants. Copper can be found in wastewater of many industrial processes such as metal-process pickling and plating baths [6]. Cramps [5], convulsions [5], irritation of the skin [6],

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dermatitis [6], hands keratinization [6], Wilson's disease [7], and cellular damage [7] may occur by exposure to the excess amounts of copper. Discharges from acid mine drainage, galvanizing plants, natural ores, and municipal wastewater treatment plants contain zinc [6]. Although zinc is an essential trace element for the regulation of the biochemical processes and for the physiological functions of the living tissue, its excess amounts bring some health problems like irritations in the skin, nausea, and anemia [5]. Wastewaters originated from battery production, metal coating, and mining industries contain commonly Cu(II) and Zn (II) together [4]. The wastewater of electroplating industry frequently contains nickel, copper, and zinc as heavy metals [8]. Vengris et al. [8] used natural and modified clay to investigate its sorption capacity for Cu(II), Ni(II), and Zn(II). They found that the removal capacity of both natural and modified sorbents was in the order of Cu(II) > Ni(II) > Zn(II). Their batch experiment results showed that modified sorbent has the capability to reduce the concentration of metal ions to sewage discharge limits [8].

The removal of heavy metal ions from industrial wastewaters have become important problem due to hazardous effect of these toxic metals on health. A number of methods including ion exchange [1,3,9], adsorption [3], electrochemical treatment [1], solvent extraction [3], complexing agent [9], and chemical precipitation [3] are used to remove heavy metal ions from metal-contaminated wastewaters. Regeneration possibility of adsorbent, the ease of the plant and high effluent quality are the some of the main advantages of adsorption process [5]. Ion exchange is also a superior conventional process because of the ease of recovery and reusability of the resin. Ion exchange resins can be classified as cationic-, anionic-, and chelating-exchange resins depending on their functional groups [10]. Since ion-exchange process offers many advantages, such as fast kinetics, effective treatment capacity, and high removal efficiency, it is extensively used for the removal of heavy metals from wastewaters [5].

While strongly acidic resins contain sulfonic acid groups ($-SO_3H$), weakly acidic counterparts have carboxylic acid groups ($-COOH$) [5,11], and both functional groups demonstrate different sorption behavior [11]. The polymers with pendant sulfonic acid group do not act like ligands [12]. The interaction between sulfonic acid groups and metal ions occurs by electrostatic manner/ionic interaction [12]. The removal of metal ions is based on the ion exchange mechanism [13], whereas the coordination bonds are favorable in the sorption properties of carboxylic acid [11]. The presence of $-SO_3^-$, $-NH$, and $-OH$ functional groups in polymer structures provides distinctive advantages in the removal process of metal ions [14]. Metal cations replace with hydrogen ions in the acidic groups of the resin. The following mechanism was proposed for the ion-exchange of metal ions and sulfonic acid groups [5].

$$nR{-}SO_3H + M^{n+} \rightarrow (R - SO_3^-)_n M^{n+} + nH^+$$

There is a difference between the selectivity of weak acid and strong cation exchange resins for the divalent ions. Sulfonic acid group is less selective for divalent alkaline ions than carboxylic acid groups [15]. In the removal processes, the presence of competing ions should be taken into account because industrial wastewaters generally contain heavy metal ions more than one [7,16]. In our previous study [17], discharge limits of Cu(II), Ni(II), and Zn(II) were explained in detail.

Synthetic resins [18], carbonaceous adsorbents [19], microbeads [20], hydrogels [21], hydrogel nanoparticles [22], and natural materials such as zeolites and silicate minerals [5] have been preferred to remove heavy metal ions from aqueous solutions. Hydrogels are cross-linked and hydrophilic networks have three dimensional structures and absorb large amounts of water without dissolving [23]. Hydrogels have attracted particular interest in the removal of heavy metal ions from wastewater due to presence of different functional groups, its reusability, and ease of removal process [16]. Functional groups, such as amide [7,16], amine [7], sulfonic [16], carboxylic acid [7,16], hydroxyl [7,16], phosphonic [16], and ammonium [7] indicate binding property toward metal ions. Therefore, hydrogels are good candidates as polychelatogens for heavy metal removal applications [7]. The presence of electron rich atoms (e.g., nitrogen, oxygen, and sulfur) in the structure of sorbent material provides advantages in terms of heavy metal ion removal from wastewaters [24].

Ion exchange, chelation, and electrostatic interaction are three modes of the adsorption process. Ion exchange process is related to the ionic radius [25,26], ionic charges [26], and electronic structure [26] of the metal ions. It is known that electrostatic interaction takes place between heavy metal ions and functional groups since metal ions and carboxylic and/or sulfonic acid groups are counter charged [25]. The process of chelation expected depends on hydration energy of metal ions [26]. 2-acrylamido-2-methyl-1-propanesulfonic acid is an ionic monomer, which is a strong electrolyte because of its complete dissociation property in whole pH range. The behaviors of the hydrogels based on AMPS differ from the counterpart hydrogels with neutral or weak acidic functionality. The hydrogels based on AMPS display different pH and ionization behavior in comparison with the counterpart hydrogels with neutral or weak acidic functionality. PAMPS hydrogels are strong polyelectrolytes, and they exhibit pH-independent swelling behavior on the contrary to weak polyelectrolyte counterparts [23]. The presence of AMPS units in copolymer hydrogels affects positively the adsorption capacity of the hydrogels [3].

There is a little information about the use of gels for the removal of Cu(II), Ni(II), and Zn(II) ions from industrial wastewaters/aqueous solutions containing all the ions together. The current study focused on the use of poly (2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) gel in the removal of Cu(II), Zn(II), and Ni(II) ions from ternary solutions. PAMPS gel was prepared by free radical chain polymerization in the presence of a cross-linker. The sorption kinetics of Cu(II), Zn(II), and Ni(II) ions by the PAMPS were determined. The pseudo-first order and pseudo-second order equations were used to determine the mechanism and kinetics of the sorption process. In addition to the correlation coefficients (R^2), the average percentage errors ($\varepsilon\%$) between the experimental and predicted value were also calculated for the confirmation of the suitability of the studied kinetic models.

2. Experimental

2.1. Materials

2-Acrylamido-2-methyl-1-propane sulfonic acid (AMPS), N,N′-methylenebisacrylamide (NMBA) and N,N,N′,N′-tetramethylethylenediamine (TEMED) were provided from

Merck Schuchardt OHG (Germany). Ammonium peroxydisulfate (APS) (Merck KGaA, Darmstadt, Germany) was used as the free radical initiator. Nickel (II) sulfate hexahydrate (Merck Darmstadt, Germany), copper (II) sulfate pentahydrate (Merck KGaA, Darmstadt, Germany), and zinc sulfate heptahydrate (Merck, Darmstadt, Germany) were used to prepare metal ion solutions. Deionized water was used in the gel synthesis and preparation of metal ion solutions.

2.2. Preparation of gel

PAMPS gel was synthesized by free radical chain polymerization reaction using AMPS monomer at 1 mol/L initial concentration in aqueous solution. The initiator APS and the cross-linker NMBA were used as 1 and 5 mol% with regard to initial total monomer concentration, respectively. Feed composition also includes accelerator of TEMED in equal amount of initiator ($W_{\text{TEMED}} = W_{\text{APS}}$). The polymerization reaction was performed in glass tubes with 1.3 cm inner diameter and 10 cm length. Nitrogen purging was applied to solution containing monomer and cross-linker for 20 min to provide inert medium. Then, the given amounts of APS and TEMED were added to the aqueous solution of monomer and the cross-linker. Polymerization was performed at 60°C using a water bath with a temperature controller (Polyscience) for 24 h. After completion of the polymerization, the obtained hydrogels were sliced into small cylinders, and they were equilibrated in deionized water to remove the unreacted reactants by changing the water twice a day. Finally, the purified hydrogels were dried initially in air and then in vacuum oven at 40°C till constant weight.

In the study of Çavuş and Gürdağ [27], PAMPS gel prepared in the presence of 3 mol% NMBA was used for the competitive removal of Pb(II), Cu(II), and Cd(II) ions from aqueous solutions. In the present study, the removal of Cu(II), Ni(II), and Zn(II) ions was performed by PAMPS gel prepared in the presence of 5 mol% NMBA, namely PAMPS gel with higher cross-link density than that used in the previous work [27].

2.3. Characterization studies and instrumentation

In order to determine metal ion concentrations in the aqueous solutions at regular intervals, a Perkin Elmer flame-graphite-furnace atomic absorption spectrometers (AAS) was used. The characterization of the gels before and after the metal sorption process (sample: 50 mg/L metal ion sorbed gel) was performed using Fourier transform infrared spectroscopy (FTIR) (Perkin-Elmer Spectrum One FTIR Spectrometer). The FTIR spectra were obtained in the wavenumber range of 450–4,000 cm^{-1} using the KBr pellet method. Following the sorption experiments, the microstructure of the gels before and after sorption was determined.

The microstructure of the PAMPS gel was analyzed by scanning electron microscopy (SEM) using Zeiss EVO® LS 10 instrument. The microstructure of the PAMPS-Me(II) was analyzed by environmental scanning electron microscopy (ESEM) with an accelerating voltage of 10.0 kV (JEOL/JSM-6335F-INCA instrument). Liquid nitrogen was used to break the gel samples, and afterward they were coated with gold to get a suitable contrast of the structure. Thermal stability of PAMPS gels both before and after the sorption of metal ions was investigated using Shimadzu, DTG 60. Thermal gravimetric analysis (TGA) experiments were performed from 25°C to 800°C at a heating rate of 20°C/min in a nitrogen atmosphere (20 mL/min). The zeta (ζ)-potentials of the PAMPS gel at pH values varied from 3 to 9 and were determined with a Particle Size Analyzer (Brookhaven Instruments BIC 90 Plus) based on the method of Alkan et al. [28].

The equilibrium swelling values of the PAMPS gel was also determined using the following equation:

$$\text{Equilibrium Swelling Value}\left(\frac{g_{\text{water}}}{g_{\text{sample}}}\right) = \frac{\left(W_s - W_d\right)}{W_d} \tag{1}$$

where W_s and W_d denote the weights of PAMPS in swollen and dry forms, respectively. The equilibrium swelling value of the PAMPS gel was found as 225 $g_{\text{water}}/g_{\text{gel}}$.

2.4. Sorption studies

The removal of Cu(II), Ni(II), and Zn(II) ions from aqueous solutions by PAMPS gel was studied by batch sorption technique. Synthetic ternary metal solutions of different initial concentrations ranging 25−100 mg/L were prepared by dissolving Nickel (II) sulfate hexahydrate, copper (II) sulfate pentahydrate, and zinc sulfate heptahydrate in deionized water. The ratio of metal ions in weight was 1:1:1 for the solutions at all concentrations. For the removal experiments, 50 mL of the metal ion solution was added to a constant amount of gel (0.1 g) in a stoppered glass erlenmeyer flask, and it was shaken by using a thermostated orbital shaker (Zhicheng, China) at constant temperature (25°C ± 2°C) with a rate of 200 rpm. The concentration of residual metal ions in the aqueous solutions was measured by AAS following the filtration using 0.45 μm Whatman filter paper.

The experimental metal ion sorption capacities of the PAMPS gel at equilibrium (q_e) and at time t (q_t) were calculated using Eqs. (2) and (3), respectively [3,17,19,29].

$$q_e = \left(C_0 - C_e\right) \times \frac{V}{m} \tag{2}$$

$$q_t = \left(C_0 - C_t\right) \times \frac{V}{m} \tag{3}$$

where q_e is the amount of metal ion sorbed at equilibrium (mg/g), q_t is the amount of metal ion sorbed at time t (mg/g), C_0 is the initial metal ion concentration (mg/L), C_e is the concentration of metal ion in solution at equilibrium (mg/L), C_t is the concentration of metal solution at any time (mg/L), V is the volume of wastewater (L) and m is the amount of the gel (g).

In order to evaluate the performance of PAMPS gel, metal ion removal efficiency (RE%) was calculated as follows [17,22]:

$$\text{RE}\ \left(\%\right) = \frac{\left(C_0 - C_e\right)}{C_0} \times 100 \tag{4}$$

R^2 and ε% were used to investigate the confirmation of the suitability of the kinetic models for the sorption of metal ions by PAMPS. ε% between the experimental and predicted values are calculated with Eq. (5).

$$\varepsilon\% = \frac{\sum_{i=1}^{N} \frac{\left| q_{e,i,\text{exp}} - q_{e,i,\text{cal}} \right|}{q_{e,i,\text{exp}}}}{N} \times 100 \tag{5}$$

While the experimental and calculated values are denoted with the subscripts "exp" and "cal," N is the number of measurements [30]. Lower values of ε% indicate greater accuracy in prediction.

For the investigation of the sorption mechanism of metal ions by any polymer adsorbent, two well-known kinetic models, that is, Lagergren's pseudo-first [31–33] and second-order kinetic models [32–34] are used. In general, the sorption process in solid/liquid systems is well described by Lagergren's pseudo-first order equation [Eq. (6)].

$$\frac{dq_t}{dt} = k_1\left(q_e - q_t\right) \tag{6}$$

where k_1 (1/min) denotes the pseudo-first order rate constant of the sorption process, while the amounts of metal ion sorbed per gram of polymer (mg/g) at equilibrium and at time t (min) are shown by q_e and q_t, respectively. The linear equation [Eq. (7)] is obtained by the integration of Eq. (6) at the initial condition of $q_t = 0$ and time (t) approaches to 0 [33].

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{7}$$

The pseudo-second order kinetic model equation and also its linearized form are given in Eqs. (8) and (9), respectively [33]. k_2 (1/min) shows the pseudo-second order rate constant for the sorption process.

$$\frac{dq_t}{dt} = k_2\left(q_e - q_t\right)^2 \tag{8}$$

$$\frac{t}{q_t} = \frac{1}{\left(k_2\, q_e^2\right)} + \left(\frac{1}{q_e}\right)t \tag{9}$$

The initial sorption rate constant, h (mg/g min), is found using the second order rate constant, k_2 (1/min) and equilibrium sorption uptake q_e (mg/g) values [27,35].

$$h = k_2 \times q_e^2 \tag{10}$$

3. Results and discussion

3.1. FTIR analysis

FTIR technique was used to characterize the gels both before (PAMPS) and after sorption of metal ions (PAMPS-Me(II)), and their spectra are shown in Fig. 1. The characteristic C=O stretching band (amide I) of AMPS is seen at 1,674 and 1,635 cm^{-1} for PAMPS and PAMPS-Me(II), respectively [3,27]. The bands at around 3,100–3,600 cm^{-1} are assigned to the stretching of O–H and N–H bonds [3,27]. The bending of N–H bond (amide II band) appears at 1,550 and 1,552 cm^{-1} in the spectra of PAMPS and PAMPS-Me(II), respectively [3,27]. Since PAMPS has –SO$_3$H groups, symmetric and asymmetric stretching bands of SO$_2$ are seen at 1,031 and 1,148 cm^{-1}, respectively [25]. In the spectrum of PAMPS-Me(II), while symmetric SO$_2$ stretching band is observed at 1,042 cm^{-1}, asymmetric one is present at 1,182 cm^{-1}. These peaks are characteristic of sulfonic acid (SO$_3$H) [13]. The peaks at 618 and 625 cm^{-1} are assigned to the stretching of C–S bond [23]. The absence of the peaks attributed to the C=C and CH$_2$= bonds indicates the completion of polymerization [17], and it demonstrates the purity of the polymer. FTIR spectra showed that both positions and intensities of the bands change due to sorption of metal ions since the metal ion sorption mechanism depends on ion exchange reaction between –SO$_3$H groups and the metal ions. The most apparent change is observed for symmetric SO$_2$ stretching band because of the sorption of the metal ions by PAMPS. The loss in the intensity of this band results from the strong interaction between metal ions and sulfonic acid groups of PAMPS gel. The shift in the position of SO$_2$ bands due to sorption of metal ions also confirms the presence of –SO$_3$H-Cu(II) + Ni(II) + Zn(II) type interaction. The intensity of C–S band decreased after metal ion sorption too.

The decrease in the intensity of amide II band is due to the change in inter-/intra-molecular hydrogen bonds indicating ion exchange mechanism. In addition, the change in the peak area of N–H and O–H bands (between 3,100 and 3,600 cm^{-1}) after ion sorption can also be assigned to the metal ion sorption by ion exchange mechanism and variation of inter-/intra-molecular hydrogen bonds [17].

3.2. Thermal stability

The changes in the thermal behavior of PAMPS gel both before and after sorption process were determined by TGA, and the analysis results are presented in Fig. 2. The TGA curves revealed that thermal stability of PAMPS-Me(II) is higher than that of pristine gel PAMPS, which can be assigned to the ionic cross-linking/attraction between metal ions (Cu(II) + Ni(II) + Zn(II)) and –SO$_3$H groups. The presence of ionic cross-linking between metal ions and –SO$_3$H groups of polymers substantially affects the thermal stability [17]. The weight loss observed at temperatures lower than 200°C

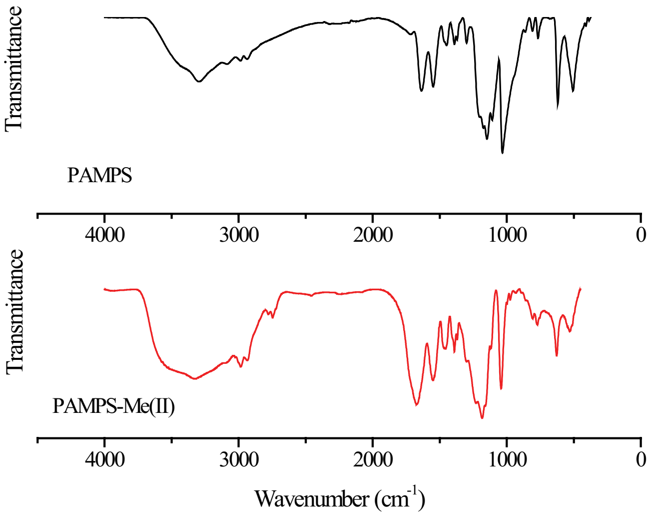

Fig. 1. FTIR spectra of PAMPS gel before and after sorption.

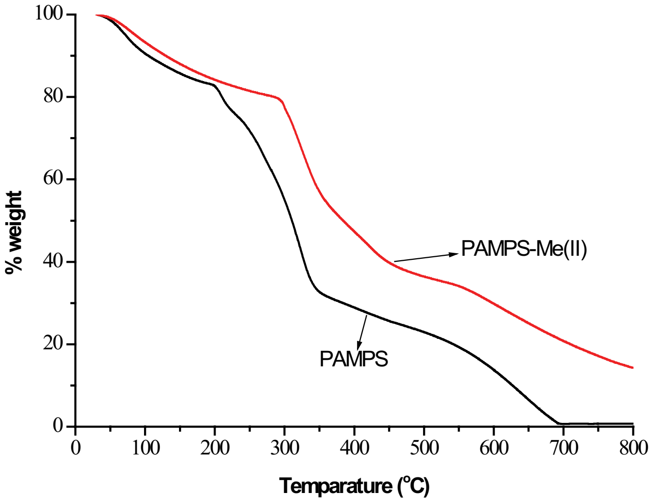

Fig. 2. TGA curves of PAMPS and metal ion adsorbed-PAMPS (PAMPS-Me(II)) gels.

can be assigned to the loss of moisture [3]. While the decomposition of $–SO_3H$ groups (SO_2/SO_3) can usually be observed between 250 and 300°C, the degradation of the main chain and the following cross-linking bridges occur approximately between 300 and 500°C [3,17]. The weight loss of PAMPS was found to be higher than that of PAMPS-Me(II). For example, at 350°C, the weight losses of PAMPS and PAMPS-Me(II) were found to be 67.3% and 42.9%, respectively. It was reported that the breakaway of SO_2 molecules from the branched chains/network structure occurs at temperatures higher than 700°C [25]. PAMPS gel completely decomposed at 700°C, whereas the weight loss of PAMPS-Me(II) was 79.2% at the same temperature.

3.3. Morphologic characterization

The electron microscopy images of the gels before (PAMPS) and after sorption (PAMPS-Me(II)) are presented

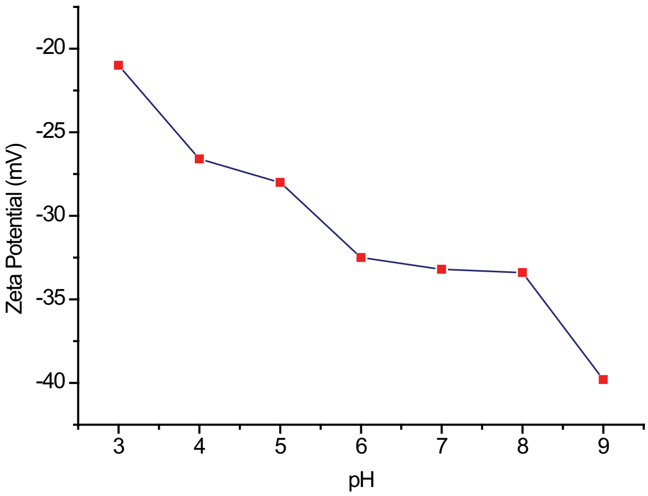

Fig. 4. Zeta potential values of PAMPS gel at different pHs.

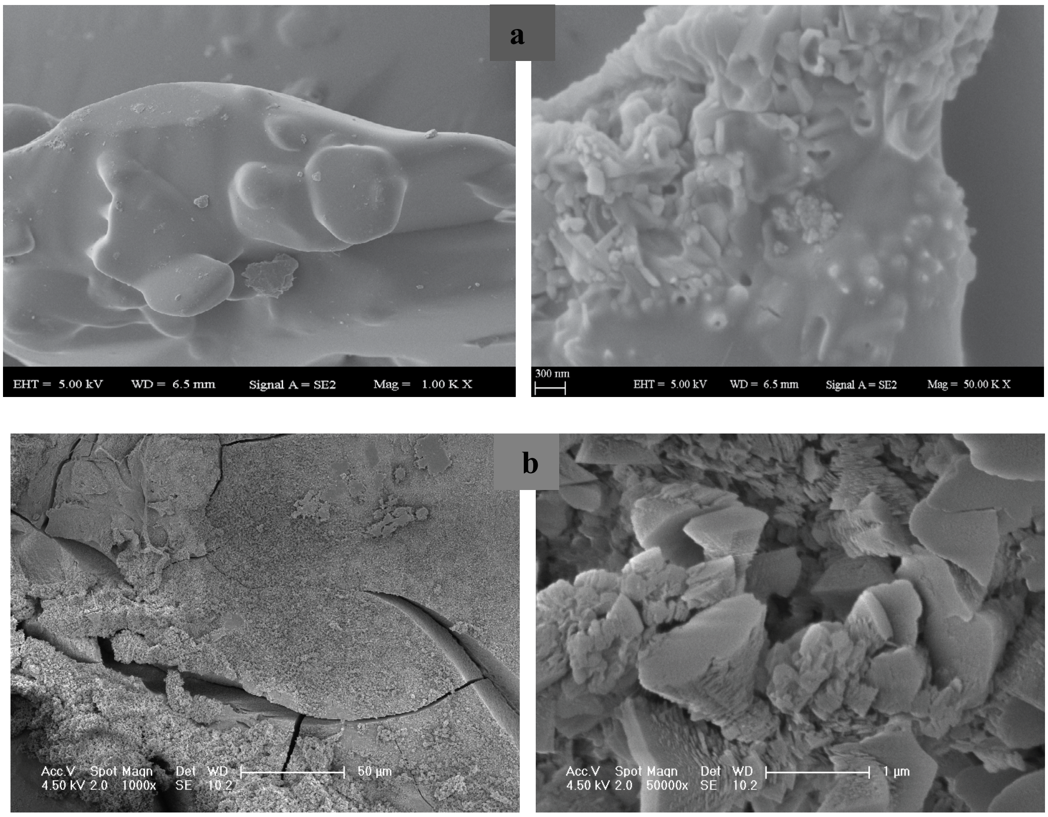

Fig. 3. SEM of PAMPS (a) ESEM of PAMPS-Me(II) (b).

in Fig. 3. The surface of PAMPS is not smooth, and it has discontinues. The deposition of the metal ions is clearly observed on the ESEM of PAMPS-Me(II). Pores with irregular shapes can indicate the ease of accession of metal ions into the gel network. It was reported that the porous structure might be resulting from high swelling property of gel [3,23]. This property indicates more accessibility of the functional groups within the network structure [3]. Zheng et al. [29] reported that surface morphology with porous nature is useful for the fast sorption equilibrium since accessibility of the reactive functional groups for the metal ions occurs more easily.

3.4. The zeta (ζ)-potential measurements

The surface charge of the PAMPS gel was measured at different pH values, and depicted in Fig. 4. PAMPS gel is negatively charged at all pH values due to the dissociation of –SO$_3$H groups. Its ζ-potentials increased from −39.8 to −21 with the decrease of pH from 9 to 3. It is well known that the sulfonic acid groups exhibit strong acidity, and a complete dissociation is observed in a wide pH range [36].

3.5. Batch experiments

A ternary aqueous solution including equivalent amounts of Cu(II), Ni(II), and Zn(II) ions was used in the batch experiments in order to determine removal mechanism of these ions. The metal ion sorption capacity of PAMPS was investigated at initial metal ion concentrations of 25, 50, 75, and 100 mg/L at 25°C ± 2°C. A series of ternary aqueous solutions (50 mL) were shaken at different contact times in the range of 5–180 min using 0.1 g gel at a rate of 200 rpm. The sorption capacities of PAMPS gel for Cu(II), Ni(II), and Zn(II) ions as a function of time are depicted in Fig. 5(a), (b), and (c). The sorption equilibrium was reached in a short time, which can be assigned to the strong affinity of sulfonic acid (–SO$_3$H) groups to bind metal ions through electrostatic interaction. The removal of Cu(II), Ni(II), and Zn(II) nearly completed within the first 10 min. It is known that a material with –SO$_3$H groups remove the heavy metal ions from aqueous solutions via electrostatic interaction [13]. It is expected that the interaction between the adsorbent and metal ions should occur rapidly for a practicable process [37]. As it can be seen from Fig. 5, the sorption affinity depends on the initial concentration of metal ion. The sorption capacity increased with the increase in initial metal ion concentration. Sorption capacity of PAMPS gel for Cu(II), Ni(II), and Zn(II) ions from ternary solutions is given in Table 1 for all studied metal ion concentrations. The total sorption capacities of PAMPS gel from ternary solutions were found to be 1.14, 2.19, 2.82, and 3.27 mek/g for 25, 50, 75, and 100 mg/L initial metal ion concentrations, respectively.

It is clear that PAMPS gel did not exhibit any apparent selectivity for the removal of these ions at low concentrations. The sorption of Cu(II), Ni(II), and Zn(II) ions from

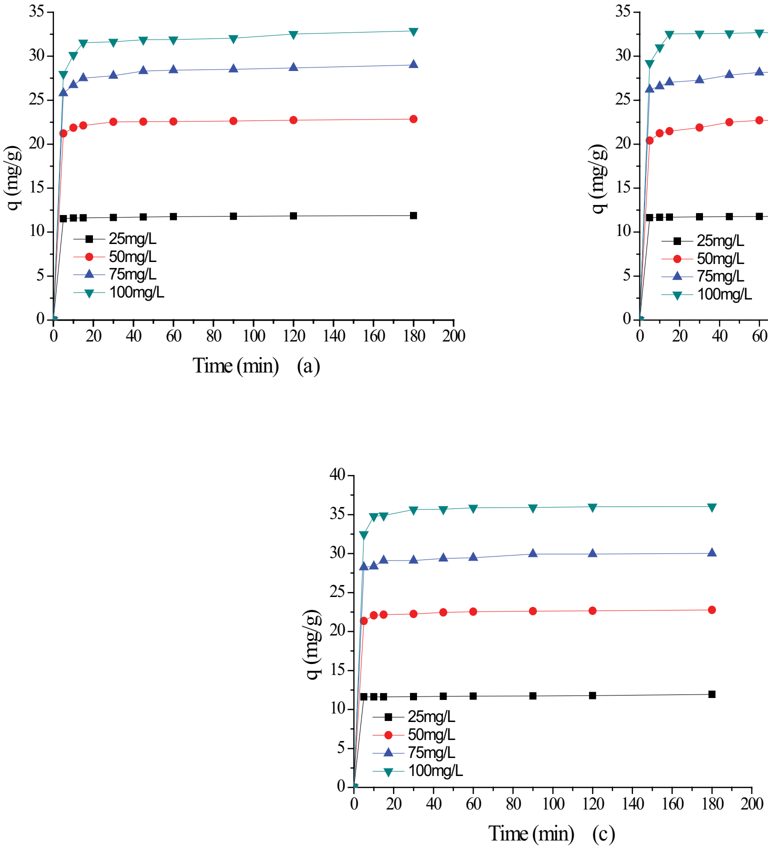

Fig. 5. The sorption capacity of PAMPS gel for (a) Cu(II), (b) Ni(II), and (c) Zn(II) ions.

Table 1
Estimated parameters for the pseudo-second order reaction kinetic model

Metal ion	Parameters	25 mg/L	50 mg/L	75 mg/L	100 mg/L
Cu(II)	q_{exp} (mg/g)	11.87	22.85	29.01	32.89
	q_{theo} (mg/g)	11.89	22.88	29.07	32.89
	k_2 (g/(mg min)	0.1943	0.07433	0.03082	0.02376
	h (mg/g min)	27.47	38.91	26.04	25.71
	R^2	1	1	0.9999	0.9999
	ε%	1.015	4.502	3.638	1.905
Ni(II)	q_{exp} (mg/g)	11.88	22.84	28.90	33.14
	q_{theo} (mg/g)	11.88	22.99	28.90	33.22
	k_2 g/(mg min)	0.2477	0.0473	0.02575	0.04119
	h (mg/g min)	34.97	25	21.50	45.45
	R^2	1	1	0.999	1
	ε%	0.925	4.556	3.7	0.640
Zn(II)	q_{exp} (mg/g)	11.94	22.77	30.02	36.02
	q_{theo} (mg/g)	11.90	22.78	30.12	36.10
	k_2 g/(mg min)	0.1300	0.0796	0.04306	0.05813
	h (mg/g min)	18.42	41.32	39.06	75.76
	R^2	0.9999	1	1	1
	ε%	2.017	4.515	3.452	0.385

aqueous solutions by PAMPS gel occurred in the order of Zn(II) (36 mg/g) > Ni(II) (33.1 mg/g) ≈ Cu(II) (32.9 mg/g) for 100 mg/L initial metal ion concentration. PAMPS gel showed slightly higher selectivity for the sorption of Zn(II) ion from ternary solutions at high concentrations. At the lowest initial concentration (25 mg/L), the equilibrium sorption capacity values were nearly the same, namely 11.9 mg/g, for each metal ion.

The effect of initial metal ion concentration on the removal efficiency of the PAMPS with respect to time is shown in Fig. 6(a), (b), (c), and (d). For all the studied metal ions, at the initial concentration of 25 mg/L, 92%–93%, removal was obtained within 5 min, which increased up to 95% in 180 min. For the initial concentration of 100 mg/L, a 56%–65% removal was obtained within 5 min, which increased up gradually to 66%–72% in 180 min. It can be concluded that the sorption equilibrium was gradually reached at high metal ion concentration. The removal efficiency for Cu(II), Zn(II), and Ni(II) ions increased as the metal ion concentration decreased, and it reached up to 95%–95.5% for 25 mg/L initial metal ion concentration. The removal efficiency at 100 mg/L was in the order of Zn(II) (72.0%) > Ni(II) (66.3%) > Cu(II) (65.8%). Presence of OH, NH, C=O and C–O–C groups in the gel structure ensures formation of complex between the gel and metal ion. Free electrons interact with these functional groups of gel to form a chelate [24]. PAMPS gel has $–SO_3H$, –NH and –C = O groups. In the case of high initial metal ion concentrations, most probably because of the saturation of functional groups, there is no adequate free functional group for the sorption of Cu(II), Ni(II), and Zn(II) ions on PAMPS gel, and as a result, the lower removal efficiencies are observed.

It was reported that sorption of Cu(II) [25,26], Ni(II) [25], and Zn(II) [26] occurs by ion-exchange mechanism. The physical properties of Cu(II), Zn(II), and Ni(II) ions strongly affect the sorption capacity and sorption rate values. In the study of Ramesh et al. [6], the sorption of Cu(II) and Zn(II) ions on hydroxyapatite was examined for both in single and binary aqueous systems. They [6] reported that sorption of the metal ions depends on effective ionic radius, and therefore, the sorption behavior of Cu(II) and Zn(II) ions should be the same since their effective ionic radius are approximately the same. El-Hag Ali [37] investigated the chelating performance of carboxymethyl cellulose/2-acrylamido-2-methyl propane sulfonic acid hydrogels depending on the initial metal ion concentration to predict their efficiency at low pollution levels. It was explained that the adsorption interactions by physical and chemical mechanisms are affected by the initial metal ion concentration. The chelating ability of carboxymethyl cellulose/2-acrylamido-2-methyl propane sulfonic acid hydrogels at low metal ion concentrations is higher because of the electrostatic interaction. In the study of Demirbas et al. [38], Amberlite IR-120 was used as a strong acidic ion exchange resin for the sorption of Cu(II), Zn(II), Ni(II), Cd(II), and Pb(II) ions. Their results showed that the ion exchange resin exhibited more selectivity for Ni(II) and Zn(II) ions over other metal ions. The ionic radius, electronegativity, size, and degree of hydration of metal ions affect amount of sorbed metal ions by the polymer. For example, ionic radius of Ni(II) is higher than that of Co(II) causing less affinity toward the polymeric ligands [14].

In our study, both removal efficiencies and sorption capacities of PAMPS gel for Cu(II), Ni(II), and Zn(II) are very close to each other at low initial metal ion concentrations. PAMPS gel showed selectivity for the sorption of Zn(II) from ternary solutions at higher concentrations. In addition,

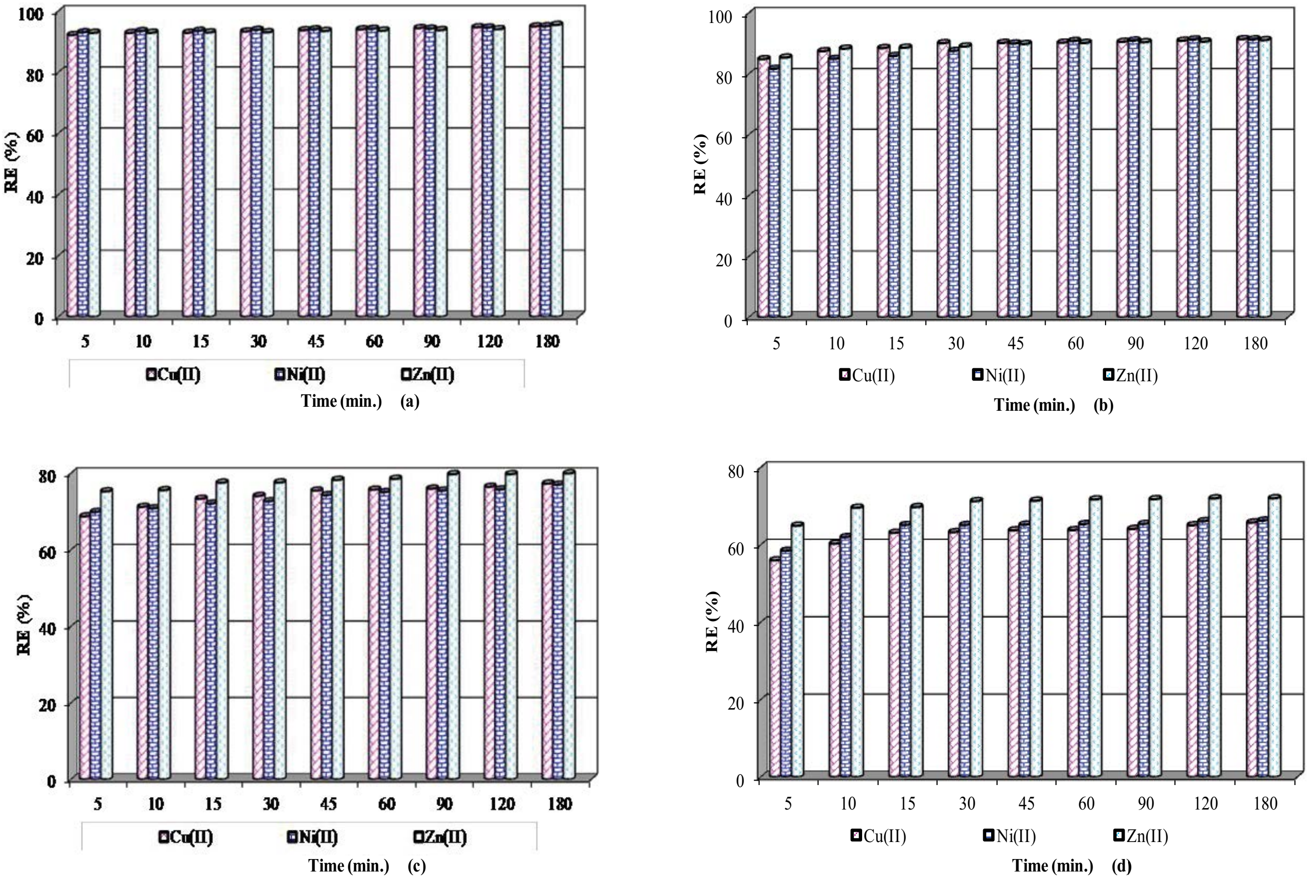

Fig. 6. The removal efficiencies of PAMPS gel for 25 mg/L (a), 50 mg/L (b), 75 mg/L (c), and 100 mg/L (d) as a function of time.

Demirbas et al. [38] reported that Amberlite IR-120 containing sulfonic acid group exhibited selectivity for Ni(II) and Zn(II) ions. In the case of our work, the ionic radius of metal ions used are nearly the same (Zn(II): 0.74Å, Cu(II): 0.71Å, and Ni(II): 0.69Å) [39]. So, it can be concluded that the initial metal ion concentration affected the selectivity of PAMPS gel, whereas physical properties of Cu(II), Ni(II), and Zn(II) did not play a role in the sorption mechanism of PAMPS toward these metals.

3.6. Sorption kinetics

Reaction based kinetic models (Lagergren pseudo-first and second-order) were used to investigate the sorption mechanism of Cu(II), Zn(II), and Ni(II) ions on PAMPS gel. Lagergren pseudo first- and second-order models are well-known models applied in the sorption systems [32,40]. Liquid sorption process is usually modeled by using the Lagergren pseudo-first order equation. In that case, there is a relation between rate of occupation of the binding sites and number of unoccupied sites on the adsorbent material [41,42]. The pseudo-second order kinetics is applied when the Lagergren pseudo-first order equation is not applicable for the fitting of the experimental data. In general, the sorption of heavy metals on different adsorbents is explained well by the pseudo-second order kinetic model [3,7,13]. This model accepts that chemisorption may be a rate-limiting step in sorption processes [34,35]. The pseudo-second order reactions are affected by the amount of metal ion(s) sorbed at equilibrium, and the amount metal ion on the surface of sorbent material [7,43].

Rate constants (k_1) and correlation coefficient values (R^2) for first order reaction kinetics were found from the plots of $\ln(q_e - q_t)$ vs. time (figure is not given). The pseudo-second order plot for the sorption of Cu(II), Ni(II), and Zn(II) ions on PAMPS is depicted in Fig. 7(a), (a), and (c). The plots of t/q_t against t exhibit linear trend for all the metal ions at all concentrations. The related kinetic parameters (pseudo-second order) for the removal of the heavy metal ions on PAMPS gel are shown in Table 1. Although the analysis of experimental data on pseudo-first order kinetics resulted in lower correlation coefficient values in comparison to second-order kinetic model, they were not too low for first-order kinetics. Especially, for some initial concentrations and metal ions, R^2 values are very close or equal to 0.99. However, it was determined that the experimental data are completely in accordance with the pseudo-second order model for the sorption of Cu(II), Zn(II), and Ni(II) ions. The coefficients for the pseudo-second order kinetic model are equal or greater than 0.9999 (Table 1), indicating the sorption process is conceivably controlled by the chemisorption via exchange of electrons between PAMPS gel and metal ions. Similar finding for SO_3H groups was reported by Qu et al. [13].

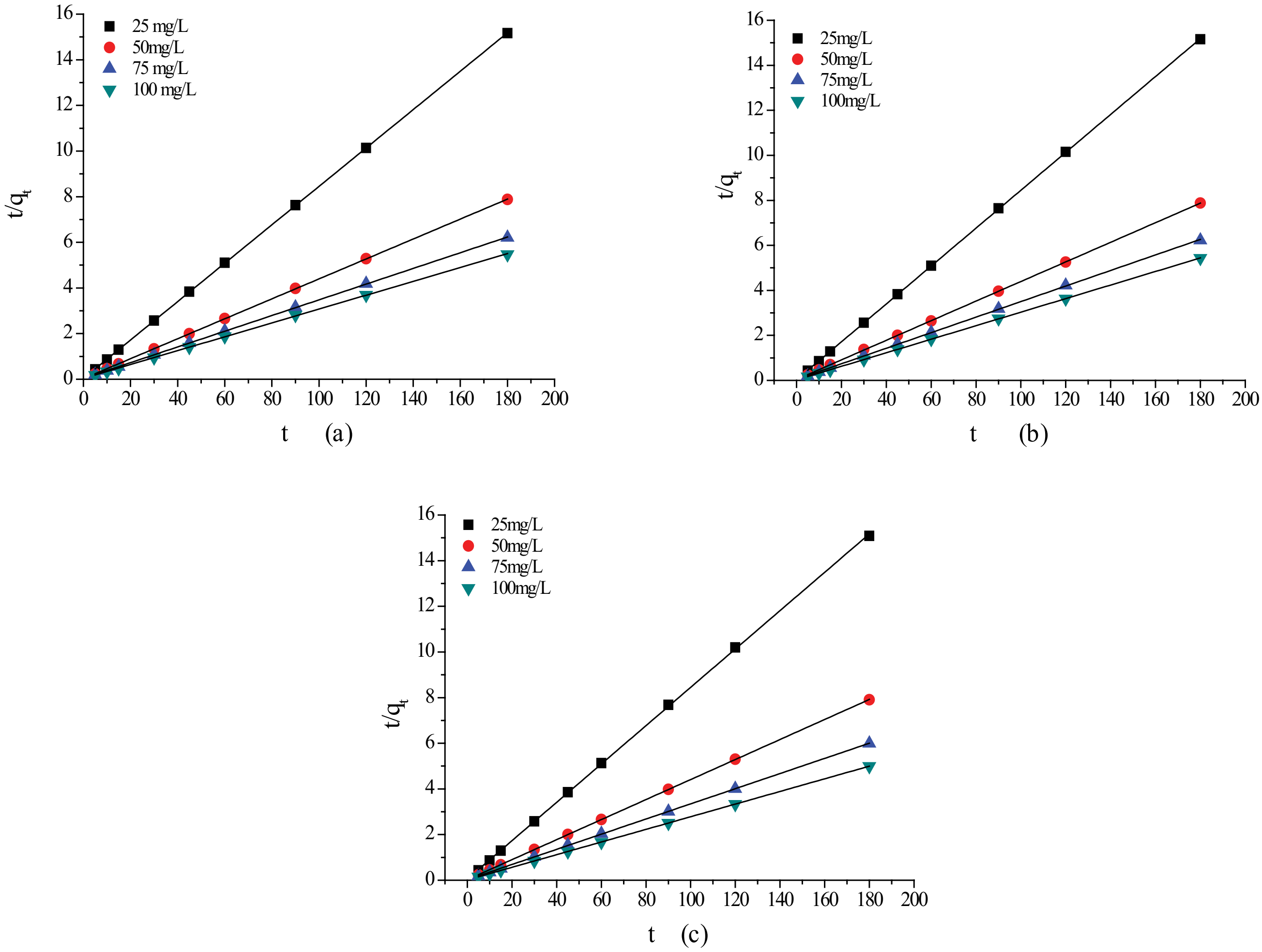

Fig. 7. Pseudo-second-order reaction kinetic model plots for the sorption of metal ions by PAMPS gel; (a) Cu(II), (b) Ni(II), and (c) Zn(II).

For the second order model, the experimental equilibrium sorption capacity values (q_{exp}) and its theoretical counterpart (q_{theo}) were found to be almost the same. It was also clear that R^2 values are very high, and ε% values are very low confirming the suitability of the second order kinetic model for the sorption process.

In general, the pseudo-second order rate constant (k_2) for the sorption of metal ions from ternary solution by PAMPS gel decreased with the increase in metal ion concentrations. So, initial metal ion concentration played an important role in the rate of sorption. The rate constant (k_2) dramatically decreased with the increase in metal ion concentration from 25 to 50 mg/L for each metal ion. Table 1 shows that the pseudo-second order rate constants (k_2) and the initial sorption rate (h) values were in the order of Zn(II) > Ni(II) > Cu(II) for the initial concentration of 100 mg/L. It is known that the driving force for mass transfer affects the initial sorption rate. High initial sorption rate decreases the time to reach the surface of the sorbent material [17,27]. On the other hand, the initial sorption rate (h) and k_2 for Zn(II) at 25 mg/L have the lowest values among them at other metal ions. Our findings showed that the sorption capacities, initial sorption rates, and pseudo-second order rate constants were dependent on the initial metal ion concentrations.

4. Conclusions

The sorption of Cu(II), Ni(II), and Zn(II) ions from ternary solutions at different metal ion concentrations by PAMPS gel was investigated. The effect of initial metal ion concentration on the sorption capacity and the removal efficiency of PAMPS gel were determined. The sorption occurs rapidly for all the metal ions, and the sorption equilibrium was attained in about 10 min. Batch sorption experiments showed that the sorption capacities of Cu(II), Ni(II), and Zn(II) ions are low at low initial metal ion concentrations compared with the high initial metal ion concentrations. PAMPS gel successfully removed metal ions (RE: 95%–95.5%) at lower initial concentrations (25 mg/L). At higher metal ion concentrations, PAMPS gel showed slightly higher selectivity for Zn(II) ion. Sorption of Cu(II), Ni(II), and Zn(II) by PAMPS gel is fitted well by the second order kinetic model. Metal ion sorption strongly affected thermal stability of the PAMPS gel due to interaction between metal ions and –SO$_3$H groups of PAMPS, namely ionic cross-linking. It can be said that PAMPS gel is a good candidatefor the removal of Cu(II), Ni(II), and Zn(II) ions from ternary aqueous solutions.

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