



The removal of heavy metal ions from aqueous solutions by novel pH-sensitive hydrogels

Ufuk Yildiz^{a,*}, Ömer Ferkan Kemik^a, Baki Hazer^b

^a University of Kocaeli, Department of Chemistry, 41380 Kocaeli, Turkey

^b Zonguldak Karaelmas University, Department of Chemistry, 67100 Zonguldak, Turkey

ARTICLE INFO

Article history:

Received 7 March 2010

Received in revised form 16 June 2010

Accepted 14 July 2010

Available online 21 July 2010

Keywords:

Crosslinking

Hydrogel

Macroinimer

Heavy metal ions

ABSTRACT

Novel non-ionic hydrogels were synthesized by radical homopolymerization of *N*-vinyl-2-pyrrolidone (VP) or by radical copolymerization of VP with methylacrylate (MA). A macroinimer (MIM) was used as a crosslinker and initiator, as well. The percentage of mass swelling ratios (S_M), the molecular weight between crosslinks (M_c) and Young's modulus of the hydrogels were investigated. The hydrogels were used as binding materials for different heavy metal ions such as Cu^{2+} , Cd^{2+} , Ni^{2+} and Zn^{2+} under varying conditions. The binding capability of the hydrogels toward the metal ions decreases in the following order: $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$.

© 2010 Elsevier B.V. All rights reserved.

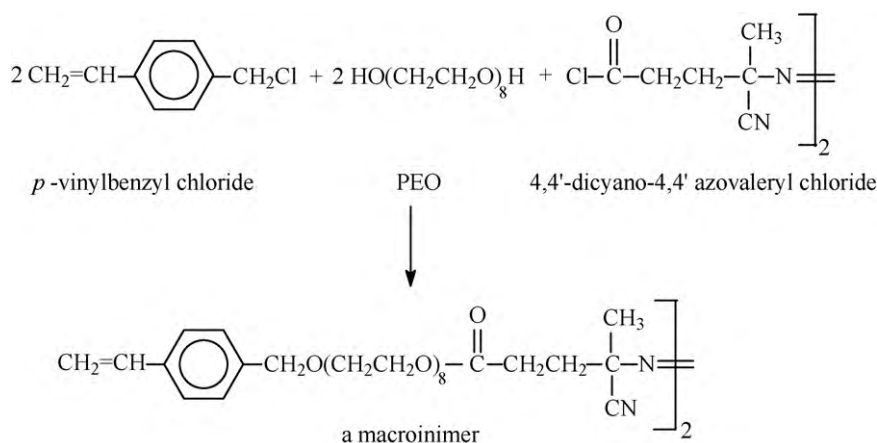
1. Introduction

In general, a hydrogel is crosslinked, hydrophilic polymer network arranged in a three-dimensional network with a great capacity for water and it can remain insoluble due to the presence of chemical or physical crosslinks [1,2]. Stimuli-responsive hydrogels have earned the reputation of "smart materials" due to their unique ability to change volume or shape in response to environmental signals. In the past decades, environmental stimuli-responsive hydrogels have been extensively investigated for their smart response to physical or chemical stimuli including temperature, electric field, ions, pH and light [3–7]. The stimuli-induced volume change usually arises from one of three major mechanisms: (1) changes in osmotic pressure or charge density (i.e., pH-responsive hydrogels); (2) changes in solvent affinity of the polymer backbone (i.e., temperature-sensitive hydrogels); or (3) changes in the polymer crosslink density [4].

Inorganic effluents from the industries contain toxic metal ions which tend to accumulate in the food chain. The toxic heavy metal ions have high solubility in the aquatic environments and thus they can be absorbed by living organisms. Once they enter the food chain, large concentrations of heavy metal ions may accumulate in the human body. If the metal ions are ingested

beyond the permitted concentration, they can cause serious health disorders [8]. Existence of heavy metal ion pollutants in water result in ecological problems even at very low concentration which increased the need for materials that can provide efficient complexing potential toward these metal ions [9]. A number of technologies have been developed over the years to remove toxic metal ions from water. The most important of these technologies include filtration, chemical precipitation, ion exchange, adsorption, electrodeposition and membrane systems. All of these technologies have their inherent advantages and limitations in applications [10]. A technique which has been used is the use of hydrogels to remove the heavy metal ions from water. Due to their capability to bind heavy metal ions through the polar functional groups which interact selectively and strongly with heavy metal ions. Moreover easy handling and reusability make hydrogels promising materials for water purification. The regular hydrogels that crosslinked by the conventional crosslinking agents have poor metal binding capacity and mechanical performance so that limiting their application significantly. In the present study we introduce novel poly(vinylpyrrolidone) and poly(vinylpyrrolidone-co-methylacrylate) hydrogels using macroinimer (MIM) which is based on poly(ethylene oxide) (PEO) and has the properties of macromonomers, macrocrosslinkers and macroinitiator in a macrostructure [11–18]. The aim of this work was not only to synthesize and characterize new type of hydrogels, but also to evaluate the usefulness and feasibility of these hydrogels for effective removal of heavy metal ions from synthetic wastewater.

* Corresponding author at: University of Kocaeli, Department of Chemistry, Umutepe Campus, 41380 Kocaeli, Turkey. Tel.: +90 262 3032035; fax: +90 262 3032003.
E-mail address: uyildiz@kocaeli.edu.tr (U. Yildiz).



Scheme 1. A macroinimer synthesis.

2. Experimental

2.1. Materials

Vinylpyrrolidone (VP), methylacrylate (MA) were supplied by Merck. Analytical grade poly(ethylene glycol) (Merck), 4,4'-dicyano-4,4'-azovaleric acid (Fluka) and 4-vinylbenzyl chloride (Sigma–Aldrich) were used to synthesize PEO based macroinimer (MIM) according to the procedure, described earlier [13]. $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was supplied by JT Baker. All other chemicals such as $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$, NaOH and PCl_5 were purchased from Merck.

2.2. Characterization techniques

Infrared (IR) spectroscopy was used for recording the spectra of the poly(vinylpyrrolidone) (PVP) and poly(vinylpyrrolidone-co-methylacrylate) (P(VP-co-MA)) hydrogels on a Shimadzu FTIR 8201 spectrometer, in the spectral range between 4000 and 400 cm^{-1} by grinding the dried samples with KBr.

^1H NMR spectrum (in CDCl_3) was recorded on Bruker 250 MHz AC Aspect spectrometer using tetramethylsilane as internal Standard.

The molecular weight of the MIM was determined by gel permeation chromatography (GPC) analysis. GPC chromatogram was taken on an Agilent Instrument (Model 1100) consisting of a pump, refractive index and UV detectors, and four Water Styragel Columns (HR 5E, HR 4E, HR 3, and HR 2) and using THF as eluent at a flow rate of 0.3 mL/min at 30°C and toluene as an internal standard. The molecular weight, M_w , of the MIM was determined by GPC as $1.1 \times 10^3 \text{ g/mol}$ ($M_w/M_n = 1.19$).

Atomic absorption spectrometer (Perkin-Elmer AAnalyst 800) was used to measure the metal ion concentration in the solutions before and after gel immersion by dilution to an appropriate concentration with distilled water.

The glass transition temperatures (T_g) and melting points (T_m) of the polymers were determined by differential scanning calorimeter (Mettler Toledo DSC 1 Star system). Sample films ranging 10–12 mg in weight were sealed in non-hermetic type aluminium pans and were ramped at a heating of $10^\circ\text{C min}^{-1}$ in nitrogen at a flow rate of 50 mL/min .

The dried specimen was examined for morphological details by using a scanning electron microscopy (SEM). Dried hydrogel was coated with a thin layer of copper during 300 s in a Baltec SCD 005 Sputter Coater, and imaged in a SEM (JEOL, JSM-6060).

2.3. Synthesis of macroinimer

A typical macroinimer (MIM) can be synthesized by the reaction of 4,4'-dicyano-4,4'-azovaleryl chloride, polyethylene oxide (PEO) and 4-vinylbenzyl chloride (Scheme 1).

2.4. Preparation of poly(vinylpyrrolidone) hydrogels

Bulk polymerization of VP was carried out at 70°C in the presence of MIM as an initiator and crosslinker, as well. The polymerization mixture consisted of VP (2 g) and MIM. The amount of MIM was varied from 5, 15, 25, 40 to 60% based on the total weight of the monomer.

In a Pyrex tube, in which given amounts of VP and MIM were charged, argon was purged a needle into the tube for 5 min. The tightly capped tube was put in an oil bath thermostatted at 70°C . After 3 h, the tube content was immersed in distilled water by changing the water every 6 h for 24 h to eliminate any water-soluble components. At the end, PVP samples were dried under vacuum at 50°C for 24 h.

Bulk polymerization of VP was also carried out in the presence of an additional initiator, 2,2'-azoisobutyronitrile (AIBN) just to see whether it has any effect or not. 0.05 g AIBN was added into the tubes which contain 2 g VP and varying the concentration of MIM as 5, 15, 25, 40 and 60% based on the total weight of the monomer. All the conditions and further treatment were as given above.

2.5. Preparation of poly(vinylpyrrolidone-co-methylacrylate) hydrogels

Bulk copolymerization of VP with methylacrylate (MA) was also carried out. VP and MA were used as received for the free radical copolymerization. P(VP-co-MA) samples were prepared with the same concentration of the crosslinker, MIM, as 15% based on the total weight of the monomers while the amounts of VP and MA were changed as: VP:MA (g:g); 1.75:0.25; 1.50:0.50; 1.25:0.75; 1.0:1.0; 0.75:1.25; 0.50:1.50 and 0.25:1.75.

In a Pyrex tube, in which given amounts of VP, MA and MIM were charged, argon was purged a needle into the tube for 5 min and then allowed to polymerization process as explained above.

Bulk copolymerization of VP and MA was also carried out in the presence of AIBN as an additional initiator. In that case, 0.05 g AIBN was added into each tube and the copolymerization was carried out as explained above.

Table 1
Gel fraction and swelling properties of the hydrogels.

Run no.	VP (g)	MA (g)	MIM (g)	AIBN (g)	Gelation (%)	S_M (%)	M_c (g/mol)	E (Mpa)
1	2.00	–	0.10	–	41.54	1500	86042	0.10
2	2.00	–	0.30	–	60.53	648	14229	0.61
3	2.00	–	0.50	–	63.83	373	3419	2.52
4	2.00	–	0.80	–	67.60	219	1037	8.31
5	2.00	–	1.20	–	71.32	199	843	10.22
1 ^a	2.00	–	0.10	0.05	19.71	1886	144054	0.06
2 ^a	2.00	–	0.30	0.05	34.27	732	16392	0.53
3 ^a	2.00	–	0.50	0.05	43.51	407	4179	2.06
4 ^a	2.00	–	0.80	0.05	54.90	278	1741	4.95
5 ^a	2.00	–	1.20	0.05	64.59	224	1078	7.99
6	0.25	1.75	0.30	–	59.77	38	40	207.08
7	0.50	1.50	0.30	–	56.82	73	109	76.29
8	0.75	1.25	0.30	–	54.28	129	309	26.96
9	1.00	1.00	0.30	–	53.45	246	1201	6.94
10	1.25	0.75	0.30	–	52.03	478	5416	1.54
11	1.50	0.50	0.30	–	50.21	618	9851	0.85
12	1.75	0.25	0.30	–	50.03	652	11150	0.75
6 ^a	0.25	1.75	0.30	0.05	59.00	39	42	196.99
7 ^a	0.50	1.50	0.30	0.05	56.18	99	188	44.39
8 ^a	0.75	1.25	0.30	0.05	53.49	174	567	14.68
9 ^a	1.00	1.00	0.30	0.05	47.04	352	2676	3.11
10 ^a	1.25	0.75	0.30	0.05	43.22	523	6665	1.25
11 ^a	1.50	0.50	0.30	0.05	39.48	654	11257	0.74
12 ^a	1.75	0.25	0.30	0.05	34.03	695	12960	0.64

^a Denotes that AIBN was added to the recipe of the run no.

2.6. Swelling properties of the hydrogels

PVP and P(VP-co-MA) hydrogels have been prepared for the purpose of removal of toxic metal ions from the aqueous solutions. That is why the swelling behaviour of the gels was investigated in the distilled water. The swelling of the hydrogel samples was carried out by storing a given amount of sample in 50 mL of water for 24 h at room temperature (25 °C). The hydrogel samples were designed as almost disc shape. The samples were weighed out to an accuracy of 0.0001 mg on the Scaltec Auto-Balance. Then the samples were soaked in 50 mL solutions of pH 7 at 25 °C for 24 h. After the hydrogel samples reached equilibrium in each solution, almost in 24 h, they were taken out and the surplus surface water was removed by filter paper. Then the percentage of mass swelling (S_M) were determined by accurately weighing each sample both in the hydrated and dried states and applying the following expression [19]:

$$\%S_M = \frac{M_t - M_0}{M_0} \times 100 \quad (1)$$

where M_0 and M_t are the initial mass and mass at different time intervals, respectively.

2.7. Determination of M_c values

Another structural parameter for characterizing the crosslinked polymers is the average molecular weight between two consecutive crosslinks (M_c) which is directly related to the crosslink density. The magnitude of the M_c affects the mechanical, physical and thermal properties of crosslinked polymers. The M_c can be determined by swelling studies. For this aim, the swelling ratio of the hydrogels, q_w , was calculated using the following equation [20]:

$$q_w = \frac{M_s}{M_d} \quad (2)$$

where M_s is the mass of the hydrogel after equilibrium and M_d is the mass of the hydrogel before swelling. Then the volume fraction ϕ of the swollen polymer was calculated using the equation [19]:

$$\phi = \left[1 + \frac{d_p}{d_s}(q_w) - \frac{d_p}{d_s} \right] \quad (3)$$

In the above equation, d_p and d_s represent the densities of polymer and solvent, respectively. M_c values of the hydrogels was determined according to the Flory–Rehner equation [21]:

$$M_c = \frac{-\{V_1 d_p (\phi^{1/3} - (\phi/2))\}}{\{\ln(1 - \phi) + \phi + \chi \phi^2\}} \quad (4)$$

where V_1 is the molar volume of solvent (18 mL/mol for water), d_p is the density of polymer (1.16 g/mL for PVP), ϕ is the volume fraction of polymer in swollen gel and χ is the Flory–Huggins interaction parameter between polymer and solvent molecules which is assumed to be 0.49 for PVP/water system [21]. The density of the P(VP-co-MA) copolymer was determined as 1.12 g/mL using Mettler Toledo XS 205 density meter.

2.8. Metal ion binding properties of the hydrogels

The binding properties of PVP and P(VP-co-MA) hydrogels for Cu^{2+} , Ni^{2+} , Zn^{2+} and Cd^{2+} metal ions were tested under non-competitive conditions by immersing the gel in a solution containing a metal ion. The adsorption experiments were performed by agitating a given amount of hydrogel in 50 mL of solution containing a metal ion concentration of 5 ppm at varying pH as 2, 5 and 8 for several time periods up to 24 h. The pH value of each solution was adjusted by either 0.1N HCl or 0.1N NaOH. The metal ion concentrations in the solutions were measured before and after the gel immersion by dilution to an appropriate concentration with distilled water and measured with atomic absorption spectrometer.

2.9. Regeneration

The P(VP-co-MA) hydrogels were exposed to acid hydrolysis by soaking the gel in 0.025 M HNO_3 for 24 h then the gel was washed several times with water and methanol and then dried under vacuum at 50 °C for 24 h.

3. Results and discussion

Macromonomeric azoinitiator, macroinimer (MIM), was synthesized as shown in Scheme 1 and characterized by FTIR,

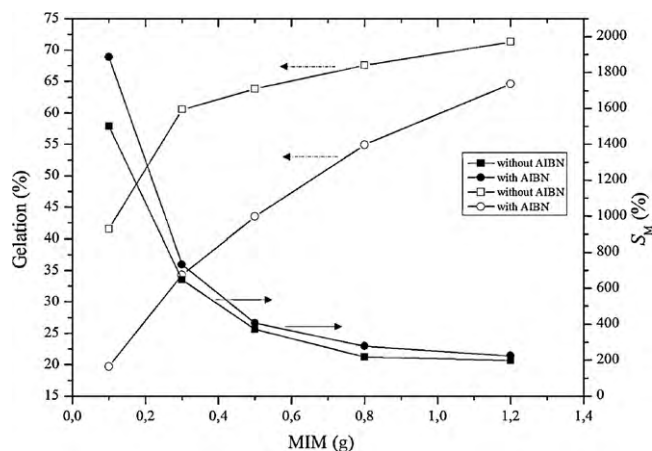


Fig. 1. Variation of gelation (open symbols) and mass swelling (filled symbols) of PVP with the amount MIM.

NMR spectroscopy and GPC chromatography. Characteristic signals of MIM in FTIR and NMR spectra confirm its structure.

IR spectrum of MIM: 1107 cm^{-1} (CH_2 -etheric bonds of PEG), 1630 cm^{-1} (vinyl and benzyl groups), 1738 cm^{-1} (carbonyls of ester groups) and 2244 cm^{-1} (bonds of $\text{C}\equiv\text{N}$).

^1H NMR spectrum of MIM: $\delta = 3.6\text{ ppm}$: $\text{CH}_2\text{CH}_2\text{O}$ groups in PEG, $\delta = 4.5\text{ ppm}$: s, CH_2 groups in vinylbenzyl groups, $\delta = 5.2$ and 5.7 ppm : m, $\text{CH}_2=\text{CH}-$ groups in vinylbenzyl groups, $\delta = 6.7\text{ ppm}$: $\text{CH}_2=\text{CH}-$ groups in vinylbenzyl groups, $\delta = 7.3\text{ ppm}$: phenyl groups in vinylbenzyl groups.

Vinylpyrrolidone based hydrogels have wide applications in many areas especially in the biomedical applications. There have been many reports on the preparation of these hydrogels by thermal, photo or irradiation polymerization [9]. The regular hydrogels which is crosslinked by the conventional crosslinking agents have poor metal binding capacity and mechanical performance, limiting their application significantly. MIM as an effective crosslinker was used to obtain novel hydrogels with higher metal ion binding capacity and mechanical performance than present hydrogels. The free radical polymerization of *N*-vinyl-2-pyrrolidone (VP) and copolymerization of VP with methylacrylate (MA) were carried out to yield PVP and P(VP-co-MA) hydrogels. Adding of MA as a hydrophobic component is due to improve the mechanical strength of the hydrogel. The effect of MA on the hydrogel efficiency was investigated by fixing MIM concentration and changing VP:MA ratio (Table 1). The network structure and swelling properties of all hydrogels were investigated. Then the hydrogels were used as binding materials for different heavy metal ions such as Cu^{2+} , Ni^{2+} , Zn^{2+} and Cd^{2+} from synthetic wastewater under varying conditions.

The obtained hydrogels were examined using FTIR to confirm their structure. The characteristic absorption bands such as carbonyl and etheric were observed in the FTIR spectra of PVP and P(VP-co-MA). The glass transition temperatures (T_g) and melting points (T_m) of the PVP and P(VP-co-MA) were determined by differential scanning calorimeter. The glass transition temperatures were 128 and 118°C while the melting points were 434 and 400°C for PVP and P(VP-co-MA), respectively. The decrease in T_g and T_m values is due to the increasing amorphous structure of the hydrogel with the addition of MA.

3.1. Swelling studies

The percentage of mass swelling ratios (S_M) were calculated using Eq. (1). Fig. 1 shows the S_M values of the PVP hydrogels. It

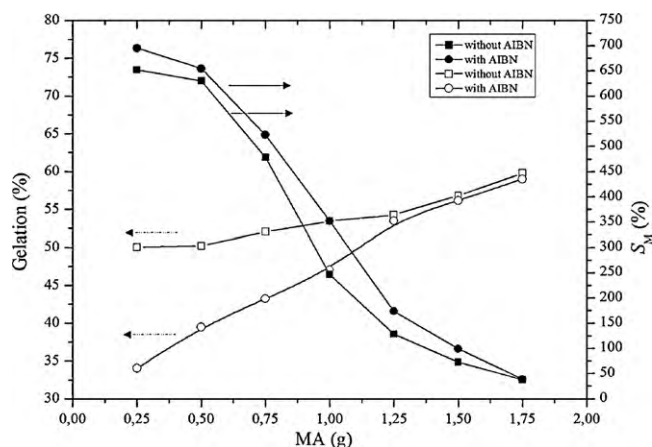


Fig. 2. Variation of gelation (open symbols) and mass swelling (filled symbols) of P(VP-co-MA) with the amount of MA.

was found that MIM concentration affects the S_M values of the hydrogels. The increasing MIM concentration decreases the S_M values due to the increasing in the crosslink density. Percentage gelation i.e., percentage conversion of monomers and crosslinking agent into insoluble networks, is based on the total weight of the crosslinking agent and monomers in the initial mixture, increases with increasing crosslinker (MIM) concentration, as expected. The molecular weight between two consecutive crosslinks (M_c) decreases/or the crosslink density increases with increasing MIM concentration (Table 1). The increase in the crosslink density leads to a decrease in the free volume and consequently lower S_M values.

In the case of P(VP-co-MA) hydrogels, decreasing the amount of MA in the copolymer increases the S_M values (Fig. 2 and Table 1). The S_M values increased from 38 to 652% with decreasing MA concentration/or increasing VP:MA (g/g) ratio from $0.25:1.75$ to $1.75:0.25$. The increase in the S_M values with decreasing MA concentration is most likely due to the increasing hydrophilicity. In addition there will be more free space available for accommodation of water with decreasing MA concentration. As mentioned by Rueda et al. [22], PVP is a very hydrophilic polymer therefore the hydrogel porosity and the hydrogel absorptive capacity for polar liquids in the copolymer hydrogels depend on the molar ratio between VP and other monomer, showing an increase with VP content.

The morphology of the prepared PVP hydrogel microstructure can be seen in Fig. 3. The microstructure of PVP is a three-dimensional network supported by crack-like and thick crystal PVP walls. Most likely, the thick walls are responsible for the high

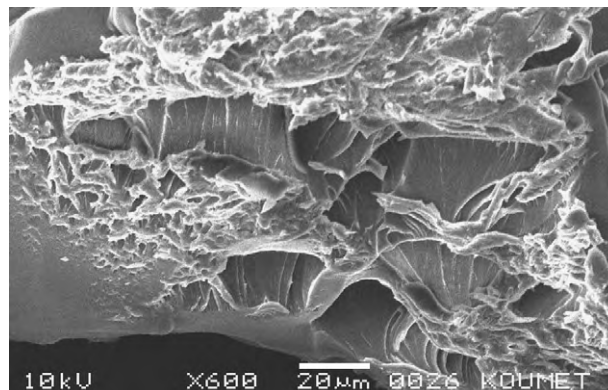


Fig. 3. SEM image of MIM initiated PVP hydrogel.

Table 2
The highest metal ion binding capacities of the hydrogels.

Metal ion	PVP			P(VP-co-MA)			P(VP-co-MA) after regeneration		
	pH 2	pH 5	pH 8	pH 2	pH 5	pH 8	pH 2	pH 5	pH 8
The highest metal ion binding capacities (mg metal ion/g hydrogel)									
Cu ²⁺	35	75	92	60	85	110	70	130	170
Ni ²⁺	15	32	39	45	67	75	75	105	130
Zn ²⁺	9	11	25	32	47	70	58	79	110
Cd ²⁺	3	12	15	15	30	50	20	40	65

mechanical strength of the hydrogels. This picture verifies that the PVP hydrogel has a porous structure. The porous structure of the hydrogels is important from the viewpoint of their application in many fields. It is supposed that these pores are the regions of water permeation and interaction sites of external stimuli with incorporated drug or hydrophilic groups of the polymers [23]. Therefore, the porous structure is the predominant reason for the high swelling of PVP.

M_c values were also determined and as is given in Table 1, M_c values increase from 40 to 11150 g/mol with decreasing MA content due to the increase in the free volume. The presence of additional initiator (AIBN) increases S_M and M_c values of the PVP and P(VP-co-MA) hydrogels. The increase in the S_M and M_c values is due to increasing in the free volume. The increase in the free volume means a decrease in the crosslinking density due to the lower crosslinking efficiency of the MIM. It is reasonable to assume that the lower crosslinking efficiency of the MIM is due to increasing the hetero-radical termination reactions between cyanoisopropyl and MIM-derived radicals. The increment in the termination reactions decreases the crosslinking efficiency of the MIM and consequently lower crosslinking density and thus higher M_c and S_M values.

3.2. Physical properties of the hydrogels

Another purpose of the work was to increase the mechanical strength of the hydrogels. In order to check the increment in the mechanical properties of the hydrogels, the Young's modulus (E) was determined. E is a material property that describes its stiffness. E values of the hydrogels were determined using swelling measurements data and Flory–Rehner equation as explained below [24].

The first relationships between macroscopic sample deformation, chain extension and entropy reduction were expressed by proposing the model of a random coil polymer chain. When the sample was stretched, the chain had extended in proportion, called an affine deformation. When the sample is relaxed, the chain has an average end-to-end distance, r_0 which increases to r_i when the sample is stretched.

Young's modulus can be written

$$E = L \left(\frac{\partial \sigma}{\partial L} \right)_{T,V} \quad (5)$$

which yields

$$E \cong 3n \frac{r_i^2}{r_0^2} RT \quad (r_i^2/r_0^2 \cong 1) \quad (6)$$

where L is the length of the chain and r_0^2 and r_i^2 represent the squares of the relaxed and stretched end-to-end distances, respectively. The quantity approximately equals to unity. The value of r_0 does not change, because it is the end-to-end distance of the equivalent free chain. The value of r_i is determined by the distance between the crosslink sites binding the chain. The quantity n in Eq. (6) represents

the number of active network chains per unit volume, called the network or crosslink density.

On the other hand the Flory–Rehner equation may be written as

$$-\ln(1 - \phi) + \phi + \chi \phi^2 = V_1 n [\phi^{1/3} - (\phi/2)] \quad (7)$$

where ϕ is the volume fraction of polymer in the swollen mass, V_1 is the molar volume of the solvent and χ is the Flory–Huggins polymer–solvent dimensionless interaction term. n values were calculated using Eq. (7) and put in Eq. (6) to determine the E values by assuming $r_i^2/r_0^2 \cong 1$. As can be seen in Table 1, Young's modulus of the polymers increases with increasing MIM and MA concentration. The E values increased from 0.10 to 10.22 Mpa (megapascal) with increasing MIM concentration. The results are good as compare to macromonomer network hydrogels [25] which have the same polyethylene oxide content. E values of the hydrogels were between 1.0 and 8.8 MPa in that work.

The addition of MA to the PVP matrix resulted in an increase in the tensile strength (Young's modulus) of P(VP-co-MA). This increase was attributed to adhesive character of MA, which occupied vacant spaces and improved the interaction between the polymeric chains. The Young's modulus values increased from 0.75 to 208 MPa with increasing MA concentration. Thus, adding of MA as a hydrophobic component increases E values which describes the mechanical performance of the hydrogels, as conformable our aim.

3.3. Metal binding efficiency of the PVP and P(VP-co-MA)

Hydrogels containing one or more electron donor atoms (Lewis base) such as N, S, O and P that can form coordinate bonds with most of the toxic metal ions (Lewis acid) [26]. In this connection the binding properties of PVP and P(VP-co-MA) hydrogels for Cu²⁺, Ni²⁺, Zn²⁺ and Cd²⁺ metal ions were tested under non-competitive conditions by immersing a sample in a solution containing a metal ion. The binding of the Cu²⁺, Ni²⁺, Zn²⁺ and Cd²⁺ ions by different PVP hydrogel compositions were illustrated in Fig. 4a and b. It is clear that the tendency of the hydrogels to bind Cu²⁺ is greater than the other metal ions examined in this study under the same conditions. The maximum Cu²⁺ binding capacity is 92 mg for PVP at pH 8 (Table 2). The higher Cu²⁺ binding capacity is due to the Jahn–Teller effect which states “For any non-linear molecule in an electronically degenerate state, distortion must occur to lower the symmetry, remove the degeneracy and lower the energy.” These distortions are called Jahn–Teller distortions and lower the energy of molecules. On the other hand, it is well known that Cu²⁺ is the easiest metal ion to be complexed with ligands containing nitrogen and oxygen [9]. Increasing the pH from 2 to 8 enhances the maximum binding capacity of the hydrogels, contrastly decreasing in the pH decreases the binding capacity of the hydrogels. This behaviour is due to the protonation of the N atoms at low pH. That is, there will be less N atoms for coordinating the metal ions at low pH. The improved binding capacity towards all the metal ions at high pH proves that the binding is occurring mostly at the nitrogen centers which are being blocked by protonation at low pH values. The binding capac-

ity of the hydrogels for the other metal ions was found to be in the order of: $\text{Ni}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$. There are several factors affecting the capacity and affinity such as: the chemical nature of the metal ion (size, valence, electron orbital structure), hydrogel (charge density,

structure of polymer chains), environmental changes (pH, temperature), morphology and so on [10]. All the conditions except for the metal ion are the same. Thus, this order is as a result of increasing in the ionic radius. The Ni^{2+} binding capacity of the hydrogels is

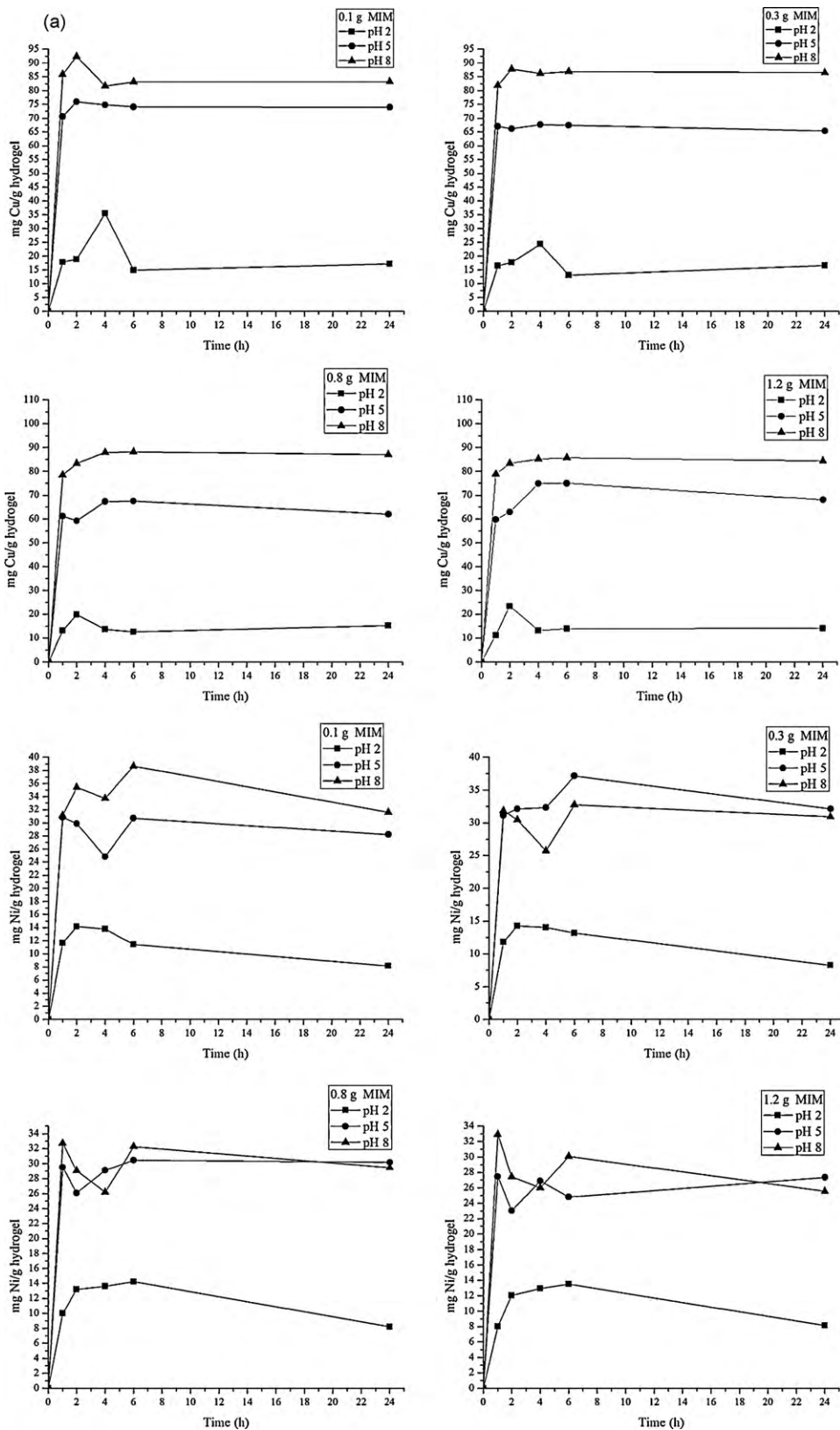


Fig. 4. (a) Effect of pH, MIM concentration and time on the Cu(II) and Ni(II) ions removal of PVP. (b) Effect of pH, MIM concentration and time on the Zn(II) and Cd(II) ions removal of PVP.

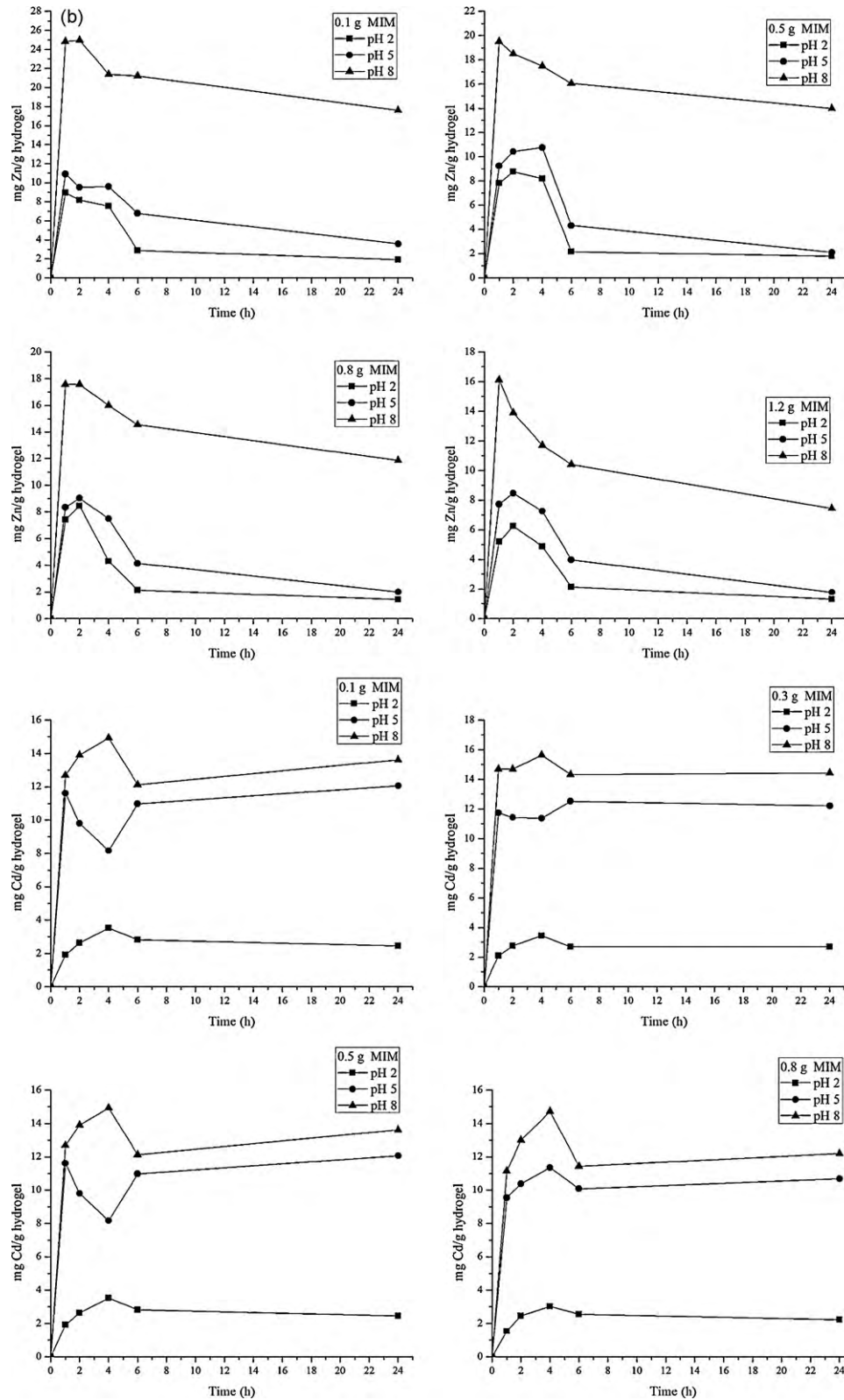


Fig. 4. (Continued).

higher than those of Zn^{2+} and Cd^{2+} due to the lower atomic mass and ionic size. The sizes of the ions for six-coordination are 0.69, 0.74 and 0.96 Å for Ni^{2+} , Zn^{2+} and Cd^{2+} , respectively [27].

The addition of AIBN as an additional initiator has no clear effect on the metal binding efficiency of the polymers.

The metal ion binding capacities of P(VP-co-MA) hydrogels were also investigated (Table 2). It is supposed that the adding of MA in the PVP matrix would increase the metal binding capability of the hydrogels. As it can be seen in Fig. 5a and b, the metal binding capacities of the copolymeric hydrogels are higher than those of

homopolymeric hydrogels. The increase in the metal binding capacities is most likely due to the presence of additional oxygen atoms which coordinate more metal ions. The result shows that MA as a hydrophobic component affects the metal binding capacity of the hydrogels.

3.4. Effect of the MIM concentration

The effect of the MIM concentration on S_M and M_c values of the hydrogels were discussed in Section 3.1. The effect of the MIM concentration on the removal of metal ions can be investigated

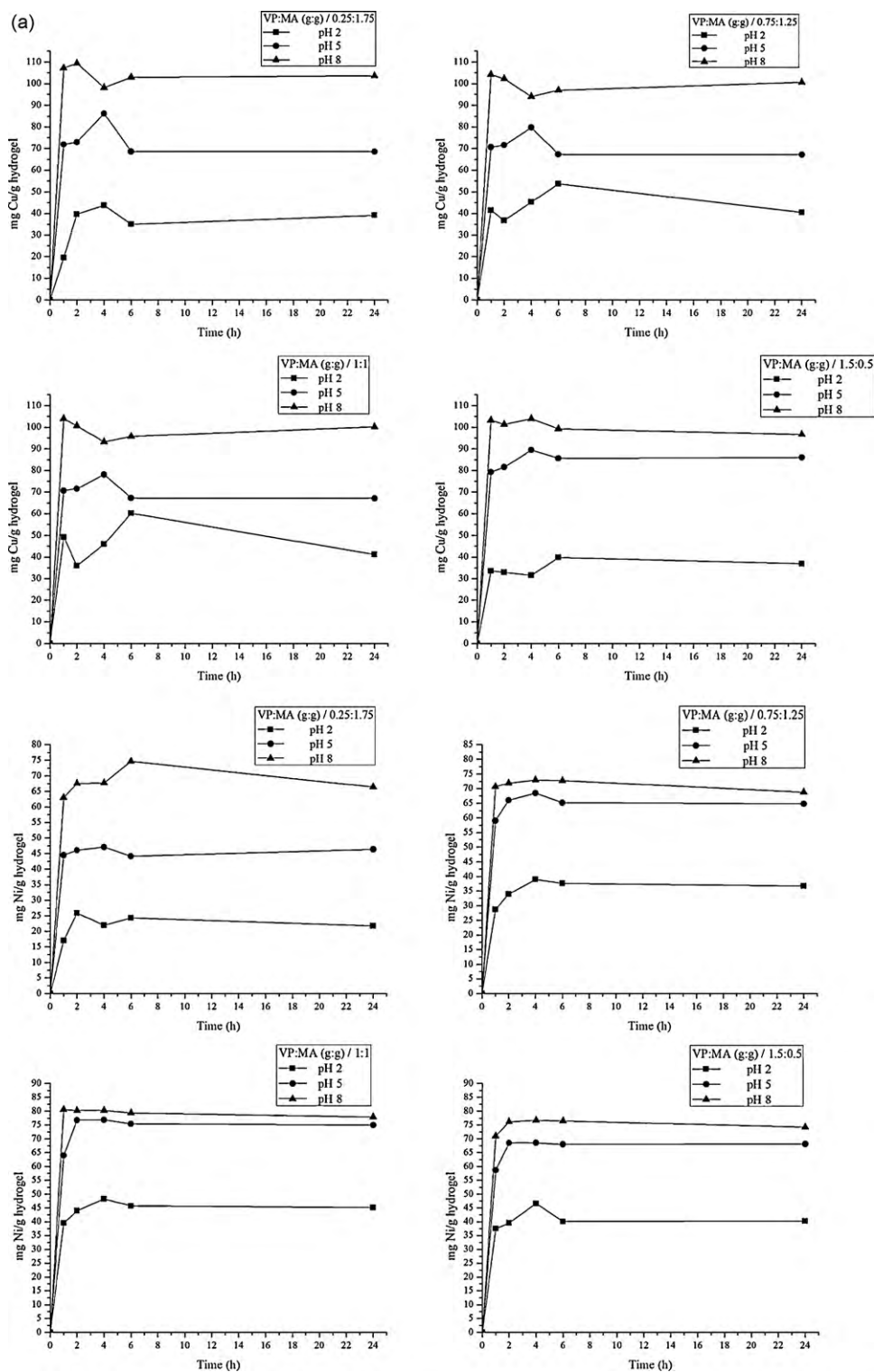


Fig. 5. (a) Effect of pH, VP:MA ratio and time on the Cu(II) and Ni(II) ions removal of P(VP-co-MA). (b) Effect of pH, VP:MA ratio and time on the Zn(II) and Cd(II) ions removal of P(VP-co-MA).

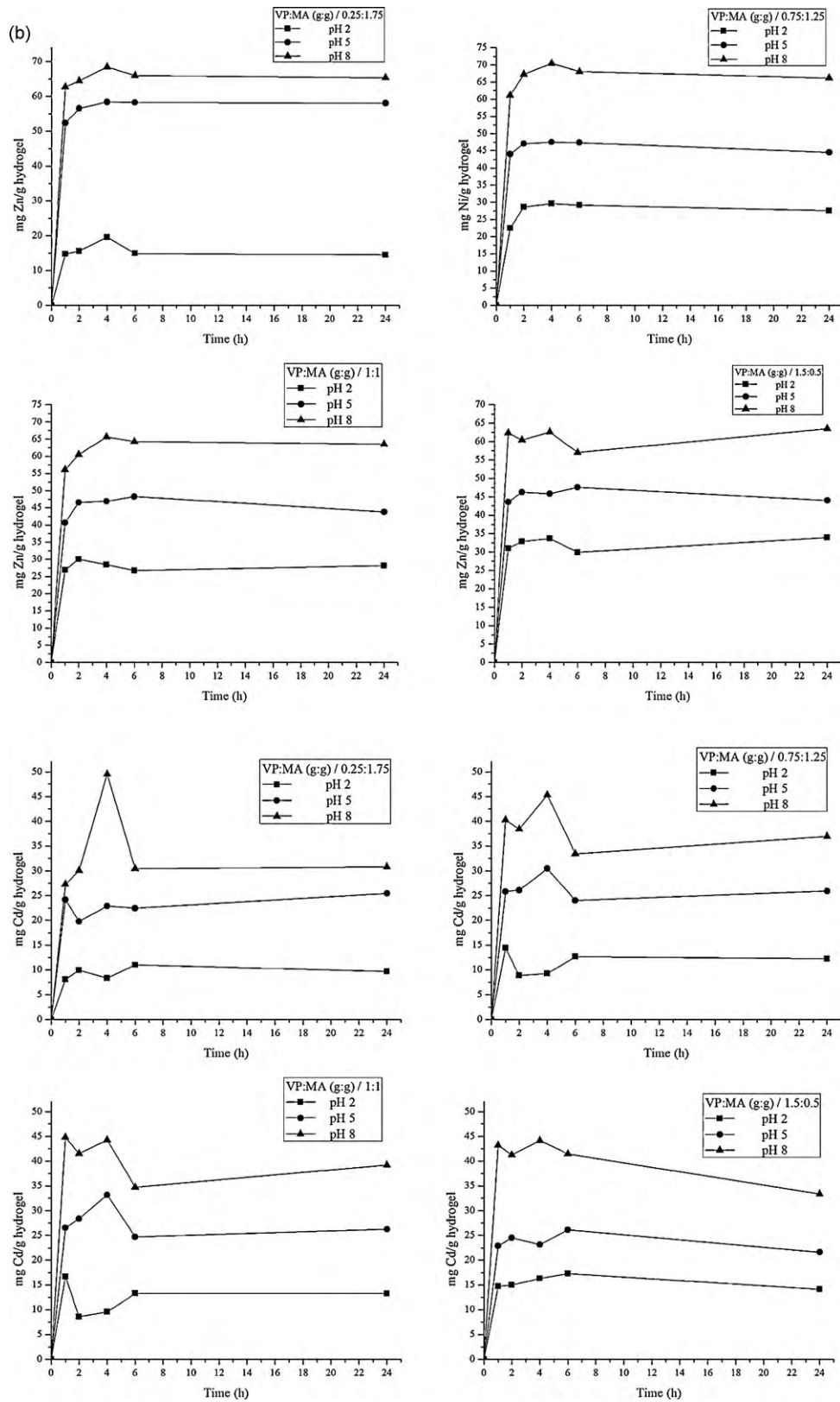


Fig. 5. (Continued).

by following the binding capacity of the hydrogel samples. The increasing MIM concentration has no clear effect on the metal binding capacity of the hydrogels. However, there is a clear decrease in the case of the highest MIM concentration (1.2 g). This behaviour

can be attributed to the increasing in the crosslink density of the hydrogels with increasing crosslinker (MIM) concentration so that leads to a decrease in the free volume and consequently lower metal binding capacity.

3.5. Regeneration

The metal ion binding capacities of P(VP-co-MA) hydrogels after regeneration were also investigated. The clear increase in the metal binding capacities of P(VP-co-MA) hydrogels after regeneration (Fig. 6a and b), is due to changing the ester groups of MA into the car-

boxylic group, which has high affinity for binding metal ions [28]. The maximum binding capacities of the hydrogels were improved (almost doubled) after regeneration, especially at pH 8. The highest metal binding capacities after regeneration were 170, 130, 110 and 65 mg metal ion/g copolymeric hydrogel for Cu^{2+} , Ni^{2+} , Zn^{2+} and Cd^{2+} , respectively (Table 2).

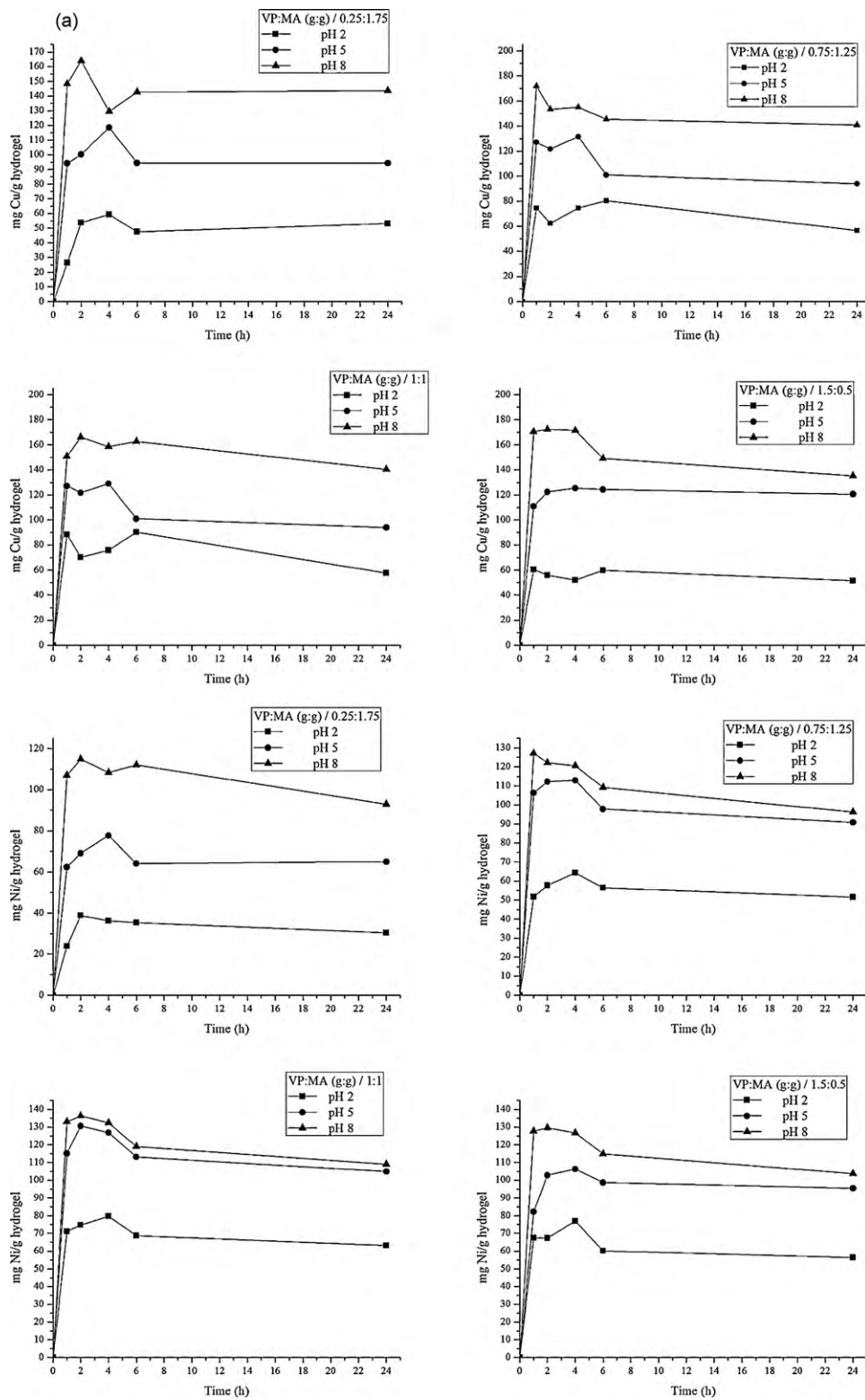


Fig. 6. (a) Effect of pH, VP:MA ratio and time on the Cu(II) and Ni(II) ions removal of P(VP-co-MA) after regeneration. (b) Effect of pH, VP:MA ratio and time on the Zn(II) and Cd(II) ions removal of P(VP-co-MA) after regeneration.

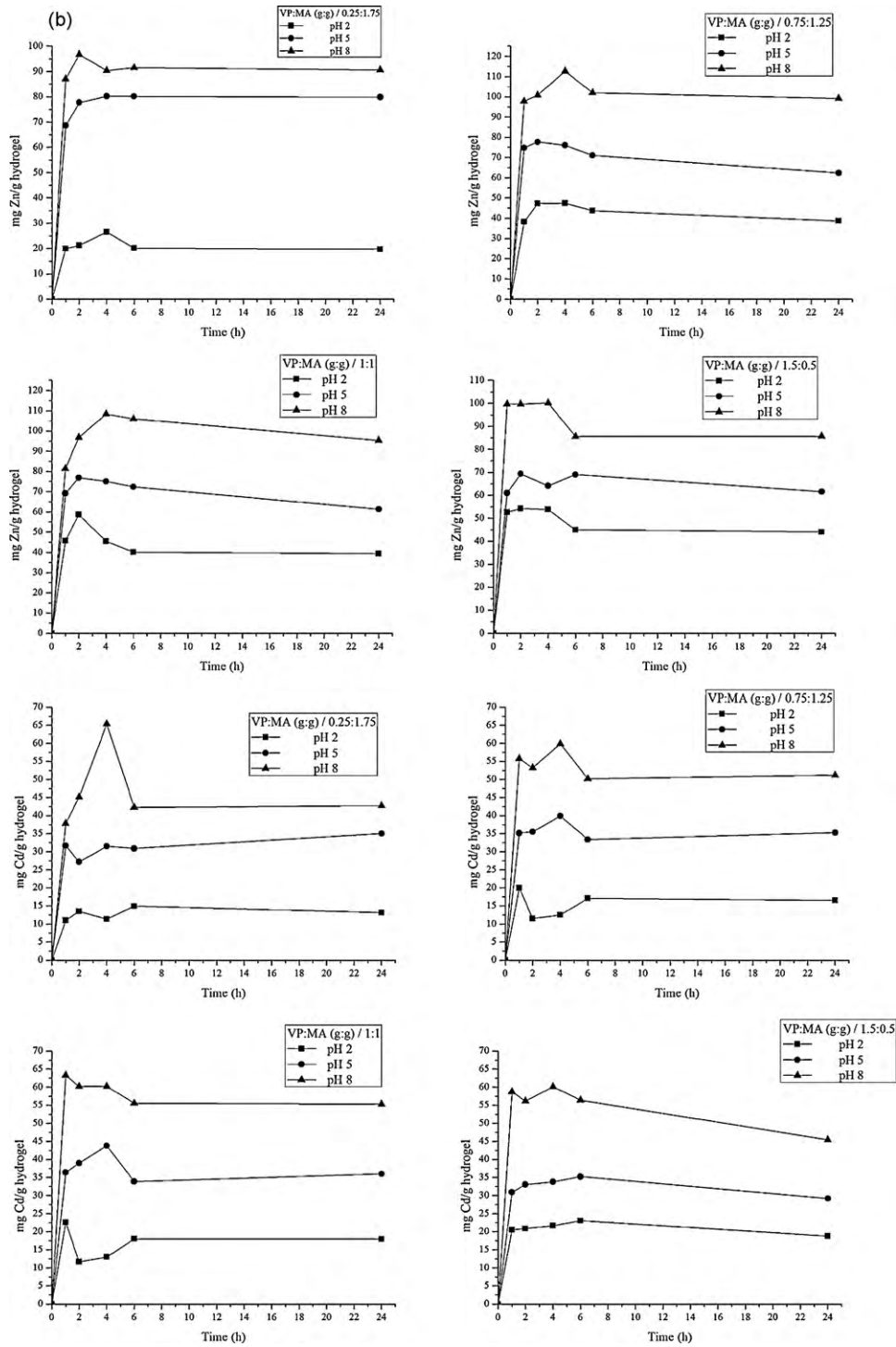


Fig. 6. (Continued).

4. Conclusions

The free radical polymerization of *N*-vinyl-2-pyrrolidone (VP) and copolymerization of VP with methylacrylate (MA) were carried out in the presence of a macroinimer to prepare novel hydrogels. The percentage of mass swelling ratio (S_M) and the molecular weight between two consecutive crosslinks (M_c) values of the hydrogels were determined. The increasing MIM concentration decreases the S_M and M_c values of the hydrogels due to the increasing in the crosslink density. The increasing in the crosslink density leads to a decrease in the free volume and consequently lower

S_M and M_c values. The decreasing the amount of MA/or increasing VP:MA ratio in the P(VP-co-MA) hydrogels increases the S_M and M_c values. The decreasing MA concentration increases the hydrophilicity and consequently S_M and M_c values. Young's modulus of the hydrogels was determined. The moduli values increase with increasing MA concentration. This increase was attributed to the adhesive character of MA, which occupied vacant spaces and improved the interaction between the polymeric chains. The binding properties of PVP and P(VP-co-MA) hydrogels for metal ions Cu²⁺, Cd²⁺, Ni²⁺ and Zn²⁺ were tested under non-competitive conditions. The maximum binding capacity of the hydrogels for the

different metal ions was in the order of $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$. The higher Cu^{2+} binding capacity is due to the Jahn–Teller effect and being the easiest metal ion to be complexed with ligands containing nitrogen and oxygen. Increasing the pH from 2 to 8 enhances the maximum binding capacity of the hydrogels, contrastly decreasing the pH decreases the binding capacity of the hydrogels due to the protonation of the N atoms at low pH. The metal binding capacities of the P(VP-co-MA) hydrogels were higher than those of PVP hydrogels. The increase in the metal binding capacities is most likely due to the presence of additional oxygen atoms which coordinate more metal ions. The metal binding capacities of P(VP-co-MA) hydrogels increase significantly after regeneration due to the changing the ester groups into the carboxylic group.

Finally, we can definitely conclude that MIM can be used to prepare hydrogels for higher mechanical strength and heavy metal ion binding capability.

The prepared novel pH-sensitive hydrogels might have great potential applications in environmental works as smart materials.

Acknowledgments

The authors would like to thank Dr. Ümit Ay for measuring metal ion concentrations by Atomic Absorption Spectrometer. For morphological investigation by scanning electron microscopy the authors thank Prof. Şadi Karagöz. The authors are also grateful for the support from the Scientific and Technical Research Council of Turkey (TÜBİTAK), Project No. TBAG-108T282.

References

- [1] X. Zhang, X. Guo, S. Yang, S. Tan, X. Li, H. Dai, X. Yu, X. Zhang, N. Weng, B. Jian, J. Xu, Double-network hydrogel with high mechanical strength prepared from two biocompatible polymers, *J. Appl. Polym. Sci.* 112 (2009) 3063–3070.
- [2] T.R.R. Singh, P.A. McCarron, A.D. Woolfson, R.F. Donnelly, Investigation of swelling and network parameters of poly(ethylene glycol)-crosslinked poly(methyl vinyl ether-co-maleic acid) hydrogels, *Eur. Polym. J.* 45 (2009) 1239–1249.
- [3] K. Wang, S.Z. Fu, Y.C. Gu, X. Xu, P.W. Dong, G. Guo, X. Zhao, Y.Q. Wei, Z.Y. Qian, Synthesis and characterization of biodegradable pH-sensitive hydrogels based on poly(3-caprolactone), methacrylic acid, and poly(ethylene glycol), *Polym. Degrad. Stabil.* 94 (2009) 730–737.
- [4] K.N. Plunkett, M.L. Kraft, Q. Yu, J.S. Moore, Swelling kinetics of disulfide cross-linked microgels, *Macromolecules* 36 (2003) 3960–3966.
- [5] K. Wang, X. Xu, Y.J. Wang, X. Yan, G. Guo, M.J. Huang, F. Luo, X. Zhao, Y.Q. Wei, Z.Y. Qian, Synthesis and characterization of poly(methoxyl ethylene glycol-caprolactone-co-methacrylic acid-co-poly(ethylene glycol) methyl ether methacrylate) pH-sensitive hydrogel for delivery of dexamethasone, *Int. J. Pharm.* 389 (2010) 130–138.
- [6] G.T. Chao, Z.Y. Qian, M.J. Huang, B. Kan, Y.C. Gu, C.Y. Gong, J.L. Yang, K. Wang, M. Dai, X.Y. Li, M.L. Gou, M.J. Tu, Y.Q. Wei, Synthesis, characterization, and hydrolytic degradation behavior of a novel biodegradable pH-sensitive hydrogel based on polycaprolactone, methacrylic acid, and poly(ethylene glycol), *J. Biomed. Mater. Res. A* 85 (2010) 36–46.
- [7] X. Xu, S.Z. Fu, K. Wang, W.J. Jia, G. Guo, X.L. Zheng, P.W. Dong, Q.F. Guo, Z.Y. Qian, Preparation and characterization of vitamin-12 loaded biodegradable pH-sensitive microgels, *J. Microencapsul.* 26 (2009) 642–648.
- [8] P.V. Dadhaniya, A.M. Patel, M.P. Patel, R.G. Patel, A new cationic poly[1-vinyl-3-ethyl imidazolium iodide], P(VEII) hydrogel for the effective removal of chromium (VI) from aqueous solution, *J. Macromol. Sci. Part A: Pure Appl. Polym. Chem.* 46 (2009) 447–454.
- [9] H.A. Essawy, H.S. Ibrahim, Synthesis and characterization of poly(vinylpyrrolidone-co-methylacrylate) hydrogel for removal and recovery of heavy metal ions from wastewater, *React. Funct. Polym.* 61 (2004) 421–432.
- [10] D. Solpan, M. Torun, (Sodium alginate/acrylamide) semi-interpenetrating polymer networks and their usability on removal of lead, cadmium, nickel ions, *J. Macromol. Sci. Part A: Pure Appl. Polym. Chem.* 42 (2005) 1435–1449.
- [11] B. Hazer, Synthesis of PS-PEG and PMMA-PEG branched block copolymers by macroinimer, *Macromol. Rep. A28* (1991) 47–52.
- [12] B. Hazer, Gelation in bulk polymerization of styrene with macroinimers, *Makromol. Chem.* 193 (1992) 1081–1086.
- [13] U. Yildiz, B. Hazer, Free radical crosslinking copolymerization. Gelation behavior of macromonomeric azoinitiators versus macrocrosslinkers, *Macromol. Chem. Phys.* 199 (1998) 163–168.
- [14] U. Yildiz, B. Hazer, Dispersion redox copolymerization of methyl methacrylate with macromonomeric azoinitiator as a macrocrosslinker, *Polymer* 41 (2000) 539–544.
- [15] K. Tauer, U. Yildiz, Reactive poly(ethylene glycol)s in aqueous radical heterophase polymerization, *Macromolecules* 36 (2003) 8638–8647.
- [16] Y. Yamamoto, W. Nakao, Y. Atago, K. Ito, Y. Yagci, A novel macroinimer of polyethylene oxide: synthesis of hyper branched networks by photoinduced H-abstraction process, *Eur. Polym. J.* 39 (2003) 545–550.
- [17] G.L. Cheng, P.W.F. Simon, M. Hartenstein, A.H.E. Muller, Synthesis of hyper-branched poly(tert-butyl acrylate) by self-condensing atom transfer radical polymerization of a macroinimer, *Macromol. Rapid Commun.* 21 (2000) 846–852.
- [18] D. Melekaskan, F. Kasapoglu, K. Ito, Y. Yagci, O. Okay, Swelling and elasticity of hydrogels based on poly(ethylene oxide) macroinimer, *Polym. Int.* 53 (2004) 237–242.
- [19] S.K. Bajpai, S. Johnson, Superabsorbent hydrogels for removal of divalent toxic ions. Part I: Synthesis and swelling characterization, *React. Funct. Polym.* 62 (2005) 271–283.
- [20] T. Caykara, I. Akcakaya, Synthesis and network structure of ionic poly(N,N-dimethylacrylamide-co-acrylamide) hydrogels: comparison of swelling degree with theory, *Eur. Polym. J.* 42 (2006) 1437–1445.
- [21] H. Kaplan, A. Guner, Characterization and determination of swelling and diffusion characteristics of poly(N-vinyl-2-pyrrolidone) hydrogels in water, *J. Appl. Polym. Sci.* 78 (2000) 994–1000.
- [22] J.C. Rueda, H. Komber, J.C. Cedron, B. Voit, G. Shevtsova, Synthesis of new hydrogels by copolymerization of poly(2-methyl-2-oxazoline) bis(macromonomers) and N-vinylpyrrolidone, *Macromol. Chem. Phys.* 204 (2003) 947–953.
- [23] A. Pourjavadi, S. Barzegar, Synthesis and evaluation of pH and thermosensitive pectin-based superabsorbent hydrogel for oral drug delivery systems, *Starch* 61 (2009) 161–172.
- [24] L.H. Sperling, *Introduction to Physical Polymer Science*, Wiley Interscience, New Jersey, 2006.
- [25] B. Stuart, *Polymer Analysis*, John Wiley & Sons, West Sussex, 2003.
- [26] A. El-Hag Ali, H.A. Shawky, H.A. Abd El Rehim, E.A. Hegazy, Synthesis and characterization of PVP/AAc copolymer hydrogel and its applications in the removal of heavy metals from aqueous solution, *Eur. Polym. J.* 39 (2003) 2337–2344.
- [27] R.T. Gephart III, N.J. Williams, J.H. Reibenspies, A.S. De Sousa, R.D. Hancock, Metal ion complexing properties of the highly preorganized ligand 2,9-bis(hydroxymethyl)-1,10-phenanthroline: a crystallographic and thermodynamic study, *Inorg. Chem.* 47 (2008) 10342–10348.
- [28] J. Heller, R.F. Helwing, R.W. Baker, M.E. Tuttle, Controlled release of water-soluble macromolecules from bioerodible hydrogels, *Biomaterials* 4 (1983) 262–266.