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

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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 (SM), 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 Cu2+, Cd2+, Ni2+ and Zn2+ under varying conditions. The binding capability of the hydrogels toward the metal ions decreases in the following order: Cu2+ > Ni2+ > Zn2+ > Cd2+.

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 macrorinitiator 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.

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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]. Cd(NO\(_3\))\(_2\)·4H\(_2\)O was supplied by JT Baker. All other chemicals such as CuCl\(_2\)·2H\(_2\)O, ZnCl\(_2\)·2H\(_2\)O, NiCl\(_2\)·2H\(_2\)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.

\(^1\)H 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 an 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\(^3\) 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 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\(^3\) g/mol (\(M_w/M_n = 1.19\)).

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.
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 (SM) were determined by accurately weighing each sample both in the hydrated and dried states and applying the following expression [19]:

\[
\%SM = \left( \frac{M_t - M_0}{M_0} \right) \times 100
\]

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]:

\[
q_w = \frac{M_t}{M_0}
\]

where \(M_t\) is the mass of the hydrogel after equilibrium and \(M_0\) is the mass of the hydrogel before swelling. Then the volume fraction \(\phi\) of the swollen polymer was calculated using the equation [19]:

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

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]:

\[
M_c = \frac{-V_1(d_p/(\phi^{1/3} - (\phi/2)))}{\left[ \ln(1 - \phi) + \phi + \phi^2 \right]}
\]

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), \(\phi\) is the volume fraction of polymer in swollen gel and \(\chi\) 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 \(\text{Cu}^{2+}\), \(\text{Ni}^{2+}\), \(\text{Zn}^{2+}\) and \(\text{Cd}^{2+}\) 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 HNO₃ 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,
Swelling studies

The free radical polymerization of 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 methacrylate (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 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...
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 \( r \) when the sample is stretched.

Young’s modulus can be written

\[
E = L \left( \frac{\partial \alpha}{\partial L} \right)_{T,V}
\]

which yields

\[
E \equiv 3n \frac{RT}{r_0^2} \left( \frac{r^2}{r_0^2} \approx 1 \right)
\]

where \( L \) is the length of the chain and \( r_0^2 \) and \( r^2 \) 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 \( r \) 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

\[
-\ln(1 - \phi) + \phi + \chi \phi^2 = V_1 n_1 (\phi^{1/3} - (\phi/2))
\]

where \( \phi \) is the volume fraction of polymer in the swollen mass, \( V_1 \) is the molar volume of the solvent and \( \chi \) is the Flory–Huggins polymer–solvent dimensionless interaction term. \( n_1 \) values were calculated using Eq. (7) and put in Eq. (6) to determine the \( E \) values by assuming \( r^2 / r_0^2 \approx 1 \). 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 Cu\(^{2+}\), Ni\(^{2+}\), Zn\(^{2+}\) and Cd\(^{2+}\) metal ions were tested under non-competitive conditions by immersing a sample in a solution containing a metal ion. The binding of the Cu\(^{2+}\), Ni\(^{2+}\), Zn\(^{2+}\) and Cd\(^{2+}\) ions by different PVP hydrogel compositions were illustrated in Fig. 4a and b. It is clear that the tendency of the hydrogels to bind Cu\(^{2+}\) is greater than the other metal ions examined in this study under the same conditions. The maximum Cu\(^{2+}\) binding capacity is 92 mg for PVP at pH 8 (Table 2). The higher Cu\(^{2+}\) 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 Cu\(^{2+}\) 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.

### Table 2

The highest metal ion binding capacities of the hydrogels.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>PVP</th>
<th>P(VP-co-MA)</th>
<th>P(VP-co-MA) after regeneration</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 2</td>
<td>pH 5</td>
<td>pH 8</td>
<td>pH 2</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>35</td>
<td>75</td>
<td>92</td>
</tr>
<tr>
<td>Ni(^{2+})</td>
<td>15</td>
<td>32</td>
<td>39</td>
</tr>
<tr>
<td>Zn(^{2+})</td>
<td>9</td>
<td>11</td>
<td>25</td>
</tr>
<tr>
<td>Cd(^{2+})</td>
<td>3</td>
<td>12</td>
<td>15</td>
</tr>
</tbody>
</table>
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 $\text{Ni}^{2+}$ binding capacity of the hydrogels is

![Graphs showing the effect of pH, MIM concentration and time on the removal of Cu(II) and Ni(II) ions from PVP.](image)

![Graphs showing the effect of pH, MIM concentration and time on the removal of Zn(II) and Cd(II) ions from PVP.](image)

**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.
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.
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 carboxylic 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 Cu²⁺, Ni²⁺, Zn²⁺ and Cd²⁺, respectively (Table 2).
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 moduli 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 Cu$^{2+}$, Cd$^{2+}$, Ni$^{2+}$ and Zn$^{2+}$ were tested under non-competitive conditions. The maximum binding capacity of the hydrogels for the
different metal ions was in the order of Cu$^{2+}$ > Ni$^{2+}$ > Zn$^{2+}$ > 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.

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