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Enhanced adsorption properties of interpenetrating polymer network hydrogels for heavy metal ion removal

Jingjing Wang · Fang Liu · Jun Wei

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Abstract In this study, sequential interpenetrating polymer network (IPN) hydrogels based on poly(polyethylene glycol diacrylate) poly(PEGDA) and poly(methacrylic acid) (PMAA) were prepared with enhanced adsorption properties for heavy metal ion removal. The swelling behavior and mechanical property of the IPN hydrogels were characterized. It was found that swelling ratio increased, and mechanical strength decreased with the PMAA content in the IPN. The IPN hydrogels were used to remove heavy metal ions from aqueous solution under the non-competitive condition. The effects of pH values of the feed solution at the range of 3–5 and PMAA content in the IPN on the adsorption capacity were investigated. The results indicated that the adsorption capacity of the IPN hydrogels increased with the pH values and PMAA content in the IPN. Furthermore, the synergistic complexation of metal ions with two polymer networks in the IPN was found in the adsorption studies. Regeneration studies suggested that metal rebinding capacity of the IPN hydrogels did not change significantly through repeated applications compared with the first run. It was concluded that the poly(PEGDA)/PMAA hydrogels could be used as fast-responsive, high capacity, and renewable sorbent materials in heavy metal removing processes.

Keywords Hydrogel · Interpenetrating polymer network · Heavy metal ion · Adsorption · Synergistic complexation

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J. Wang (✉) · F. Liu · J. Wei
Department of Polymer Materials and Engineering, School of Material Engineering, Key Laboratory for Advanced Technology in Environmental Protection of Jiangsu Province, Yancheng Institute of Technology, Yancheng 224051, People's Republic of China
e-mail: jjwang1@hotmail.com

Introduction

In recent years, the presence of heavy metal ions in water streams has readily increased as a result of industrialization and urbanization. Therefore, an effective removal of heavy metal ions from industrial effluents or water streams is very crucial due to their toxic nature and other adverse effects on many life forms. Several treatment methods such as ion exchange, reverse osmosis, adsorption, and precipitation have been extensively investigated to remove metal ions from wastewater [1–3]. Among these methods, adsorption is generally preferred due to its high efficiency, easy handling, and availability of different adsorbents. Many publications concentrated on the use of hydrogels [4–9] having amide, amine, carboxylic acid, or ammonium groups which can bind with heavy metal ions, as the adsorbent to remove the heavy metal ions due to their swelling response to ionic strength, pH, and temperature [10]. In addition, high adsorption capacities, the ease of operation, especially regeneration abilities encourage their applications in waste water treatment.

However, hydrogels prepared from either natural or synthetic sources usually exhibited poor mechanical properties. Because their crosslinking points are distributed irregularly and the polymer chains between the crosslinking points have different lengths. Therefore, stress on the gels can not be evenly distributed between the polymer chains, and cracks develop easily [11]. There are different ways to improve the mechanical properties of hydrogels, including copolymerization with hydrophobic monomers [12] and formation of interpenetrating polymer network (IPN) [13–15].

IPN, describing as an intimate entanglement of two crosslinked networks, has been the most useful method to improve the mechanical strength of hydrogels [13–15]. Consisting of two or more network polymers, with at least one polymerized and/or crosslinked in the immediate presence of others, the interlocked structures of the crosslinked components are believed to ensure the stability of the bulk and surface morphology [16].

In this study, IPN hydrogels based on poly(polyethylene glycol diacrylate) poly(PEGDA) and poly(methacrylic acid) (PMAA) were synthesized by sequential interpenetrating technology. The swelling behavior and mechanical property of the IPN hydrogels were investigated. Adsorption properties of the IPN hydrogels were examined for the removal of Cu(II), Cd(II), and Pb(II) ions from aqueous solutions under the non-competitive condition. Finally, the regeneration abilities of the IPN hydrogels were evaluated.

Experimental section

Materials

Polyethylene glycol diacrylate (PEGDA, M_n 575) and methacrylic acid (MAA) were purchased from Sigma-Aldrich Chemicals and used without further purification. Free radical photoinitiator Darocur 1173 was obtained from Ciba Co. Copper sulfate ($CuSO_4 \cdot 5H_2O$), cadmium nitrate [$Cd(NO_3)_2 \cdot 4H_2O$], and lead acetate [$Pb(CH_3COO)_2 \cdot 3H_2O$] used in sorption experiments were purchased from Shanghai Chemical Reagents Co., China.

Preparation of IPN hydrogels

PEGDA was first dissolved in ethanol, and then the free radical photoinitiator Darocur 1173 (0.5% w/w based on the weight of PEGDA) was added. The mixture was introduced between two glass plates and cured under a high-pressure mercury lamp for 1 h. Then the obtained poly(PEGDA) membranes were extracted by ethanol and dried completely under vacuum.

Monomer MAA (5, 10, 15, 20, 25, 30, 35, 40, and 45% w/w based on solvent ethanol) and the free radical photoinitiator Darocur 1173 (0.5% w/w based on MAA) were mixed and dissolved in ethanol. The mixture was allowed to swell the poly(PEGDA) membranes until equilibrium had reached (approximately 24 h) in vial. The vials containing the poly(PEGDA) membranes and the remaining MAA solution were placed under the UV lamp for a period of 1 h. Subsequently, the membranes were removed from the MAA solution and extracted using ethanol. Finally, the membranes were hydrated to equilibrium in distilled water, and the IPN hydrogels were obtained. The content of the PMAA incorporated into the IPN hydrogel was calculated by the following formula:

$$\mathrm{PMAA}(\%) = \frac{m_{\mathrm{IPN}} - m_{\mathrm{poly(PEGDA)}}}{m_{\mathrm{IPN}}} \times 100\%$$

where $m_{\mathrm{poly(PEGDA)}}$ and m_{IPN} were the weights of poly(PEGDA) and IPN hydrogels at the dry state, respectively.

Swelling ratio studies

Swelling ratio (SR) was determined by the gravimetric method. Dried IPN hydrogel samples were immersed in 0.01 mol/L citrate buffer solution and the weight of the wet sample (W_{w}, g) was measured after carefully removing moisture on the surface with filter paper. The weight of the dried sample (W_{d}, g) was determined after drying samples at 105 °C for 24 h. The SR of samples was calculated as follows:

$$\mathrm{SR}(\%) = \frac{W_{\mathrm{w}} - W_{\mathrm{d}}}{W_{\mathrm{w}}} \times 100\%.$$

Mechanical property studies

Stress–strain measurements were carried out using an Instron series IX materials testing system at room temperature. Dog-bone shaped samples were cut from the hydrogels (5 mm wide at the narrowest point with a gage length of 15 mm). Thickness of the samples was measured with a digital micrometer having a precision of 1 μm. A crosshead speed of 10 mm/min was used and at least triplicate was tested for each sample.

Adsorption capability studies

Adsorption studies were carried out in magnetically stirred (160 rpm), thermostated (25 °C) cylindrical glass vessels in batch conditions. Fifty milligram of sample was added into Cu(II), Cd(II), or Pb(II) ion solutions (0.005 mol/L metal ion, 50 mL) to determine the metal ion adsorption capacity of the samples under non-competitive conditions. The pH of the metal feed solutions was adjusted before the hydrogels were applied for the adsorption process. Amount of the residual metal ion in the solution was determined by atomic absorption using a Perkin-Elmer 560 spectrophotometer (Perkin-Elmer Cetus Instruments, Norwalk, CT) after 24 h. Amount of adsorbed metal ion (Q, mmol/g) was calculated from the following equation:

$$Q = \frac{(C_0 - C)V}{m}$$

where C_0 (mmol/L) and C (mmol/L) were the metal ion concentrations in the initial solution and after the adsorption for different periods of time, respectively. V (L) was the volume of the solution added and m (g) was the amount of sample used.

Adsorption rate studies

Batch studies were carried out using the prepared IPN hydrogels with the PMAA content of 20.2 and 38.4% to determine the effect of time duration on the chelation of metal ions. Fifty milligram of sample was added into Cu(II), Cd(II), or Pb(II) ion solutions (0.005 mol/L metal ion, 50 mL). At regular intervals, amount of adsorbed metal ions was determined as mentioned above.

Regeneration studies

The metal-complexed hydrogels were freed from metals by treating with 1 mol/L HCl. The acid-treated hydrogels were filtered and washed with distilled water and bicarbonate solution to remove HCl. The concentration of desorbed metals was determined as mentioned above. The desorption ratio was calculated as follows: desorption ratio = (amount of metal ion desorbed into solution/amount of metal ion bound to hydrogels) × 100%. A second metal binding cycle was repeated with these regenerated hydrogels. Reuse of the IPN hydrogels = (amount of metal ion adsorbed in the second run/amount of metal ion adsorbed in the first run) × 100%.

Results and discussion

Preparation of IPN hydrogels

IPN hydrogels were prepared by swelling poly(PEGDA) until equilibrium in MAA solutions with different concentrations followed by photoinitiated polymerization. In order to optimize the PMAA content, several fabrication parameters, including the initiator concentration during the poly(PEGDA) membrane curing procedure,

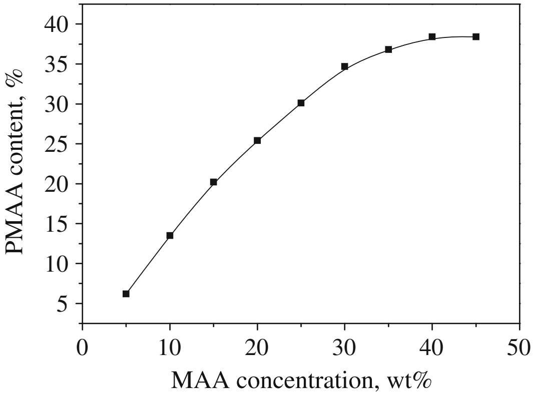


Fig. 1 Influence of MAA concentration on the PMAA content incorporated into the IPN hydrogels

and the effect of MAA and initiator concentrations during the MAA incorporation step were examined. The PMAA content of the resultant networks was found to be relatively unaffected by the concentration of the initiator during both of the processes of poly(PEGDA) membrane curing and MAA incorporation (results not shown). However, increasing the MAA concentration made the amount of PMAA incorporated into the IPN become larger (as shown in Fig. 1), and the highest content of PMAA incorporated was about 38.4%.

Swelling behavior

When a hydrogel is exposed to the aqueous medium, water will be absorbed by the hydrogel. Metal ions diffused primarily through the water phase in the hydrogel during the adsorption process. Therefore, the adsorption capacity increased with the swelling ratio of the hydrogel. The swelling behavior of the IPN hydrogels was investigated as a function of PMAA content in the IPN by immersion of the gels in buffered solutions at pH = 3, 4, and 5. Figure 2 illustrates the swelling ratio increased with the PMAA content and pH values at room temperature (25 °C). This could be attributed to the more completely dissociation of the acid groups of MAA with the increase of the pH value and stronger water uptake ability of PMAA than

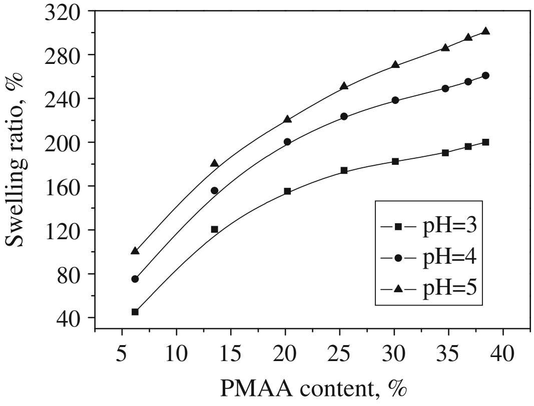


Fig. 2 Swelling isotherms of IPN hydrogels as a function of PMAA content in the IPN

poly(PEGDA). Therefore, the behavior observed was the consequence of the ionizable groups of the PMAA, which enhanced the repulsive forces of the carboxylic groups among the neighboring chains [7].

Mechanical property

In order to remove the influence of water content, the mechanical strength of poly(PEGDA) and IPN hydrogels were examined at dry state. The results are summarized in Fig. 3. The IPN hydrogels exhibited enhanced tensile strength compared with the poly(PEGDA), falling in the range from 2.2 to 6.9 MPa. Increases in the tensile strength with PMAA content in the IPN were found for the IPN hydrogels. It may be deduced to the fact that the crosslinked PMAA network was entrapped within the poly(PEGDA) network, resulting in an effective transfer of stress between the two polymer networks in the IPN hydrogels.

Adsorption studies

Metal ion adsorption capacity of poly(PEGDA) and PMAA at different pH values is listed in Table 1. The amount of adsorbed Pb(II) was more than Cu(II) or Cd(II). This could also be related to the atomic radius (slightly smaller for lead than for copper or cadmium), which would affect the availability of adsorption sites and diffusivity kinetics of the metal ions.

Figures 4 and 5 respectively illustrate the influence of PMAA content in the IPN and PH of the feed solution on the adsorption capacity. The theoretical adsorption values of IPN hydrogels, which were used to reach certain conclusions about the effect of interpenetrating network structure on the adsorption capacity, were also calculated. Briefly, theoretic values in Figs. 4 and 5 were obtained as follows: first, metal ion adsorption capacity of poly(PEGDA) and PMAA obtained from Table 1 was used in calculations. Then, the values of poly(PEGDA) and PMAA contents in the IPN were multiplied by adsorption values of each respective polymer. Finally, both values were added to obtain theoretical results.

Fig. 3 Mechanical strength of the IPN hydrogels

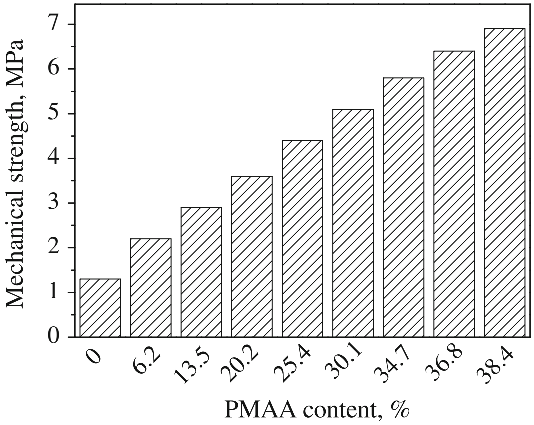


Table 1 Metal ion adsorption capacity of poly(PEGDA) and PAA at different pH values from the single metal ion solution (0.005 mol/L), mmol/g

Metal ions	Poly(PEGDA)			PMAA		
	pH = 3	pH = 4	pH = 5	pH = 3	pH = 4	pH = 5
Pb(II)	0.45	0.51	0.55	1.32	1.65	2.25
Cu(II)	0.28	0.32	0.36	0.64	0.85	1.24
Cd(II)	0.21	0.28	0.33	0.55	0.71	1.08

In order to investigate the relationship between adsorption capacity of the hydrogels and PMAA content in the IPN, the adsorption studies of the IPN hydrogels for Cu(II), Cd(II), and Pb(II) ions were conducted from single solutions (0.005 mol/L) fixing pH at 5. It was seen that the adsorption capacity increased with the PMAA content for all metal ions, and the highest sorbing capacity for metal ions was observed for the IPN hydrogel having the largest amount of PMAA content. The results may also be attributed to the fact that PMAA exhibited higher adsorption capacity compared with poly(PEGDA). Therefore, the more amount of PMAA in the IPN, the more the amount of metal ion adsorbed.

The influence of pH values on the metal ion absorption capacity of the IPN hydrogels was studied at various pH values with a fixed PMAA content of 34.7%. Seen from the results in Fig. 5, the absorption of metal ions was strongly dependent on the pH, which was consistent with a polyelectrolyte system. The dissociation constant (p*K*a) of MAA was 4.66. When the pH values ranged from 3 to 5, the swelling ratio and the absorption capacity tended to increase due to the dissociation of the carboxylic acid group. Therefore, the metal ion binding was in agreement with the exchange between the metal ions in the external solution and the hydrogen ions from the carboxylic groups of PMAA.

Furthermore, it was found that the experimental value was larger than the corresponding theoretical value for the metal ion adsorption. The phenomena may be explained by synergistic complexation of metal ions with two polymer networks in the IPN. Synergism is defined as the cooperative action of different ligands in producing an effect greater than the sum of the effects of all ligands acting separately. In the current research two ligands, –COOH in the PMAA and –O– in the poly(PEGDA), cooperated in the complexation of metal ions, leading to the enhanced amount of metal ion adsorption.

Adsorption rate

The rapid adsorption of metal ions by the adsorbent is of great importance for practical use, shortening the treatment of wastewater during filtration. IPN hydrogels with PMAA content of 20.2 and 38.4% were selected for the adsorption rate studies. The change in amount of adsorbed metal ions with time for the IPN hydrogels is shown in Figs. 6 and 7. It was observed that the adsorption process was very fast and the equilibrium was approached within the first 5 min of the process. After this period, the adsorption rate was fairly slow and saturation was reached

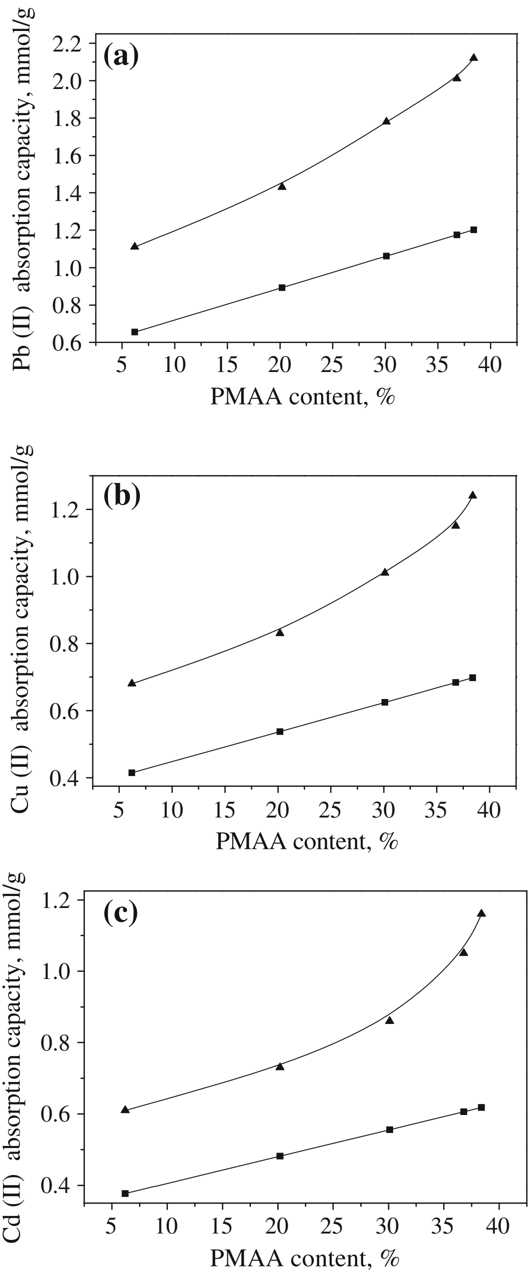
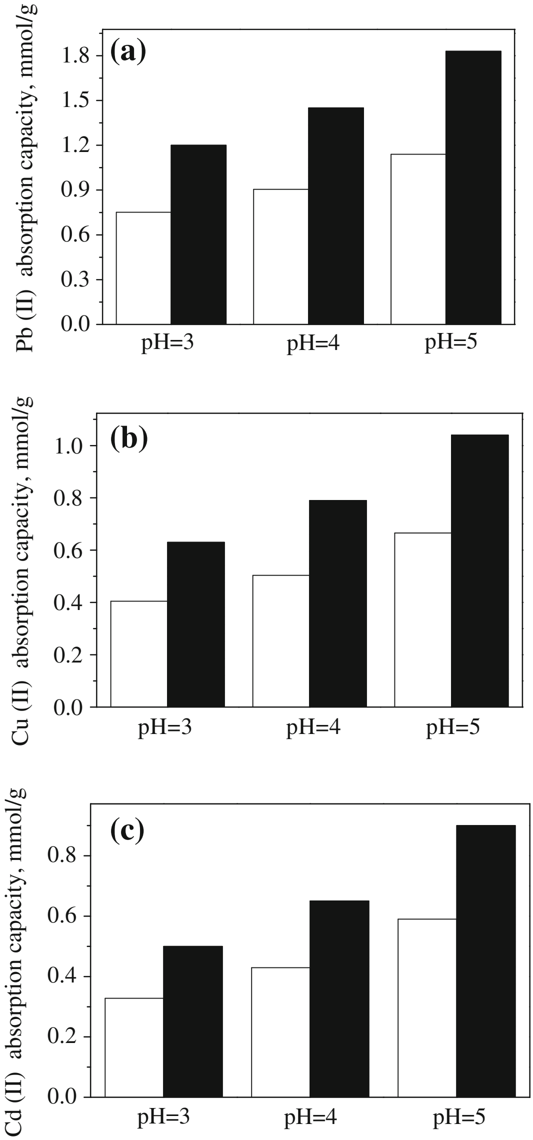


Fig. 4 Influence of PMAA content in the IPN on **a** Pb(II), **b** Cu(II), **c** Cd(II) adsorption capacity, fixing pH at 5; (*filled squares*) theoretic values, (*filled triangles*) experimental values

within approximately 15 min for all metal ions. This high initial rate suggested that the adsorption occured mainly on the surface [17].

In previous reports, crosslinked polyacrylamides hydrogels adsorbed heavy metal ions with different adsorption rates changing between 30 min and 24 h [18]. The adsorption rates of the IPN hydrogels in this research for removal of Cu(II), Cd(II),

Fig. 5 Effect of pH values on **a** Pb(II), **b** Cu(II), **c** Cd(II) adsorption capacity of the IPN hydrogel having PMAA content of 34.7%; (*open bars*) theoretic values, (*filled bars*) experimental values



and Pb(II) ions were very fast compared with previous studies [18], probably because of the synergistic complexation of heavy metal ions with two polymer networks in the IPN hydrogels as shown in Figs. 4 and 5.

Regeneration studies

The capacity of hydrogels to be used in repeated operations is greatly influenced by the ability to easily desorb the bound metals under suitable conditions. The

Fig. 6 Adsorption rates of metal ions by the IPN hydrogel having PMAA content of 20.2%

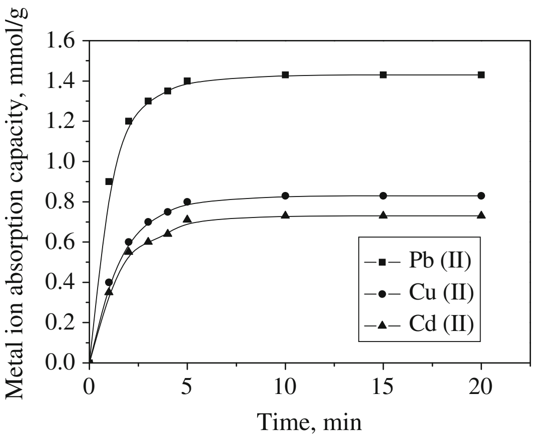
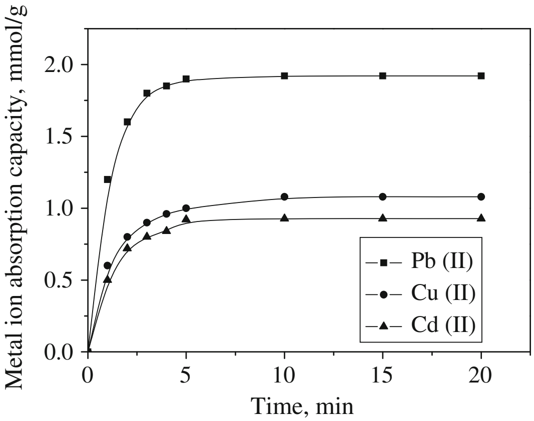


Fig. 7 Adsorption rates of metal ions by the IPN hydrogel having PMAA content of 38.4%



desorption of metal ions from IPN hydrogels using dilute HCl as desorbing agent was studied for Cu(II), Cd(II), and Pb(II). The data presented in Table 2 showed that the desorption ratio was higher than 96%, which meant that there was no difficulty in desorbing the metals from the IPN hydrogels, and both the strongly and weakly sorbed metals could be easily removed by the dilute acid. The dilute acid used for desorption leaded to breaking the coordination bonds between the metal ions and the ligands (–COOH and –O–). Therefore, it leaded to the release of the metal ions from hydrogels into solution.

Easy removal of metal ions from the binding sites demonstrated that the IPN hydrogel might be reused several times without significant loss of its metal ion capacity. The IPN hydrogels with different PMAA content which were regenerated with dilute HCl were used again in adsorption of metal ions to observe the reuse properties of the hydrogels. The results of Table 3 indicated that metal rebinding capacity of the IPN hydrogels for all metals did not change significantly through

Table 2 Desorption ratio of metal ions (%)

Sample	Cu(II)	Pb(II)	Cd(II)
IPN hydrogel 1[a]	98.0	97.3	96.9
IPN hydrogel 2[a]	96.8	98.4	97.4
IPN hydrogel 3[a]	97.5	96.7	98.1
IPN hydrogel 4[a]	97.3	97.9	97.5
IPN hydrogel 5[a]	98.2	98.8	98.0
IPN hydrogel 6[a]	97.8	98.5	96.7
IPN hydrogel 7[a]	98.1	98.2	97.8

[a] IPN hydrogels 1, 2, 3, 4, 5, 6, and 7 having PMAA content of 6.2, 13.5, 20.2, 25.4, 30.1, 34.7, 36.8, and 38.4% in the IPN, respectively

Table 3 Reuse of the IPN hydrogels (%)

Sample	Cu(II)	Pb(II)	Cd(II)
IPN hydrogel 1[a]	94.1	93.3	92.9
IPN hydrogel 2[a]	93.8	93.6	93.4
IPN hydrogel 3[a]	93.5	92.7	93.1
IPN hydrogel 4[a]	92.3	92.9	92.5
IPN hydrogel 5[a]	93.2	91.8	92.8
IPN hydrogel 6[a]	91.8	92.5	91.7
IPN hydrogel 7[a]	93.1	93.2	91.8

[a] IPN hydrogels 1, 2, 3, 4, 5, 6, and 7 having PMAA content of 6.2, 13.5, 20.2, 25.4, 30.1, 34.7, 36.8, and 38.4% in the IPN, respectively

repeated applications compared with the first run. This character of the possibility for reusing the IPN hydrogels several times made it economically suitable for use.

Conclusions

IPN hydrogels based on poly(PEGDA) and PMAA were synthesized by sequential interpenetrating technology. The swelling ratio increased and mechanical strength decreased with the PMAA content in the IPN. The metal ion adsorption capacity of the IPN hydrogels increased with the pH values of the feed solution between 3 and 5 and PMAA content in the IPN. Furthermore, the synergistic complexation of metal ions with two polymer networks in the IPN was found in the adsorption studies. Regeneration studies suggested that the IPN hydrogel may be reused several times without significant loss of its metal ion capacity. In a word, the poly(PEGDA)/PMAA hydrogels could be used as fast-responsive, high capacity, and renewable sorbent materials in heavy metal removing processes.

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References

1. Jesús EPA, Marcos AS (2010) Effect of the presence of lignin or peat in IPN hydrogels on the sorption of heavy metals. Polym Bull 65:495–508
2. Ngah WS, Endud CS, Mayanar R (2002) Removal of copper(II) ions from aqueous solution onto chitosan and crosslinked chitosan beads. React Funct Polym 50:181–190
3. Saliba R, Gauthier H, Gauthier R, Petit-Ramel M (2000) Adsorption of copper(II) and chromium(II) ions onto amidoximated cellulose. J Appl Polym Sci 75:1624–1631
4. Bekiari V, Sotiropoulou M, Bokias G, Lianos P (2008) Use of poly(*N*,*N*-dimethylacrylamide-co-sodium acrylate) hydrogel to extract cationic dyes and metals from water. Colloids Surf A Physicochem Eng Aspects 312:214–218
5. Pourjavadi A, Amini-Fazl MS (2007) Optimized synthesis of carrageenan-graft-poly(sodium acrylate) superabsorbent hydrogel using the Taguchi method and investigation of its metal ion absorption. Polym Int 56:283–289
6. Selva C, Gülten G (2009) Noncompetitive removal of heavy metal ions from aqueous solutions by poly[2-(acrylamido)-2-methyl-1-propanesulfonic acid-*co*-itaconic acid] hydrogel. Ind Eng Chem Res 48:2652–2658
7. Jeria-Orell M, Pizarro GDC, Marambio OG, Geckeler KE (2009) Novel hydrogels based on itaconic acid and citraconic acid: synthesis, metal ion binding, and swelling behavior. J Appl Polym Sci 113:104–111
8. Guilherme MR, Reis AV, Paulino AT, Moia TA, Mattoso LHC, Tambourgi EB (2010) Pectin-based polymer hydrogel as a carrier for release of agricultural nutrients and removal of heavy metals from wastewater. J Appl Polym Sci 117:3146–3154
9. Chauhan GS, Kumar S, Kumari A, Sharma R (2003) Study on the synthesis, characterization, and sorption of some metal ions on gelatin- and acrylamide-based hydrogels. J Appl Polym Sci 90:3856–3871
10. Mohan YM, Premkumar T, Joseph DK, Geckeler KE (2007) Stimuli-responsive poly(*N*-isopropylacrylamide-co-sodium acrylate) hydrogels: a swelling study in surfactant and polymer solutions. React Funct Polym 67:844–858
11. Reddy TT, Takahara A (2009) Simultaneous and sequential micro-porous semi-interpenetrating polymer network hydrogel films for drug delivery and wound dressing applications. Polymer 50:3537–3546
12. Essawy HA, Ibrahim HS (2004) Synthesis and characterization of poly(vinylpyrrolidone-co-methylacrylate) hydrogel for removal and recovery of heavy metal ions from wastewater. React Funct Polym 61:421–432
13. Zhang XZ, Wu DQ, Chu CC (2004) Synthesis, characterization and controlled drug release of thermosensitive IPN-PNIPAAm hydrogels. Biomaterials 25:3793–3805
14. Tang Q, Sun X, Li Q, Wu J, Lin J (2009) A simple route to interpenetrating network hydrogel with high mechanical strength. J Colloid Interface Sci 339:45–52
15. Tang Q, Sun X, Li Q, Wu J, Lin J (2009) Fabrication of a high-strength hydrogel with an interpenetrating network structure. Colloids Surf A Physicochem Eng Aspects 346:91–98
16. Liu L, Sheardown H (2005) Glucose permeable poly (dimethyl siloxane) poly (*N*-isopropyl acrylamide) interpenetrating networks as ophthalmic biomaterials. Biomaterials 26:233–244
17. KaşgÖz H, Özgümüş S, Orbay M (2003) Modified polyacrylamide hydrogels and their application in removal of heavy metal ions. Polymer 44:1785–1793
18. Mathew B, Pillai VNR (1993) Polymer–metal complexes of amino functionalized divinylbenzene-crosslinked polyacrylamides. Polymer 34:2650–2658