Preparation and Characterization of Photocured Thiol-Ene Hydrogel: Adsorption of Au(III) Ions from Aqueous Solutions

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ABSTRACT: In this study, photocured a novel thiol-ene hydrogels based on P(Penta3MP4/PEG-DA/HEMA) were investigated for adsorption of Au(III) ions from aqueous solutions purposes. The photopolymerization kinetics of thiol-ene-based formulations was investigated by real-time infrared spectroscopy. The chemical composition and surface morphology of hydrogels were also characterized. The effect of different parameters on Au(III) adsorption efficiency was examined in detail. Better adsorption behavior was achieved for Au(III) by P(Penta3MP4/PEG-DA/HEMA) F1 hydrogels. The maximum uptake for Au(III) was at pH 0.5. Both Langmuir and Freundlich adsorption isotherm models were applied and the reusability of thiol-ene hydrogels investigated. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: thiol-ene; hydrogel; pentaerythritol tetrakis (3-mercaptopropionate); Au(III) adsorption

INTRODUCTION

Gold is known for its uses in art, jewelry, and coinage although it is widely used in industry, dentistry, and has medical applications. The most important industrial use of gold is in the manufacture of electronics. As a highly efficient conductor, it can be melted, alloyed with many other metals. All these properties make gold an important metal which ought to be recovered.[1–4]

Because of the low concentration of gold in environmental, geological and metallurgical materials and insufficient sensitivity, separation and recovery of gold is neither practical nor simple. Many conventional methods have been used to recover gold ions from wastewater including coprecipitation,[5] ion exchange,[6–8] zinc-dust cementation,[9] carbon adsorption and solvent extraction[10,11] and adsorption.[12–14] However, these methods are too expensive, and low-cost techniques are required.[15] Among these techniques, adsorption is the most significant and promising technique for the removal of heavy metal ions because of its high efficiency, easy handling and the availability of different adsorbents.[16–20] In the past few decades, a large number of cross-linked polymers have been reported to be used as adsorbents for removal of Au(III) ions from aqueous solutions. Hydrogels which consist of a special class of three-dimensional cross-linked and hydrophilic polymeric networks were also used as polymeric adsorbents.[21] There have been various polymeric adsorbents used to recover Au(III) ions from aqueous solutions. Polymers functionalized with groups containing sulfur donor atoms can be highly efficient in the selective sorption of precious metals.[22,23] The hydrogels with functional group including sulfur and oxygen donor atoms are very efficient at chelating with precious metals according to hard-soft acid-base (HSAB) theory by Pearson. Au^{3+} is a soft metal ion and shows affinity to soft bases with donor atoms as O < N < S. Oxygen atoms in a hydrogel can be protonated and then they can show ionic interaction with anionic metal ions such as $AuCl^{-4}$. Moreover, S is poor in protonation and it is effective in coordinating with soft metal ions.[24] Some attempts have been made to synthesize polymers containing donor sulfur atoms, such as thiol,[23,24] thiosemicarbazide,[25] 2-mercaptobenzothiazole,[26] and thiohydrate.[27] But thiol-ene-based hydrogels have not been reported in the metal adsorption literature. This new approach for the preparation of the metal adsorbent hydrogel matrix has many advantages over conventional preparation techniques. Thiol-ene-based photocurable systems exhibit very rapid rates of polymerization. In the presence of air, rates of thiol-ene copolymerization are much greater than those

TABLE I
The Composition and Properties of Hydrogels

Formulation	Penta3MP4 (mmol)	PEG-DA (mmol)	HEMA (mmol)	Irq-184 (%)	H_2O (%)	Gelation %
F1	1	1.75	0.5	3	20	94.6
F2	1	1.25	0.5	3	20	99.7
F3	1	1.00	0.5	3	20	96.7
F4	1	0.50	0.5	3	20	95.5

attained by traditional multifunctional acrylates. Even in the absence of an added photoinitiator, rapid copolymerization (thiol-acrylate) and homopolymerization (acrylate) rates of a multifunctional thiol and a difunctional acrylate are recorded in the air.[28] Homopolymer hydrogels are cross-linked networks of one type of hydrophilic monomer unit, whereas copolymer hydrogels are produced by cross-linking of two comonomer units. Synthetic hydrogels and cross-linked hydrophilic synthetic polymers (synthetic polymer networks), are versatile materials with a growing number of novel applications. Despite their usefulness, the structure of the most synthetic hydrogels is poorly controlled. Such randomly cross-linked polymer networks have usually been produced using free radical polymerization methods. In this study, we used two acrylate monomers to prepare random copolymer hydrogels.[29,30]

From this perspective, our interest has turned to use thiol-ene-based-hydrogels for adsorption. Therefore, the main objectives of the study are as follows:

- synthesize a novel thiol-ene-based hydrogel to use in adsorption studies,
- characterize the synthesized hydrogel, and
- determine the optimum conditions of maximum Au(III) adsorption capacity.

EXPERIMENTAL

Chemicals and materials

The monomers pentaerythritol tetrakis(3-mercaptopropionate) (Penta3MP4, Merck), 2-hydroxyethyl methacrylate (HEMA, Merck), poly(ethylene glycol) dimethacrylate (PEGDA, Fluka) and the photoinitiator, 1-hydroxycyclohexyl-phenyl-ketone (Irgacure 184, Ciba Specialty Chemicals) were used as received. For adsorption studies 1000 mg L^{-1} $AuCl_4^{-}$ stock standard solution was purchased from Merck. Other standard solutions were prepared from this stock solution daily. Sodium hydroxide pellets and hydrochloric acid (37%) (Merck) were used to adjust the pH of sample solutions. Sulfuric acid and thiourea (TU) supplied by Merck, were used as the desorption agents in the desorption study. Water was deionized using a Milli Q-water purification system (Millipore, Anamed, Turkey) to

a resistance of 18.2 MΩ cm before used to prepare all of the solutions.

Preparation of thiol-ene hydrogels

A 1 g batch was prepared consisting of ratios given in Table I. The homogeneous mixture was transferred to a Teflon® mold (R = 4 mm). Then, the formulations were irradiated for 90 s under a high pressure UV lamp (OSRAM 300 W, λ_{max} = 365 nm). Scheme 1 demonstrates the chemical structure of all compounds and the preparation of hydrogels. The UV-cured hydrogels were taken out of the mold and were immersed in a large excess of deionized water for 1 day to wash out any unreacted monomers and the initiator, and
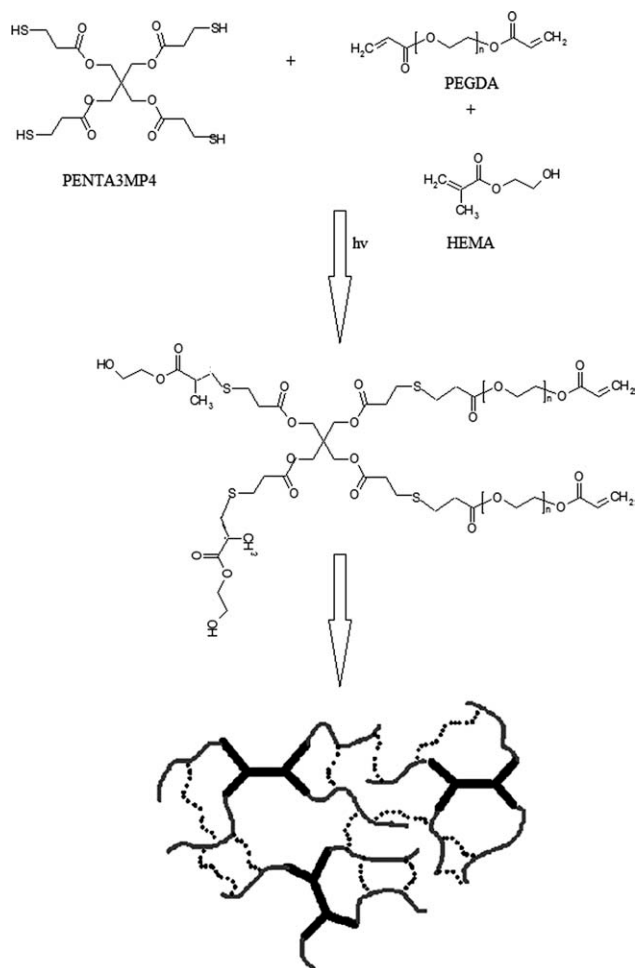
Scheme 1 Preparation of thiol-ene-based hydrogels.

then dried in a vacuum oven at 30°C for several days until a constant weight was reached. The dry gel samples were weighed (W_i) before soaking into 25 mL of deionized water at room temperature 20.0 ± 0.1°C. The swollen hydrogel samples were taken out and dried in a vacuum oven at 40°C for 1 day. All samples were reweighed (W_d). The percentage of gelation was calculated with the following formula:

$$\text{Gelation } (\%) = (W_d/W_i) \times 100 \qquad (1)$$

where W_d is the dried weight of hydrogel after extraction and W_i is the initial weight of the prepared hydrogel.

Characterization

FTIR spectrum of synthesized thiol-ene hydrogel was recorded on Perkin Elmer Spectrum 100 ATR-FTIR spectrophotometer to define the chemical composition of the hydrogels. The polymerization conversion was followed by real-time infrared spectroscopy. Conversion rates were calculated according to the decrease of IR absorption band at 2570 cm^{-1} for thiol and 1630 cm^{-1} for acrylate groups. The mixtures were spread on KBr discs and the absorption data were collected while UV light was applied to samples. The percent conversion was calculated by using the following equation:

$$\text{Conversion } \% = 100[1 - (A_t/A_o)] \qquad (2)$$

where A_o is the initial absorbance of acrylate or thiol bonds and A_t is the absorbance of the functional groups at time t.

The thermal properties of hydrogels were investigated by thermogravimetric analysis (TGA) using a Perkin-Elmer Thermogravimetric analyzer Pyris 1 TGA model. The temperature range was from ambient to 700°C at a heating rate of 10°C/min under a nitrogen atmosphere. The morphology of the hydrogels was investigated using a Philips XL30 ESEM-FEG/EDAX. The specimen was prepared for SEM by freeze fracturing in liquid nitrogen and applying a gold coating.

Swelling behavior of the hydrogels

The swelling behavior of dried hydrogels was studied by a general gravimetric method. Dry hydrogels were incubated in vials filled with 10 mL of deionized water or different buffer solutions at various pH mediums ranging from 0.5 to 10.0 at various temperatures and the swollen weight for each sample was recorded at regular time intervals after the excess surface water was blotted carefully with moistened filter paper. The procedure was repeated
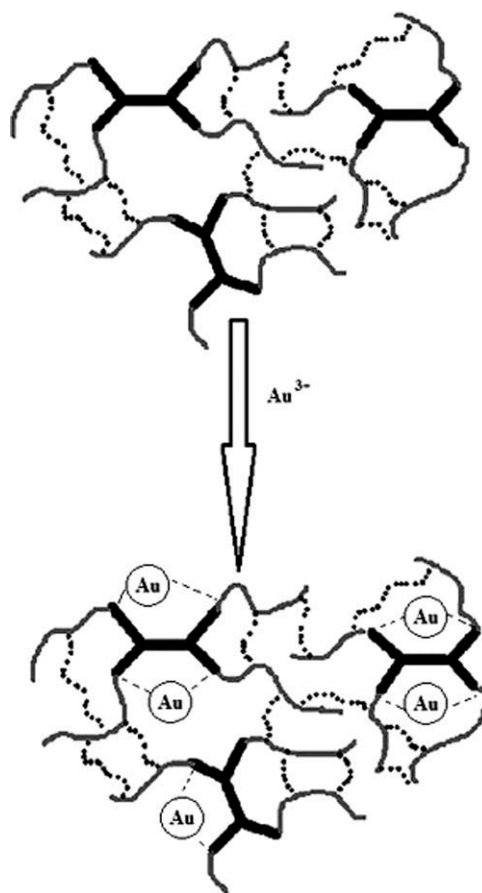
**Scheme 2** Complexation of gold ions on thiol-ene-based hydrogels.

until there was no further weight increase. The mass swelling of the hydrogels was calculated with the following formula:

$$\text{Swelling percentage } (\%) = [(m_t - m_i)/m_i] \times 100 \qquad (3)$$

m_i is the mass of dry hydrogel and m_t is the mass of the hydrogel at time t.

Adsorption of Au(III) ions

Adsorption of Au(III) ions from aqueous solutions was carried out separately in a batch system at the ambient temperature. To investigate the optimum conditions for maximum adsorption capacity, 0.05 g of P(Penta3MP4/PEG-DA/HEMA) hydrogel samples were immersed in 25 mL reagent bottles containing 10 mL of Au(III) ion solutions at various concentrations. The sample pH was adjusted to the desired value with HCl or NaOH solution. To determine the optimum pH on maximum adsorption, the dry gel samples were immersed in a 250 mg L^{-1} single ion solution which proved to be a sufficient concentration to reach equilibrium at pH 0.5–5.0 at room temperature for 24 h. For all experiments the bottles were
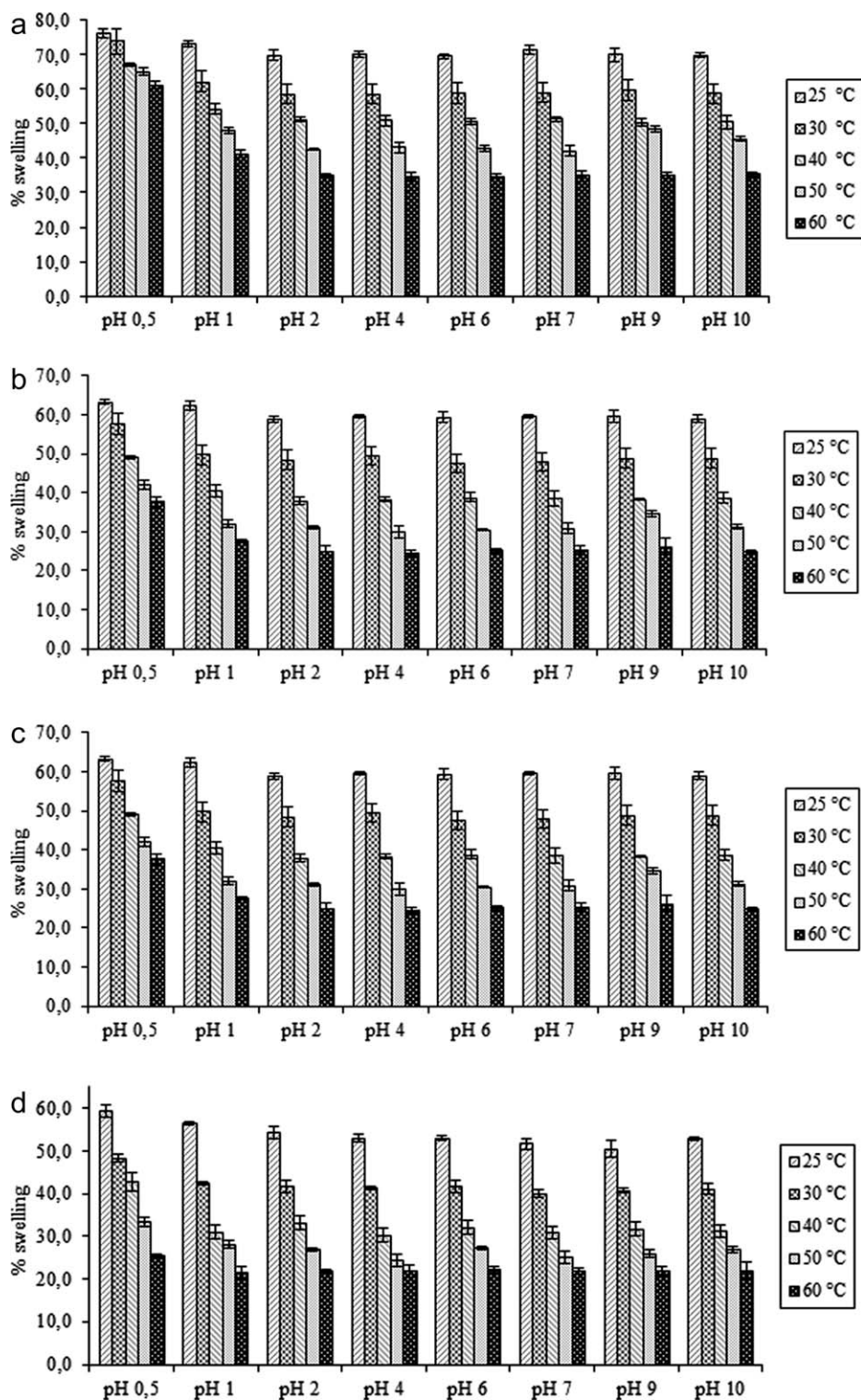
Figure 1 (a) pH and temperature depended swelling ratio of F1 hydrogel. (b) pH and temperature depended swelling ratio of F2 hydrogel. (c) pH and temperature depended swelling ratio of F3 hydrogel. (d) pH and temperature-depended swelling ratio of F4 hydrogel.

agitated at 250 rpm using a mechanical shaker to reach equilibrium. To investigate the effect of contact time, hydrogels were immersed in a solution containing a metal ion concentration of 250 mg L^{-1} at pH 0.5 for several time periods up to 24 h. Adsorption isotherm experiments were conducted with different initial metal ion concentrations in the range of 5–1000 mg L^{-1} but with the same solution pH value of 0.5 for 2 h. The maximum adsorption capacity (Q_m) was calculated from these isotherm data. To
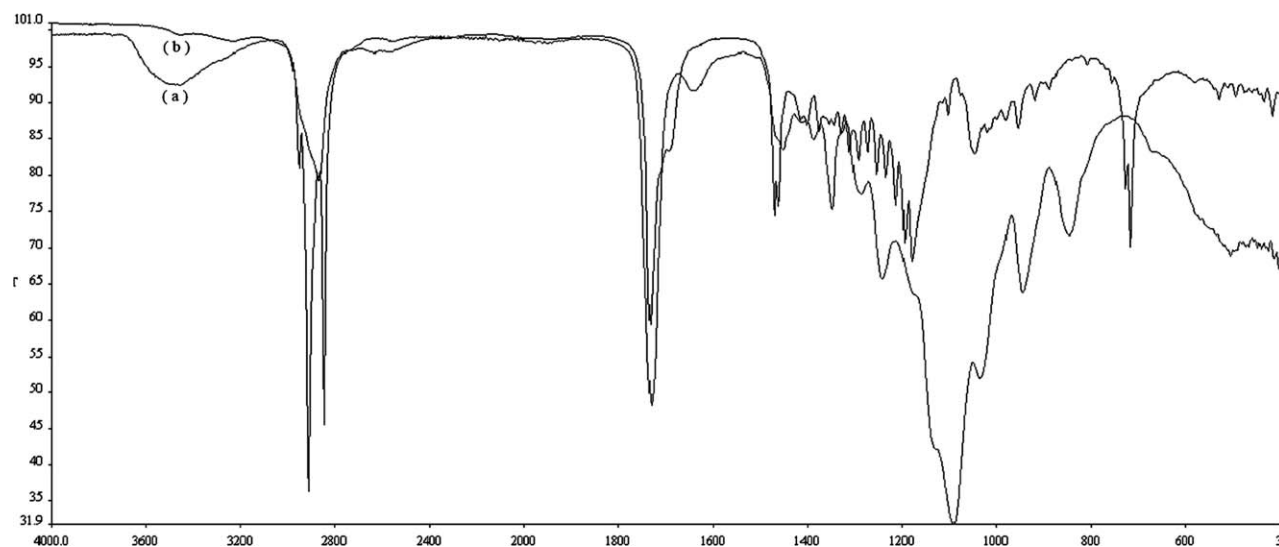
Figure 2 FTIR spectrum of P(Penta3MP4/PEG-DA/HEMA) hydrogel (F1) (a) Wet formulation (b) Cured hydrogel.

investigate the effect of initial solution volume, P(Penta3MP4/PEG-DA/HEMA) hydrogels were immersed in solutions at 10, 20, 50, 100 mL containing a metal ion concentration of 100 mg L^{-1}. Each value reported in this study is an average of at least three separate measurements. After equilibrium was attained, the aqueous phases were separated from the hydrogels and the final concentration of Au(III) ion was analyzed using an Analytikjena Zeenit 700 Flame Atomic Absorption Spectrophotometer (FAAS) equipped with deuterium lamp for continuous background correction. Adsorbed Au(III) per unit mass of the hydrogel (mg Au(III) g^{-1} dry hydrogel) was calculated by the following formula.

$$\text{The amount of metal ion adsorbed (mg/g)} = [(C_0 - C) \times V]/(m \times 1000) \quad (4)$$

where C_0 and C are the concentrations of the metal ions in the aqueous phase before and after the adsorption period, respectively (mg L^{-1}); V is the volume of the aqueous phase (mL) and m is the amount of dry hydrogel used (g).

Scheme 2 illustrate of complexation for gold ions.

Recovery and reuse studies

To determine the desorption behaviors of Au(III) ions from P(Penta3MP4/PEG-DA/HEMA) hydrogel (F1), metal ion-loaded samples were subjected to acid leaching to regenerate the hydrogel. To determine the optimum desorption agent, $0.8M$ thiourea and $3M$ HCl, $3M$ HCl, $5.10^{-3}M$ thiourea and $1M$ H_2SO_4 and $0.8M$ thiourea solutions acidified to pH 0.5, 1, 2, and 3 respectively were prepared for desorption studies. Loaded hydrogels added into 10 mL of various desorption solutions in a flask for

ion desorption. The contents of a flask were stirred (250 rpm) at room temperature for 2 h, and metal ion concentrations in the solution were analyzed at various times. After the maximum desorption ratio was obtained with $0.8M$ thiourea solution acidified to pH 0.5, the effect of the solution volume was examined. The hydrogels were loaded with 100 mg L^{-1} Au(III) solutions at 10, 20, 50, and 100 mL and
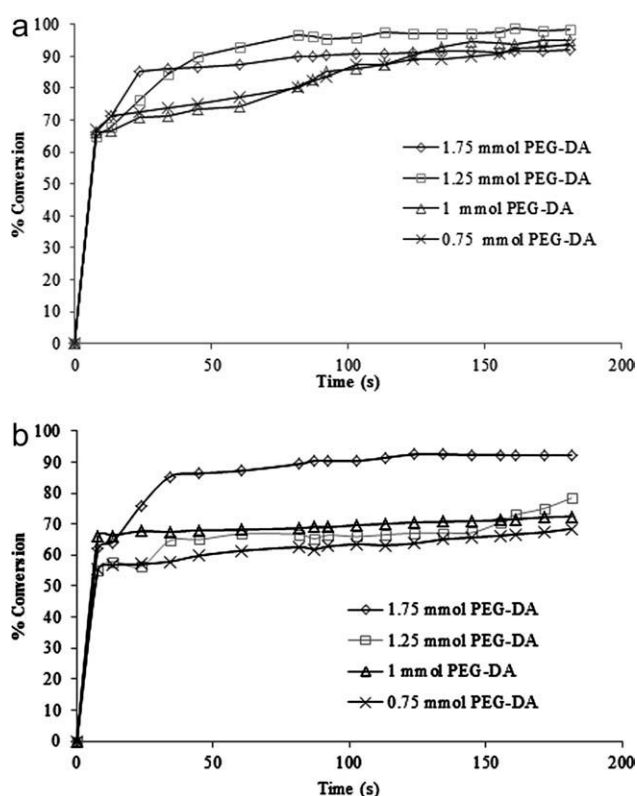
Figure 3 (a) Double bond conversion of the hydrogel versus irradiation time. (b) Thiol conversion of the hydrogel versus irradiation time.
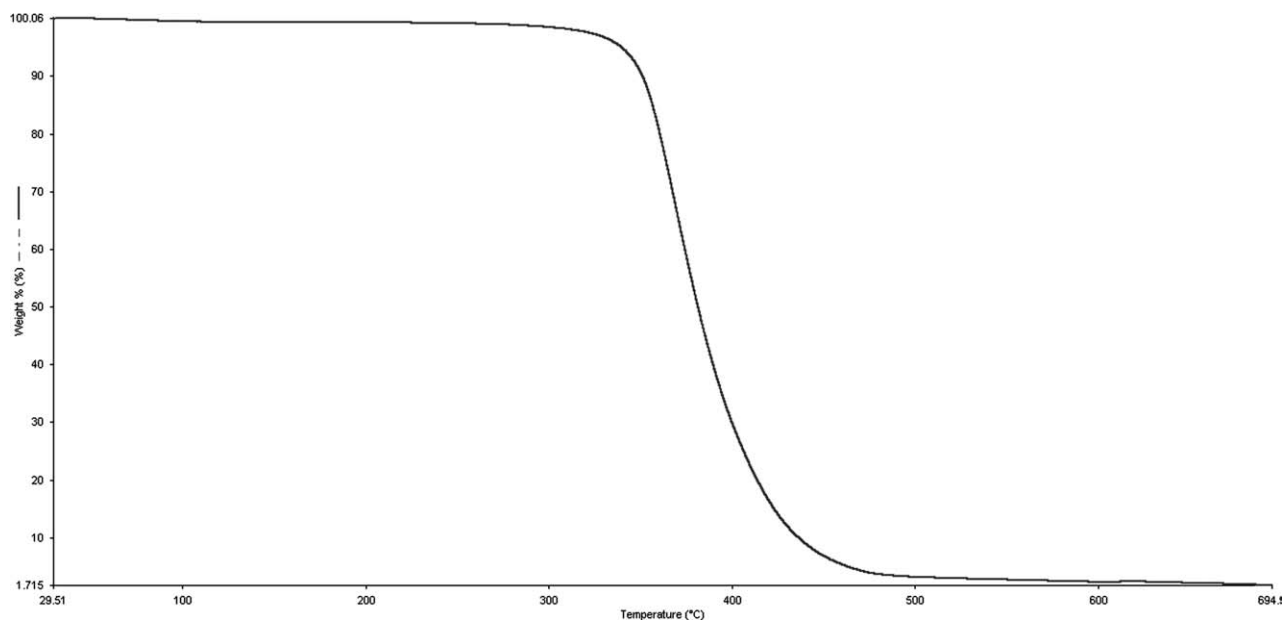
Figure 4   Thermogram of the P(Penta3MP4/PEG-DA/HEMA) hydrogel (F1).

then immersed in 0.8M thiourea solutions acidified to pH 0.5 at 10, 20, 50, and 100 mL. The released metal ion amount was determined using a FAAS according to the guidelines of the manufacturers.

RESULTS AND DISCUSSION

Characterization

Composition and swelling of hydrogels

The compositions and gelation ratios of P(Penta3MP4/PEG-DA/HEMA) hydrogels can be seen from Table I and the results demonstrate that gelation ratios of prepared hydrogels were higher than 94.6%.

The swelling ratios of the hydrogels can be seen in Figure 1(a–d). As it can be seen from the figures, there was less significant difference between water

uptakes of the P(Penta3MP4/PEG-DA/HEMA) hydrogels when pH changes from 2.0 to 10.0. On the other hand, the temperature appears to impact extent of swelling more significantly.

FTIR spectroscopic studies

In order to identify the hydrogel structure, FTIR spectrum of P(Penta3MP4/PEG-DA/HEMA) hydrogel (F1) was taken (Fig. 2). As it can be seen from FTIR spectra of P(Penta3MP4/PEG-DA/HEMA) hydrogel has the characteristic absorption peaks at 3475, 2870, 1731, and 1638 cm^{-1}, 1453 cm^{-1} and 1349 cm^{-1} respectively (a-spectrum: uncured wet hydrogel formulation). These can be summarized as: the peak at 3475 cm^{-1} shows the hydroxyl group of HEMA, the peak at 2870 cm^{-1} shows typical R—CH , the peak at 1731 cm^{-1} which is due to the presence of O—C=O group of Penta3MP4, PEG-DA, and HEMA, the strong peak at 1638 cm^{-1} indicates the —C=C— group of acrylates, and the peaks at 1453 cm^{-1} and 1349 cm^{-1} show the —C—O groups of Penta3MP4,
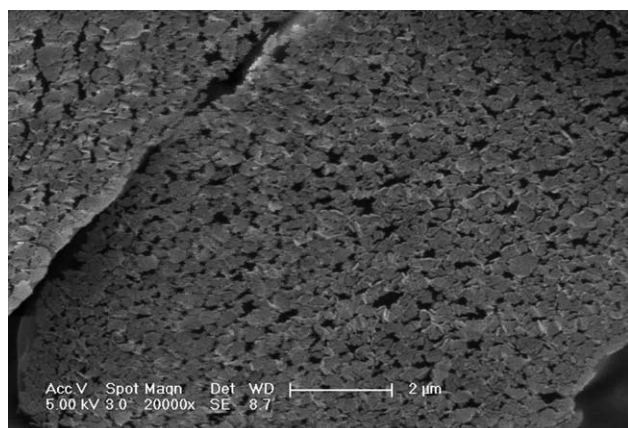

Figure 5   Scanning electron microscope (SEM) image of the P(Penta3MP4/PEG-DA/HEMA) hydrogel.
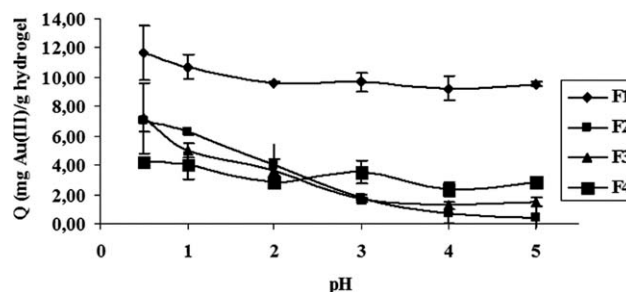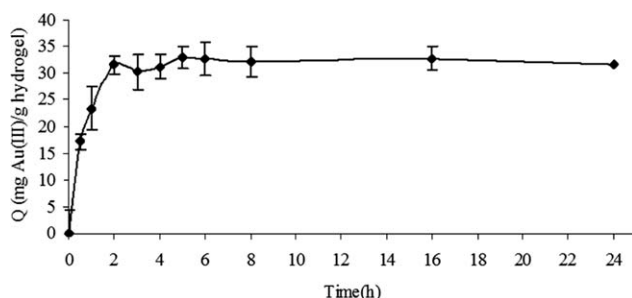

Figure 6   pH and chelating ligand effect.

**Figure 7** Saturation time for Au(III) uptake of P(Penta3MP4/PEG-DA/HEMA) hydrogel (mg/g).

PEG-DA, and HEMA in the case of FTIR spectrum of P(Penta3MP4/PEG-DA/HEMA) hydrogel.[31,32]

Double-bond conversion

The photopolymerization kinetics of the P(Penta3MP4/PEG-DA/HEMA) hydrogel was investigated by following the decrease in a thiol band at 2570 cm^{-1} and double band at 1638 and 810 cm^{-1}. Figure 3(a,b) shows the plot of conversion of acrylate and thiol, respectively. From the plots, it can be seen that within the first 60 s, nearly 90% conversion was reached the hydrogel (F1). As can be seen in both figures, acrylate-thiol systems do not reach full conversion. It was previously reported that, in certain cases where the thiol concentration was high enough to produce a sufficiently fast polymerization rate, overcoming the inhibition reaction and complete conversion was achieved.[33] The relatively low conversion of the double bonds is due to the oxygen inhibitions which cause the initiator to be consumed before full conversion.

Thermogravimetric analysis

The thermal degradation behavior of the P(Penta3MP4/PEG-DA/HEMA) hydrogel (F1) was assessed by TGA in nitrogen atmosphere. Figure 4 shows the thermogram of P(Penta3MP4/PEG-DA/HEMA) hydrogel (F1). One can observe that the hydrogel starts to degrade above 344°C, followed by a rapid loss at that
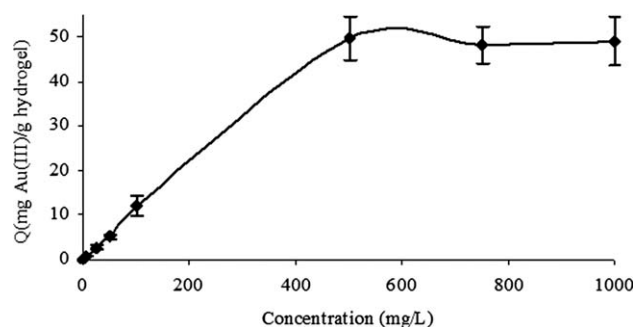
Figure 8 Effect of initial metal ion concentration on adsorption capacity of P(Penta3MP4/PEG-DA/HEMA) hydrogel.
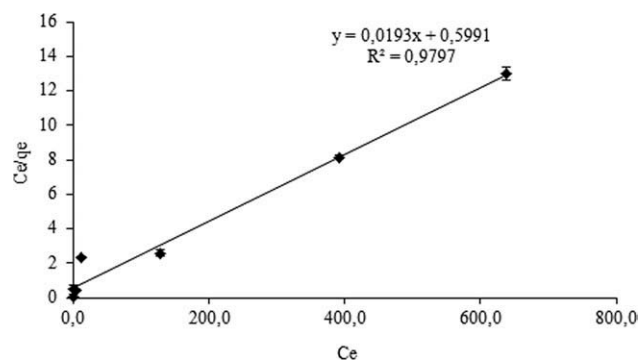
Figure 9 Langmuir isotherm plot for the adsorption of Au(III) ions on P(Penta3MP4/PEG-DA/HEMA) hydrogel.

temperature. Therefore, it is shown that the hydrogel has good thermal stability for adsorption studies.

SEM investigation

The surface morphology of the P(Penta3MP4/PEG-DA/HEMA) hydrogel was investigated by the scanning electron micrograph in Figure 5. Surface morphology and pore size of the hydrogels are affected by the nature of cross-linker. In this study Penta3MP4 was used as a cross-linking agent and this tetradental ligand may be provided to the hydrogel uniform porosity. In this case Penta3MP4 makes the surface appear as a continuous phase. The uniform and very few small pores on the surface should be considered as a factor providing a greater surface area. In addition, these pores reduce mass transfer resistance and facilitate the diffusion of metal ions because of high internal surface area. This also provides higher metal chelation capacity.

Adsorption studies

Effects of pH and hydrogel formulation

As it is widely known metal ion adsorption on chelating adsorbents critically depends on pH.[16] According
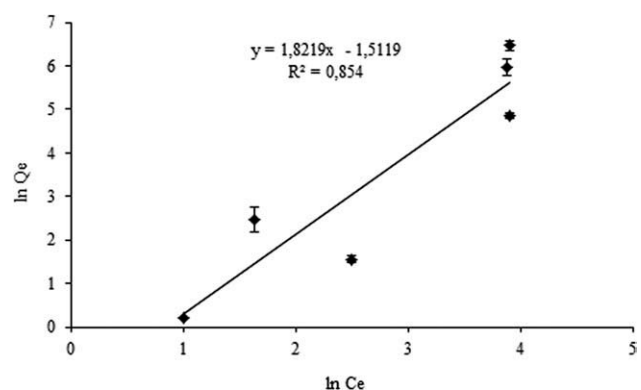
Figure 10 Freundlich isotherm plot for the adsorption of Au(III) ions on P(Penta3MP4/PEG-DA/HEMA) hydrogel.

TABLE II
Adsorption Isotherm Equations of P(Penta3MP4/PEG-DA/HEMA) Hydrogels

Freundlich		Langmuir			
Model	R^2	Model	R^2	Q_0	k_L
$\ln q_e = 0.4687 \ln C_e + 1.1173$	0.854	$C_e/q_e = 0.0193C_e + 0.5991$	0.979	51.813	0.032

to the preliminary experiments, adsorption of Au(III) ions was achieved in acidic solutions. Figure 6 shows that adsorption of Au(III) from aqueous solution decreases to a small extent with the increase of pH. It is because the competitive adsorption between Cl^- and $AuCl_4^-$ influenced the Au(III) adsorption on the positively charged sites of P(Penta3MP4/PEG-DA/HEMA) hydrogels when there is a high concentration of Cl^- (pH 1.0–2.0). When the pH was greater than 3.0, the adsorption capacity of hydrogels for Au(III) decreased with increasing pH. From the point of chemical structure of chloro gold complexes, evidence shows that the predominant gold complex is $AuCl_4^-$ at pH below 3.0.[34] To investigate the influences of pH and hydrogel formulation on the adsorption of Au(III) by P(Penta3MP4/PEG-DA/HEMA) hydrogels, they were studied at an initial concentration of 250 mg L^{-1}. The results show that maximum adsorption for Au(III) was obtained with F1 hydrogel at pH 0.5.

Effect of time

The relationship between adsorption capacity and adsorption time was also studied. To study the equilibrium adsorption time, the hydrogels were treated with 10 mL of 250 mg L^{-1} Au(III) ion solutions at pH 0.5 for 24 h at 250 rpm. The results shows in Figure 7 that at the beginning of adsorption, the increase in adsorption capacity of hydrogel was very fast, after 2 h, equilibrium was established. Obviously, about 90% of the maximum uptake capacity
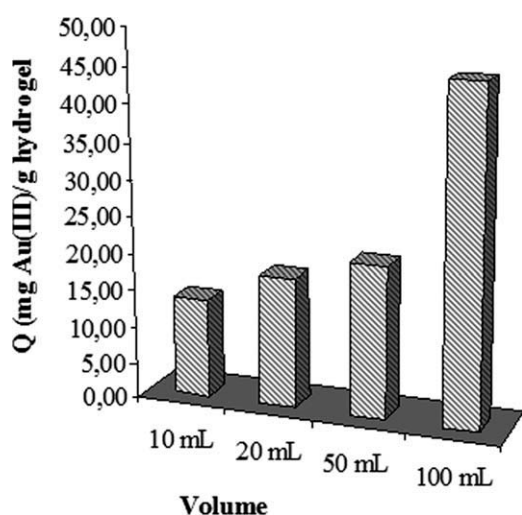
was achieved within 2 h for P(Penta3MP4/PEG-DA/HEMA) hydrogels. All these results show that the adsorption time is compared favorably with the values in the literature for applications with a high level of Au(III) ion recovery.

Effect of initial metal ion concentration

To determine the applicability of the hydrogel, it is useful to know its adsorption capacity and efficiency towards Au(III) ions. Therefore, initial metal ion concentration is really important in order to find the adsorption capacity of the adsorbed species on hydrogels. These can be carried out by equilibrating a fixed amount of the hydrogel with a series of metal ion solutions of gradually increasing concentration. To examine the effect of the initial concentration of the Au(III) ions on the adsorption capacity of the P(Penta3MP4/PEG-DA/HEMA) hydrogels, different initial concentrations of Au(III) ions in between 5 and 1000 mg L^{-1} at pH 0.5 were used. Figure 8 shows the Au(III) adsorption curves of the hydrogels. As it can be seen from the figure, equilibrium metal ion concentration increases with the increase of initial metal ion concentration. Then, it reaches saturation and gives a plateau after 500 mg L^{-1}.

Adsorption isotherms

When adsorbent gets in contact with an aqueous solution, adsorbent begins to remove solutes until equilibrium is established between the phases. This equilibrium is described by adsorption isotherm and distribution coefficients. Adsorption isotherms also
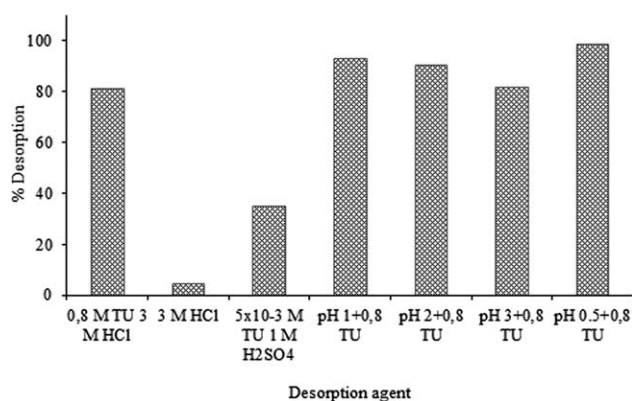
Figure 11 Effect of initial solution volume.

Figure 12 Desorption ratios of different agents.

TABLE III
Adsorption and Desorption Capacity of
P(Penta3MP4/PEG-DA/HEMA) Hydrogel

Cycle	Adsorption (mg Au(III)/g hydrogel)	Desorption %
1	45.29	99.94
2	44.78	97.32
3	44.35	96.34

known as equilibrium data are related to the equilibrium concentration of the solute in the aqueous solution and inside the adsorbent. The distribution coefficient of a solute between two phases is calculated as the ratio of the concentration of the solute in one phase to the concentration of the solute in the other phase under equilibrium conditions. The adsorption data were applied to Langmuir and Freundlich isotherms. To investigate the equilibrium data of Au(III) on the P(Penta3MP4/PEG-DA/HEMA) hydrogels, Langmuir or Freundlich isotherms, given by the following equations respectively, are commonly used:

$$q_e = \frac{Q_m \cdot k_L \cdot C_e}{1 + k_L \cdot C_e} \qquad (5)$$

$$\ln q_e = \ln K_F + \frac{1}{n}(\ln C_e) \qquad (6)$$

where q_e is the equilibrium uptake capacity of hydrogels, C_e is the concentration of metal ions in the supernatant after sorption, n and K_F are the empirical constants, Q_m and k_L are Langmuir's constants related to the capacity and energy of the adsorption.[16]

Langmuir and Freundlich isotherm plots for the adsorption of metal ions from aqueous solution by the hydrogel are presented in Figures 9 and 10, and the constants of adsorption isotherms are summarized in Table II. The Langmuir equation was originally developed to describe individual chemical adsorbents, and is applicable to physical adsorption which is monolayer within a low concentration range.[16] The results indicate that the Langmuir equation fits well to the adsorption of Au(III) on the hydrogel, and this shows that the adsorption behavior of Au(III) is a monolayer.

Effect of initial solution volume

The same amount of dry P(Penta3MP4/PEG-DA/HEMA) hydrogels (about 0.05 g) were treated with

TABLE IV
Comparative Data for Adsorption of Au(III)

System	Studied metal	pH	Adsorption time (h)	Adsorption capacity (mg Au(III)/g hydrogel)	Reference
Glycine modified crosslinked chitosan resin	Au(III), Pt(IV) and Pd(II)	2.0 (for Au)	3	169.98	33
Bisthiourea/formaldehyde resin	Ag(I) and Au(III)	6.5 (for Au)	5	715	34
Poly(acrylamide-1-allyl-2-thiourea) hydrogels	Au(III)	0.5	90	940	35
Chelating resins with amine, thio and amine/mercaptan functionalities	Au(III)	2.0	3	443.18	36
Poly((N-(hydroxymethyl) methacrylamide)–1-allyl-2-thiourea) hydrogels	Au(III)	0.5	30 min for 100 mg L^{-1} 4 h for 1000 mg L^{-1}	698	37
Poly(p-chloromethylstyrene-divinylbenzene) polymeric microbeads	Au(III), Ag(I), Pt(II) and Pd(II)	0.5 (for Au)	5	960	38
Crosslinked chitosan was modified with 4-amino-4′-nitroazobenzene	Au(III) and Pb(II)	3.0 (for Au)	14	69.93	39
Carboxymethylchitin (CMCht) and carboxymethylchitosan (CMChts) hydrogels	Au(III)	3.9	4	37.59 for CMChts 11.86 for CMCht	40
Poly[N-isopropylacrylamide-co-[2-(methylthio)ethyl methacrylate]]	Au(III)	3.0	3	12.39 for homogenous gel (62.8 μmol Au(III)) 63.42 for heterogenous gel (322 μmol Au(III))	41
Carboxymethyl cellulose/carboxymethyl chitosan blend hydrogels	Au(III) and Pb(II)	4.0	24	–	42
P(Penta3MP4/PEG-DA/HEMA) hydrogels	Au(III)	0.5	2	45.19	This work

a different volume of the Au(III) ion solution, containing 100 mg L^{-1} Au(III). Up to 50 mL of Au(III) solution, there was no significant change in the adsorption capacity of the hydrogels. On the other hand, at 100 mL of Au(III) solution the amount of adsorbed metal ions increased up to 45 mg Au(III)/g hydrogels. These results (Fig. 11) showed that the adsorption capacity of the P(Penta3MP4/PEG-DA/HEMA) hydrogels almost reached its maximum value when 100 mL Au(III) ion solution was used in the adsorption experiments.

Recovery and reuse

Desorption of the adsorbed precious metal ions from the P(Penta3MP4/PEG-DA/HEMA) hydrogel (F1) was studied by the batch method using different concentrations of thiourea, HCl and thiourea–HCl and H_2SO_4-thiourea solutions. The results are presented in Figure 12. It was found that $0.8M$ thiourea solution acidified to pH 0.5 provided efficient desorption of Au(III) from the P(Penta3MP4/PEG-DA/HEMA) hydrogel.

Table III shows the adsorption–desorption cycles of Au(III) on the P(Penta3MP4/PEG-DA/HEMA) hydrogel. The results demonstrate that, the amount of adsorption of Au(III) on P(Penta3MP4/PEG-DA/HEMA) hydrogel did not significantly change up to three cycles and the desorption efficiencies were above 95% (Table III). Therefore, the P(Penta3MP4/PEG-DA/HEMA) hydrogels could be successfully applied to the recovery of Au(III) ions from water and wastewater.

Comparison with other methods

A comparison of the proposed system with the other systems is given in Table IV. Some obtained parameters were comparable to those of other methods described in the literature.[35–42] As seen from the data in Table IV, the proposed method of using a hydrogel system has relatively low adsorption capacities, but the method reaches equilibrium faster than the other methods reported in Table IV. As can be seen from Figure 9, even though the maximum adsorption was gained at pH 0.5, the metal solution pH has not a significant effect on the adsorption capacity. This is advantage, because sorbents have no or low affinity for metals, particularly in strong acidic solutions.

CONCLUSIONS

Thiol-ene-based hydrogels have not been reported in the metal adsorption literature, yet. In this study, photocured a novel thiol-ene hydrogels based on P(Penta3MP4/PEG-DA/HEMA) were investigated for adsorption of Au(III) ions from aqueous solutions purposes.

P(Penta3MP4/PEG-DA/HEMA) hydrogel demonstrated the applicability of thiol-ene-based hydrogel to remove Au(III) ions with a maximum uptake of 45 mg/g by optimizing the adsorption conditions such as suitable copolymer composition, pH, equilibrium time, initial metal ion concentration, and initial solution volume. Also the prepared hydrogel formulation shows good chemical and mechanical stability that facilitate the adsorption at low pH values and desorption of metal ions from the hydrogel without losing its original activity for at least three cycles.

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