Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Removal of Lead and Cadmium Ions from Aqueous Solutions Using Sulphur and Oxygen Donor Ligand Bearing Hydrogels

Melike Fırlak[a]; Ece Kök Yetimoğlu[a]; Memet Vezir Kahraman[a]; Nilhan Kayaman Apohan[a]; Sabahattin Deniz[a]
[a] Faculty of Art and Science, Chemistry Department, Marmara University, İstanbul, Turkey

To cite this Article Fırlak, Melike , Yetimoğlu, Ece Kök , Kahraman, Memet Vezir , Apohan, Nilhan Kayaman and Deniz, Sabahattin(2010) 'Removal of Lead and Cadmium Ions from Aqueous Solutions Using Sulphur and Oxygen Donor Ligand Bearing Hydrogels', Separation Science and Technology, 45: 1, 116 — 128

To link to this Article: DOI: 10.1080/01496390903256208

URL: http://dx.doi.org/10.1080/01496390903256208

Separation Science and Technology, 45: 116–128, 2010
Copyright © Taylor & Francis Group, LLC
ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390903256208

Taylor & Francis
Taylor & Francis Group

Removal of Lead and Cadmium Ions from Aqueous Solutions Using Sulphur and Oxygen Donor Ligand Bearing Hydrogels

Melike Fırlak, Ece Kök Yetimoğlu, Memet Vezir Kahraman, Nilhan Kayaman Apohan, and Sabahattin Deniz
Faculty of Art and Science, Chemistry Department, Marmara University, İstanbul, Turkey

A new thiourea and urea functional monomers were synthesized. A series of hydrogels were prepared by photopolymerization. The hydrogels were used for the removal of Pb(II) and Cd(II) ions from aqueous solutions. The influence of the uptake conditions such as the pH, the time, and the initial feed concentration on the metal ion binding capacity of hydrogel was tested. The selectivity of the hydrogels towards the different metal ions was also tested. The adsorption isotherm models were applied. The limits of detection and quantification were calculated. The usability of the hydrogels for preconcentration studies were also investigated.

Keywords adsorption; heavy metal; hydrogel; preconcentration; sulfonamide

INTRODUCTION

The removal of toxic and polluting metal ions from water and wastewater has a potentially wide range of applications in the preservation of the environment. Filtration, precipitation, neutralization, evaporation, liquid-liquid extraction, ion-exchange resins, bio sorption, reverse osmosis, electrodialysis, and adsorption are the best known treatment techniques. The adsorption is the most important method for the removal of heavy metal ions preferred among others (1). For the recovery and the removal of heavy metal ions polymeric adsorbents are more effective due to their structure, cost effectiveness, reusability, chemical and mechanical strength, and easy handling (2).

Hydrogels are a special class of cross-linked polymers that can swell in water. They alter their dimensions upon a small change in the environmental condition, such as temperature, pH etc. Hydrogels can be prepared by the simple reaction of one or more monomers or by association bonds such as hydrogen bonds and strong van der Waals interactions between chains (3–4). UV-induced crosslinking can be preferred over the wet chemical crosslinking when fast curing rate, little side products, low heat productions, and homogeneous network formation are demanded (5–7). The main advantage of hydrogel sorbents is their easy loading and complexation ability via active groups on their structure. Metal ion chelating polymers called polychelatogens, contain one or more electron donor atoms such as sulphur and oxygen that can form coordinate bonds with most of the toxic heavy metals (8). It is well known that thiourea, urea, and their N-substituted derivatives can coordinate with transition metal ions. These ligands may coordinate via nitrogen, oxygen, or sulphur atoms, often giving complexes with different stereochemistries depending on quiet small changes in the environment of the donor atom (9–11). The low NH- acidity, as well as the possibility of increasing the electron density at sulphur atoms by means of resonance effects, lead to a selective complexing behavior, which can be influenced by adjustment of the pH of the aqueous solution (12).

This paper reports the synthesis of UV-curable polychelatogen hydrogels composed of thiourea and urea modified 2-Acrylamido-2-methylpropane-sulfonic acid, N-vinyl-2-pyrrolidone, acrylic acid and 2-hydroxyethyl methacrylate. N,N′-methylene-bisacrylamide was used as a cross linker. The pH dependent swelling and the gel percentage of the hydrogels was measured. Thermal and morphological behaviors of the hydrogels were determined. The influence of the functional monomer content, the pH, the treatment time, and the initial feed concentration on the amount of the metal ions removed was investigated. Reuse ability and the adsorption capacities of hydrogels under competitive conditions were examined. Preconcentration factor, limits of detection (LOD), and limits of quantification (LOQ) values were calculated and the adsorption isotherm models were applied to the experimental data.

EXPERIMENTAL

Materials

The monomers N-vinyl-2-pyrrolidone (Aldrich), Acrylic acid (Merck), 2-Hydroxyethyl Methacrylate (HEMA), the crosslinker N,N′-methylene-bisacrylamide (MBAAm, Sigma),

---

Received 2 April 2009; accepted 16 July 2009.

Address correspondence to Ece Kök Yetimoğlu, Faculty of Art and Science, Chemistry Department, Marmara University, Stanbul, Turkey. Tel.: +90 216 3479641; Fax: +90 216 3478783. E-mail: ece.kok@gmail.com

and the photoinitiator, 1-hydroxy-cyclohexyl-phenyl-ketone (Irgacure 184, Ciba Specialty Chemicals) were used as received. 2-Acrylamido-2-methylpropane sulfonic acid (AMPS, Sigma), thiourea (TU, Merck), urea (U, Merck), bromine (Br_2, Merck), and triphenylphosphine (Ph_3P, Merck) were used for chelating ligand synthesis. Atomic absorption spectrophotometry standard solutions of 1000 mg L^{-1} Cd(II) and Pb(II) were purchased from Merck. Other dilute standard solutions were prepared from these stock solutions daily. All the other chemicals were of analytical grade and used without further purification. An acetate buffer solution was prepared from acetic acid and NaOH were obtained from Merck. Hydrochloric acid, nitric acid, and thiourea, supplied by Merck, were examined as the desorption agents in the desorption study. Water was distilled using a Milli Q-water purification system (Millipore, Anamed-Turkey) to a resistance of 18.2 MΩcm before use to prepare all of the solutions.

Characterization

FT-IR spectra of modified monomers were recorded on a Shimadzu 8300 FT-IR Spectrometer using the potassium bromide disc method, to define the structure of the products. Thermal properties of hydrogels were investigated by Thermogravimetric analysis (TGA) using a NETZCH Thermogravimetric analyzer. The temperature range was from ambient to 700°C at a heating rate of 10°C/min under nitrogen atmosphere. Morphology of the hydrogels was investigated using a JEOL SEM. The specimen was prepared for SEM by freeze fracturing in liquid nitrogen and applying a gold coating of approximately 300°A. An Analytikjena Zeenit 700 Flame Atomic Absorption Spectrophotometer equipped with a deuterium lamp for continuous background correction was employed.

Synthesis of the Thiourea (AMPSTU) and Urea (AMPSU) Modified Monomers

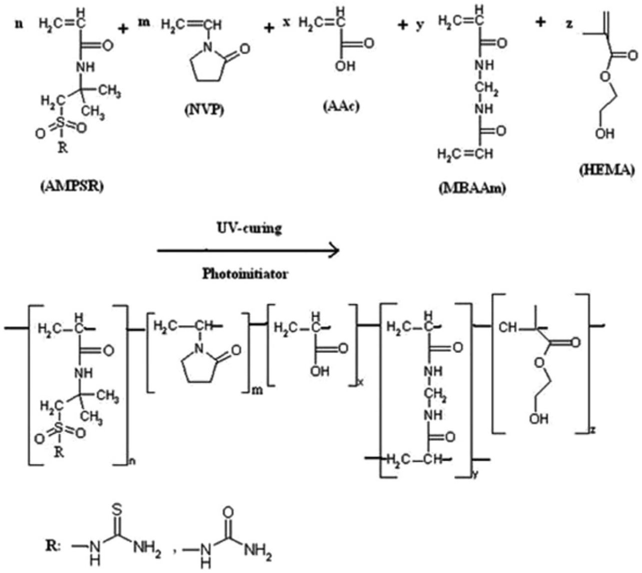
A three necked 1 L flask and a reflux condenser was used as a reactor. First, Ph_3P (10 mmol) and methanol were charged into the reactor and the mixture was stirred until having a suspension. Then to the suspension Br_2 was added drop wise at 0°C. 2-Acrylamido-2-methylpropane-sulfonic acid (10 mmol) was added in portions to the well-stirred reaction mixture. After 1 h at 0°C, the reaction continued at room temperature for an additional 1 h. In the second step, the reaction mixture was cooled down to 0°C again and thiourea (10 mmol) in methanol was added dropwise. After the addition of 10 mmol triethylamine into the flask, the reaction was stirred 1 h at 0°C and 1 h at room temperature. The by-product was completely removed by dissolving the reaction mixture in water and extracting three times with ethyl acetate. The organic layer was then dried over $MgSO_4$ and the solvent was evaporated. Finally, the thiourea modified 2-Acrylamido-2-methyl-propane-sulfonic acid (AMPSTU) monomer was dried at vacuum oven at 30°C for 24 h. The urea modified monomer (AMPSU) was synthesized by using the same procedure (13).

Preparation of Hydrogels

A 1 g batch was prepared consisting of ratios given in Table 1. The P(AMPSTU/NVP/AAc/HEMA) and P(AMPSU/NVP/AAc/HEMA) hydrogels were prepared by dissolving the modified 2-acrylamido-2-methylpropane-sulfonic acid, N-vinyl-2-pyrrolidone, acrylic acid, 2-hydroxyethyl methacrylate in 20 wt% deionized water with various compositions. Then N,N′-methylenebisacrylamide was added as a crosslinker and 1-hydroxycyclohexyl-phenyl-ketone (Irgacure 184) was added as a photoinitiator. Then, the homogenous mixture was transferred to a Teflon® mold. Finally, the formulations were irradiated 10 minutes under a high pressure UV lamp (OSRAM 300 W, $\lambda_{max} = 365$ nm). Scheme 1 shows the synthesis of the thiourea and urea functional hydrogels. The UV-cured hydrogels were taken out from the mold and were immersed in a large excess of deionized water for 1 day to wash out any unreacted monomers and initiators and then dried in a vacuum oven at 30°C for several days until reaching a constant weight. The dry gel samples

TABLE 1
The compositions of hydrogels

Hydrogel	AMPSU (g)	AMPSTU (g)	AAc (g)	NVP (g)	HEMA (g)	MBAAm (g)	Irgacure-184 (g)	H_2O (ml)
U-H0	0	–	0.60	0.15	0.15	0.1	0.03	0.2
U-H5	0.05	–	0.55	0.15	0.15	0.1	0.03	0.2
U-H10	0.10	–	0.50	0.15	0.15	0.1	0.03	0.2
U-H20	0.20	–	0.40	0.15	0.15	0.1	0.03	0.2
TU-H0	–	0	0.60	0.15	0.15	0.1	0.03	0.2
TU-H5	–	0.05	0.55	0.15	0.15	0.1	0.03	0.2
TU-H10	–	0.10	0.50	0.15	0.15	0.1	0.03	0.2
TU-H20	–	0.20	0.40	0.15	0.15	0.1	0.03	0.2



SCH. 1. Synthesis of the thiourea and urea functional hydrogels.

were weighed (Wi) before soak into 25 ml of deionized water at room temperature 20.0 ± 0.1°C. The swollen hydrogel samples were taken out and dried in vacuum oven at 40°C for 1 day. All samples were reweighed (Wd). The percentage of gelation was calculated with the following formula;

$$\text{Gelation (\%)} = (\text{Wd}/\text{Wi}) \times 100 \qquad (1)$$

Swelling Behavior of the Hydrogels

The swelling behavior of dried hydrogel 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 range from 2.0–8.0 at 20°C, 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 until there was no further weight increase. The mass swelling of the hydrogels was calculated from the following formula;

$$\text{Mass Swelling (\%)} = [(m_t - m_0)/m_0] \times 100 \qquad (2)$$

m_0, the initial mass of the hydrogel; m_t, the mass of the hydrogel at time t.

Single-Component Heavy Metal Adsorption Studies

The adsorption properties of hydrogels for metal ions Cd(II) and Pb(II) from aqueous solutions were investigated in batch experiments. The effects of the initial heavy-metal ion concentration and the pH of the medium on the equilibrium adsorption time and adsorption capacity were studied. To investigate the optimum hydrogel formulation for maximum adsorption, the dry gel samples were immersed in a 100 mgL^{-1} single ion solutions at pH 2.0–6.0 at room temperature for 24 h. The time-dependent Pb(II) and Cd(II) ion concentration in aqueous solutions during the removal experiments was measured with solutions containing a metal ion concentration of 500 mgL^{-1} at pH 5.0 for 48 h by using the optimum hydrogel formulations. After the adsorption equilibrium time was determined, the samples were contacted with different concentration of metal ion solutions (100–3000 mg/L) in acetate buffer at pH 5.0 with continuous stirring at 25°C for those predetermined time periods. Metal ion concentrations remaining in the solution after every adsorption stage was determined by using an Analytikjena Zeenit 700 Flame Atomic Absorption Spectrophotometer via applying a deuterium background correction. The instrument response was periodically checked with known heavy metal solution standards. The adsorption experiments were repeated three times and the average value was reported. Metal ion concentrations adsorbed per unit mass of the hydrogel (mg metal ion g^{-1} dry hydrogels) were calculated by using the following expression.

$$\text{The amount of metal ion adsorbed (mg/g)} = [(C_0 - C) \times V)]/(m \times 1000) \qquad (3)$$

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

Multi-Component Heavy Metal Adsorption

It is hoped that in the presence of different metal ions, one metal ion could be selectively adsorbed by a chelating agent. The adsorption capacity of a polymeric ligand towards the different metal ions, the effect of pH of the feed metal solutions, and adsorption equilibrium time are important factors over the selectivity properties of ligands in competitive adsorption. To investigate such items, competitive adsorption of Cd(II), Pb(II), Hg(II), and Au(III) ions by the P(AMPSTU/NVP/AAc/HEMA) and P(AMPSU/NVP/AAc/HEMA) hydrogels from solutions containing them together was carried out. The concentration of each metal ion in the mixture was 1 mmol L^{-1}. The pH of this solution was adjusted to 5.0 and in order to adjust salinity, 700 mg/L NaCl was added to the synthetic wastewater (2). In experiments, a fixed amount of hydrogels was equilibrated with the mixture of metal ion solutions and the adsorption of each metal ion was followed up to 24 h contact time.

Recovery and Reuse

Elution of the metals from the hydrogels was carried out in 10 mL of 0.8 M thiourea and 3 M HCl, 0.5 M HNO_3 and 1 M HNO_3 solutions for several times up to 72 h. The hydrogels (0.05 g) were placed in the elution medium and stirred with a magnetic stirrer at 150 rpm at room temperature. The released metal ion amount was determined using a FAAS according to the guidelines of the manufacturers. Thereafter, the hydrogel was washed with deionized water and again subjected to adsorption processes in order to determine the reusability of the hydrogels. To determine the reusability of the hydrogels, consecutive adsorption-elution cycles were repeated five times by using the same hydrogels. The desorption ratio was calculated by the following equation;

$$\text{Desorption Ratio} = \frac{\begin{array}{c}\text{Amount of metal ions desorbed}\\ \text{into the elution medium}\end{array}}{\begin{array}{c}\text{Amount of metal ions adsorbed}\\ \text{onto the hydrogels}\end{array}} \times 100 \tag{4}$$

Thereafter, the hydrogel was washed with deionized water and again subjected to adsorption processes in order to determine the reusability of the hydrogels.

Preconcentration Factor

Pb(II) and Cd(II) ion solutions were used for the preconcentration of the metal ions on the hydrogels. In order to investigate the efficiency of the hydrogels for the enrichment of Cd(II) and Pb(II) from different concentrations (1–0.1 mg/L) and different volumes (50–500 ml) were prepared and the hydrogels were immersed in the solutions and stirred for 24 h at 150 rpm. Then the hydrogels were separated from the adsorption medium and transferred into 5 ml 0.5 M HNO_3 solution and stirred with 150 agitation rate at room temperature for 24 h. After all, the concentration of desorption solutions were measured by FAAS and the preconcentration factor is calculated by the ratio of the highest sample volume and the desorption agent volume (5 ml).

RESULTS AND DISCUSSION

In this work, a new thiourea/urea modified AMPS based hydrogels were prepared by UV-curing technique and their metal adsorption capacity were investigated.

Characterization

The chemical structures of the thiourea and urea modified AMPS monomers (AMPSTU, AMPSU) were characterized by FT-IR spectroscopy. Figure 1(a,b) displays the FT-IR spectra of AMPSTU and AMPSU monomers. As seen in Fig. 1, the characteristic peaks for amide II and C=C double bonds appear at 1670 cm^{-1} and 1620 cm^{-1} respectively. At 1418 cm^{-1} the $-CH_2$ group adsorption bond can be seen in which $-CH_2$ group is attached to SO_2. CH_3 groups vibration can be seen in 1385 cm^{-1} beside FT-IR spectra consist of other peaks located at 1118 cm^{-1} and 980 cm^{-1} for asym. and sym. SO_2 stretching. In addition NH bonding vibrations of urea and thiourea groups appear at 1576 cm^{-1} and a shoulder. The characteristic absorption peaks of thiourea and urea units can be seen also at 1440 cm^{-1} due to strong C=S and C=O linked to nitrogen atom. The peaks at 1200 cm^{-1} and 1170 cm^{-1} are related to the sulfonamide groups. In addition N-H plane bonding peak can be seen in 780 cm^{-1} (8,10).

The feed compositions are collected in Table 1 and the gelation and equilibrium swelling percentages are summarized in Table 2. The gel percentages of thiourea and urea modified hydrogels varied between 89–93 wt% and 86–89 wt%, respectively. A decrease in equilibrium swelling percentage was observed with the replacement of acrylic acid monomer with thiourea/urea modified AMPS monomer. The ionic groups on the network chains are responsible for higher swelling due to the osmotic pressure exerted by counter-ions. For thiourea/urea modified hydrogels the decrease in swelling may be attributed to the formation of H-bonding between the C=O groups of acrylic acid and N-H groups of thiourea/urea modified AMPS. This leads to the existence of osmotically passive counter-ions inside the swollen gel, which do not contribute to the swelling process (11). The thermal degradation behaviors of the thiourea/urea modified hydrogels were assessed by TGA analysis in nitrogen atmosphere. Figure 2(a,b) shows TGA thermograms of the TU-H5 and U-H10 hydrogel samples. The thermograms showed that the polymers have good thermal stability. One can see that hydrogels begin to degrade after 100°C followed by rapid loss around 380°C. The weight loss around 100°C ($\sim$5 wt%) can be emerged from the evaporation of physically absorbed water. The SEM image of vacuum dried hydrogel (TU-H5) is shown in Fig. 3. Fractured surface morphology of the hydrogel displays nonuniform pore sizes. It is known that the pore size is greatly affected by the drying method and the freezing rate (12). Figure 4 displays pH dependence of the equilibrium swelling percentage of P(AMPSTU/AAc/NVP/HEMA) hydrogel (TU-H5) and P(AMPSU/AAc/NVP/HEMA) hydrogel (U-H10) at 20°C in buffer solutions from pH = 2 to 8. It can be seen that the percent swelling of hydrogels increased with increasing pH. The maximum swelling was found at pH 8 for both hydrogels.

pH and Chelating Ligand Effect

The thiourea/urea modified AMPS affects the removal capacity of the hydrogels. It is well known that the pH

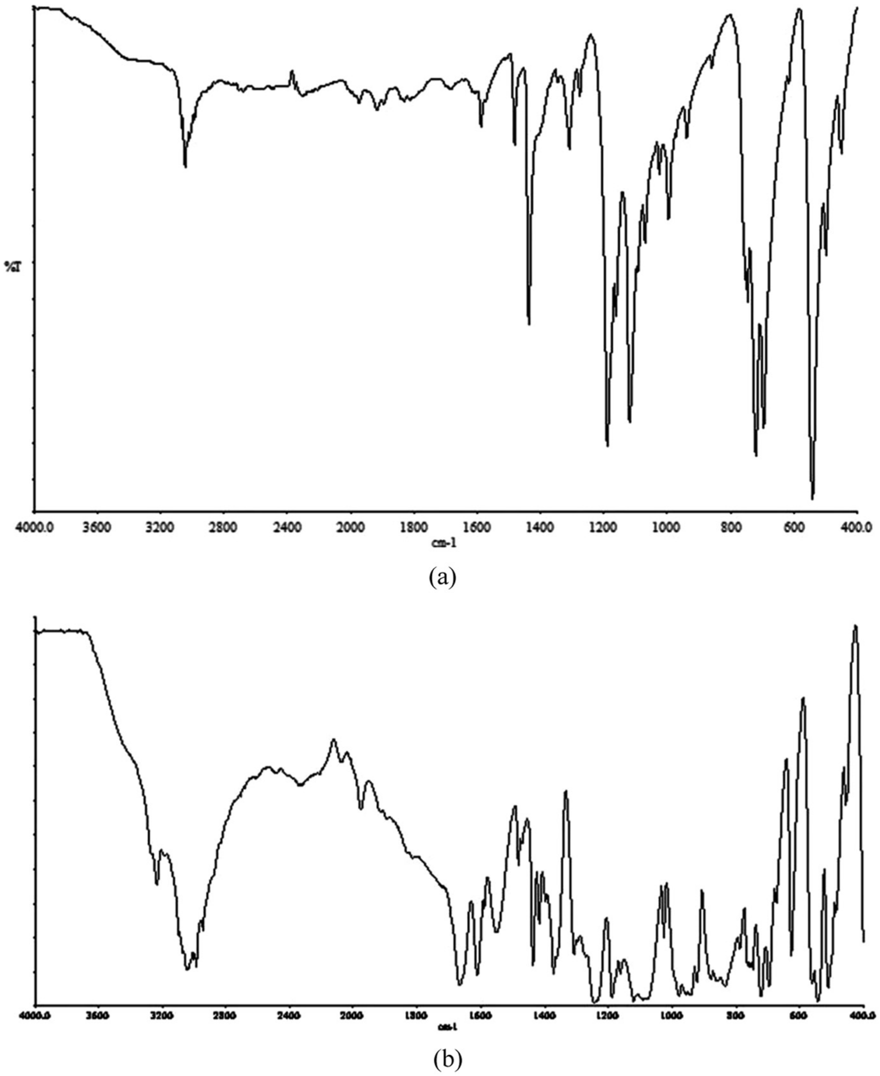
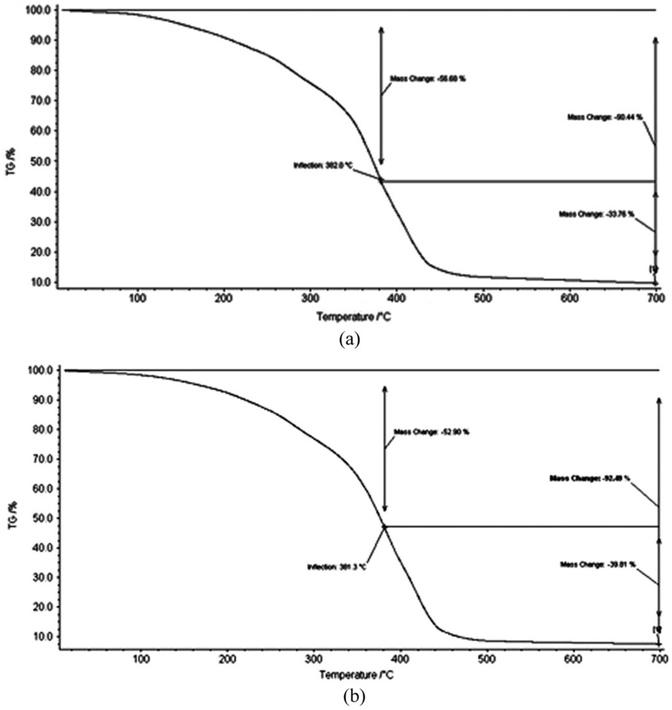


FIG. 1. FT-IR spectrum of AMPSTU monomer (a) and AMPSU monomer (b).

is also a critical parameter that can affect the hydrogel performance by influencing its swelling and ion uptake capability. For selective adsorption, besides the use of a specific ligand modified sorbent, selectivity could be achieved by adjusting medium pH to different values (14). Chelating of a metal ion by a polymeric ligand is highly dependent on the pH of the medium. Since most of the metal ions are prone to precipitation at higher pH, investigations were limited to those pH values where precipitation was just prevented. The pH of the medium has two kinds of influence on metal uptake: an effect on solubility and speciation of metal ion in aqueous solution, and an overall charge of the ligand of the adsorbent (15). In this study, to evaluate the effect of the pH on the adsorption capacity of polymers, the adsorption experiments were carried in solutions having different pH values and the results were given in Fig. 5(a,b,c,d). The maximum metal ion uptake was achieved by using TU-H5 and U-H10 hydrogels. The thiourea/urea modified AMPS in the hydrogel structure is primarily responsible for the specific binding

TABLE 2
Gelation and swelling percentages of hydrogels

Hydrogel	Gelation (%)	Swelling (%)
U-H0	86.77	55.27
U-H5	87.62	49.84
U-H10	88.73	42.46
U-H20	89.98	40.26
TU-H0	90.92	65.72
TU-H5	91.08	48.20
TU-H10	93.67	35.66
TU-H20	89.96	28.57



(a)

(b)

FIG. 2. TGA curves of thiourea (a) and urea (b) functional hydrogels.

of metals due to the coordination between sulphur, oxygen and metal ions and functional groups. Moreover, as can be seen in Fig. 5(a,b,c,d), the adsorption capacity of the hydrogels was increased with increasing pH. This can be explained by the increasing electrostatic effects between protonated sulfonamide groups and metal ions. At lower pH values the functional groups are most protonated and cannot bind with metal ions, on the other hand at weak acidic medium the adsorption capacities of hydrogels are maximum because of weakly protonated hydrogels.

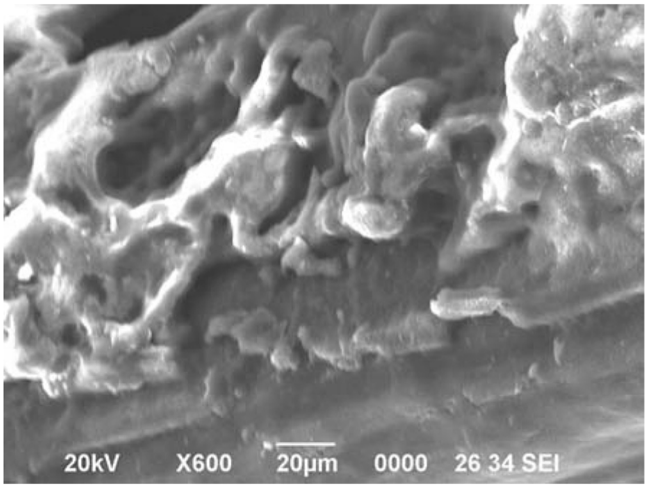
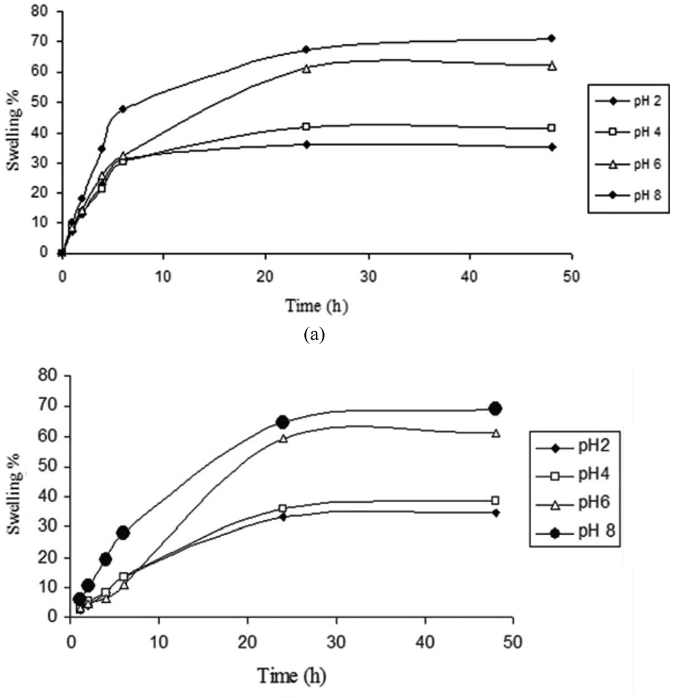


FIG. 3. Scanning electron microscope (SEM) image of the (TU-H5) hydrogel.



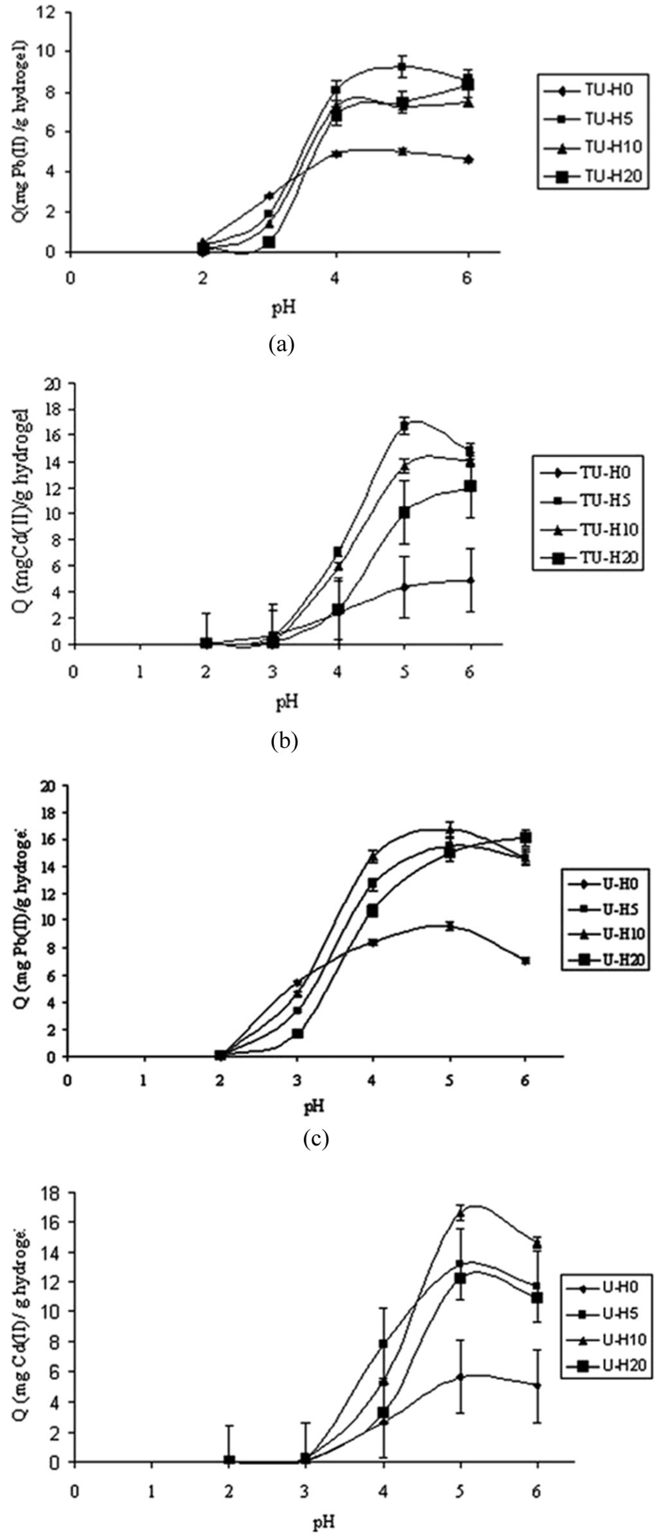
(a)

(b)

FIG. 4. Swelling behavior of thiourea (a) and urea (b) functional hydrogels.

Initial Metal Ion Concentration Effect

To determine the effect of initial metal ion concentration on adsorption capacity, the hydrogels were equilibrated with a serious of metal ion solutions of gradually increasing concentration. Adsorption capabilities of the hydrogels towards Cd(II) and Pb(II) ions with different initial ion solution concentrations varying from 100–3000 $\mathrm{mg\,L^{-1}}$ was given in Fig. 6. All measurements were performed at optimum pH. Sorption capacities of the hydrogels are presented as a function of initial concentration of metal ions within the aqueous solutions in Fig. 6. It can be seen that the equilibrium metal ion concentration increases with increasing initial acid concentration. First, the metal uptake increases rapidly with increasing initial metal ion concentration, then it reaches saturation and gives a plateau after 300 mg/L. From these plateaus values, one can easily estimate the maximum load capacities as 34.67 ± 1.20 and $35.87 \pm 2.70\,\mathrm{mg\,g^{-1}}$ dry hydrogel for Pb(II) and Cd(II) ions respectively in the case of thiourea modified hydrogel, and $24.31 \pm 1.85\,\mathrm{mg\,g^{-1}}$ and $24.68 \pm 3.12\,\mathrm{mg\,g^{-1}}$ dry hydrogel for Pb(II) and Cd(II) ions respectively in the case of urea modified hydrogel.



(a)

(b)

(c)

(d)

FIG. 5. Effect of pH, AMPSTU percent on Pb(II) (a) and Cd(II) (b) and AMPSU percent on Pb(c) and Cd(II) (d) uptake capacities of thiourea/urea modified hydrogels.

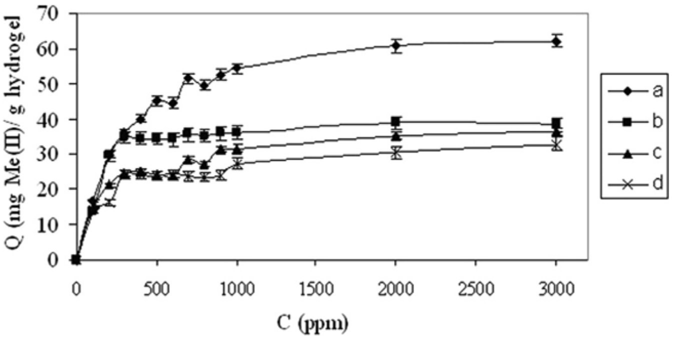


FIG. 6. Effect of initial metal ion concentration on adsorption capacity of thiourea/urea modified hydrogels; (a) TU-H5: Cd(II), (b) TU-H5 Pb(II), (c) U-10 Cd(II), (d) U-10 Pb(II).

Adsorption Isotherms

The interaction between the adsorbents and the adsorbates can be described with adsorption isotherms, so adsorption isotherms are critical in optimizing the use of adsorbents (16). When an adsorbent is in contact with the surrounding fluid of a certain composition, adsorption takes place and after a sufficiently long time, the adsorbent and the surrounding fluid reach equilibrium (17). The correlation of equilibrium data is necessary to the practical design and operation of adsorption systems (16). Results obtained from the adsorption isotherm were evaluated by means of the Langmuir and Freundlich adsorption models. The Langmuir equation was originally developed to describe individual chemical adsorbents, and is applicable to physical adsorption (monolayer) within a low concentration range. The Freundlich equation is an empirical approach for adsorbents with very uneven adsorbing surfaces. This model is applicable to adsorption of a single solute system within a fixed range of concentration (18). The equations of the above two types of sorption isotherms are expressed as follows:

$$\ln q_e = \ln K_F + \frac{1}{n}(\ln C_e) \tag{3}$$

$$q_e = \frac{Q_m \cdot k_L \cdot C_e}{1 + k_L \cdot C_e} \tag{4}$$

where q_e is equilibrium uptake capacity of hydrogels, C_e is the concentration of metal ions in the supernatant after sorption, n and K_F are empirical constants, Q_0 and k_L are Langmuir's constants related to the capacity and energy of the adsorption. In order to investigate the effect of the initial metal ion concentration on the adsorption capacity of the hydrogels, the experiments were carried out at initial metal ion concentrations between 100 and 3000 mg/L. The adsorption study was carried out at 25°C for 24 h. Langmuir and Freundlich isotherm plots

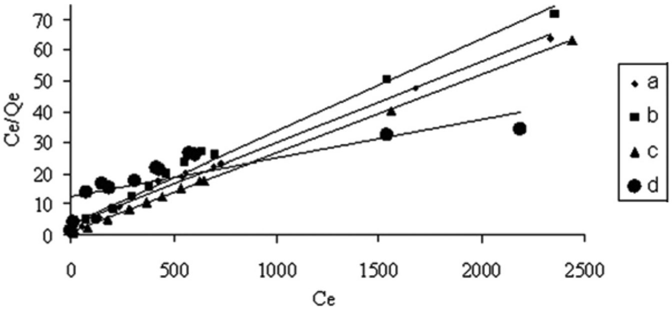


FIG. 7. Langmuir isotherm plots for the adsorption of Pb(II) and Cd(II) ions on thiourea/urea modified hydrogels; (a) U-10: Cd(II), (b) U-10: Pb(II), (c) TU-5: Pb(II), (d) TU-5: Cd(II).

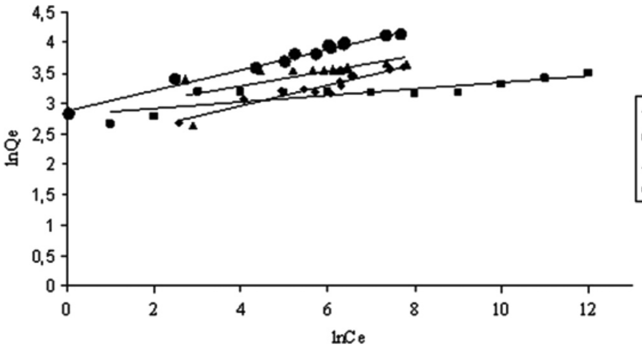


FIG. 8. Freundlich isotherm plots for the adsorption of Pb^{2+} and Cd^{2+} ions on thiourea/urea modified hydrogels.

for the adsorption of metal ions from aqueous solution by the hydrogels are presented in Figs. 7 and 8 and the constants of adsorption isotherms are summarized in Table 3. It can be seen from the data of Table 3 that the Langmuir equation fits well for metal ion adsorption on the hydrogels.

Adsorption Kinetics

The rapid adsorption of metal ions by the adsorbent is important for the feasible processes, shortening the treatment of wastewater during filtration. Therefore, the saturation time for metal uptake of the thiourea and urea modified hydrogels are determined keeping the initial metal ion concentration constant. The change in amount of adsorbed metal ions with time for hydrogels is shown in Fig. 9. The figure represents the maximum binding of the all-metal ions occurred within the 24 h and remained uniform throughout the 48 h. It was observed that the adsorption process was very fast and the equilibrium was approached within the first 24 h of the process. After this period, the adsorption rate was very slow and saturation was reached within approximately 48 h for all metal ions. This type of adsorption behavior in the later stage is typical of the specific adsorption process in which the adsorption rate is dependent upon the number of available adsorption sites on the surfaces of the adsorbent and the amount of adsorption is usually controlled by the attachment of the metal ions on the surfaces, most probably through the chelating interaction mechanism (19). The adsorption behavior of metal ions is directly related to some experimental factors such as the pH, the characteristics and the porosity of hydrogel, the dimensions of the metal ion, and the properties of donor ligands (20).

Multi-Component Heavy Metal Chelation

Chelating of heavy metals from synthetic wastewater was carried out in a batch system. The results show that, the binding capacities of all ions were decreased under the competitive conditions. The competitive adsorption of Pb(II), Cd(II), Hg(II), and Au(III) by hydrogels was found to be Pb(II)>Au(III)>Cd(II)>Hg(II) for both thiourea/urea modified hydrogels (Table 4).

Recovery and Reuse

The adsorption and desorption processes were repeated to examine the potential of thiourea/urea modified hydrogels for practical applications. The desorption behavior of hydrogels was studied using acidic desorption solutions, and the results are summarized in Table 5. We used an acidic desorption agent because it is known that metal ion uptake drops significantly at low pHs. While the functional groups of hydrogels are protonated the metal ions cannot coordinate with these groups. For this reason, the metal ions can be recovered by decreasing the pH. In this

TABLE 3
Equations of adsorption isotherms of thiourea/urea modified hydrogels

	Freundlich		Langmuir			
Hydrogel and adsorbed metal ion	Model	R^2	Model	R^2	Q_m	k_L
TU-5 Pb(II)	$\ln q_e = 0.126 \ln C_e + 2.778$	0.512	$C_e/q_e = 0.026C_e + 0.865$	0.999	38.46	0.030
TU-5 Cd(II)	$\ln q_e = 0.169 \ln C_e + 2.871$	0.982	$C_e/q_e = 0.016C_e + 1.224$	0.996	62.50	0.013
U-10 Pb(II)	$\ln q_e = 0.133 \ln C_e + 2.403$	0.842	$C_e/q_e = 0.030C_e + 3.696$	0.987	33.33	0.080
U-10 Cd(II)	$\ln q_e = 0.168 \ln C_e + 2.294$	0.932	$C_e/q_e = 0.027C_e + 3.776$	0.991	37.04	0.030

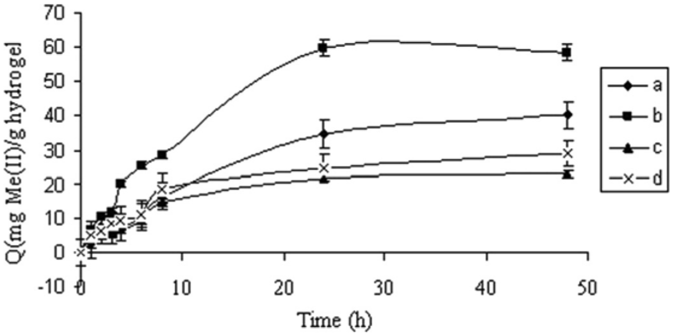


FIG. 9. The saturation time for metal uptake of thiourea/urea functional hydrogels; (a) TU-H5: Cd(II), (b) TU-H5 Pb(II), (c) U-10 Cd(II), (d) U-10 Pb(II).

experiment the thiourea and urea modified hydrogels were completely saturated with the metal ions at the optimum pH, initial metal ion concentration and time. Then, adsorbed metal ions were desorbed by using 0.5 M HNO_3. The desorption ratio of thiourea modified hydrogel for Cd(II) ions is 85% and as shown in Table 5 it is the lowest desorption value measured when compared other hydrogel-metal combinations. In the case of Pb(II), nearly 100% desorption percentage was obtained. This large difference can be explained in terms of hard-soft acid-base effects. Although exceptions exist, the general rule is that hard acids bind preferentially to hard bases and soft acids to soft bases. Cd(II) is a soft metal center and so the hard oxygen ligand of AMPSU units interacts only poorly with it. On the other hand, softer sulfur ligand such as AMPSTU monomer prefers soft acids while the hard oxygen ligand AMPSU is preferring hard acids. AMPSTU and Cd(II) are both soft base and acid respectively and can be stabilized by covalent-like bonds. The Cd(II) ion will bind more avidly to the exposed soft ligand of AMPSTU than intermediate acid Pb(II) (21). In order to obtain the reusability of the thiourea and urea modified hydrogels, the adsorption-desorption cycles were repeated at least 5 times by using the same hydrogel without loss of adsorption capacity. Table 5 represents the regeneration procedure by treatment with 0.5 M HNO_3 solution showed that desorption efficiency was generally high and the modified polymers could be used five times without loss of their adsorption capacities.

Preconcentration Factor (PF)

The enrichment factor was studied by a recommended procedure using increasing volume of metal ion solution and keeping the total amount of loaded metal ions constant to 10 mg/L for Pb(II) and Cd(II). The preconcentration factors were calculated from experimental results. As can be seen from Table 6, the results demonstrated that the recoveries were quantitative ($\geq$93) up to 250 ml initial volume, except thiourea based hydrogel with Cd(II). In the case of TU-H5 hydrogel recovery of Cd(II) changed between 37 and 89% at different spike levels. Insufficient recovery is probably due to the strong complexation between thiourea based hydrogel and the Cd(II). The recovery values decreased with increasing the initial sample volume. Preconcentration factors of both TU-H5 and U-H10 modified hydrogels were found 50 for Pb(II). It was found to be 20 for TU-H5 for Cd(II) and it was found to be 50 for U-H10 for Cd(II).

Limits of Detection and Quantification

0.50 mg/L, 1.00 mg/L, 1.50 mg/L, 2.00 mg/L, 2.50 mg/L, 3.00 mg/L 5.00 mg/L standard solutions of Pb(II) and 0.01 mg/L, 0.10 mg/L, 0.2 mg/L, 0.40 mg/L, 0.60 mg/L, 0.80 mg/L, 1 mg/L standard solutions of Cd(II) were prepared. LOD and LOQ values were calculated using the standard deviation value of the replicate measurements of lowest concentration in the linear calibration plot ($k = 7$ and $n = 10$). The limits of detection (LOD) calculated by the following equation:

$$\mathrm{LOD} = 3 \times s_b/m \tag{5}$$

where, s_b is standard deviation of solutions and m is the slope.

The limit of detection and limit of quantification values were summarized in Table 7.

TABLE 4
Multi-component heavy metal adsorption capacities

	P(AMPSTU/AAc/NVP/HEMA)				P(AMPSU/AAc/NVP/HEMA)			
	Q_1 (mmol/g)	Q_2 (mmol/g)	Q_3 (mmol/g)	$Q_{average}$ (mmol/g)	Q_1 (mmol/g)	Q_2 (mmol/g)	Q_3 (mmol/g)	$Q_{average}$ (mmol/g)
Pb(II)	0.052	0.067	0.069	0.063	0.058	0.055	0.048	0.054
Cd(II)	0.008	0.010	0.011	0.010	0.007	0.005	0.006	0.006
Hg(II)	0.009	0.007	0.010	0.009	0.002	0.002	0.001	0.002
Au(III)	0.025	0.032	0.034	0.030	0.026	0.021	0.022	0.023

TABLE 5
The results of adsorption and desorption capacities of hydrogels

	Thiourea modified hydrogel				Urea modified hydrogel			
Cycle	Adsorption (mg Cd(II)/g hydrogel)	Desorption %	Adsorption (mg Pb(II)/g hydrogel)	Desorption %	Adsorption (mg Cd(II)/g hydrogel)	Desorption %	Adsorption (mg Pb(II)/g hydrogel)	Desorption %
1	36.32	87.68	34.68	99.65	26.32	96.45	20.86	99.74
2	35.79	87.45	35.92	99.02	26.22	96.32	20.72	99.13
3	35.88	84.95	36.21	98.73	26.09	96.18	19.56	98.56
4	35.26	85.23	35.81	98.24	26.05	95.84	19.28	98.02
5	34.84	83.27	35.66	97.86	25.89	95.46	19.32	97.87

TABLE 6

Pb(II) and Cd(II) recovery results for ultra pure water with thiourea/urea modified hydrogels

			Thiourea modified hydrogel		Urea modified hydrogel	
Pb(II) spike (mg/L)	Initial volume (ml)	Enrichment factor	Pb(II) found (mg/L)	Recovery (%)[a,b]	Pb(II) found (mg/L)	Recovery (%)[a,b]
1.0	50.0	10.0	9.971 (±0.2)	99.71 (±2)	9.998 (±0.1)	99.98 (±1)
0.5	100.0	20.0	9.748 (±0.4)	97.48 (±4)	9.507 (±0.3)	95.07 (±3)
0.2	250.0	50.0	9.443 (±0.3)	94.43 (±3)	9.328 (±0.5)	93.28 (±5)
0.1	500.0	100.0	9.206 (±0.7)	92.06 (±7)	8.527 (±0.6)	85.27 (±6)

			Thiourea modified hydrogel		Urea modified hydrogel	
Cd(II) spike (mg/L)	Initial volume (ml)	Enrichment factor	Cd(II) found (mg/L)	Recovery (%)[a,b]	Cd(II) found (mg/L)	Recovery (%)[a,b]
1.0	50.0	10.0	8.93 (±0.3)	89.34 (±3)	9.83 (±0.3)	98.34 (±3)
0.5	100.0	20.0	8.84 (±0.2)	88.41 (±2)	9.74 (±0.2)	97.43 (±2)
0.2	250.0	50.0	5.53 (±1.0)	55.37 (±10)	9.53 (±0.4)	95.37 (±4)
0.1	500.0	100.0	3.55 (±0.8)	37.50 (±8)	9.25 (±0.3)	92.50 (±3)

[a] Final volume: 10.0 ml.

[b] n = 3.

TABLE 7
Analytical characteristics of the method

Element	Concentration range (mg/L)	Regression equation	R^2	LOD (mg/l)	LOQ (mg/l)
Pb	0.50–3.00	$y = 0.0174x + 0.0016$	0.9916	0.30	0.90
Cd	0.05–1.00	$y = 0.2706x + 0.0027$	0.9997	0.01	0.03

TABLE 8
Comparative data from some recent studies for adsorption of heavy metals by polymeric adsorbent systems

System	Studied metal	pH	Adsorption capacity mg/g	PF	LOD mg L^{-1}	Reference
2,3-dihydroxybenzaldehyde functionalized Amberlite XAD-4	Cu, Co, Ni, Cd, Pb	6.0	–	13.3	0.01–0.10	22
N-vinylpyrrolidone/acrylic acid/2-acrylamido-2-methylpropane sulfonic acid	Cd, Cu, Fe	5 (2.5 for Fe)	25–74	–	–	7
o-Aminophenol functionalized amberlite XAD-2	Cu, Cd, Co, Ni, Zn, Pb	5.6–7.2 (for Cd), 5.0–6.0 (for Pb)	3.32–3.42	40–50	2.00–30.00*	23
Poly(vinyl pyridine-poly ethylene glycol methacrylate-ethylene glycol dimethacrylate)	Cu, Cd, Cr, Pb	6.0–8.0	16.50–18.23	–	–	24
Poly(glycidyl methacrylate-aspartic acid)	Cu, Cd	4.0–5.0	1.28–1.40	–	–	25
Thiourea functional hydrogel	Pb, Cd	5	35–41	50	0.01–0.30	This work
Urea functional hydrogel	Pb, Cd	5	26	20–50	0.01–0.30	This work

*μg/L^{-1}

Comparison with Other Methods

A comparison of the proposed systems with other systems is given in Table 8. Some parameters obtained were comparable to those presented by other methods described in the literature. As seen from the data in Table 8, the proposed method developed by using modified AMPS monomers systems have relatively high adsorption capacities and higher pH values in comparison to other methods reported in Table 8.

CONCLUSIONS

In this study, thiourea and urea modified AMPS monomers (AMPSTU, AMPSU) were synthesized and the preparation of the novel thiourea/urea modified hydrogels prepared by UV-curing technique and their selective metal binding properties were investigated. It has been found that the adsorption capacity of hydrogels increases with increasing AMPSTU and AMPSU content in the gel structure and then decreases. The decrease in adsorption by further increase in AMPSTU and AMPSU monomer content has been explained by the formation of H-bonding between the functional groups in the network chain and consequent lower swelling capacity of the gels. The effects of pH, time, and initial metal ion concentration were investigated. The optimum conditions obtained were: pH value = 5.0, contact time = 24 h, initial concentration = 300 mg/L for the adsorption experiments. Regeneration studies showed that the modified polymers could be used at least five times without loss of their adsorption capacities. The desorption ratios of Pb(II) ions from hydrogels were higher than the desorption ratios of Cd(II) ions. The results indicate that the Langmuir equation fits well to the sorption of metal ions onto hydrogels. The results show that the theoretical maximum adsorption capacities are nearly equal to the values which were found empirically. The relatively high preconcentration factors reveal that trace metal ions in mg/L level can be determined by using these hydrogels as adsorbent. Moreover, the limits of detection and the quantification values demonstrate that the thiourea/urea modified hydrogels show a promising application potential for wastewater treatment.

ACKNOWLEDGEMENTS

This work was supported by Marmara University, Commission of Scientific Research Project under grant FEN-BGS-290506-0116.

REFERENCES

1. Rether, A.; Schuster, M. (2003) Selective separation and recovery of heavy metal ions using water-soluble *N*-benzoylthiourea modified PAMAM polymers. *Reactive and Functional Polymers*, *57*: 13–21.
2. Kara, A.; Uzun, L.; Beşirli, N.; Denizli, A. (2004) Poly(ethylene glycol dimethacrylate-*n*-vinyl imidazole) beads for heavy metal removal. *J. Hazardous Materials*, *106B*: 93–99.
3. Kılıç, A.G.; Malcı, S.; Çelikbıçak, Ö.; Şahiner, N.; Salih, B. (2005) Gold recovery onto poly(acrylamide-allylthiourea) hydrogels synthesized by treating with gamma radiation. *Analitica Chimica Acta*, *547*: 18–25.
4. Ratner, B.D.; Hoffman, A.S.; Schoen, F.J.; J. Lemons, E. (1996) *Biomaterials Science An Introduction to Materials in Medicine*, 1st Ed.; Academic Press, New York.
5. Chen, K.S.; Ku, Y.A.; Lin, H.R.; Yan, T.R.; Sheu, D.C.; Chen, T.M.; Lin, F.H. (2005) Preparation and characterization of pH sensitive poly(*N*-vinyl-2-pyrrolidone/itaconic acid) copolymer hydrogels. *Materials Chemistry and Physics*, *91*: 484–489.
6. Lopergolo, L.C.; Lugao, A.B.; Catalani, L.H. (2003) Direct UV photocrosslinking of poly(*N*-vinyl-2-pyrrolidone) (PVP) to produce hydrogels. *Polymer*, *44*: 6217–6222.
7. Kök Yetimoğlu, E.; Kahraman, M.V.; Ercan, Ö.; Akdemir, Z.S.; Kayaman Apohan, N. (2007) *N*-vinylpyrrolidone/acrylic acid/2-acrylamido-2-methylpropane-sulfonic acid based hydrogels: Synthesis, characterization and their application in the removal of heavy metals. *Reactive & Functional Polymers*, *67*: 451–460.
8. Hag Ali, A.E.; Shawky, H.A.; Abd El Rehim, H.A.; Hegazy, E.A. (2003) Synthesis and characterization of PVP/AAc copolymer hydrogel and its applications in the removal of heavy metals from aqueous solution. *European Polymer Journal*, *39*: 2337–2344.
9. Tarantelli, T.; Chiary, B. (1976) Transition metal complexes of sulfur-oxygen chelating ligands Synthesis and characterisation of polymethylen-1-(phenylthiourea)-*n*-(phenylurea) complexes of cobalt(II). *Journal of Inorganic Nuclear Chemistry*, *39*: 1549–1553.
10. Refat, M.S.; Teleb, S.M.; S Sadeek, A. (2004) A novel method for preparation of cobalt(II) and lead(II) carbonates. *Spectrochimica Acta Part A*, *60*: 2803–2805.
11. Okay, O.; Sarıışık, S.B.; Zor, S.D. (1998) Swelling behavior of anionic acrylamide-based hydrogels in aqueous salt solutions: Comparison of experiment with theory. *Journal of Applied Polymer Science*, *70*: 567–575.
12. Beyer, L.; Hoyer, E.; Liebscher, J.; Hartmann, H. (1981) Komplexbildung mit N-Acylthioharnstoffen. *Z. Chem.*, *21*: 2181.
13. Kataoak, T.; Iwama, T.; Setta, T.; Takagi, A. (1998) Preparation of sulfonamides from sodium sulfonates: $Ph_3P.Pr_2$ and Ph_3P.cıota 2 as a mild halogenatıng reagent for sulfonyl bromıdes and sulfonyl chlorides. *Synthesis*, *4*: 423–426.
14. Rivas, B.L.; Pooley, S.A.; Maturana, H.A.; Villegas, S. (2001) Metal ions uptake of acrylamide derivatives resins. *Macromol. Chem. Phys.*, *202*: 443–447.
15. Pekel, N.; Güven, O. (2004) Separation of heavy metal ions by complexation on poly (N-vinyl imidazole) hydrogels. *Polymer Bulletine*, *51*: 307–314.
16. Wong, Y.C.; Szeto, Y.S.; Cheung, W.H.; McKay, G. (2003) Equilibrium studies for acid dye adsorption onto chitosan. *Langmuir*, *19*: 7888–7894.
17. Suzuki, M. (Tokyo) (1990) *Adsorption Engineering*; Kodansha LTD.
18. Meghea, A.; Rehner, H.H.; Peleanu, I.; Mihalache, R. (1998) Test-fitting on adsorption isotherms of organic pollutants from waste waters on activated carbon. *J. Radioanal. Nucl. Chem.*, *229*: 105–110.
19. Oktar, C.; Yılmaz, L.; Özbelge, H.Ö.; Bıçak, N. (2008) Selective mercury uptake by polymer supported hydroxyethyl sulfonamides. *Reactive and Functional Polymers*, *68*: 842–850.
20. Kaşgöz, H. (2006) New sorbent hydrogels for removal of acidic dyes and metal ions from aqueous solutions. *Polymer Bulletine*, *56*: 517–528.
21. Marusak, R.A.; Doan, K.; Cummings, S.D. (2007) *Integrated Approach to Coordination Chemistry An Inorganic Laboratory Guide*; John Wiley& Sons Inc.
22. Kara, D.; Fisher, A.; Hill, S. J. (2009) Determination of trace heavy metals in soil and sediments by atomic spectrometry following preconcentration with Schiff bases on Amberlite XAD-4. *Journal of Hazardous Materials*, *165*: 1165–1169.
23. Kumar, M.; Rathore, D. P. S.; Singh, A. K. (2000) Amberlite XAD-2 functionalized with *o*-aminophenol: Synthesis and applications as extractant for copper(II), cobalt(II), cadmium(II), nickel(II), zinc(II) and lead(II). *Talanta*, *51*: 1187–1196.
24. Duran, A.; Soylak, M.; Tuncel, S. A. (2008) Poly(vinyl pyridine-poly ethylene glycol methacrylate-ethylene glycol dimethacrylate) beads for heavy metal removal. *Journal of Hazardous Materials*, *155*: 114–120.
25. Chen, C. Y.; Lin, M. S.; Hsu, K. R. (2008) Recovery of Cu(II) and Cd(II) by a chelating resin containing aspartate groups. *Journal of Hazardous Materials*, *152*: 986–993.