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Uranyl ion binding properties of poly(hydroxamic acid) hydrogels

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Summary

Poly(hydroxamic acid) (PHA) hydrogels, obtained from the synthesis of crosslinked poly(acrylamide) (PAAm) gels have been prepared, and their uranyl ion binding properties from two different sources were investigated. Swelling and binding parameters of crosslinked PHA gels were determined from swelling and uranyl ion adsorption studies. The effect of uranyl ion concentration, pH, temperature and mass of adsorbent on the uranyl ion adsorption were examined. The binding process between PHA and uranyl ions complies with the S type adsorption according to Giles classification. Free energies of the adsorptions found as negative values indicating spontaneous adsorption process. The structure and hydrophilicity of the used crosslinkers, the ionogenity of PHA polymers and the source of uranyl ions found to be effective on the swelling and binding behaviors of PHA hydrogels.

Key words: poly(hydroxamic acid), adsorption, uranyl ion, swelling, binding

Introduction

Polymeric substrates are being continuously developed and used for the purpose of complexation with metal ions either for ion-exchange or selective adsorption purposes. These polymeric ligands are tailored synthesized to remove certain metal ions or groups from aqueous media [1]. To recover uranium from seawater, mining water or wastewater, many different polymeric chelates used, but there are relatively fever studies related with hydrogels designed and synthesized for the uranyl ion adsorption from aqueous solutions. For the separation, in the use of chelating functional group containing hydrogels, some features of adsorbent such as durability, reusability, and practical applicability are very important. In this aspect, hydrogels have some advantages over other systems [2]. For the purpose of uranyl ion adsorption from aqueous solutions, we have synthesized different diprotic containing acrylamide based hydrogels with radiation technique [3, 4]. As know from literature hydroxamic acid groups have the ability to form stable complexes with various metal ions. There are numerous studies for the preparation hydroxamic acid functionality containing adsorbent from various polymers with different methods. Since there are no easily avaible monomers with pendant hydroxamic acid groups, these types of polymers were synthesized by polymer-polymer conversion reaction with suitable reactions.

Here, in this study it is aimed to prepare poly(hydroxamic acid) (PHA) polymers from poly (acrylamide) (PAAm) crosslinked with N, N' methylenebisacrylamide (N) or ethylene glycol dimethacrylate (E). And also the influence of hydrogel ionogenity on the swelling behavior and the adsorption of the uranyl ions in the aqueous solution of both uranyl acetate and uranyl nitrate were investigated.

Experimental

Acrylamide (Merck, Darmstadt, Germany), N, N' methylenebisacrylamide and ethylene glycol dimethacrylate (Sigma, St. Louis, US), ammonium persulfate (AP) (Merck, Darmstadt, Germany), N, N, N', N'-tetramethylethylenediamine (TEMED), hydroxylamine hydrochloride and sodium hydroxide (Sigma, St. Louis, US), uranyl nitrate (UN), uranyl acetate (UA) and sodium salicylate (Merck, Darmstadt, Germany) were analytical reagent-grade and used as received.

Preparation of Hydrogels

An aqueous solution of AAm and N or E (95:5 in mole ratio in 0.4 mol water) with 0.01 mmole AP and 2.5 mmole TEMED were mixed and placed in PVC straws of 4 mm diameter at +4 °C. A gel formed after 20 min of reaction. After 24 h the hydrogel rods were cut into pieces 3-4 mm length. (*N-0* and *E-0*). For preparation of acid form of PHA, a solution of hydroxylamine hydrochloride (3 M, 100 mL) was added to 20 g crosslinked PAAm in 300 mL distilled water. The resulting mixture was stirred for 2 hours at ambient temperature (*N-1* and **E-1**). For preparation of salt form of PHA, a solution of NaOH (7.5 M 50 mL) was added to 20 g acid-form of PHA in 300 mL distilled water and stirred for 24 h (N-2 and E-2). N-0, N-1, N-2, E-0, E-1 and E-2 polymers washed with distilled water and dried in air and vacuum, and stored for later use.

The swelling of dried polymers is carried out by immersion in doubly distilled water, and in the solutions of UN and UA in the concentration of 500 mg U L^{-1} at 25±0.1 °C in a water bath. The solution absorbed is determined by weighing the samples, after blotting, at various time intervals.

Binding of uranyl ions to PHA polymers

For the study of the binding kinetics of uranyl ions, 0.2 g dry PHA polymers were transferred into 100 mL of the solutions containing 500 mg U L^{-1} of UA or UN for 24 h at 25 °C. The concentration of uranyl ions was determined at various time intervals.

All the following experiments below were performed at 25 °C for 24 hours otherwise is not specified.

To examine the influence of the adsorbate concentration, 0.1 g dried PHA polymers were transferred into 50 mL of the aqueous solutions of UA and UN in the concentration range 100-1000 mg U L^{-1}. In order to see the effect of temperature on the binding ratio, 0.1 g dried PHA polymers put into 50 mL of aqueous solutions of 1000 mg U L^{-1} UA or UN, and treated for 24 h at the temperature range 15-40 °C. For the examination of the effect of pH on the binding ratio, 0.1 g dried PHA hydrogels were transferred into 50 mL 1000 mg U L^{-1} aqueous solutions of UA or UN, treated at desired pHs in acetate buffer solutions (acetic acid + sodium carbonate). To investigate the influence of the mass of adsorbent, different amount of dried PHA hydrogels (0.05-0.50 g) were placed in 50 mL of aqueous solutions of UA or UN containing 1000 mg U L^{-1}.

For the desorption studies, with an initial mass of 0.1 g PHA hydrogels loaded from 50 mL 900 mg U L^{-1} solutions of UA and UN were used. Following the removal of adsorbent from adsorption media, uranyl ion loaded samples left in distilled water and 0.1 M H_2SO_4.

The concentration of uranyl ions was determined by spectrophotometric method. After decantation of adsorbent from adsorption media, 1 mL of 1 g L^{-1} sodium salicylate was added to 10 mL of the uranyl solutions, and allowed to stand for 30 min. Spectrophotometric measurements were carried out using a Hitachi model UV-VIS spectrophotometer at ambient temperature at a wavelength of 327 nm.

Results and Discussion

Bindings of uranyl ions to PHA hydrogels

To observe the binding of uranyl ions onto the PHA polymers, hydrogels were placed into the aqueous solutions of corresponding uranyl ion sources, and allowed to equilibrate for two days. At the end of this time, PHA hydrogels in the solutions showed the yellow-orange colorations, while PAAm hydrogels have not sorbed any detectable uranyl ion. Since poly(acrylamide) is a non-ionic polymer [5], ionizable groups on the polymer were increased by forming hydroxamic acid groups from the acrylamide polymers. So, these hydrogels have many ionizable hydroxamic acid groups that can increase the interaction between the uranyl ions and the hydroxamic acid groups in hydrogel network. The solutions of uranyl ions were used in the experiments of adsorption. Two different uranyl ions sources such as uranyl nitrate and uranyl acetate were chosen for the investigation of the effect of anionic groups of uranyl salts on the adsorption.

Fig 1 shows the FT-IR spectra of PHA derivatives/uranyl ions systems. The peak at 930 cm^{-1} is related to the stretching frequency of linear structure of O=U=O [6] or enol type-hydroxamic acid groups [7]. In Fig 1, the sharp peak at 930 cm^{-1} is related to the stretching frequency of linear structure of O=U=O, and this peak has not been seen in the IR spectra of uncomplexed PHA hydrogels [8]. So, binding process of uranyl ions to PHA derivatives was formed keto-type of hydroxamic acid groups on the PHA hydrogels. The possible interactions between uranyl ions and PHA polymers are shown in Scheme 1.

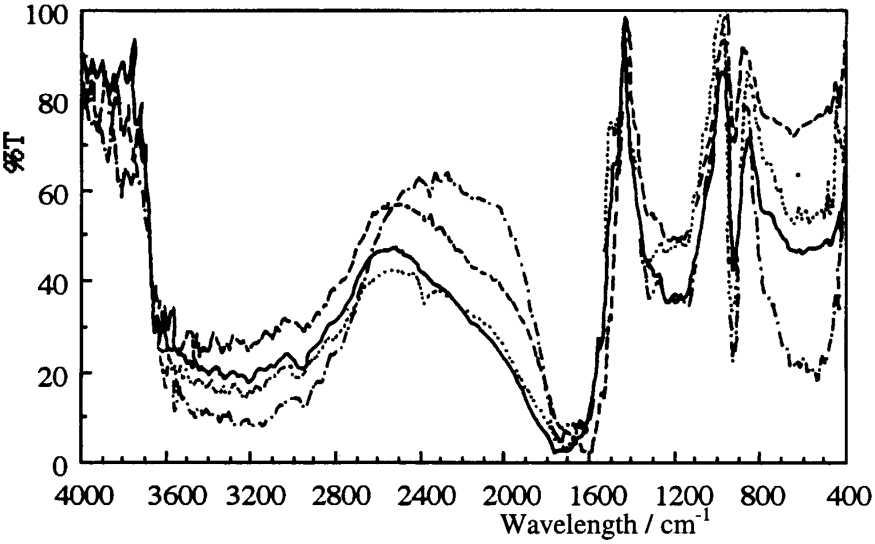
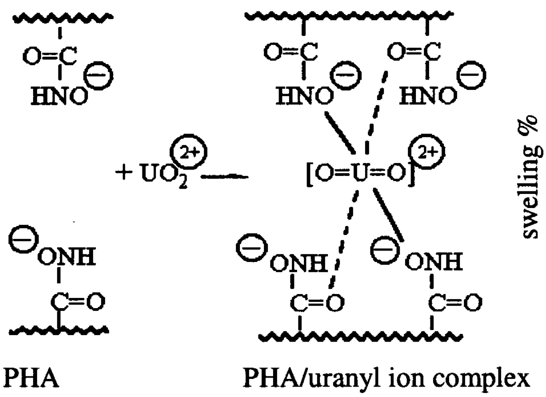


Fig 1 IR spectra of PHA/U binding systems. — ; E-1,···; E-2 in UA and - -; E-1, - · - E-2 in UN



Scheme 1 The possible interactions between uranyl ions and PHA polymers

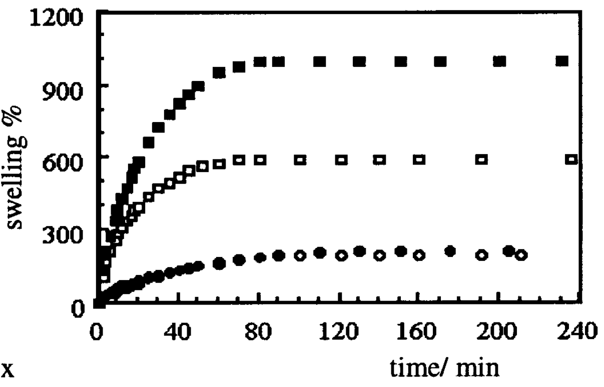


Fig 2 Time depending swelling of PHA hydrogels, ●; N-2/UA, ○; N-2/UN, ■; E-2/UA, □; E-2/UN.

Swelling studies in the solutions of uranyl ions

The swelling (S%) of PHA polymers in the aqueous solutions of UA and UN is calculated from the following relation: $S\% = [(m_t-m_0)/m_0]x100$, where m_0 is the mass of dry gel at time 0, m_t is the mass of swollen gel at time t. Swelling curves of the hydrogels were plotted and, the curves are presented in Fig 2. The values of equilibrium swelling, S_{eq} % are given Table 1.

Fig 2 and Table 1 show that the swellings of E-type hydrogels are higher than N-type of hydrogels in the uranyl solutions. Since the same amount of crosslinkers used during the synthesis of hydrogels, the differences should be due to the structural and flexibility differences of cross-linkers in hydrogels, so these swelling results are conceivable. And also as indicated in previous paper [8], the conversion amount of amide groups of PAAm hydrogels having E-type crosslinker to hydroxamic acid groups much more than that of N-type crosslinked PAAm hydrogels. In other words, the extent of hydroxamic acid group in E-1 is higher than N-1. In addition, crosslinker E is flexible, while crosslinker N is semi-flexible, and also crosslinker E is more hydrophilic than the crosslinker N. Thus, flexible crosslinker E can be retain the fluids more than the semiflexible crosslinker N. On the other hand, the swelling of the hydrogels in the uranyl solutions is in following order; type-1<type-2 hydrogel. Since type-2 is the sodium salt form of hydroxamic acid, it is the most ionogenic form of the other type. Thus, type-1 PHA contains the ionic groups as only as the ionizing degree of PHA. It is evident that, the more the ionogenic content of a hydrogel the more the swelling degree gets.

In addition to the crosslinkers and the form of PHA hydrogels, the acetate and nitrate anions of the uranyl salts affected swellings. The uranyl acetate dissolves as molecule in the aqueous solution while uranyl nitrate dissolves as ions in the aqueous solution. Thus, the cation of the salt having nitrate anion have interacted with the hydroxamic acid groups in the hydrogels, so the swelling of these hydrogels in the aqueous solution of the nitrate salt is low because of high ionic strength of this solution compared to acetate solution. An increase in ionic strength generally decreases the swelling, because the difference in the concentration of mobile ions between the gel and the solution is reduced with a decrease in the osmotic swelling pressure of these ions inside the gel. These interactions can be electrostatic, such as ionic or ion-dipole in nature [9].

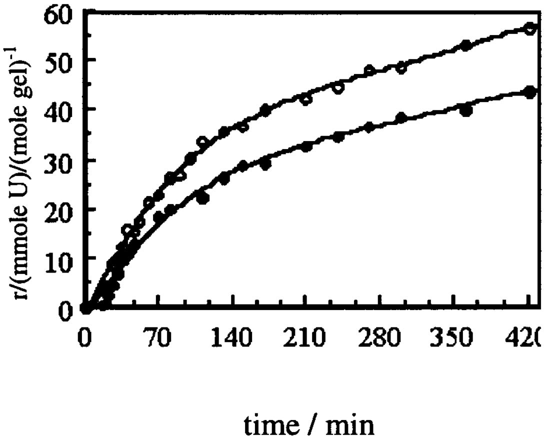


Fig 3 Time depending binding of uranyl ions, ●; N-2/UN, ○; N-2/UA.

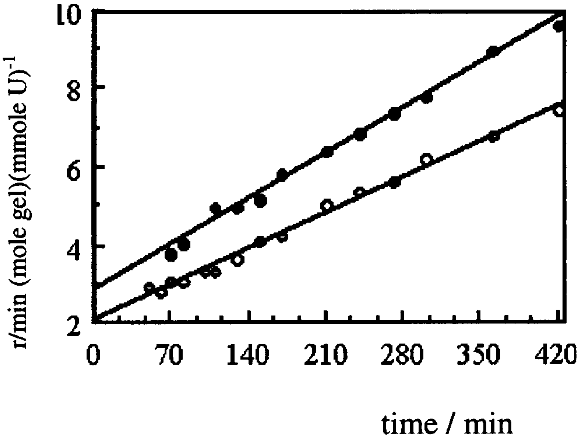


Fig 4 Binding kinetics for PHA/U systems, ●; N-2/UN, ○; N-2/UA.

Adsorption of Uranyl Ions

The purpose of this investigation is the uptake of uranyl ions onto the PHA hydrogels and the usability as a sorbent for uranyl ions. For this, binding kinetics between uranyl ions and PHA hydrogels, and the influences of concentration of uranyl ions, pH, temperature and mass of adsorbent on the adsorption equilibrium were examined.

In a batch adsorption system, total cosolute concentration (C_I, mole L^{-1}) is $C_I=C_B+C$, where, C_B is the cosolute on the adsorbent in mole per liter (bound solute concentration) and C is the cosolute in the solution in mole L^{-1} (free solute concentration). Therefore the bound amount can be conveniently expressed as the binding ratio, r, defined as $r=C_B/P$. Thus with C_B in mole L^{-1} and P in base mole (moles of monomer units) per liter, r then represents the average number of molecules of solute bound each monomer unit at that free solute concentration.

i. Adsorption kinetics

To investigate binding kinetics of uranyl ions to PHA hydrogels, the graphs r versus the interaction time t were plotted and representative curves are illustrated in Fig 3.

The PHA hydrogels show similar binding kinetics behavior in all cases. The kinetic curves are similar in shape but differ in size and position. Fig 3 shown that binding ratio is rapidly increased by time to 140 min, and then it is slowly increased. The equilibrium time of the binding process between PHA hydrogels and uranyl ions ranged between 8 and 10 hours.

For second order binding kinetics of polymers, the following relation can be written; $t/r = A+b\ t$ where A is the reciprocal of equilibrium binding ratio (r_{eq}) and, $B=l/(dr/dt)_o$ is the reciprocal of initial binding rate (r_o).

Fig 4 shows the linear regression of the binding kinetics curves obtained by means of the final equation. The values of r_o [mol U (mole gel)$^{-1}$ min^{-1}] and r_{eq} [mole U (mole gel)$^{-1}$] of the PHA derivatives are calculated from the slope an intersection of the lines and, are presented in Table 1.

From Table 1, it can be clearly seen that the values of equilibrium binding ratio of the hydrogels are in good agreement with the results of swelling of the gels. The explanations in the swelling evaluations are also valid in the binding process. Binding processes of the hydrogels having E crosslinker is faster than the binding rate of the hydrogels having N crosslinker in the solution of uranyl ions.

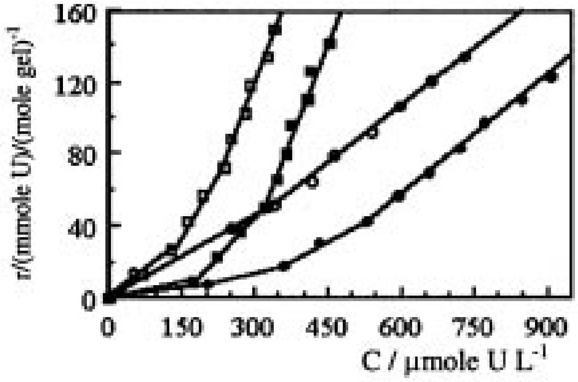


Fig. 5 Influence of concentration on the adsorption, □; E-1/UN,■ ; N-1/UN, ○ ; E-1/UA, ●; N-1/UA.

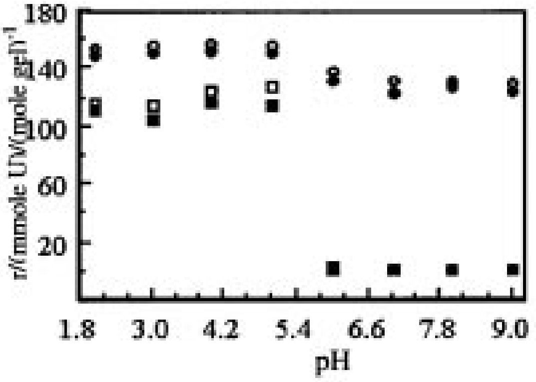


Fig. 6 Influence of pH on the adsorption, ○;E-2/UA,●; N-2/UA, □;E-2/UN, ■; N-2/UN

ii. Adsorption equilibrium

In this stage of the work, the influences of the concentration of uranyl ions, pH, temperature and the mass of adsorbent to adsorption equilibrium were investigated.

Influence of concentration

Representative plots of the binding ratio versus the free concentrations of uranyl ions in the solutions are shown in Fig 5. From this figure, the adsorption of the uranyl ions into PHA hydrogels are in accordance with S type adsorption isotherms in the Giles classification system for the adsorption of a solute from its solution [10, 11].

Adsorption equilibrium constants (K) of uranyl ion-PHA hydrogel systems were obtained from the linear portion of the curves [12] from Fig 5. Free energies of the adsorption processes were calculated using the equation of $\Delta G = - RT \ln K$. The values of K [L mole gel^{-1}] and ΔG [kJ mole^{-1}] are postulated in Table 1.

In the uranyl ions-PHA hydrogels binding process, the K values are higher than unity, and the values of ΔG were found as negative values indication of spontaneous adsorption process.

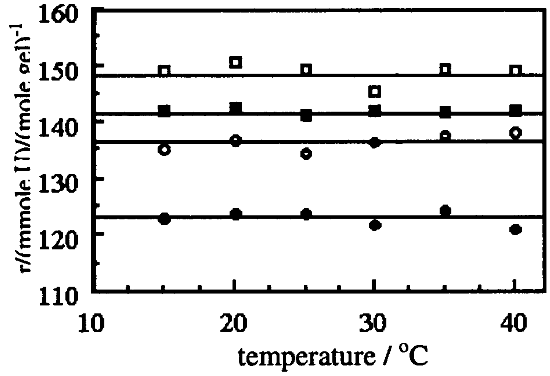


Fig. 7 Influence of temperature on the adsorption, adsorption,
□; E-1/UN, ■; E-1/UA, ○; N-1/UN, ●; N-1/UA

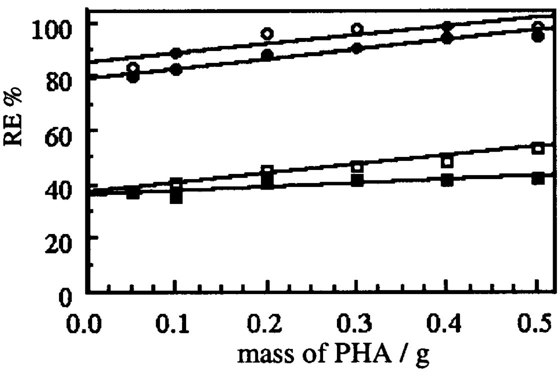


Fig. 8 Influence of gel mass on the
○; E-2/UA, ●; E-1/UA, □; N-2/UN, ■; N-1/UN

Table 1 Swelling, binding kinetics and thermodynamic parameters of PHA hydrogels

Solution	Uranyl acetate					Uranyl nitrate				
hydrogel	S$_{eq}$%	r$_o$x10^3	r$_{eq}$x10^3	K	?G / kJmole^{-1}	S$_{eq}$%	r$_o$x10^3	r$_{eq}$x10^3	K	?G / kJmole^{-1}
N-1	185	49.7	63.9	216.4	– 13.3	180	43.1	60.3	691.1	– 16.2
N-2	215	48.3	76.1	181.7	– 12.9	195	35.2	62.5	900.0	– 13.3
E-1	245	66.8	82.3	214.7	– 13.3	220	1.7	74.9	38.7	– 9.1
E-2	990	97.3	94.3	217.9	– 13.3	595	34.8	126.0	47.1	– 9.5

Influence of pH

Representative plots of the binding ratio versus pH are presented in Fig 6. pH was not effective on the binding processes between uranyl ions and PHA polymers up to 5. Over pH 5 values, the binding ratio was sharply dropped to zero in the solution of uranyl nitrate, while these ratios decrease were slightly pronounced in the solution of uranyl acetate. The uranyl cation, UO_2^{2+} is hydrolized in aqueous solution within this range of the binding system pH. In the range of acidic to near neutral pH values, four major hydrolized complex ions, UO_2^{2+}, $(UO_2)_2(OH)_2^{2+}$, UO_2OH^+, $(UO_2)_3(OH)_5^+$ and dissolved solid schoepite ($4UO_3 \cdot 9H_2O$), a hydrous uranium oxide, exist in the solution. Hydrolyzed ion forms of uranium are found in the aqueous solutions to pH 5, while neutral forms of uranium are found after pH 5 [13].

Influence of temperature

Representative plots of the binding ratio versus temperature (°C) are shown in Fig 7. There is not important influence of the temperature on the binding process between uranyl ions and PHA derivatives.

Influence of the mass of hydrogel

Some representative graphs of the removal efficiency [$RE\%=(C_B/C_I)x100$] versus the mass of dried PHA polymers are shown in Fig 8. The values of RE% of the polymers were increased very low with increase of PHA mass. So, it can be said that, the increase of mass of the used polymers did not affect the binding process.

The adsorption amount of uranyl ions from the solutions of UA is higher than UN. Same interactions that are responsible for the swelling properties of the hydrogels are also effective here on the adsorptions of UN and UA into the PHA hydrogels. These interactions could be very well electrostatic, ion-ion and/or ion-dipole among the corresponding groups.

Some researchers have studied on the adsorption of uranyl ions to some inorganic and organic polymers such as TriSyl silicas [14], radiation induced pre-arranged acrylamide/maleic acid (p-AAm/MA) [15], acrylamide/itaconic acid (AAm/IA) [4], acrylamide/maleic acid (AAm/MA) [3] and N-vinyl 2-pyrrolidone/ itaconic acid (VP/IA) [1] hydrogels. As a comparison of our results with the results of other researchers in 500 mg U L^{-1} of the initial concentration of uranyl ions, it is observed that the adsorption of uranyl ions to PHA hydrogels are generally higher than that of others. The amount of binded U (mg U (g polymer)$^{-1}$) increased in the solutions of UA in the following order; E-2>E-1>N-2>AAm/IA>N-1>AAm/MA> PAAm/MA>TriSyl, while the values increased in the solutions of UN in the following order; E-2>E-1>N-2> AAm/IA>N-1>AAm/MA>VP/IA>TriSyl. Consequently, PHA hydrogels are better adsorbents than the others for uranyl ions.

Desorption of Uranyl ions

Elution experiment was carried out in 0.1 M H_2SO_4. To see the nature of binding between hydroxamic groups and uranyl ion, maximum amount of uranyl ion adsorbed hydrogels were taken out from uranyl ion solutions and kept in distilled water for 3 days and could not find any amount of measurable uranyl ions. These hydrogels were not shown any colorization while uranyl ion loaded hydrogels, which were originally clear (transparent) showed decolorization from yellow-orange to the original form in the acidic elucition medium.

Conclusion

PAAm hydrogels were synthesized using two different type of crosslinker. To impart the uranyl ion adsorptivity, amide groups of PAAm converted to hydroxamic acid groups in the presence of $NH_2OH \cdot HCl$. From the swelling studies of PHA hydrogels in two different uranyl ion sources, it was found that salt, crosslinker type and ionogenity of the PHA are effective on the swelling behavior. From the values of equilibrium swelling in the uranyl solutions, PHA hydrogels having N type crosslinker swelled low (between 180 and 215%), while E-type crosslinker used for PHA hydrogels swelled higher (between 220 and 990%) in UN and UA solution, respectively. As a result, the structure and the hydrophilicity of the crosslinkers, as well as the ionogenity of PHA and source of uranyl ions such as UN and UA have great effect on the swelling of polymers. In addition to these factors, concentration of uranyl ions, and pH of the medium were found to be effective, while temperature and mass of adsorbent were not very effective for the uranyl ion binding process. Uranyl ion adsorption studies showed S Type adsorption isotherms. The adsorption capacity of E-2 is 126 mmole U (mole gel)$^{-1}$ and 94.3 mmole U (mole gel)$^{-1}$ for UN and UA, and 62.5 mmole U (mole gel)$^{-1}$ and 76.1 mmole U (mole gel)$^{-1}$ for N-2, respectively.

Consequently, it can be concluded that PHA hydrogels can be used as efficient sorbent for removal of water pollutant such as uranyl ions and others with fast adsorption rates. These types of adsorbents are very promising because of their high adsorption capacity, reusability and the easiness of handling with the safety to environment.

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