

Polyelectrolyte CASA Hydrogels for Uptake of Uranyl Ions from Aqueous Solutions

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ABSTRACT: In this study, uranyl ion adsorption from aqueous solutions has been investigated by chemically crosslinked acrylamide/sodium acrylate (CASA) hydrogels. Adsorption studies were investigated by the spectroscopic method. CASA hydrogels with various compositions were prepared from ternary mixtures of acrylamide (A), sodium acrylate (SA), and water by free radical polymerization in aqueous solution, using multifunctional crosslinkers such as ethylene glycol dimethacrylate (EGDMA). Uranyl ion adsorption from aqueous solutions was studied by the batch sorption technique at 25°C. The effect of uranyl ion concentration and mass of adsorbent on the uranyl ion adsorption were examined. In experiments of sorption, L-type sorption in the Giles classifica-

tion system was found. Some binding parameters, such as initial binding constant (K_i), equilibrium constant (K), monolayer coverage (n), site-size (u), and maximum fractional occupancy (\bar{O}) for the CASA hydrogel–uranyl ion binding system, were calculated using the Langmuir linearization method. Finally, the amount of sorbed uranyl ion per gram of dry hydrogel (q) was calculated to be 4.44×10^{-4} – 14.86×10^{-4} mol uranyl ion per gram for CASA hydrogels. Adsorption of uranyl ion (percentage) was changed within a range of 12.86–46.71%. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 200–204, 2007

Key words: acrylamide; hydrogel; swelling; sorption; uranyl ion

INTRODUCTION

Removal of toxic heavy metals, in connection with wastewater treatment strategy, remains a major topic of current research. Many methods have been proposed for the removal of heavy metals and other hazardous materials. Adsorption or ion exchange using different polymeric materials and synthetic resins is the method of choice in many wastewater treatment processes for the removal of dyes from chemical process industries in certain developed countries. Chemical precipitation, membrane extraction, coagulation, complexing, solvent extraction, ion change, and adsorption are some of the commonly used processes, but each has its own advantages and disadvantages in its applications. Adsorption, solvent extraction, and ion-exchange techniques have been applied primarily to the uptake and separation of some metal ions, such as uranyl ions.^{1–5} Some disadvantages of solvent extraction and ion-exchange techniques, as an alternative approach, some crosslinked polymers or copolymers have been suggested by several researchers by direct adsorption of the heavy metal ions into macroporous polymeric supports. Stud-

ies have been reported on the use of hydrogels or hydrophilic characteristic crosslinked polymers or copolymers as adsorbents for the removal of heavy metals, for the recovery of dyes, for removal of toxic or radioactive elements from various effluents, and for metal preconcentration for environmental sample analysis from aqueous solutions.^{6–12}

Uranium is an element of considerable technological importance. Nuclear power is derived from uranium, which has no significant commercial use other than as a fuel for electricity generation. Uranium is dissolved in seawater at a concentration of $\sim 3 \text{ mg m}^{-3}$ in the ionic form of uranyl tricarbonate ions. Atomic power plants continuously require uranium resources; therefore, 4.5 billion tons of total uranium in seawater can be recovered for atomic power utilization.¹³ Crosslinked polymeric hydrogels will therefore be potential ion-exchange support material for recovery of uranium ions from seawater, using several techniques.

The use of polymer hydrogels for the removal of uranyl ion from wastewater has been continued to attract considerable attention in recent years. In this study, novel hydrogels prepared with acrylamide and sodium acrylate were used to increase the adsorption capacity of acrylamide hydrogels for uranyl ions. Crosslinked acrylamide/sodium acrylate (CASA) hydrogels were prepared by free radical crosslinking copolymerization.

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EXPERIMENTAL

Materials

Acrylamide (A), the initiator, ammonium persulphate (APS), the activator *N,N,N',N'*-tetramethylethylenediamine (TEMED), the crosslinker, ethylene glycol dimethacrylate (EGDMA), uranyl acetate (UA) and sodium salicylate as a complexing agent were supplied by Merck (Darmstadt, Germany) and anionic *co*-monomer, SA, was supplied by Aldrich Chemical Co. (Milwaukee, WI). All chemicals were used as received. The sources of water, the monomers, acrylamide (A) and sodium acrylate (SA) were given before.¹⁴

Preparation of CASA hydrogels

CASA hydrogels were prepared by free radical crosslinking copolymerization of A monomer with the addition of an anionic *co*-monomer such as SA (10–80 mg SA per gram A) and a multifunctional crosslinker such as EGDMA. The modes of purification and specifications of the sources of water; monomers A and SA; crosslinker, EGDMA; initiator, APS; and the activator, TEMED, were given in our related study.¹⁴ Some of the details of preparation are as follows. To prepare highly swelling hydrogel systems, acrylamide weighing 1 g was dissolved in 1 mL aqueous solutions containing 0 or 10 mg, (or 20, 30, 40, 50, 60, 70, and 80 mg) SA. For synthesis, 0.25 mL of 1% concentration EGDMA solution was added to this aqueous solution. Then, 0.20 mL of APS (5 g/dL water) and 0.25 mL of TEMED (1 mL/dL water) were added to the solution. The solutions were placed in PVC straws of 3-mm diameter. Fresh hydrogels obtained in long cylindrical shapes were cut into pieces 3–4 mm in length. Polymerization and crosslinking took 1 h in gelation of CASA hydrogels. However, for all hydrogel systems, a waiting period of 24 h has good gelation. They were washed and thoroughly rinsed with distilled water, blot dried with filter paper, dried in air and vacuum, and stored for swelling studies.

Sorption studies

Solutions of UA, containing 2.4×10^{-3} – 1.0×10^{-2} M UA in distilled water, were prepared. CASA hydrogels containing 50 mg SA were used in a known volume of uranyl ion solution until equilibrium was reached. For the SA effect on the uranyl ion sorption, UA solution of concentration of 0.01 M was used.

After sorption, UA solution was separated by decantation from the hydrogels; 1.0 mL solution of sodium salicylate with a concentration 1.0 g L^{-1} was added to 10 mL of the UA solution and allowed to stand for 30 min. Then, the spectrophotometric method

was applied to UA solutions. Spectrophotometric measurements were carried out using a Shimadzu UV 1601 model UV-VIS spectrophotometer at ambient temperature. The absorbance of these uranyl–complex (UA–sodium salicylate) solutions was read at 414 nm.¹⁵ Distilled water was chosen as the reference.

The equilibrium concentrations of the uranyl–complex solutions were determined by means of precalibrated scales. The amounts of uranyl ion sorbed and the adsorption percentage were determined from the initial and final concentrations of the solutions, calculated from the measured absorbance.

The adsorption percentage (Ads%) was calculated as

$$\text{Ads\%} = \frac{C_0 - C}{C_0} \times 100, \quad (1)$$

where C_0 and C are the concentrations of UA in the initial solution and the aqueous phase after treatment for a certain period time, respectively (mol L^{-1}).

The amount (mol) of sorption per unit mass of the CASA hydrogels (q) was evaluated with the following equation:^{1,12}

$$q = \frac{(C_0 - C)v}{m}, \quad (2)$$

where q is the amount (mol) of uranyl ions sorbed onto unit dry mass of the CASA hydrogels (mol g^{-1}), v is the volume of the aqueous phase (L), and m is the amount of dry CASA hydrogel (g).

Binding studies

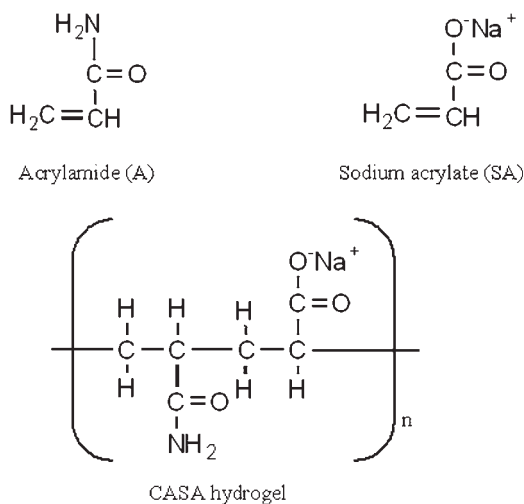
In the sorption system at equilibrium, the total solute (uranyl ion) concentration, C_0 , is as shown in the following equation:

$$C_0 = C_b + C, \quad (3)$$

where C_b is the equilibrium concentration of the solute (uranyl ion) on the sorbent per liter solution (bound solute concentration), and C is the equilibrium concentration of the solute in the solution (free solute concentration). The value of the bound concentration may be obtained using eq. (3). For a fixed free solute concentration, C_b is proportional to the polymer concentration on the binding system; the amount bound can therefore be conveniently expressed as the binding ratio r , defined by

$$r = C_b/P. \quad (4)$$

Thus, with \ln and P is base mol (moles of monomer units) per liter solute represents the average number of molecules of solute bound each monomer unit at that free solute concentration.^{16,17} The binding data were interpreted on the basis of the uniform site-binding



Scheme 1 Molecular formula of acrylamide, sodium acrylate, and possible crosslinked acrylamide/sodium acrylate copolymer (CASA hydrogel).

(USB) model, which in statistical–thermodynamic terms corresponds to a formation of an ideal localized one-dimensional monolayer of solute on the polymer chains.^{16,17} This leads to the hyperbolic (Langmuir) form of the binding isotherm, which applies to many polymer/solute (uranyl ion) binding systems:

$$r = \frac{nKC}{1 + KC}, \quad (5)$$

where K is the binding constant, i.e., the equilibrium constant for the attachment of a uranyl ion onto a site by a specific combination of noncovalent forces. Here n is the site density (the limiting value of r for monolayer coverage) which is therefore of density of the sites along the polymer chain. To the reciprocal of n is the site-size, u , which may be taken to represent either the average number of monomer units occupied by the bound solute molecule, or more generally the average spacing of solute molecules when the chain is saturated. The initial binding constant, K_i is the initial slope of the binding isotherm, and therefore the average binding strength of a solute molecule by a single monomer unit on an occupied chain. K_i is equal to the product Kn .

To get the best values for the binding parameters from the experimental data, the linearization methods of eq. (5) have been developed by such researchers as Klotz, Scatchard, and Langmuir.^{16,17}

Langmuir linearization method

Mathematical analysis of eq. (5) yields

$$\frac{C}{r} = \frac{1}{nK} + \frac{C}{n}, \quad (6)$$

where a plot of C/r vs. C should be a straight line of slope $1/n$, ordinate intercept $1/nK$.^{16,17}

The related binding parameter is the maximum fractional occupancy, \hat{O} :

$$\hat{O} = r/n. \quad (7)$$

Using the value of r at the maximum experimental free uranyl ion concentration, maximum fractional occupancy can be calculated.

RESULTS AND DISCUSSION

CASA hydrogels were prepared by free radical crosslinking copolymerization of the A monomer with the addition of SA and a multifunctional cross-linker such as EGDMA.^{18–20} Possible copolymerization mechanism is presented in Scheme 1.

Binding characterization

To observe the sorption of uranyl ions, CASA hydrogels were placed in aqueous solutions of UA and allowed to equilibrate for 4 days at 25°C. At the end of this period, CASA hydrogels in the UA solutions showed the yellow coloration (the color of UA salt). But acrylamide hydrogel did not sorb any uranyl ions from UA solutions.

To determine the sorption kinetics of uranyl ion into CASA hydrogels, the binding ratio (r) is plotted against the free concentration of uranyl ions in Figure 1 for CASA hydrogels crosslinked by EGDMA. Figure 1 shows that sorption of uranyl ions within CASA hydrogels corresponds to L-type sorption isotherms in the Giles classification system for sorption of the uranyl ion from its solution.²¹ In this type of adsorption isotherm, the initial curvature shows that it becomes increasingly difficult for a bombarding uranyl ion to find an available vacant site, as more and more sites on the crosslinked CASA hydrogels are filled. This implies that either the adsorbed uranyl

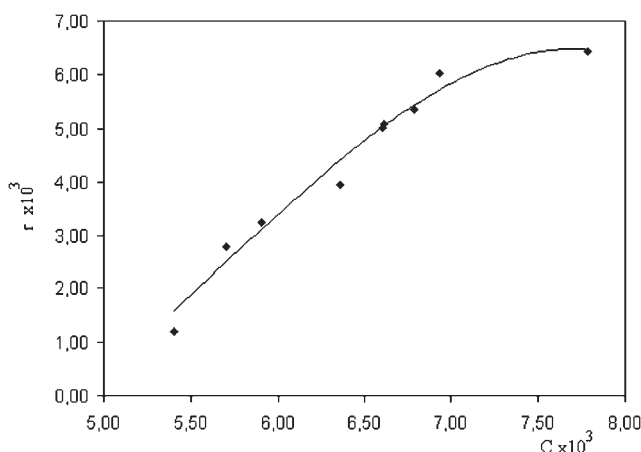


Figure 1 Binding isotherm of CASA hydrogel–uranyl ion binding system.

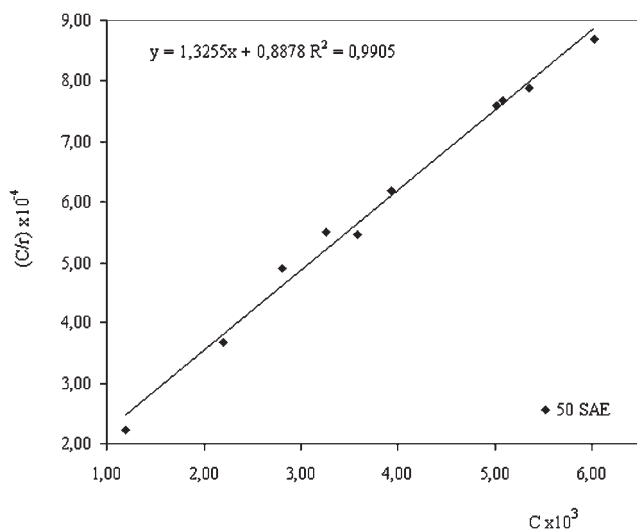


Figure 2 Langmuir plot of CASA hydrogel-uranyl ion binding system.

nyl ion molecule is not oriented vertically or there is no strong competition from the solvent, water.

To get the best values for the binding parameters from the experimental data, Langmuir linearization method was used. The Langmuir plots of CASA hydrogel-uranyl ion binding systems is shown in Figure 2, and the binding parameters for CASA hydrogel-uranyl ion binding systems are calculated from the intercept and slopes of the binding isotherm method.

The binding parameters K_i , K , n , u , and \hat{O} are listed in Table I, for CASA hydrogel-uranyl ion binding systems. There has been shown good accordance to the linear regression of the experimental data. The correlation coefficient of regression is 0.9905 for Langmuir plot of CASA hydrogel-uranyl ion binding system.

Equilibrium adsorption studies

The adsorption percentage and the amount of sorption uranyl ion per unit mass of the CASA hydrogels were evaluated by using eqs. (1) and (2). The amount of uranyl ion sorbed onto unit dry mass of the gel was calculated for uptake of uranyl ion within the hydrogel in 1.0×10^{-2} mol uranyl ions in L of aqueous solutions. Equilibrium uranyl ion adsorption isotherm of CASA hydrogels is presented in Figure 3, which shows that the amount of sorption uranyl ion per unit mass of the CASA hydrogels are increased with the

TABLE I
Some Binding Parameters of CASA Hydrogel-Uranyl Ion Binding System

| Binding parameters | K | n | K_i | θ | u |
|--------------------|--------|-------|-------|----------|--------|
| | 147.22 | 7.547 | 11111 | 1.0308 | 0.1325 |

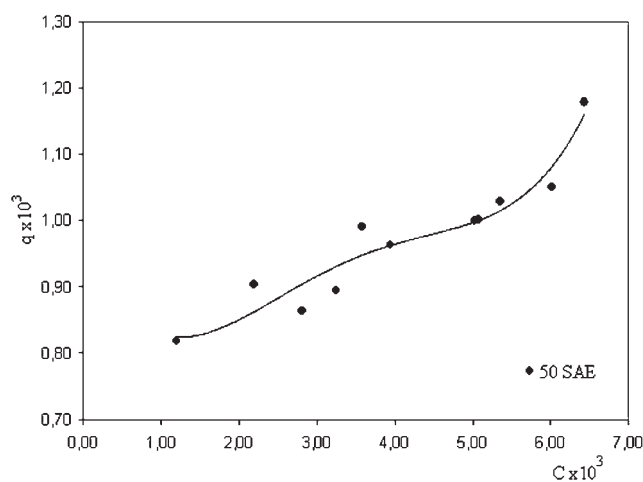


Figure 3 Equilibrium uranyl ion adsorption isotherm of CASA hydrogels.

increasing concentration of uranyl ion. The results have shown good accordance to the swelling results of CASA hydrogels.¹⁴

In later experiments, it was investigated that the effects of SA contents on sorption of uranyl ions onto the CASA hydrogels. As a result of some calculations about equilibrium adsorption studies, some results are tabulated in Table II, which shows that the amount of uranyl ions sorbed onto unit dry mass of the CASA hydrogels ($4.44 \times 10^{-4} - 14.86 \times 10^{-4}$ mol g^{-1}), q are increased. The amount of uranyl ions sorbed onto unit dry mass of the CASA hydrogels gradually increased with the increase of content of SA in CASA hydrogels. The percentage sorptions of uranyl ions onto CASA hydrogels are changed among 12.86–46.71%.

There may be several reasons for noncovalent interactions in the binding of uranyl ions by CASA hydrogels. These interaction types are represented as possible as simply interactions in Figure 4. The main interactions between the hydrogel and uranyl ions may be hydrogen bonding. In particular, hydrogen bonding will be expected to occur between uranyl ions and oxygen and nitrogen atoms as the amine and carbonyl groups on the repeating monomeric unit of crosslinked polymer. With the incorporation SA groups into crosslinked copolymeric structure, the hydrophilicity of CASA copolymers becomes

TABLE II
Amount of Uranyl Ion Sorbed onto Unit Dry Crosslinked Polymer and Adsorption Percentage of CASA Hydrogel-Uranyl Ion Binding System

| | SA (mg) | | | | | | | |
|------------------------------------|---------|-------|-------|-------|-------|-------|-------|-------|
| | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 |
| $q \times 10^4$ (mol g^{-1}) | 4.47 | 7.65 | 7.83 | 9.11 | 11.78 | 13.69 | 14.47 | 14.86 |
| Ads% | 12.86 | 19.82 | 21.49 | 31.19 | 35.62 | 33.96 | 37.84 | 46.71 |

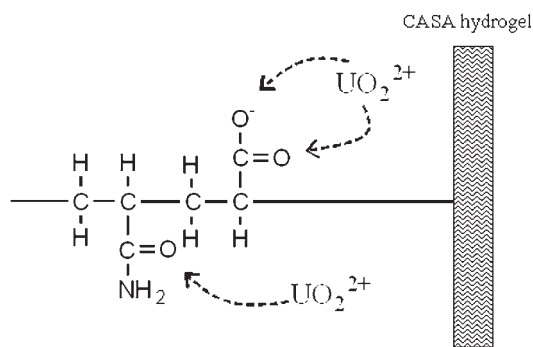


Figure 4 Possible binding/interaction mechanism of UO_2^{2+} to CASA hydrogel.

greater than that of crosslinked acrylamide, so the swelling of CASA hydrogels is greater than the swelling of crosslinked acrylamide hydrogels in water or aqueous media.¹⁴ It was reported that the percentage swelling degree of CASA hydrogels were 1690–12870%, but for crosslinked A hydrogels, the percentage swelling degree was 770%.¹⁴

The results of swelling studies represent parallel behavior to the results of sorption studies.¹⁴ The ionic charge content in the polymeric structure is important. SA contains many ionic units ($-\text{COONa}$). The swelling degrees of the hydrogels increase due to increase of the hydrophilic units on hydrogel structure (Scheme 1). Therefore, CASA hydrogels have many ionic groups that can increase the interaction between the uranyl and anionic groups of hydrogels. It can be seen that the sorption capability of CASA hydrogels is increased with increasing SA content in copolymeric structure. The most important effect is the hydrophilicity of copolymeric gels. Hydrophilicity of CASA copolymers becomes greater than that of crosslinked acrylamide, when the addition of SA to the copolymeric structure.

CONCLUSION

The present work provides quantitative information on the binding characteristic of uranyl ions with CASA hydrogels. CASA hydrogels have sorbed the uranyl ions, while crosslinked acrylamide hydrogels do not. L-type sorption isotherm in the Giles classification system is found. For good characterization of the binding isotherms, the Langmuir linearization method was

used. Some binding parameters were found. This linearization method (i.e., Langmuir) can be used in the hyperbolic binding system for the uranyl ion–polymer binding process.

Sorption of uranyl ions is increased with the SA content in the hydrogels. The moles of sorbed uranyl ions per gram of dry hydrogel (q) were calculated as 4.44×10^{-4} – 14.86×10^{-4} mol uranyl ion per gram for CASA hydrogels. The percentage sorption of uranyl ions onto CASA hydrogels is changed in 12.86–46.71%. At the end of this study, it is seen that chemically crosslinked CASA hydrogels may be used a sorbent for removal of uranyl ions. It can be said that CASA hydrogels are potential sorbents at a wide range area of biotechnology.

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