The Preparation of p(acrylonitrile-co-acrylamide) hydrogels for uranyl ion recovery from aqueous environments

Sulu ortamlardan uranil iyonu kazanımı için p(akrilonitril-ko-akrilamit) hidrojellerinin hazırlanması

Research Article

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ABSTRACT

The synthesis of poly(acrylonitrile-co-acrylamide) (p(AN-co-AAm)) hydrogels with different amounts of acrylonitrile (AN) and acrylamide (AAm) monomers were carried out by concurrent use of redox and microemulsion polymerization techniques. The prepared hydrogels were amidoximated for sorption of uranyl ion from aqueous medium. Batch type UO_2^{2+} ion sorption by p(AN-co-AAm) (0.25:1 mole ratio) was carried out and an sorption capacity of 220 mg UO_2^{2+} mg/g dried hydrogel was found. The highest amount of UO_2^{2+} ion sorption, 277 mg/g dry gel was accomplished at pH 4.

Key Words
Hydrogel, amidoximation, uranyl ion sorption, p(AN-co-AAm).

ÖZET

Değişik miktarlarda akrilonitril (AN) ve akrilamit (AAm) monomerleri içeren poli(akrilonitril-ko-akrilamit) ((p(AN-co-AAm)) hidrojelleri eş zamanlı redoks ve microemülsiyon polymerizasyon teknikleri kullanılarak gerçekleştirilmiştir. Hazırlanan hidrojeller sulu ortamdan uranil iyonları soğurumu için amidoxime reaksiyonuna tabii tutulmuşlardır. P(AN-co-AAm) (0.25:1 mole oranında) tarafından batch tipi UO_2^{2+} iyonu çalışmaları yapılmış ve kuru hidrojel başınan 220 mg/g soğurma kapasitesi bulunmuştur. En fazla uranil iyonu soğurma kapasitesi pH 4 de gram kuru jel başına 277 mg/g olarak gerçekleştirilmiştir.

Anahtar Kelimeler
Hidrojel, amidoksimasyon, uranil iyonu soğurumu, p(AN-ko-AAm).

INTRODUCTION

Toxic metal ions, especially radioactive ones contaminate the environments are generally the results of industrial activities, mining plants, and accidents [1-3]. Uranium (U) and thorium (Th) are among the most common metal ions [3,4] that threaten the environment with both toxic, radioactive nature and suspected for teratogenic effects on unborn childs [2,3,5,6]. Even catastrophic events cause to the leak of toxic radioactive metal ions such as UO_2^{2+} and Th^{4+} threatening the living organism and eco systems needs urgent measures to be taken [3,7,8]. The form of UO_2^{2+}, $UO_2(OH)^+$, $UO_2(OH)_2$ and $UO_2(OH)_3^-$ from soil, rock, mines can exist and create environmental problems. The form of these metal ions is strongly depend on the pH of the medium and the presence of other ions [3,6,8-11]. For the removal of UO_2^{2+} from aqueous environments various materials such as clays, ion exchange resins, ashes, activated carbon and polymeric structures has been widely used [5,7,8,11]. Hydrogels are capable of absorbing water up to a hundred times their dry weights, and in some cases even thousands of times [3]. The ability to operate in aquatic environments provide many advantages for hydrogels to be used in many applications such as bioengineering, pharmaceuticals, medicine, food industry, water purification, sensors and so on [3,12,14-16]. There are many investigations in the literature reported the use of hydrogels in the removal of toxic metal ions [2-3,5,17-19]. Especially some hydrogels are chemically modifiable for specific purpose to adopt additional characteristics such as higher removal of toxic contaminant metal ions [3,16,20].

European Union (EU) plan to introduce a legal limit for the maximum concentration of uranium in drinking water, however different national health authorities and the World Health Organization (WHO) recommends between 10 -15 µg/L [21]. As one of the important actinide as a fuel in nuclear industry, the geochemical pathways of uranium is extremely important due to its long term toxic implications. Together with the other toxic metal ions such as Cu, Zn, Pb, Cd, and Hg, the removal of UO_2^{2+} is extensively investigated [1-6,8-10,12,17, 19, 22]. Several techniques have been developed for determination uranium including spectrometry, neutron activation, spectrophotometer, molecular fluorescence spectrometry, gas chromatography, complex metric titration and voltammeter [22-24]. There are many complexing agents such as sodium salicylate, chloranilic acid, cupferron, propyl gallate, catechol, potassium hydrogen phthalate, 8-hydroxyquinoline, pyromellitic acid, arsenazo (III), and humic acid [22-25] for uranium to be complexed and quantification. Several absorbent materials containing amidoxime groups from the amidoximation of nitrile groups [26] such as N-vinyl 2-pyrrolidone/acrylonitrile copolymeric hydrogels [20], poly(hydroxamic acid) [17] were used in the recovery and enrichment of uranium from aqueous media as well as some other absorbents [19, 27-30].

In this study, p(AN-co-AAm) hydrogels were synthesized via redox and microemulsion polymerization technique and used in UO_2^{2+} recovery after amidoximation reactions. The hydrogels were characterized by swelling experiments, thermogravimetric analyzer, and FT-IR spectroscopy.

Materials and Method

Materials

Acrylonitrile (AN) and acrylamide (AAm) (99% Sigma–Aldrich), as monomers, N, N methylene bisacrylamide (MBA) (99%, Sigma) as crosslinkers, ammoniumpersulfate (APS) (98%, Aldrich) as an initiator, sodium dodecylsulfate (SDS,) as anionic surfactant and N, N, N', N'-tetramethyl ethylenediamine (TEMED) (Across) as an accelerator were used in the hydrogel preparation. Hydroxylamine hydrochloride ($NH_2OH.HCl$, Merck) and sodium hydroxide (NaOH) were used for the amidoximation reactions. Uranium (UO_2^{2+}) solution was prepared from uranium acetate dihydrate, $UO_2(CH_3COO)_2.2H_2O$ by dissolution in water to obtain 2000 ppm stock solution. This solution was diluted with DI water to obtain 100 ppm diluted (UO_2^{2+}) concentrations. Sodium salicylate (SS) (Merck) was prepared in deionized water (DI) and used as complexing agent for spectrophotometric experiments. All the reagents were of analytical grade or

highest purity available, and used without further purification. The DI water was 18.2 MΩ.cm (Millipore Direct-Q3 UV) and was used throughout the experiments. The pHs of the solution were adjusted by the addition of 0.1 M HCl and 0.1 M NaOH to the medium and the measurements were performed using a Sartorius Documenter pH meter. UV-Vis (T80+UV-VIS Spectrometer, PG Ins. Ltd) spectrophotometer was used to quantify uranium complex with SS at 327 nm for sorption studies.
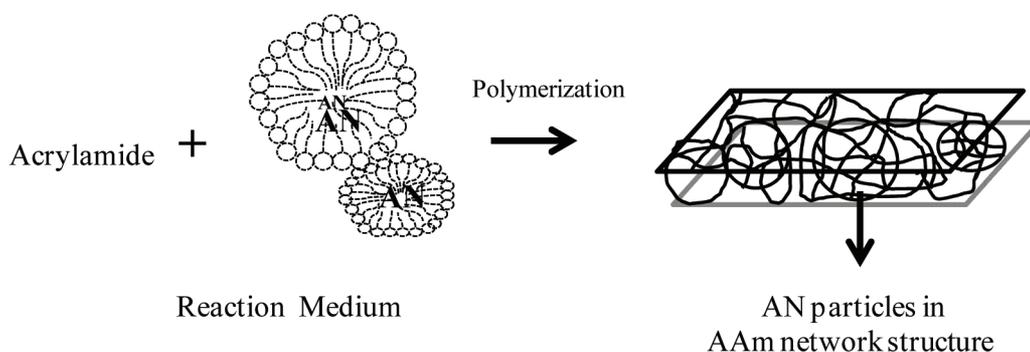
Synthesis of p(AN-co-AAm) based hydrogels

The hydrogels of p(AN-co-AAm) were synthesized by combination of the redox and micro emulsion polymerization technique as shown in Figure 1. In brief; to a constant weight of AAm (0.555 g) mixed with various amount of AN, and 0.05 mol % MBA with respect to total monomer amounts as a crosslinking agent was dissolved by mixing thoroughly via vortex mixer in 1 M 2 mL aqueous SDS. The mole ratio of AN to AAm were 0:1, 0.25:1, 0.5:1, 1:1, 1.5:1, 2:1. Then to these solutions, 5 μl TEMED was added and finally, the initiator solution, 200 μl APS (0.75 mol % with respect to total monomer) in water was added to this hydrogel precursor. After mixing carefully, the solution was injected into plastic straws with 5 mm diameter and allowed to polymerize and crosslink to complete the reaction at ambient temperature. Then, hydrogels were removed from the plastic straws, cut into 6 mm long cylinders. The hydrogels were washed with 1 M and 5 M NaCl by replenishing the NaCl solutions every 8 h for 24 h to remove SDS from hydrogel network, and washed with DI placing in DI water every 6 h for 72

h. After the cleaning procedure, hydrogels were dried in an oven at 40°C to a constant weight, and kept in sealed containers for sorption experiments and swelling studies. In this study, sorption term is used for the combination of absorption and adsorption terms. The synthesis mechanism is given in Figure 1.
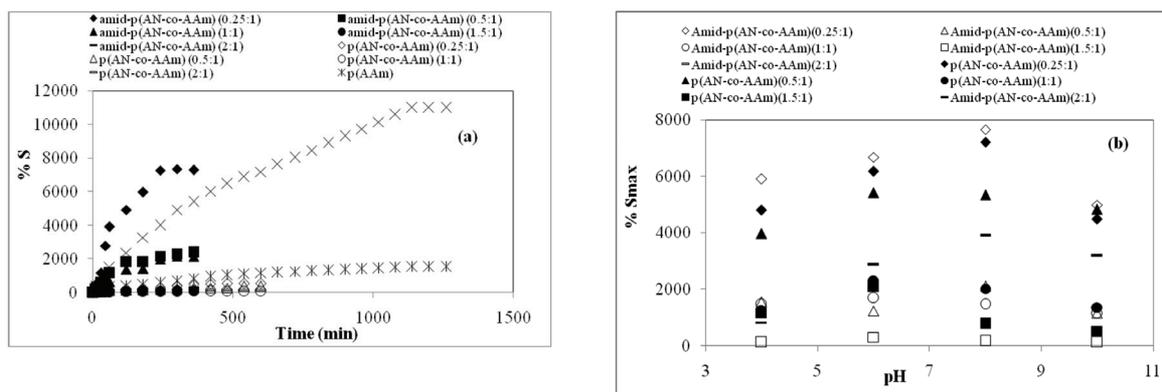
In the amidoximation reaction, the conversion of hydrophobic nitrile groups from AN moieties were converted to hydrophilic amidoxime groups within p(AN-co-AAm). The excess amounts (at least 3 fold) of 10 wt % of $NH_2OH.HCl$ (based on nitrile groups) neutralized by NaOH were prepared and reacted with the polymeric hydrogels under constant stirring at 150 rpm for 24 h at room temperature. The amidoximated bulk hydrogels were washed with copious amount of DI water and were dried in an oven at 40°C to a constant weight.

Characterization and swelling behavior of hydrogels

Swelling studies of hydrogels were carried out in triplicate at room temperature by placing certain amounts of dried hydrogels in DI water and buffer solutions with different pH values. The mass increase was periodically measured by weighing the hydrogels after blot drying with filter paper to remove the superficial water, and returned into the same swelling media. Hydrogels were kept in swelling medium for 24 h to determine the maximum swelling values, % S_{max}. The % S values can be calculated by subtracting the dry weight of the hydrogel from the water swollen weight at time and dividing by dried weight and then

Acrylamide + [Reaction Medium] → Polymerization → AN particles in AAm network structure

Figure 1. The schematic representation of p(AN-co-AAm) hydrogel synthesis.

Figure 2. (a) Percent swelling degrees of hydrogels with time in DI water (% S vs time), and (b) Swelling of hydrogels as a functional of pH.

by multiplying the overall result by 100. Swelling characterization was also studied as a function of pH between 4 and 10 by adjusting the pH of the solutions with 0,1 M HCl and 0,1 M NaOH by kepting them 24 h in acidic/basic solutions to determine the effect of medium pH on hydrogel swellings.

The FT-IR spectra of hydrogels were obtained from a Perkin Elmer Spectrum 100 instrument using ATR apparatus with 4 cm^{-1} resolution between 4000 and 650 cm^{-1}. The thermal behavior of the prepared hydrogels were investigated using a thermo gravimetric analyzer (SII TG/DTA 6300 model). Approximately 4-6 mg dried samples were placed in ceramic crucibles and heated up to 1000 °C from 50 °C under N$_2$ atmosphere with 100 mL/min flow rate at 10 °C/min heating rate.

Sorption studies from aqueous media

The sorption experiments were carried in a room temperature at 25 °C from aqueous UO$_2^{2+}$ solutions. The maximum sorption amounts of hydrogels prepared at different mole compositions of AN and AAm were determined by placing 0.05 g hydrogel into 100 ppm 50 mL UO$_2^{2+}$ ion solution for 24 h. To investigate the time dependent sorption of the hydrogels, 0.05 g of hydrogel was placed in 100 ppm 200 mL UO$_2^{2+}$ ions solutions under constant mixing rate. The UO$_2^{2+}$ solution of about 3 ml were taken from the sorption medium at certain time intervals, and mixed with 1000 ppm 0.3 ml SS, and the absorbance values of this complex were measured using UV-Vis spectrometer after diluting with DI water by 1 to 1 volume ratio. The absorbed amounts of UO$_2^{2+}$ was determined

from a calibration constructed at 327 nm for the complex between the uranium ions and SS.

Results and Discussion

Characterization and swelling behavior of hydrogels

The percent swelling (% S) degree before and after amidoximation as the function time is given in Figure 2(a). The % swelling ratio (% S) was calculated as:

$$\% S = \left(\frac{(M_t - M_o)}{M_o} \right) * 100 \qquad (1)$$

Where M$_o$ and M$_t$ are the initial mass and the mass of hydrogels at time t, respectively [15]. All the experiments were carried out in triplicates. As can be seen from the Figure 2, the swelling values increased drastically the amidoximation reaction and reached to 7290 % from 530 % for amid-p(AN-co-AAm) (0.25:1) and p(AN-co-AAm) (0.25:1), respectively. Due to the hydrophobic nature of AN in the copolymeric network, the swelling degrees were increased with the amidoximation reaction. However, as the amount of AN content of the systems is increased the complete amidoximation can not be possible as shown in Figure 2 (a) from the swelling experiments. Also, medium pH versus %S$_{max}$ swellings were investigated as a function of pH (pH 4-10) as shown in Figure 2(b). Form Figure 2(b) the maximum swelling values were obtained at pH 8 and 6 for all hydrogels. This interval about the neutral pH and the amidoximated materials has ionization pH ranges about these pHs [16, 19, 25].
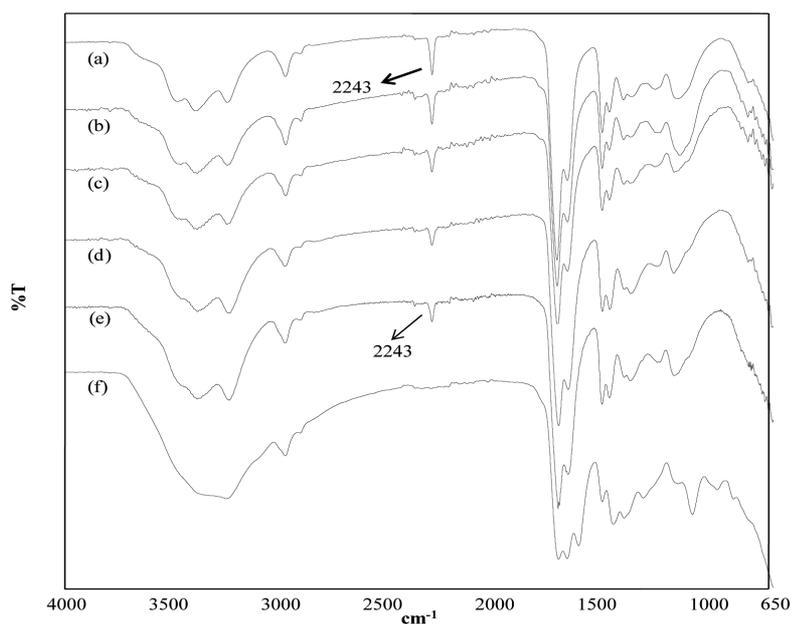
Figure 3. FT-IR analysis of (a) p(AN-co-AAm)(0.25:1), (b) p(AN-co-AAm)(0.5:1), (c) p(AN-co-AAm) (1:1), (d) p(AN-co-AAm)(1.5:1), (e) p(AN-co-AAm)(2:1) (f) p(AN-co-AAm) (2:1) after the amidoximation reaction.

To determine the functional groups in the hydrogel and their copolymeric froms, FT-IR spectra of hydrogels before and after amidoximation was taken and given in Figure 3. In Figure 3(a-e), the characteristic nitrile stretching band due to AN stretching at about 2243 cm^{-1} can be clearly seen. As there is no obvious increase in the intensity of AN bands for these hydrogel systems, the AN content of the copolymeric hydrogels may not increase with the increase in the feed ratio during synthesis. In the Figure 3(f), the nitrile peak is disappeared due to the amidoximation reactions. The peaks belonging to the AAm monomer and cross linker at 3353 cm^{-1}, 3500 cm^{-1} can be assigned for N-H stretching vibration of the amide group [4,31]. The peaks observed at 2941 cm^{-1}, 2929 cm^{-1} and 2926 cm^{-1} in the spectrum belong to the –CH stretching vibrations, and the peaks at 1641 cm^{-1}, 1646 cm^{-1} and 1643 cm^{-1} in the spectrum belong to the C=O stretching vibrations, whereas, the peaks at 1479 cm^{-1}, 1480 cm^{-1} can be assign to the C-N stretching vibrations, respectively for the both amid-p(AN-co-AAm), p(AN-co-AAm), p(AAm) hydrogels and cross-linker.
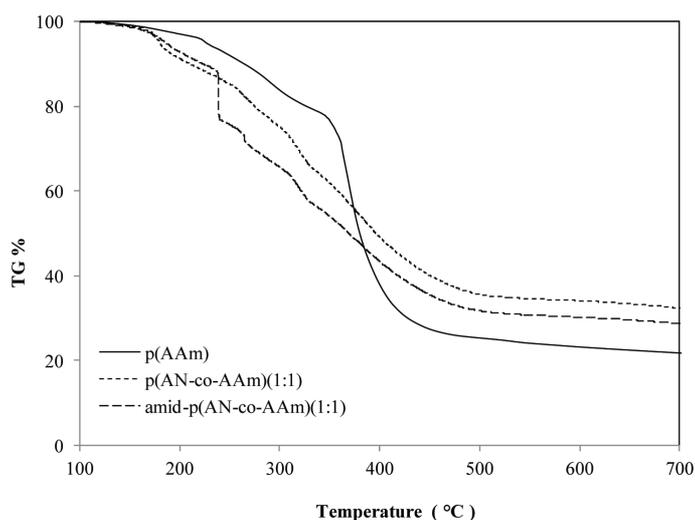
Figure 4. Thermogravimetric analysis of p(AAm), p(AN-co-AAm)(1:1), amid-p(AN-co-AAm) (1:1) .

Thermal behavior of the bulk hydrogels before and after amidoximation reaction is given Figure 4. In the previous research the temperature depended of homopolymeric p(AN) weight loss demonstrated two step degradations at 211°C and 378 °C (18). As shown in Figure 4, p(AN-co-AAm)(1:1) have six degradation temperature. And, 11 and 77 % of the weights were lost at 238 and 900 °C, respectively. The amid-p(AN-co-AAm)(1:1) hydrogel have seven degradations temperatures with weight losses of 27% up to 264°C, 32% at 290°C, 39% at 320°C, 52% at 380°C, and 78% at end of 900°C. Individual p(AAm) have also four degradation temperatures, and lost 83% of the original weight the end of 900°C.

Equilibrium Sorption Studies

In the metal ion sorption studies, the maximum metal ion concentration absorbed per unit mass of the hydrogel, qe (mg/g) was calculated using the following equation [32]:

$$q_e = \frac{(C_o - C_e) * V}{W} \qquad (2)$$

Where C_o and C_e are the initial and equilibrium metal ion concentrations (mg/L), V is volume of metal ion solution and W is the weight (as gram) of the p(AN-co-AAm), Amid-p(AN-co-AAm) and p(AAm) used.

Upon amidoximation reaction, the hydrophobic nitrile groups in the hydrogel converted to hydrophilic amidoxime groups. The amounts of absorbed UO_2^{2+} ion with time from 50 mL 100 ppm UO_2^{2+} ion at absorbent dosage 0.05 g is shown in Figure 5. In the figure, the UO_2^{2+} ion sorption of p(AN-co-AAm)(0.25:1) before and after amidoximation reaction is given. It is obvious that the amidoximation significantly increases the sorption capacity of the hydrogels, and all reaches maximum sorption amounts in about 10 h. The maximum UO_2^{2+} ion sorption of p(AN-co-AAm)(0.25:1) is 62 mg/g and after amidoximation this value increases 221 mg/g. This shows the high binding tendency of amidxoime groups for the UO_2^{2+} ions.

The UO_2^{2+} removal by the prepared hydrogel system is given in Table 1. Before UO_2^{2+} sorption studies, the prepared hydrogels were washed with 1 M and 5 M NaCl to remove SDS surfactants. The amounts of absorbed UO_2^{2+} ions by the prepared hydrogels were given in Table 1. As can be seen from the table, the amidoximated hydrogels absorb more UO_2^{2+} ions and upon washing the prepared hydrogel with 5 M NaCl hydrogel, the sorption capacity increased significantly in comparison to the hydrogel that were washed 1 M NaCl. As the wash with higher salt concentration removes more SDS from the system, the amidoximation reaction and the UO_2^{2+} ion sorption become more effective.
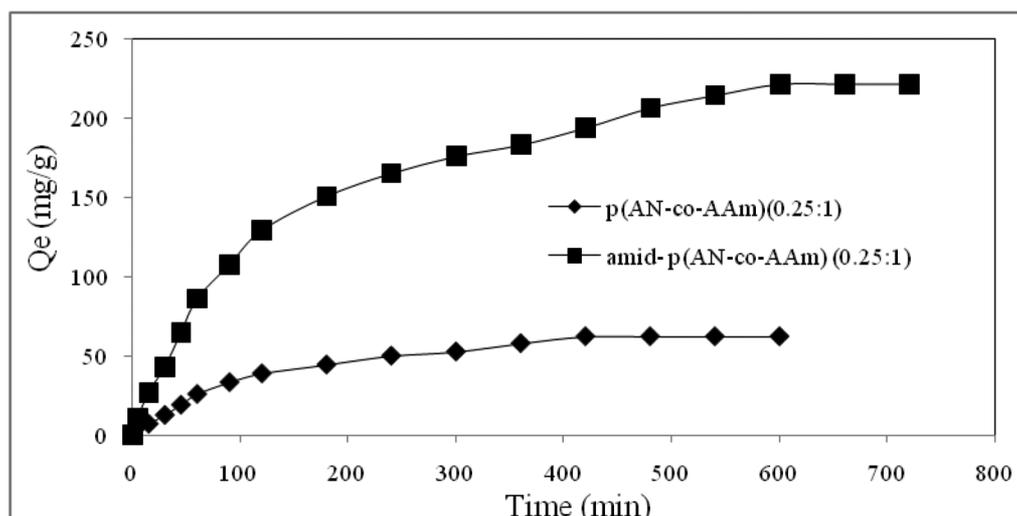

Figure 5. The amounts of absorbed UO_2^{2+} with time by p(AN-co-AAm) (0.25:1) and amid-p(AN-co-AAm) (0.25:1) hydrogels. [UO_2^{2+} concentration; 50 mL, 100 mg L^{-1}, and adsorbent dosage :0.05 g].

Table 1. The amount of UO_2^{2+} ion sorption of p(AN-co-AAm) hydrogels washed DI water, 1 M NaCl and 5 M NaCl. [UO_2^{2+} concentration: 100 mg L^{-1} 50 mL,. adsorbent dosage :0.05 g with 24 h contact time].

Hydrogels	ID Water (Qe (mg/g))	1 M NaCl Qe (mg/g)	5 M NaCl Qe (mg/g)
p(AN-co-AAm) (0.25:1)	27	46	62
Amid -p(AN-co-AAm) (0.25:1)	72	84	220
p(AN-co-AAm) (0.5:1)	15	52	59
Amid -p(AN-co-AAm) (0.5:1)	52	70	130
p(AN-co-AAm) (1:1)	14	42	48
Amid -p(AN-co-AAm) (1:1)	23	67	85

In general, as the mole ratio of AN increase in the hydrogels, the UO_2^{2+} sorption capacity does not increase. Upon amidoximation the UO_2^{2+} adsorption capacity of the hydrogels were increased. However, as the AN content of hydrogels were increased in the amidoximated hydrogels, the UO_2^{2+} sorption capacity do not increase either, this could be due to the more hydrophobic nature and incomplete amidoximation reactions. The optimum ratio for p(AN-co-AAm) hydrogel was found as 0.25:1 amongst the prepared hydrogels with 220 mg/g absorbed UO_2^{2+} ion.

The effect of pH on UO_2^{2+} sorption was also investigated, and the corresponding data are shown in Fig 6. As can be seen from the figure, the maximum amounts of UO_2^{2+} ions were absorbed by the hydrogel at about pH 4, and slightly decrease upon the increase in the medium pH around 6 and 7 was observed. It is known that uranyl ions can precipitate at higher pH [2, 10, 16, 17, 19], therefore the reduction in the sorption capacity of the prepared hydrogels with high pH values is reasonable.
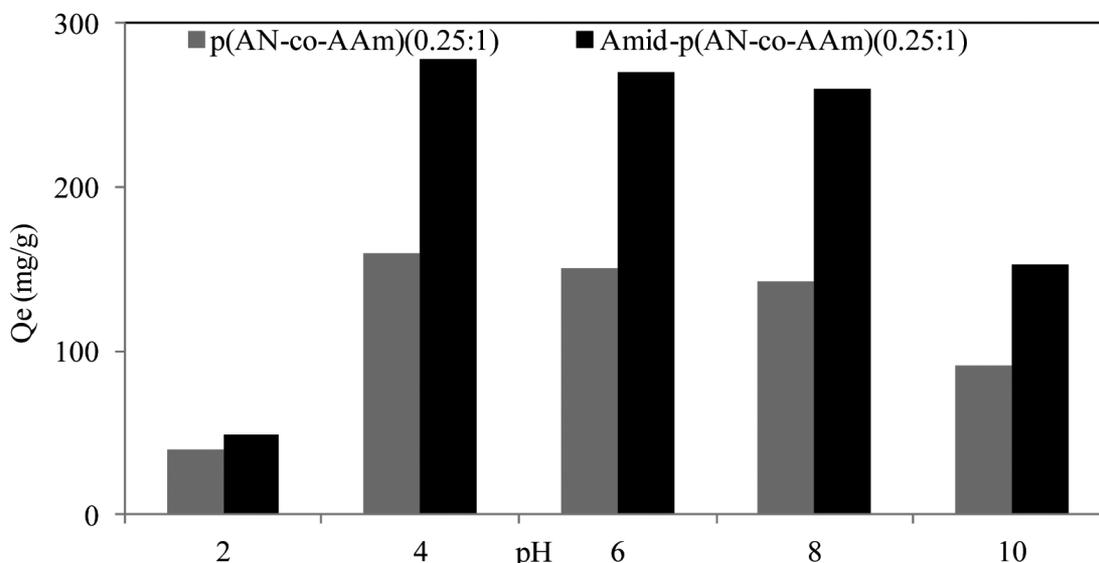
Figure 6. The effect of pH (2-10) on the sorption of UO_2^{2+} into p(AN-co-AAm) (0.25:1) and amid-p(AN-co-AAm)(0.25:1) [UO_2^{2+} concentration: 50mL, 100 mgL^{-1} absorbent dosage :0.05 g].

Conclusions

Here, we report the use of p(AAm) hydrogel matrix containing p(AN) moieties with different content. These combined p(AN-co-AAm) with different mole ratio can be readily prepared and amidoximated for uptake of uranyl ions from different aquatic environments.

Acknowledgements

References

1. D. James, G. Venkateswaran, T. Prasada Rao, Removal of uranium from mining industry feed simulant solutions, Micropor. Mesopor. Mater. 119 (2009) 165.

2. U. Ulusoy, R. Akkaya, Adsorptive features of polyacrylamideeapatite composite for Pb^{2+}, UO_2^{2+} and Th^{4+}, J. Hazard. Mater., 163 (2009) 98.

3. O. Ozay, S. Ekici, N. Aktas, N. Sahiner, P(4–vinyl pyridine) hydrogel use for the removal of UO_2^{2+} and Th^{4+} from aqueous environments, J. Environ. Management, 92 (2011) 3121.

4. A. Denizli, R. Say, B. Garipcan, S. Patır, Methacryloylamidoglutamic acid functionalized poly(2–hydroxyethyl methacrylate) beads for UO_2^{2+} removal, React. Funct. Polym., 58 (2004) 123.

5. R. Han, W. Zou, Y. Wang, L. Zhu, Removal of uranium(VI) from aqueous solutions by manganese oxide coated zeolite: discussion of absorption isotherms and pH effect, J. Environ. Radioact., 93 (2007) 127.

6. A.M. Donia, A.A. Atia, E.M.M. Moussa, A.M. El–Sherif, M.O. Abd El–Magied, Removal of uranium (VI) from aqueous solutions using glycidyl methacrylate chelating resins, Hydrometallurgy, 95 (2009) 3.

7. S. Kundakcı, O.B. Uzum, E. Karadağ, A New composite sorbent for water and dye uptake: highly swollen acrylamide/2–acrylamido–2–methyl–1–propanesulfonic acid/clay hydrogels crosslinked by 1,4–butanediol dimethacrylate, Polym. Composite., 30 (2009) 29.

8. B. Boonchayaanant, D. Nayak, X. Du, C.S. Criddle, Uranium reduction and resistance to reoxidation under iron–reducing and sulfate–reducing conditions, Water Res., 43(2009) 4652.

9. G. Atun, S. Ortaboy, Adsorptive removal of uranium from water by sulfonated phenol "formaldehyde resin, J. Appl. Polym. Sci., 114 (2009) 3793.

10. E. Karadağ, O.B. Uzum, S. Kundakcı, D. Saraydın, Polyelectrolyte casa hydrogels for uptake of uranyl ions from aqueous solutions, J. Appl. Polym. Sci., 104 (2007) 200.

11. O. Ozay, S. Ekici, Y. Baran, N. Aktas, N. Sahiner, Removal of toxic metal ions with magnetic hydrogels, Water Res., 43 (2009) 4403.

12. O. Ozay, S. Ekici, Y. Baran, S. Kubilay, N. Aktas, N. Sahiner, Utilization of magnetic hydrogels in the seperation of toxic metal ions from aqueous environments, Desalination, 260 (2010) 57.

13. O.B. Uzum, S. Kundakci, E. Karadağ, Uranyl ion uptake from aqueous solutions by chemically cross–linked polyelectrolyte CAMA hydrogels, Polym. Plastic. Technol. Eng., 46 (2007) 775.

14. N. Sahiner, M. Singh, In situ micro/nano–hydrogel synthesis from acrylamide derivates with lecithin organogel system, Polymer, 48 (2007) 2827.

15. M.A. Barakat, N. Sahiner, Cationic hydrogels for toxic arsenate removal from aqueous environment, J. Environ. Management, 88 (2008) 955.

16. N. Pekel, N. Sahiner, O. Güven, Thermodynamics of absorption of uranyl ions onto amidoximated poly(acrylonitrile)/poly(N–vinyl 2–pyrrolidone) interpenetrating polymer networks, J. Polym. Sci. Part B–Polym. Phys., 42 (2004) 986.

17. D. Saraydın, Y. Isikver, N. Sahiner, Uranyl ion binding properties of poly(hydroxamic acid) hydrogels, Polym. Bull., 47 (2001) 81.

18. S. Ortaboy, E. Acar, G. Atun, S. Emik, T. Iyim, G. Guclu, S. Ozgumus S, Performance of acrylic monomer based terpolymer/montmorillonite nanocomposite hydrogels for UO(VI) removal from aqueous solutions, Chem. Eng. Res. Design, 91 (2013) 670.

19. N. Pekel, N. Sahiner, P. Akkas, O. Guven, Uranyl ion adsoptivity of N–vinyl 2–pyrrolidine/acryonitrile copolymeric hydrojels containing amidoxime groups, Polym. Bull., 44 (2000) 593.

20. C. Liu, L. Zhong, J.M. Zachara, Uranium(VI) diffusion in low–permeability subsurface materials, Radiochim. Acta, 98 (2010) 719.

21. J. Schafer, H.P. Nirmaier, P. Schmoll, K.H. Bauer, A. Meyer, Ultratrace determination of uranium (VI) drinking water by adsorptive stripping voltammetry according to DIN38406–17.

22. S. Sahoo, A.K. Satpati, A.V.R. Reddy, Stripping voltammetric determination of uranium in water samples using hg–thin film modified multiwall carbon nanotube incorporated carbon paste electrode, Am. J. Anal. Chem., 4 (2013) 141.

23. M.B. Gholivand, H. Rashidi Nassab, H. Fazeli, Cathodic adsorptive stripping voltammetric determination of uranium (VI) complexed with 2, 6–pyridinedicarboxylic acid, Talanta, 65 (2005) 62.

24. S. Sander, G. Henze, Absorption voltammetric tehniques for the determination of uranium (VI) with 2,5–dichloro–3,6–dihydroxy–1,4 benzoquinone as complex forming agent, Fresenius J. Anal. Chem. 349 (1994) 654.

25. H. Güler, N. Sahiner, G.A. Aycık, O. Güven, Development of novel adsorbent materials for recovery and enrichment of uranium from aqueous media, J. Appl. Polym. Sci., 66 (1997) 2475.

26. N. Sahiner, S. Butun, P. Ilgin, Soft hydrogel particles with high functional value, Colloid. Surf. A: Physicochem. Eng. Aspect., 381 (2011) 74.

27. T.B. Mostafa, Chemical modification of polypropylene fibers grafted vinyl imidazole/acrylonitrile copolymer prepared by gamma radiation and its possible use for the removal of some heavy metal ions, J. Appl. Polym. Sci., 111 (2009) 11.

28. N. Pekel, Z.M.O. Rzaev, O. Güven, Synthesis and characterization of poly (N–vinylimidazole–co–acrylonitrile) and determination of monomer reactivity ratios, Macromol. Chem. Phys., 205 (2004) 1088.

29. N. Sahiner, P. Ilgın, Synthesis and characterization of soft polymeric nanoparticles and composites with tunable properties, J. Polym. Sci. Part A: Polym. Chem., 48 (2010) 5239.

30. O. Ozay, N. Aktas, N. Sahiner, Hydrogels as a potential chromatographic system: absorption, speciation, and separation of chromium species from aqueous media, Sep. Sci. Technol., 46 (2011) 1450.