NUCL SCI TECH (2017) 28:45
DOI 10.1007/s41365-017-0198-7

Amidoxime-based adsorbents prepared by cografting acrylic acid with acrylonitrile onto HDPE fiber for the recovery of uranium from seawater

Lu Xu[1] · Jiang-Tao Hu[1] · Hong-Juan Ma[1] · Chang-Jian Ling[1] · Mou-Hua Wang[1] · Rong-Fang Shen[1] · Xiao-Jing Guo[1] · Yin-Ning Wang[2] · Jing-Ye Li[1] · Guo-Zhong Wu[1]

Received: 6 July 2016 / Revised: 13 December 2016 / Accepted: 11 January 2017 / Published online: 27 February 2017

Abstract An amidoxime-based polymeric adsorbent was prepared by pre-irradiation grafting of acrylonitrile and acrylic acid onto high-density polyethylene fibers using electron beams, followed by amidoximation. Quantitative recovery of uranium was investigated by flow-through experiment using simulated seawater and marine test in natural seawater. The maximum amount of uranium uptake was 2.51 mg/g-ads after 42 days of contact with simulated seawater and 0.13 mg/g-ads for 15 days of contact with natural seawater. A lower uranium uptake in marine test can be attributed to the short adsorption time and the contamination of marine microorganisms and iron. However, the high selectivity toward uranium against vanadium may be beneficial to harvest uranyl ion onto adsorbents and the economic feasibility for recovery of uranium from seawater.

Keywords Radiation-induced grafting · Amidoxime · Acrylonitrile · Uranium · Selectivity

1 Introduction

Despite the seawater uranium concentration of just 3.3 ppb, the total amount of uranium in seawater is about 4.5 billion tons, presenting an almost inexhaustible uranium resource. If the recovery of uranium from seawater can be achieved, it will provide an alternative source of uranium to terrestrial mining for future nuclear fuel consumption [1–4]. The recovery of uranium from seawater has been intensively researched in many laboratories, and important achievements have been made [5–9]. Comparing with solvent extraction, ion exchange, flotation and other approaches, the adsorption of uranium on various adsorbents is advantageous [1, 3, 10–12] and has been performed extensively. Among many kinds of adsorbents, fibrous polymeric adsorbents containing amidoxime [AO, –C(NOH)NH_2] groups are considered as a potential candidate due to its high selectivity and capacity for uranyl ions, rapid adsorption rate and safety for environment [1–3, 13–16].

Radiation-induced grafting polymerization (RIGP) is a powerful method for preparing functional polymers, as polymer chains with functional groups can be anchored to substrate polymers upon existing form such as film or fibers without obvious property changes, such as strength and swelling [2, 13, 17]. Okamoto et al. [18] and Omichi et al. [19] firstly reported that the fibrous adsorbents containing amidoxime groups were prepared by RIGP of acrylonitrile (AN) onto fibers followed by amidoximation with hydroxylamine. Upon amidoximation, the cyano groups can be converted into AO groups [20–22]. Furthermore, as the diffusion of uranyl ions determines the overall adsorption of uranium, cografting of hydrophilic monomers such as acrylic acid (AA) or methacrylic acid (MAA)

This work was supported by the National Natural Science Foundation of China (Nos. 21676291, 21306220, 11275252, 11305243 and 11405249). The research was also in part supported by the "Knowledge Innovation Program of Chinese academy of sciences".

✉ Jing-Ye Li
lijingye@sinap.ac.cn

✉ Guo-Zhong Wu
wuguozhong@sinap.ac.cn

[1] Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China

[2] Nuclear and Radiation Safety Center, Ministry of Environmental Protection of the People's Republic of China, Beijing 100035, China

with AN onto fibers is suggested to enhance the diffusion of uranyl ions into AO adsorbents [6, 22, 23].

In our previous work, an AO-based adsorbent was prepared by cografting AA and AN onto ultrahigh molecular weight polyethylene (UHMWPE) fibers [9, 16]. Actually it is not easy to cograft AA and AN onto UHMWPE fibers due to its long stretched molecular chain, which may restrict the migration of radicals. Moreover, the high cost of UHMWPE fibers limits its application in uranium recovery from ocean. In this work, an inexpensive and easily prepared amidoxime-based polymeric adsorbent was prepared by RIGP of AA and AN onto high-density polyethylene fibers (HDPE) and followed by an amidoximation treatment. The uranium adsorption of AO-based adsorbent was evaluated by flow-through experiment and marine test. The degree of grafting was controlled at 230–250 wt%. Flow-through experiment was conducted using simulated seawater, and marine test was performed in natural seawater in a seawater desalination plant.

2 Experimental section

2.1 Materials

HDPE fibers in average molecular weight of 1.5×10^6 and an average diameter of 30 μm, made via a melt spinning method, were supplied by Donghua University and used as trunk polymer for grafting. Acrylic acid (AA), acrylonitrile (AN) and other chemical agents, all of analytical grade, were purchased from Sinopharm Chemical Reagent Co. Ltd.. All agents were used without further purification.

2.2 Adsorbent preparation

The amidoxime-based polymeric adsorbents were prepared by RIGP of AA and AN onto HDPE fibers and subsequent amidoximation modifications as shown in Fig. 1. HDPE fibers were pre-irradiated by electron beam to 200 kGy in air at room temperature. The irradiated fibers were immersed into a 60 wt% DMF solution of AN/AA comonomer and deaerated by nitrogen. The mole ratio of AN/AA was set as 80/20. Cografting of AN and AA onto the irradiated HDPE fibers was performed at 70 °C for several hours. After repeated rinsing by dimethylformamide and deionized water, the grafted fibers were vacuum-dried and weighed. The degree of grafting was calculated by $\mathrm{DG} = [(W_1 - W_0)/W_0] \times 100\%$, where W_0 and W_1 are the weights of HDPE fiber before and after grafting, respectively.

Various degrees of grafting of HDPE were prepared and screened; the grafted HDPE-*g*-PAA-*co*-PAN fibers with DG at 230–250 wt% were selected for amidoximation. They were treated by hydroxylamine hydrochloride (NH_2-OH·HCl) solution of pH 7.0 at 80 °C for 2 h to covert the grafted cyano groups to AO groups. After reaction, the obtained HDPE-*g*- PAA-*co*-PAO adsorbents were washed by deionized water for several times and vacuum-dried.

2.3 Characterization

Chemical structures of the pristine HDPE fiber, HDPE-*g*-PAA-*co*-PAN fiber and HDPE-*g*-PAA-*co*-PAO fiber were analyzed with Fourier transform infrared spectroscopy on a Bruker Tensor 27 FTIR spectrometer (Bruker Optics, Germany) in the range of 600–4000 cm^{-1}.

2.4 Flow-through test

The adsorbent performance in simulated seawater was carried out on a laboratory scale 1.5 m^3/day simulated seawater adsorption system as shown in Fig. 2.

Simulated seawater was prepared by sea salt in DI water followed by adjusting of salinity (35 psu), metallic ion concentrations (Table 1) and pH of solution. For characterization of kinetic adsorption data on the amount of uranium and other coexisting ions as a function of time, a series of adsorption experiment over 6 weeks was performed using this system. Seven columns of HDPE-*g*-PAA-*co*-PAO fiber adsorbents were placed in parallel in this continuous flow-through system. Amidoxime-based HDPE adsorbents (0.2 g) were freely dispersed and packed in each column, and the empty space was filled up with polyethylene terephthalate (PET) fibers. The simulated seawater was drawn from a reservoir and forced through the manifold using a pump with all fluorine plastic components in the pump head and PPH tubing feed lines. With a thermostatic water tank kept at 25 ± 2 °C, the simulated seawater adsorption was performed at a flow rate of 35 ± 2 mL min^{-1} using actively pumping systems. Adjustments were made when the temperature increased by 2 °C and the flow rate increased by 10%. The adsorbent in each column was periodically removed at intervals of 6–8 days.

2.5 Adsorption in seawater

The seawater testing was performed in a seawater desalination plant (Zhejiang, China). The seawater with precipitation treatment was pumped through 4 g adsorbents fixed on the canal bed at the flow rate of 80 cm/s at 21 ± 2 °C. After 15 days of exposure, the adsorbents were taken out of canal. The trace metal concentrations in seawater are given in Table 1.

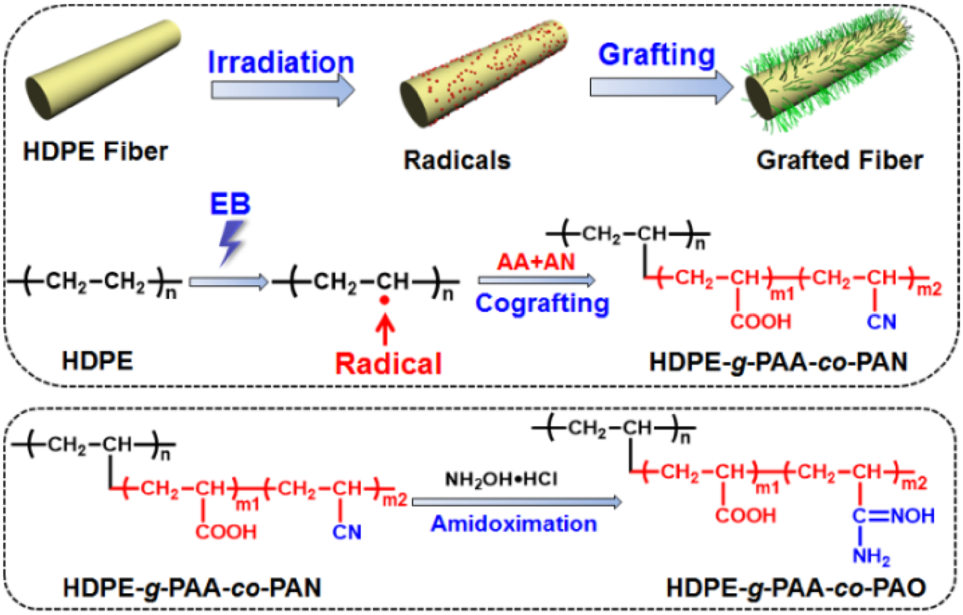

Fig. 1 Preparation of amidoxime-based polymeric adsorbents by RIGP of AA and AN onto HDPE fibers and subsequent amidoximation

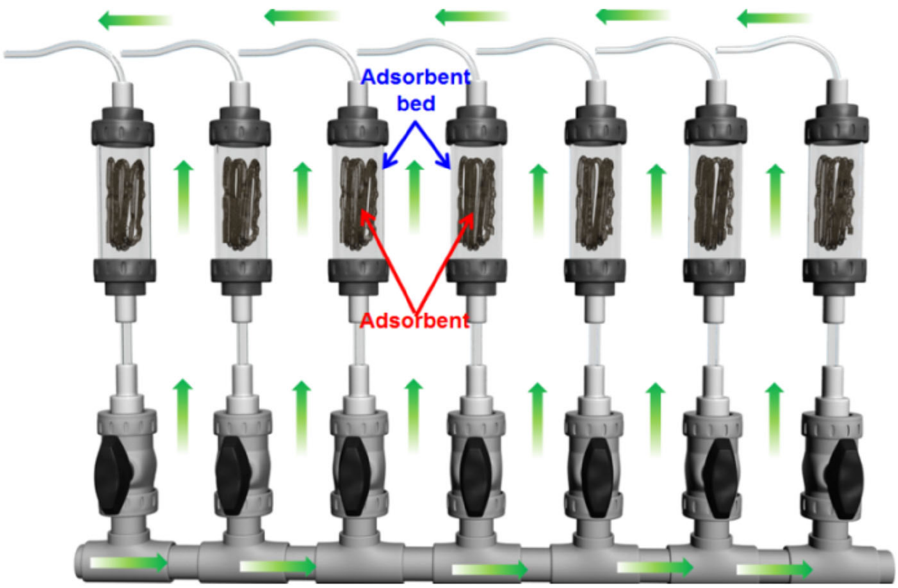

Fig. 2 Schematic diagram of continuous flow-through system

Table 1 Concentration of various elements in simulated water and natural seawater

Elements	U	V	Fe	Co	Ni	Cu	Zn	Pb
Simulated water								
Ion valence	UO_2^{2+}	VO_3^-	Fe_3^+	Co_2^+	Ni_2^+	Cu_2^+	Zn_2^+	Pb_2^+
Ion conc. (ppb)	3.6	1.9	40.6	0.3	1.1	5.4	8.2	31.6
Natural seawater (ppb)	2.61	2.54	85.6	0.21	1.85	4.3	8.69	1.48

2.6 Analysis process

The exposed adsorbent fibers were collected from adsorbent columns, washed with DI water to remove salts and vacuum-dried at 60 °C. The dried adsorbents (100 mg) were digested with 10 mL high-purity concentrated nitric acid in an MARS6 Microwave Digestion System (CEM, USA). High-purity DI water (Optima, Fisher Scientific) was added to make a 50-mL dilute acid solution and to give desired concentration range of uranium for analysis. Inductively coupled plasma atomic emission spectrometry (ICP–AES, Thermo Scientific X-Series II) was used for quantitative analysis of uranium. Each sample was analyzed twice against a four-point calibration curve. The adsorbed amounts of uranium (Q) were calculated by $Q = C \times V/W$, where C is the uranium concentration in digested solution (V), and W is the weight of initial adsorbents.

3 Results and discussion

3.1 Chemical structure of HDPE-*g*-PAA-*co*-PAO adsorbents

In order to prepare HDPE-*g*-PAA-*co*-PAO fiber, AA and AN were first grafted onto HDPE fibers through RIGP method. HDPE-*g*-PAA-*co*-PAN fiber was then amidoximated to give the amidoxime-based adsorbent. The changes in chemical structures of the grafted fiber were confirmed by FTIR spectra.

Figure 3 shows FTIR spectra of HDPE, HDPE-*g*-PAA-*co*-PAN and HDPE-*g*-PAA-*co*-PAO fibers. Compared with the FTIR–ATR spectrum of virgin HDPE fibers, two new peaks appeared in the spectrum of HDPE-*g*-PAA-*co*-PAN fibers at 2243 and 1731 cm^{-1}, corresponding to the $C\equiv N$ groups of AN and C=O of AA grafted onto HDPE, respectively [17, 24]. After amidoximation, the $C\equiv N$ band at 2243 cm^{-1} disappeared completely, while a new and strong C=N stretching vibration at 1645 cm^{-1} appeared, indicating the completely transformation of nitrile into amidoxime groups.

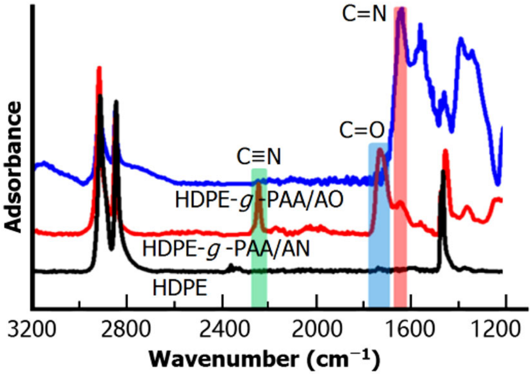

Fig. 3 FTIR spectra of HDPE, HDPE-*g*-PAA-*co*-PAN and HDPE-*g*-PAA-*co*-PAO fibers

3.2 Uranium adsorption in simulated seawater

Flow-through experiments in simulated seawater were performed to investigate the uranium adsorption behavior, and the adsorbent with DG of 252% was employed for this experiments. The uranium adsorption kinetic data are shown in Fig. 4a. The amount of uranium on adsorbents increased nonlinearly with the exposure time. After 42 days of exposure, the uranium uptake was about 2.51 mg/g-ads, but the adsorption equilibrium was still not reached. The initial uranium uptake rate of HDPE adsorbent was 0.25 mg g^{-1} day^{-1} (Fig. 4b) and decreased by 50% at day 6, where the decrease rate began to slow down considerably. The rapid initial uranium uptake rate could be attributed to the chemical adsorption between uranium ions and AO groups on the surface of adsorbents. Upon contacting with simulated seawater, the hydrophilic AO groups on the adsorbent surface reacted immediately with uranium ions with the assistance of carboxylate groups [13] and hence a rapid uptake rate. When adsorption on adsorbent surface reached saturation, the diffusion of metal ions to the inner part of adsorbents appeared. However, this process could be hampered by the metal ions adhered on surface of adsorbents, consequently, leading to the low uptake rate of uranium.

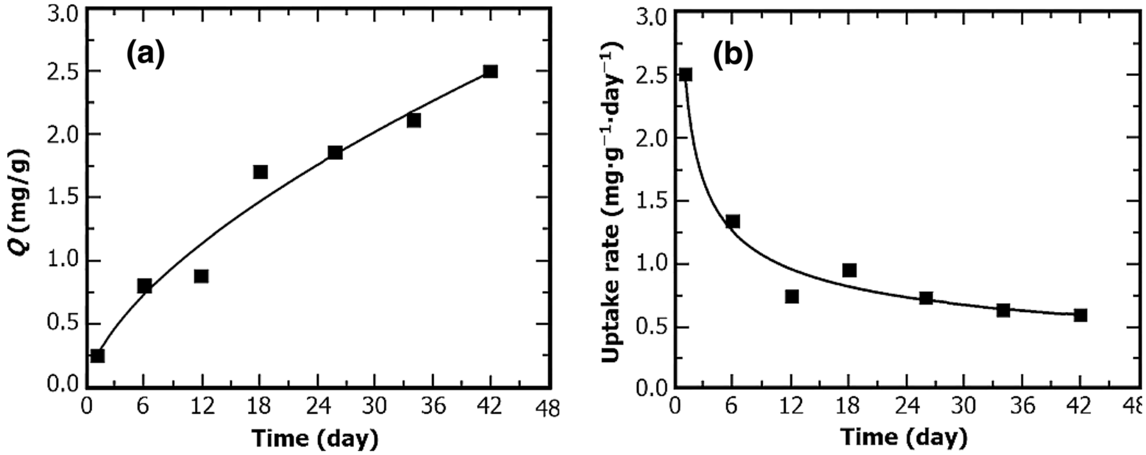

Fig. 4 Uranium adsorption kinetic data (**a**) and uranium uptake rate (**b**) from flow-through tests in simulated seawater

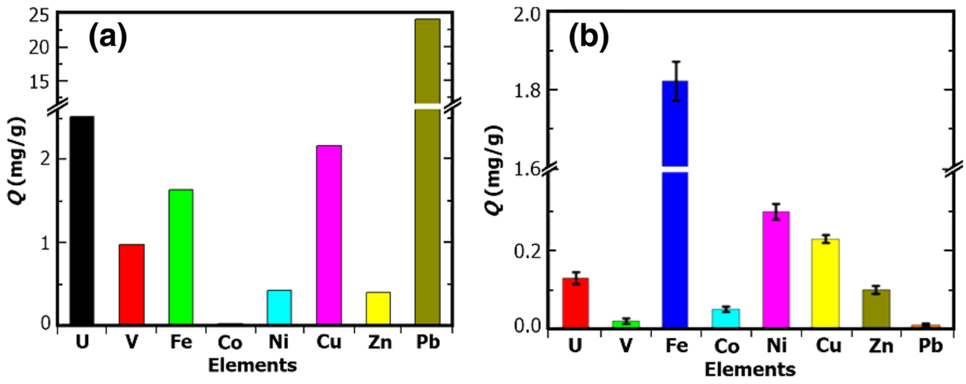

Fig. 5 Uptake capacity of metal ions in flow-through experiments (**a**) and marine test (**b**)

The uptake capacities of metal ions for 42 days of adsorption are summarized in Fig. 5a. The uranium adsorption capacity is the highest of all metal ions except lead ions (whose very high capacity could be attributed to the high Pb concentration in simulated seawater). This indicates that HDPE-*g*-PAA-*co*-PAO adsorbents possess good selectivity for the uranyl ion.

3.3 Uranium adsorption in natural seawater

To further conform the above results and to evaluate the adsorption capacity of uranium in natural seawater, the adsorption experiment in real seawater was carried out. After 15 days of exposure, the adsorbents were taken out from the canal and analyzed. As shown in Fig. 5b, the maximum uranium uptake for 15 days was 0.13 mg/g-ads. The low uranium uptake could be attributed to the short adsorption time and the contamination of marine microorganisms. Furthermore, the concentration of iron in seawater is very high (Table 1), indicating that the seawater used in this work might be polluted by iron or steel parts of facilities. Consequently, the iron uptake is the highest of all, which could affect the adsorption of uranium. It should be noticed that the uranium adsorption capacity is about 6 times higher than that of vanadium, consistent well with the result of flow-through experiment and suggesting high selectivity toward uranium against vanadium. The U/V selectivity of HDPE-*g*-PAA-*co*-PAO fiber in real seawater was far higher than that of JAEA and ORNL fibers [25]. This is meaningful for its use of harvesting uranyl ion onto adsorbents and improving the economic feasibility for uranium recovery from seawater.

4 Conclusion

An amidoxime-based polymeric adsorbent was prepared by RIGP of AA and AN onto high-density polyethylene fibers (HDPE) and a subsequent amidoximation treatment. Uranium adsorption was investigated by flow-through system and marine test. The results in flow-through test showed a maximum uranium uptake capacity of 2.51 mg/g-ads after 42 days of contact with simulated seawater and the initial uptake rate of 0.25 mg g^{-1} day^{-1}. Moreover, this adsorbent also shows high selectivity for uranium. A lower uranium uptake of 0.13 mg/g-ads was observed in marine test, for 15 days of contact with natural seawater, which can be attributed to the short adsorption time and the contamination of marine microorganisms. The high concentration of iron in seawater may also show negative influence on adsorption of uranium. However, the high U/V selectivity of adsorbent shows important advantages for recovery of uranium from seawater. Further investigation of uranium adsorption at ocean site will be carried out.

References

1. A.Y. Zhang, T. Asakura, G. Uchiyama, The adsorption mechanism of uranium(vi) from seawater on a macroporous fibrous polymeric adsorbent containing amidoxime chelating functional group. React. Funct. Polym. **57**, 67–76 (2003). doi:10.1016/j.reactfunctpolym.2003.07.005
2. K. Saito, T. Hori, S. Furusaki et al., Porous amidoxime-group-containing membrane for the recovery of uranium from seawater. Ind. Eng. Chem. Res. **26**, 1977–1981 (1987). doi:10.1021/Ie00070a007
3. X.Y. Liu, H.Z. Liu, H.J. Ma et al., Adsorption of the uranyl ions on an amidoxime-based polyethylene nonwoven fabric prepared by preirradiation-induced emulsion graft polymerization. Ind. Eng. Chem. Res. **51**, 15089–15095 (2012). doi:10.1021/ie301965g
4. H.J. Schenk, L. Astheimer, E.G. Witte et al., Development of sorbers for the recovery of uranium from seawater. 1. Assessment of key parameters and screening studies of sorber materials. Separ. Sci. Technol. **17**, 1293–1308 (1982). doi:10.1080/01496398208056103
5. J. Kim, C. Tsouris, Y. Oyola et al., Uptake of uranium from seawater by amidoxime-based polymeric adsorbent: field experiments, modeling, and updated economic assessment. Ind. Eng. Chem. Res. **53**, 6076–6083 (2014). doi:10.1021/ie4039828
6. T. Saito, S. Brown, S. Chatterjee et al., Uranium recovery from seawater: development of fiber adsorbents prepared via atom-transfer radical polymerization. J. Mater. Chem. A **2**, 14674–14681 (2014). doi:10.1039/c4ta03276d

7. D. Shao, J. Li, X. Wang, Poly(amidoxime)-reduced graphene oxide composites as adsorbents for the enrichment of uranium from seawater. Sci. China Chem. **57**, 1449–1458 (2014). doi:10.1007/s11426-014-5195-7
8. S. Xie, X. Liu, B. Zhang et al., Electrospun nanofibrous adsorbents for uranium extraction from seawater. J. Mater. Chem. A **3**, 2552–2558 (2015). doi:10.1039/c4ta06120a
9. Z. Xing, J. Hu, M. Wang et al., Properties and evaluation of amidoxime-based UHMWPE fibrous adsorbent for extraction of uranium from seawater. Sci. China Chem. **56**, 1504–1509 (2013). doi:10.1007/s11426-013-5002-x
10. M. Kanno, Present status of study on extraction of uranium from sea-water. J. Nucl. Sci. Technol. **21**, 1–9 (1984). doi:10.3327/Jnst.21.1
11. I. Tabushi, Y. Kobuke, T. Nishiya, Extraction of uranium from seawater by polymer-bound macrocyclic hexaketone. Nature **280**, 665–666 (1979). doi:10.1038/280665a0
12. W.J. Williams, A.H. Gillam, Separation of uranium from seawater by adsorbing colloid flotation. Analyst **103**, 1239–1243 (1978). doi:10.1039/An9780301239
13. T. Kawai, K. Saito, K. Sugita et al., Comparison of amidoxime adsorbents prepared by cografting methacrylic acid and 2-hydroxyethyl methacrylate with acrylonitrile onto polyethylene. Ind. Eng. Chem. Res. **39**, 2910–2915 (2000). doi:10.1021/Ie990474a
14. S.H. Choi, Y.C. Nho, Adsorption of uo22+ by polyethylene adsorbents with amidoxime, carboxyl, and amidoxime/carboxyl group. Radiat. Phys. Chem. **57**, 187–193 (2000). doi:10.1016/S0969-806x(99)00348-5
15. Q.H. Gao, J.T. Hu, R. Li et al., Radiation synthesis of a new amidoximated UHMWPE fibrous adsorbent with high adsorption selectivity for uranium over vanadium in simulated seawater. Radiat. Phys. Chem. **122**, 1–8 (2016). doi:10.1016/j.radphyschem.2015.12.023
16. J. Hu, H. Ma, Z. Xing et al., Preparation of amidoximated ultrahigh molecular weight polyethylene fiber by radiation grafting and uranium adsorption test. Ind. Eng. Chem. Res. **55**, 4118–4124 (2016). doi:10.1021/acs.iecr.5b03175
17. S.H. Choi, Y.C. Nho, Radiation-induced graft copolymerization of binary monomer mixture containing acrylonitrile onto polyethylene films. Radiat. Phys. Chem. **58**, 157–168 (2000). doi:10.1016/S0969-806x(99)00367-9
18. J. Okamoto, T. Sugo, A. Katakai et al., Amidoxime-group-containing adsorbents for metal-ions synthesized by radiation-induced grafting. J. Appl. Polym. Sci. **30**, 2967–2977 (1985). doi:10.1002/app.1985.070300720
19. H. Omichi, A. Katakai, T. Sugo et al., A new type of amidoxime-group-containing adsorbent for the recovery of uranium from seawater. Separ. Sci. Technol. **20**, 163–178 (1985). doi:10.1080/01496398508058357
20. S. Das, A.K. Pandey, A. Athawale et al., Chemical aspects of uranium recovery from seawater by amidoximated electron-beam-grafted polypropylene membranes. Desalination **232**, 243–253 (2008). doi:10.1016/j.desal.2007.09.019
21. T. Saito, Y. Oyola, C.J. Janke, Investigation of polymer structure and properties of amidoxime-functionalized hydrophilic random copolymers on performance of uranium recovery from seawater. Abstr. Pap. Am. Chem. Soc. **244** (2012)
22. H.W. Yu, S.S. Yang, H.M. Ruan et al., Recovery of uranium ions from simulated seawater with palygorskite/amidoxime polyacrylonitrile composite. Appl. Clay Sci. **111**, 67–75 (2015). doi:10.1016/j.clay.2015.01.035
23. S. Das, A.K. Pandey, T. Vasudevan et al., Adsorptive preconcentration of uranium in hydrogels from seawater and aqueous solutions. Ind. Eng. Chem. Res. **48**, 6789–6796 (2009). doi:10.1021/ie801912n
24. C.K. Na, H.J. Park, B.G. Kim, Optimal amidoximation conditions of acrylonitrile grafted onto polypropylene by photoirradiation-induced graft polymerization. J. Appl. Polym. Sci. **125**, 776–785 (2012). doi:10.1002/app.35059
25. S. Brown, Y.F. Yue, L.J. Kuo et al., Uranium adsorbent fibers prepared by atom-transfer radical polymerization (atrp) from poly(vinyl chloride)-co-chlorinated poly(vinyl chloride) (pvc-co-cpvc) fiber. Ind. Eng. Chem. Res. **55**, 4139–4148 (2016). doi:10.1021/acs.iecr.5b03355