

# Chemical aspects of uranium recovery from seawater by amidoximated electron-beam-grafted polypropylene membranes

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## Abstract

The amidoximated macroporous membranes (AO membranes) were prepared by post irradiation grafting of acrylonitrile (AN) onto thermally bonded non-woven matrix of poly(propylene) sheet using electron beams. These precursor membranes were reacted with hydroxylamine to convert AN to AO groups, and conditioned by treating them with 2.5% KOH at 80°C for 1 h. The water uptake capacity in seawater, Na<sup>+</sup>-exchange capacity, and uranium loading capacity from seawater of AO membranes were found to be 200±10 wt.%, (3.1±0.2)×10<sup>-4</sup> mol/g, and (1.60±0.18)×10<sup>-3</sup> mol/g, respectively. The expected functional group density based on the degree of AN grafting (125 wt.%) and its subsequent conversion to AO groups (80%) was found to be 7.8×10<sup>-3</sup> mol/g. The comparison of the expected functional group density and uranium uptake capacity seems to suggest that UO<sub>2</sub><sup>2+</sup> forms a complex with AO groups in 1:4 proportion. The uranium could be quantitatively desorbed (>90%) from the AO membrane in Na<sub>2</sub>CO<sub>3</sub> and mineral acids like HCl in the equilibration times of 60 min and 40 min, respectively. Alkaline conditioning was found to be necessary for reuse of the membrane equilibrated with acid. However, AO membranes equilibrated with Na<sub>2</sub>CO<sub>3</sub> could be reused without any conditioning for uranium sorption.

**Keywords:** Amidoxime membrane; Pre-concentration; Uranium; Seawater; Sorption; Desorption

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## 1. Introduction

Functionalized polymeric materials in the forms of resins, beads, gels, or membranes have potential applications in selective pre-concentration or separation of target metal ions from multi-component aqueous feed such as seawater. One of the interesting applications of these functionalized materials is in the recovery of uranium from seawater. Seawater is an electrolyte solution of pH = 7.5–8.5. The concentration of uranium in seawater is of the order of  $1.4 \times 10^{-8}$  mol/L ( $3.3 \text{ mg/m}^3$ ) [1] and is found to be present principally as the anionic tricarbonato-uranate (VI)  $[\text{UO}_2(\text{CO}_3)_3]^{4-}$  species under the prevailing conditions [2,3]. The uranophiles such as poly (acrylamidoxime) [4], 2-2'-dihydroxyazo-benzene attached to polymer matrices [5], calixarenes [6,7] and macrocyclic hexacarboxylic acid [8] have been found to be promising for the recovery of uranium from seawater. Calixarene and macrocyclic derivatives have been found to be highly selective towards  $\text{UO}_2^{2+}$ , but the major problem associated with these ligands is their slow rate of complexation with uranyl ions under seawater conditions. The poly(acrylamidoxime) (AO) was found to be more suitable for uranium recovery from seawater due to: (i) its selectivity towards uranium, (ii) high uranium loading capacity, (iii) good mechanical strength, and (iv) ease with which amidoxime (AO) can be anchored to different polymer matrices of various shapes and sizes [9–16].

The economic viability of recovery of uranium from seawater still critically depends upon the kinetics of sorption of uranium in AO sorbents. It is desirable that the uranium species present in seawater should be instantaneously sorbed when it comes in contact with the surface of a sorbent. Therefore, the major challenge for making uranium recovery economically viable is to develop a sorbent that has a very high uranium sorption rate. In order to enhance the kinetics of uranium ions sorption, AO groups have been anchored in

the variety of substrates with different co-monomers [9–21]. Since  $[\text{UO}_2(\text{CO}_3)_3]^{4-}$  species is bulky ( $10 \text{ \AA}$ ), the diffusion of this species in the sorbent matrix is highly dependent on the physical composition of the sorbent (free volume and pore structure in the polymer matrix) and hydrophilicity of the sorbent [17–21]. It has been reported that the kinetics of uranium ion sorption from seawater could be enhanced by anchoring AO groups on thermally bonded fibrous poly(propylene) and poly(ethylene) substrates [17]. There are two possible methods that can further improve the rate of sorption of uranium species in the matrix of the polymer sorbent. These are: (a) alkaline treatment of AO-grafted sorbent, and (b) co-grafting of hydrophilic monomers along with acrylonitrile in the sorbent. The uranium uptake in alkaline-treated sorbents has been found to be 2–3 times higher than that obtained with the untreated grafted polymer (AO or AO-co-hydrophilic monomer) [4,18]. This is due to the fact that the alkaline treatment of grafted polymers at high temperatures changes the polymer structure in such a way as to enlarge the space between polymer chains, which facilitates the sorption of water [18]. The study of amidoxime sorbents prepared by co-grafting of acrylonitrile along with monomers such as methacrylic acid (MAA), 2-hydroxyethyl methacrylate (HEMA), acrylic acid (AAc), N,N-dimethylacrylamide (DMAAm) has indicated that the presence of acidic groups in the polymer chain enhances the kinetics of uranium complexation with AO functional groups [18,20,21]. This was attributed to a possibility that  $\text{H}^+$  ions from acidic groups may facilitate the decomplexation of  $[\text{UO}_2(\text{CO}_3)_3]^{4-}$  to  $\text{UO}_2^{2+}$ , which forms a complex with AO groups anchored in the polymeric materials. An attempt has been made to understand the sorption mechanism of U(VI) from seawater on a macroporous polymeric sorbent containing amidoxime chelating functional groups [22]. However, the exact role of the acidic group on the kinetics of uranium sorption in AO-functionalized substrate has not been confirmed.

In spite of extensive studies on AO containing polymeric materials, the knowledge of many important chemical aspects involved in extraction of uranium from seawater is inadequate. The objectives of the present work are to study: (i) uranium-loading capacity of AO-containing sorbents from seawater, (ii) time and concentration of acid required for complete desorption of uranium, and (iii) whether alkali treatment can be avoided in reuse of amidoxime polymer. Prolonged exposure of an AO membrane with acids can lead to degradation of AO groups. Unnecessary exposure of the AO membrane with acids can be avoided if kinetics of desorption of  $\text{UO}_2^{2+}$  from the membrane is known. In the present work, the precursor membrane has been prepared by electron-beam irradiation of a poly(propylene) sheet, and followed by grafting of acrylonitrile (AN). This AN-grafted membrane has been treated with hydroxylamine to convert acrylonitrile groups to amidoxime groups. The AO membrane thus prepared has been characterized for: (i) water uptake capacity, (ii)  $\text{Na}^+$ -exchange capacity, (iii) sorption of uranyl ions in the membrane as a function of pH of the equilibrating solution, and (iv) uranium uptake capacity from seawater spiked with  $^{\text{nat}}\text{U}+^{233}\text{U}$ . The extent of desorption of U(VI) from the AO membrane with different reagents has been studied. The time required for the equilibrium sorption of U(VI) in the AO membrane from well-stirred seawater, and quantitative uranium desorption from the membrane by acid and  $\text{Na}_2\text{CO}_3$  have also been measured. The results of these studies are described in this paper.

## 2. Experimental

### 2.1. Materials

AR grade chemicals and deionized water (18  $\text{M}\Omega/\text{cm}$ , gradient A-10 model, Milli-Q USA) were used in the present study. Non-woven thermally bonded poly(propylene) fibers in the form of sheet were obtained from NK Filter Fabric, Mumbai, India. Radiotracers were obtained from the Board

of Radiation and Isotope Technology, Mumbai, India. Locally available thermally bonded non-woven polypropylene macroporous sheet was used as a substrate for grafting acrylonitrile. The specifications for this fibrous substrate are: thickness = 2 mm; density  $\approx 0.26 \text{ g/cc}$ ; bursting strength =  $30\text{--}35 \text{ kg/cm}^2$ . The thickness of the each membrane sample in an appropriate ionic form was measured using a digital micrometer (Mitutoyo, Japan) with an accuracy of 0.001 mm. The pH of the aqueous samples was monitored by the pH meter (420 A, Thermo Orion, USA), which was calibrated using pH = 4, pH = 7, and pH = 10 standard buffer solutions (Hamilton). The  $\gamma$ -activity of the radiotracer was monitored by a well-type NaI(Tl) detector connected to a multichannel analyzer. The  $\alpha$ -radioactivity of  $^{233}\text{U}$  in equilibrating aqueous solutions was monitored by taking out a 50  $\mu\text{L}$  sample, and adding it in a vial containing 5 mL of scintillation cocktail-O (2,5-diphenyl oxazole = 10 g, 1,4-di-2-(5-phenyloxazolyl) benzene = 0.25 g, and naphthalene = 100 g in 1000 mL toluene, 10 v/v % HDEHP). The liquid scintillation counting was carried out in home built liquid scintillation counter with EMI 9514 photomultiplier tube (13 stages) coupled to an amplifier and a single channel analyser via a discriminator.

### 2.2. Preparation and characterization of the grafted membrane

The acrylonitrile (AN) was grafted on the matrix of the poly(propylene) fibrous sheet by the post irradiation grafting method as described elsewhere [23]. The samples of thermally bonded non-woven porous poly(propylene) substrate were irradiated with electron beams (electron energy = 2 MeV; dose rate = 10 kGy/pass) in air at the electron accelerator facility, BARC, Mumbai-85, India. The total dose of 200 kGy was given to each membrane sample. The time required for transferring the irradiated membrane samples from the irradiation assembly to the grafting facility was 15 min. The grafting of AN was carried out by

immersing the membrane samples in the deaerated dimethyl formamide (DMF) solution containing 70 v/v% of AN for 3 h. The temperature of the grafting solution was kept at 50°C. Finally, this precursor membrane was washed and vacuum dried to the obtained weight of the grafted membrane. The degree of AN-grafting in the membrane samples was determined from the knowledge of weights of membrane samples before ( $W_{\text{initial}}$ ) and after grafting ( $W_{\text{final}}$ ) using the following gravimetric relation:

Degree of grafting (%)

$$= \frac{(W_{\text{final}} - W_{\text{initial}})}{(W_{\text{initial}})} \times 100 \quad (1)$$

The  $\text{C}\equiv\text{N}$  groups in the precursor membrane were converted to AO groups by soaking it in the 3% hydroxylamine solution (methanol:water = 1:1) at 60°C for 8 h. After amidoximation, the membrane samples were washed thoroughly with water. The conversion of AN groups to AO groups was confirmed by FTIR. The conversion of  $\text{C}\equiv\text{N}$  to AO in the membrane was estimated chemically and found to be 75–80% as reported elsewhere [23]. The AO membrane samples were conditioned by treating them with 2.5% KOH at 80°C for 1 h. The water uptake capacity of the AO membrane in deionized and seawater was determined gravimetrically using the following equation:

Water uptake capacity (%)

$$= \frac{(W_{\text{wet}} - W_{\text{dry}})}{(W_{\text{dry}})} \times 100 \quad (2)$$

where  $W_{\text{wet}}$  is the weight of the wet AO membrane sample equilibrated with deionized/seawater for overnight, and  $W_{\text{dry}}$  is the weight of the same AO membrane sample dried under vacuum.

### 2.3. U(VI) uptake in the AO membrane

The uptake studies of U(VI) in the AO mem-

brane from aqueous solutions having pH = 4–8 and seawater were carried out using  $^{233}\text{U}$  radiotracer. The amount of  $^{233}\text{U}$  spiked in seawater and aqueous samples having different pH was 9.54  $\mu\text{g/mL}$ . This amount of  $^{233}\text{U}$  was taken to obtain sufficient  $\alpha$ -scintillation counts ( $\approx 10,000$  cpm) in a 50  $\mu\text{L}$  sample of the aqueous feed added to the liquid scintillation cocktail. In order to keep the pH of the aqueous feed unaltered, the known volume of  $^{233}\text{U}$  radiotracer solution was dried under the IR lamp, and 100 mg/mL  $\text{NaHCO}_3$  solution was added to prevent the precipitation of uranium from the aqueous feed. The uptake of U(VI) in the membrane sample (2 cm  $\times$  1 cm) was monitored by liquid scintillation counting of samples (50–100  $\mu\text{L}$ ) of feed solution (15 mL) taken before and after equilibration with the membrane. The uptake of U(VI) in the membrane was obtained from the following equation:

$$\text{U(IV) uptake (\%)} = \frac{(C_{\text{before}} - C_{\text{after}})}{(C_{\text{before}})} \times 100 \quad (3)$$

where  $C_{\text{before}}$  and  $C_{\text{after}}$  are the  $\alpha$ -scintillation counts (counts/s) of  $^{233}\text{U}$  in the samples taken from the feed solution before and after equilibrating the AO membrane sample, respectively.

The equilibration time required for the optimum uptake of U(VI) in the AO membrane sample was determined by spiking known amount of  $^{233}\text{U}$  radioactivity in 15 mL seawater, and equilibrating this solution with the membrane sample (2 cm  $\times$  1 cm) with constant stirring using magnetic stirrer at room temperature. The uptake of  $^{233}\text{U}$  in the membrane was monitored by  $\alpha$ -scintillation counting of 50  $\mu\text{L}$  samples taken from the equilibrating solution at regular time intervals. The U(VI) loading capacity of the AO membrane was measured by drying a fixed volume of the solution containing a known concentration of uranyl nitrate ( $^{\text{nat}}\text{UO}_2(\text{NO}_3)_2$ ) spiked with required radioactivity of  $^{233}\text{U}$ , and 15 mL of seawater was added to equilibrate the membrane sample of the known weight for 250 min with constant stirring.  $^{233}\text{U}$

radiotracer sorbed in the membrane samples was obtained from the difference in the total radioactivity of  $^{233}\text{U}$  in the solution and the residual radioactivity of  $^{233}\text{U}$  in the solution left after equilibrating the membrane sample. U(VI) loading capacity of the AO membrane was calculated from the standard radioactivity comparison method, and knowledge of the weight of the membrane sample using the following equation:

$$\begin{aligned} &\text{U(VI) uptake capacity (mol/g)} \\ &= \frac{(A_{\text{mem}})}{(A_{\text{std}})(w_{\text{mem}})} \end{aligned} \quad (4)$$

where  $A_{\text{mem}}$  is the radioactivity (counts/s) of  $^{233}\text{U}$  sorbed in the membrane sample,  $A_{\text{std}}$  is the radioactivity of  $^{233}\text{U}$  (counts/s) of 1 mol of uranium having the same proportion of  $^{\text{nat}}\text{U}$  and  $^{233}\text{U}$  as used for loading uranium in the membrane, and  $w_{\text{mem}}$  is the weight of the dry membrane sample. The value of  $A_{\text{std}}$  was obtained by taking 100  $\mu\text{L}$  sample of the stock solution having the known concentration of uranium ( $^{233}\text{U} + ^{\text{nat}}\text{U}$ ) in seawater, and subjecting it to liquid scintillation counting as described above.

#### 2.4. $\text{Na}^+$ -exchange capacity of the AO membrane

The  $\text{Na}^+$ -exchange capacity of the AO membrane was measured by equilibrating the membrane sample of the known weight with 0.1 M NaCl containing the known amount of  $^{22}\text{Na}$  radioactivity for 3–4 h with constant stirring.  $^{22}\text{Na}$  radioactivity in the samples was measured by  $\gamma$ -counting using a well-type NaI(Tl) detector based gamma spectrometer. In order to obtain the amount of  $\text{Na}^+$  ions sorbed in the membrane, the standard sample was prepared by drying the required volume of the solution containing known amounts of NaCl, containing the same proportion of  $^{22}\text{Na}$  radioactivity as that used for equilibrating the membrane, on the Whatman-41 filter paper having the same dimensions as that of the membrane samples. The amount of  $\text{Na}^+$  ions

sorbed in the membrane samples was obtained by measuring  $\gamma$ -activities of the membrane samples and the standards under identical samples to detector geometry, and comparing the  $\gamma$ -activity of the membrane sample with that of standard.

#### 2.5. Desorption of $\text{UO}_2^{2+}$ from the AO membrane

Desorption studies were carried by loading the membrane samples with uranium having known radioactivity of  $^{233}\text{U}$  as described above. The release of  $^{233}\text{U}$  from the AO membrane sample in 15 mL well-stirred solution containing the known concentration of desorbing reagents was monitored by taking out 50  $\mu\text{L}$  solution as a function of time, and measuring radioactivity of  $^{233}\text{U}$  by liquid scintillation counting. HCl (0.25–1.0 M),  $\text{Na}_2\text{CO}_3$  (0.25–1.0 M), and  $\text{NaHCO}_3$  (1.0 M) were used as desorbing reagents.

### 3. Results and discussion

The properties of AO membrane samples are given in Table 1. The electron beam grafting of the acrylonitrile (AN) by the post irradiation method was found to be  $\approx 125$  wt.% on a thermally bonded poly(propylene) fibrous membrane. The conversion of grafted AN to amidoxime groups (AO) on treating the membrane with the hydroxylamine solution was found to be  $\approx 80\%$ . The alkali treated AO membrane samples readily sorbed the water. As can be seen from Table 1 that the water uptake capacity of the membrane was lower in the seawater (200 wt.%) as compared to that in deionized water (260 wt.%). This can be attributed to shrinking of AO bearing polymer chains due to high salt concentration in seawater. The uptake of uranium in the AO membrane sample from aqueous solutions having pH = 4–8 and seawater was studied by spiking the solution with the known radioactivity of  $^{233}\text{U}$  radiotracer. The uptake of uranium species, existing in these equilibrating solutions, in AO membrane samples was found to be more than 90%.



Table 1  
Characterization of the AO membrane

Property	Experimental measurement
Degree of AN grafting, wt. %	125
Amidoximation, %	≈80
Calculated functional group density, mol/g	$7.8 \times 10^{-3}$
Na <sup>+</sup> -exchange capacity, mol/g	$(3.1 \pm 0.2) \times 10^{-4}$
Water uptake capacity (in deionized water), wt. %	260 ± 10
Water uptake capacity (in seawater), wt. %	200 ± 10
<sup>233</sup> U uptake (seawater), %	96 ± 3
<sup>233</sup> U uptake (pH 4–8), %	90 ± 4

The Na<sup>+</sup>-exchange capacity of the AO membrane sample was found to be  $(3.1 \pm 0.2) \times 10^{-4}$  mol/g, which is significantly lower than the calculated

functional group density as given in Table 1. This indicated that amidoxime groups bearing polymer chains act as a weak polyelectrolyte. The saturation uranium uptake in the AO membrane samples was determined by equilibrating them in the solution containing 3–4 times in excess of uranium than the amount of uranium required for saturating the calculated functional groups in the membrane. The profile of the sorption rate of uranium in the membrane sample from seawater is shown in Fig. 1. It is seen from Fig. 1 that the equilibration time required for the saturation loading of uranium in the membrane sample was about 200 min. This clearly indicated that the sorption of uranium in the membrane was quite slow even though the membrane had high water content. The volume of equilibrating seawater was 15 mL that could be well stirred along with the membrane sample (1 cm × 2 cm) using a magnetic stirrer. Since uranium concentration in equilibrating so-

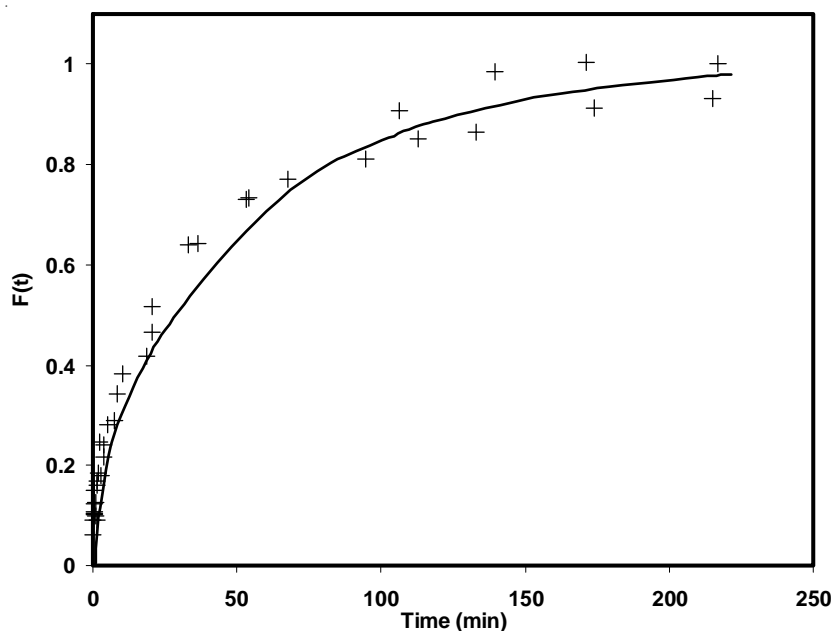


Fig. 1. The fractional attainment of the equilibrium uptake of uranium ( $F(t)$ ) in the AO membrane from seawater spiked with  $^{233}\text{U} + ^{\text{nat}}\text{U}$  as a function of the equilibration time. The value of  $F(t)$  were obtained from the ratio of radioactivity of  $^{233}\text{U}$  in the equilibrating solution as a function of time  $t$  to that at  $t = \infty$ .

lution was 3–4 times higher than that required for saturated loading in the membrane sample, the equilibration time required for saturation loading of uranium from seawater under the present experimental condition could be due to the diffusion of uranium species in the membrane matrix and reaction kinetics involved in the decomplexation of  $[\text{UO}_2(\text{CO}_3)_3]^{4-}$  and subsequent complexation of  $\text{UO}_2^{2+}$  with the AO groups in the membrane. However, the data obtained in the present work are not sufficient to identify the rate determining process in the sorption of U(VI) in the AO membrane from seawater.

The saturation loading of uranium in the AO membrane samples from seawater is given in Table 2. It can be seen from this table that the variation of uranium loading capacity in the AO membrane samples taken from the same batch was 10–12%. This indicated that the distribution of the AO groups in the membrane was fairly uniform. The average uranium loading capacity in the AO membrane samples from seawater was found to be  $(1.60 \pm 0.18) \times 10^{-3}$  mol/g. Therefore, the AO membrane studied in the present work has a high uranium loading capacity (0.38 g of U/g of the membrane). The calculated functional group density in the AO membrane, 125 wt.% AN grafting and 80% conversion of AN to AO, is  $7.8 \times$

$10^{-3}$  mole/g. As can be seen from Fig. 2, there are many reported possibilities of  $\text{UO}_2^{2+}$  complexation with AO groups in the membrane [23–25]. However, the comparison of the experimental U-loading capacity and the calculated functional group density indicates that probably  $\text{UO}_2^{2+}$  ions form a complex with AO groups in 1:4 proportion as shown in structure C of Fig. 2.

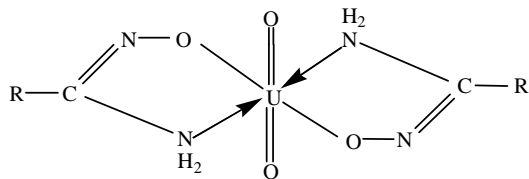
The desorption of  $\text{UO}_2^{2+}$  from the membrane was studied by using mineral acids,  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$ . The  $\text{UO}_2^{2+}$  desorption rate profiles from the AO membrane sample to the equilibrating solution containing  $\text{NaHCO}_3$  or  $\text{Na}_2\text{CO}_3$  are shown in Fig. 3. It can be seen from Fig. 3 that >90% of uranium can be desorbed from the membrane within 60 min of the equilibration time in 0.5 M  $\text{Na}_2\text{CO}_3$  with constant stirring. The desorption of uranium from the membrane sample with 1.0 M  $\text{NaHCO}_3$  was found to be 85%, and kinetics of  $\text{UO}_2^{2+}$  desorption from the membrane was slower in  $\text{NaHCO}_3$  as compared to that in  $\text{Na}_2\text{CO}_3$ . It was observed that  $\text{UO}_2^{2+}$  loading and subsequent desorption from the membrane sample did not require any alkaline treatment or conditioning as the sorption and desorption rate profiles remained the same in three cycles.

The uranium from the AO membrane was also desorbed quantitatively (>90%) in 40 min equili-

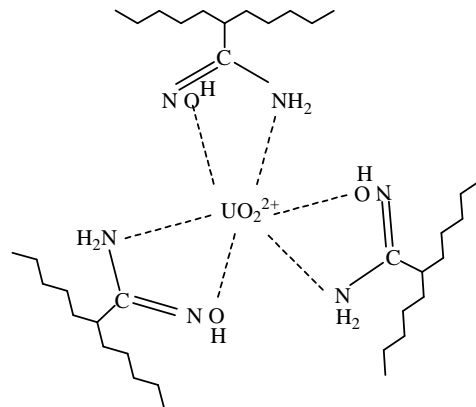
Table 2  
Uranium loading capacity of the AO membrane from seawater

Sample No.	Weight of membrane (g)	Uranium loaded (g)	U-loading capacity ( $\times 10^{-3}$ mol/g)
1	0.3134	0.1229	1.56
2	0.3592	0.1313	1.54
3	0.2678	0.1419	1.83
4	0.2957	0.1199	1.70
5	0.3259	0.0932	1.20
6	0.5733	0.1878	1.38
7	0.2558	0.1058	1.74
8	0.2730	0.1082	1.67
9	0.3005	0.1202	1.68
10	0.2889	0.1156	1.68

Structure A



Structure B



Structure C

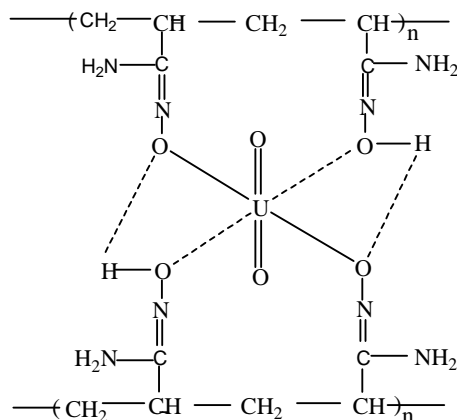


Fig. 2.  $\text{UO}_2^{2+}$  complexation with poly(amidoxime). The structures shown in A, B and C are taken from references [24], [25] and [26], respectively.

bration in the well stirred solution containing 1.0 M HCl, 1.0 M  $\text{HNO}_3$ , and 0.5 M  $\text{H}_2\text{SO}_4$ . As shown in Fig. 4, the desorption of  $\text{UO}_2^{2+}$  from the AO membrane was reduced to 40% on decreasing the concentration of HCl from 1 M to 0.25 M. This indicated that 1 M of monobasic mineral acid is required to desorb the  $\text{UO}_2^{2+}$  quantitatively from the AO membrane. After desorption of  $\text{UO}_2^{2+}$  with acid, the alkaline treatment of the AO membrane was required as uranium was not found to sorb in

the membrane even after conditioning with 0.5 M NaCl. This can be attributed to the fact that amidoxime groups are quaternized on equilibration of the membrane with the acid as shown in Fig. 5. Hence, the alkaline treatment is required to de-quaternize the amidoxime groups. The desorption of uranium from the AO membrane with  $\text{Na}_2\text{CO}_3$  does not change the chemical structure of the AO groups in the membrane and thus alkaline treatment was not needed.



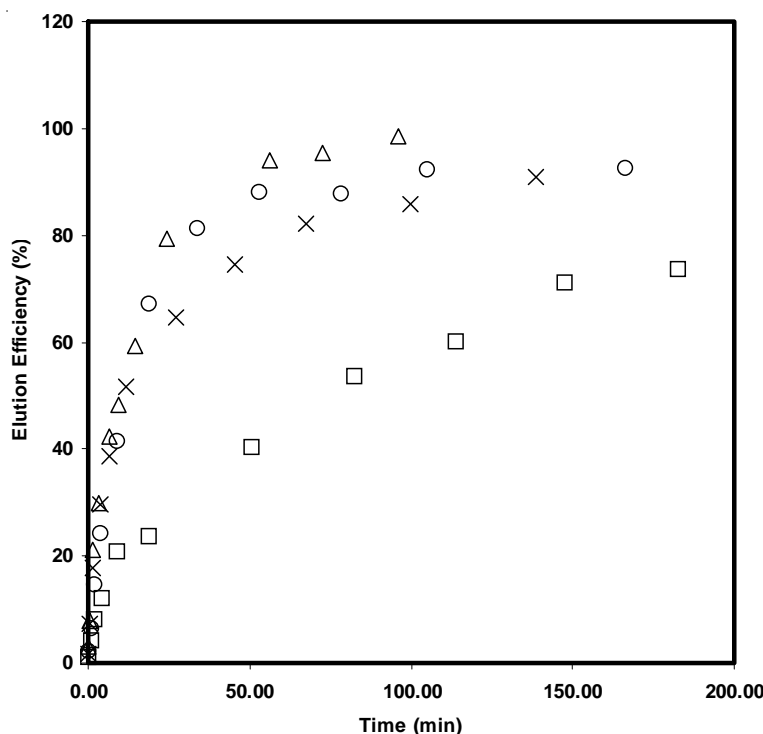


Fig. 3. Desorption of  $\text{UO}_2^{2+}$  from the AO membrane samples as a function of the equilibration time in  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$ . The symbols  $\times$ ,  $\triangle$ ,  $\circ$ , and  $\square$  represent  $\text{NaHCO}_3$  (1 M),  $\text{Na}_2\text{CO}_3$  (1 M),  $\text{Na}_2\text{CO}_3$  (0.5 M), and  $\text{Na}_2\text{CO}_3$  (0.25 M), respectively.

#### 4. Conclusions

The experiments carried out in the present work indicated that uranium could be loaded in the AO membrane in high amounts (0.38 g of U/g of the membrane). The uranium from the AO membrane could be quantitatively desorbed in  $\text{Na}_2\text{CO}_3$  (0.5 M) and mineral acids like HCl (1 M) in the equilibration times of 60 min and 40 min, respectively. Therefore, a long exposure of the AO membrane in acid could be avoided for uranium desorption as AO groups are degraded during the prolonged equilibration with acid. The alkaline treatment of the AO membrane sample equilibrated with acid was required for its reuse in uranium pre-concentration. However, the AO membrane equilibrated with  $\text{Na}_2\text{CO}_3$  could be reused without any conditioning for uranium sorption.

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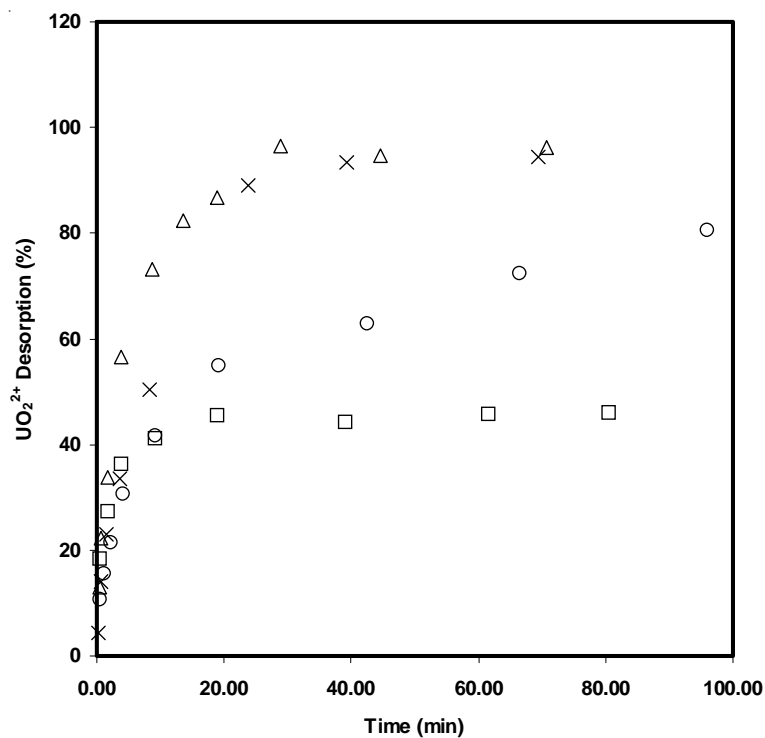


Fig. 4. Desorption of  $\text{UO}_2^{2+}$  from the AO membrane samples as a function of the equilibration time in 0.25 M HCl ( $\square$ ), 0.5 M HCl ( $\circ$ ), 1 M HCl ( $\triangle$ ), and 0.5 M  $\text{H}_2\text{SO}_4$  ( $\times$ ), respectively.

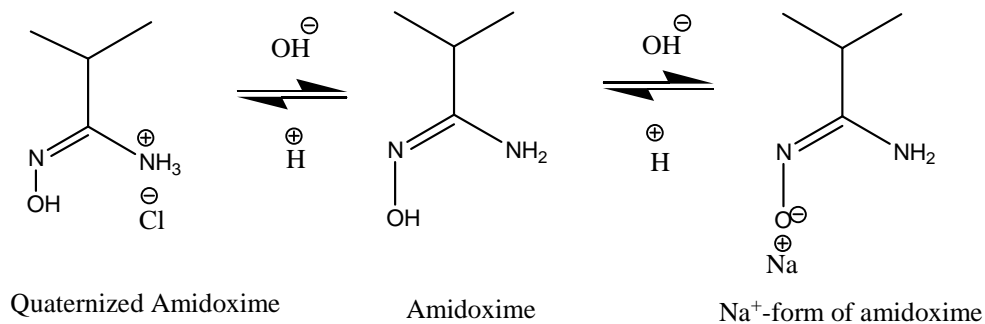


Fig. 5. Changes in the chemical structure of amidoxime groups on equilibration with acid and alkali.

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