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Uranium preconcentration from seawater using phosphate functionalized poly(propylene) fibrous membrane

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ABSTRACT

The poly(ethylene glycol methacrylate phosphate) macroporous membranes (PEGMP-membrane) were prepared by grafting of ethylene glycol methacrylate phosphate onto the poly(propylene) fibrous sheets using UV-irradiation and electron beam. The PEGMP-membrane samples thus prepared were characterized in terms of water uptake capacity, uranium uptake efficiency under seawater conditions, uranium distribution in the membrane samples, desorption and reusability of the membrane for uranium preconcentration. The uranium sorption capacity of the PEGMP membrane was found to be appropriate (1.4×10^{-3} mol/g) for using it in adsorptive mode for preconcentration of uranium from the lean aqueous feed. The functional group density based on the gravimetrically measured weight of PEGMP anchored in the membrane sample was calculated to be 3.2×10^{-3} mol/g. The comparison of expected functional group density and uranium uptake capacity seems to suggest that UO_2^{2+} forms complex with EGMP units in 1:2 proportion in the membrane. The uranium could be desorbed from PEGMP-membrane quantitatively (>95%) by equilibration in well-stirred 0.5 M Na_2CO_3 for 10 min. The membrane could be reused without any conditioning for uranium re-sorption. The studies carried out in the present work indicated potential applications of the PEGMP-membrane for adsorptive preconcentration of uranium from seawater and other natural waters.

Keywords: Ethylene glycol methacrylate phosphate; Fibrous poly(propylene) membrane; Adsorption; Preconcentration; Uranium; Seawater

1. Introduction

Seawater has uniform uranium(VI) concentration of the order of 1.4×10^{-8} mol/l (3.3 ppb), which is present principally as the anionic uranyl tricarbonato species $[UO_2(CO_3)_3]^{4-}$ having high stability under the prevailing seawater conditions [1–4]. The presence of uranium in the dissolved state makes its recovery possible from seawater. The uniform concentration of uranium throughout the sea indicates existence of a dynamic equilibrium between dissolved uranium and insoluble sedimentary uranium. Therefore, the recovery of uranium from seawater may lead to dissolution of uranium present in the seabed [5]. It has been indicated that insoluble uranium fraction on the seabed exceeds soluble fraction by thousand times. However, the technological challenge lies in making the recovered uranium cost competitive with other established routes [6]. Due to low concentration of uranium in seawater, enormous volume (≈3×10^8 m^3) has to be processed for recovery of 1 ton of uranium which is highly

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energy intensive. Thus, the conventional processes requiring large energy for pumping are not economically viable. Most possible approach is in situ application of suitable sorbents to take up uranium under real life situation i.e., submerging the sorbent in seawater for sufficient time to facilitate saturation uptake of uranium [7]. As seawater is a bio-aggressive multicomponent feed, the sorbent cannot be exposed for long time without curbing biofouling of the sorbent. Therefore, a large inventory of sorbent is needed for meaningful recovery of uranium from seawater.

First major attempt to develop a sorbent for uranium recovery was reported by Davies et al. in 1964 [5]. They evaluated several organic and inorganic sorbents, and found hydrous titanium(IV) oxide as a promising sorbent for the uranium recovery from seawater. Since then several sorbents have been explored [8–21]. The major problem associated with hydrous titanium(IV) oxide was preparation of matrix supported titanium(IV) oxide for large scale applications. Also, the suitable sorbents containing macrocyclic uranophiles, dihydroxyphosphino groups, and 2,2′-dihydroxy azobenzene have not been reported in sheet form using simple synthetic chemistry [8–10,12–14]. These functional groups could be anchored in beads that were not suitable for large scale applications. The poly(amidoxime) (PAO) has been found to be one of the most promising adsorbents. Since biofouling is a major problem for long exposure of the sorbent in seawater, the sorbent should exhibit a rapid rate of uranium sorption to reduce the sorbent inventory. Therefore, considerable efforts have been made to enhance the sorption kinetics of the PAO-based sorbent. These efforts were focused to improve the physical structure of the sorbent as well as co-grafting of hydrophilic/acidic co-monomers with PAO [21–25]. The other potential sorbents for selective preconcentration of toxic metal ions from natural waters can be the renewable biosorbents. These are materials of bacterial, fungal, plant or animal origin. Biosorption and bioaccumulation, involve interactions and concentration of toxic metals or organic pollutants (e.g., dyes) in the biomass, either living (bioaccumulation) or non-living (biosorption) [26]. However, the biomaterial for selective preconcentration uranium under seawater conditions has not been reported in the literature. There are indications that spent or viable chitinous biomasses might offer good performances because of the fact that removal of uranium from seawater by Talaromyces emersonii biomass was not depressed by the ionic species present in the seawater [27].

In the present work, the poly(ethylene glycol methacrylate phosphate) (PEGMP) membrane has been explored as an alternative to PAO based membranes. The presence of two hydroxyl groups along with phosphoryl oxygen (P=O), that has strong affinity towards uranyl ions, would be having better uranium sorption properties under seawater condition. One of the hydroxyl groups having higher pK_a would provide H^+ ions to catalyze the decomplexation of $[UO_2(CO_3)_3]^{4-}$ ions. There are several features that make large scale production of PEGMP-membrane easier than PAO-based membrane. For example, EGMP is acrylate based functional monomer and can be easily grafted via free radical mechanism on poly(propylene) matrix. Thus, the production of PEGMP-membrane is one step process. Unlike acrylonitrile used in the PAO-membrane, the EGMP monomer is neither volatile nor toxic. In present study, the ethylene glycol methacrylate phosphate (EGMP) has been anchored in the poly(propylene) fibrous sheet by electron-beam and UV-initiator induced grafting. The membrane samples thus prepared have been characterized and studied for their efficacy for uranium preconcentration from seawater.

2. Experimental

2.1. Reagents and apparatus

Analytical reagent grade chemicals and de-ionized water (18 M /cm) purified by model QuantumTM from Millipore (Mumbai, India) were used throughout the present studies. Ethylene glycol methacrylate phosphate (EGMP), N-N′-methylene-bis-acrylamide (MBA), and α,α′-dimethoxy-α′-phenyl acetophenone (DMPA) were obtained from Sigma-Aldrich (Steinheim, Switzerland). Tetrahydrofuran (THF) and N-N′ dimethylformamide (DMF) were obtained from Merck (Mumbai, India). Thermally bonded non-woven poly(propylene) macroporous fibrous sheet (NK Filter Fabric, Mumbai, India) was used as a substrate for grafting EGMP. The specifications for this fibrous substrate were: thickness ≈2 mm; density ≈0.26 g/cm^3; bursting strength = 30–35 Kg cm^2. The γ-activity of the radiotracer was monitored by a well-type NaI(Tl) or HPGe detector connected to a multichannel analyzer. The α-radioactivity of ^{233}U in equilibrating aqueous solutions were monitored by taking out 50 μl sample, and adding it in a vial containing 5 ml of scintillation cocktail-O. The composition of cocktail-O was: 2,5-diphenyl oxazole = 10 g, 1,4-di–2-(5-phenyloxazolyl) benzene = 0.25 g, and naphthalene = 100 g in 1000 ml toluene, and 10 v/v% bis(2-ethylhexyl) phosphoric acid (HDEHP). The liquid scintillation counting was carried out in home built liquid scintillation counter with EMI 9514 photomultiplier tube (13 stage) coupled to an amplifier and a single channel analyzer via a discriminator. A microprocessor based pH meter model PHAN from Lab India (Mumbai, India) was used for pH measurements.

2.2. Preparation and characterization of membranes

For UV-initiator induced grafting, the PP fibrous sheets (6 × 6 cm) were soaked for overnight in the polymerizing solution containing monomer (EGMP), crosslinker methylenebisacrylamide (MBA), and an UV-initiator α,α-dimethoxy-α-phenyl acetophenone (DMPA) dissolved in the mix solvent having 1:3 proportions of tetrahydrofuran (THF) and N-N`dimethylformamide (DMF), respectively. The amounts of crosslinker and monomer were adjusted in the polymerization solution to get 5 mol.% cross-linking. The amount of UV-initiator was taken as 1 wt.%. The polymerizing solution filled membrane samples were sandwiched between two transparent polyester sheets to prevent any possible loss of solution filled in the pores. Care was taken to remove excess of solution and air bubbles trapped between membrane and polyester sheet covering the membrane surface. Finally, the sandwiched membrane was exposed to 365 nm UV light in a multi-lamp photoreactor (Heber Scientific, model No. HML-SW-MW-LW-888) for a period of 20 min. The photoreactor contained six UV lamps (8 watt) arranged in a circle. The EGMP was also anchored in fibrous poly(propylene) membrane by electron-beam initiated in situ graft polymerization method. The fibrous poly(propylene) membrane samples were soaked in DMF solution of monomer EGMP. These monomer filled membranes were exposed to 10 MeV electron beam (3.4 Hz scanning frequency, power 20 W, scanning area 4 cm × 1 m) for 15 min at Electron-Beam Facility at Kharghar, Navi Mumbai. The cumulative dose was measured by EPR method developed by Actinide Spectroscopy Section, RCD, BARC, Mumbai which was found to be 0.5 kGy. The electron-beam grafted poly(acrylamidoxime) (PAO) membrane samples were provided by Radiation Technology Development Section (RTDS), BARC, Mumbai, India. This membrane was prepared by grafting acrylonitrile (AN) on the matrix of poly(propylene) fibrous sheet by post electron-irradiation grafting method, and subsequent treatment with hydroxylamine as described elsewhere [28].

After irradiation in the photoreactor, the membrane samples were washed thoroughly with THF, methanol and distilled water to remove the ungrafted components. The degree of EGMP grafting in the membrane samples was determined from the knowledge of weights of membrane sample before (W_{initial}) and after functionalization by grafting (W_{final}) using following gravimetric relation:

$$\text{Degree of grafting (\%)} = \frac{(W_{\text{final}} - W_{\text{initial}})}{(W_{\text{initial}})} \times 100$$

The water uptake capacity of the PEGMP-membrane samples in deionized and seawater was determined by gravimetrically using following equation:

$$\text{Water uptake capacity (\%)} = \frac{(W_{\text{wet}} - W_{\text{dry}})}{(W_{\text{dry}})} \times 100$$

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

The presence of required functional groups in the final membrane was confirmed by FTIR spectroscopy. The dried membrane samples were powdered in liquid nitrogen, mixed with KBr in 1:50 ratio, and homogenized with a mortar and pestle. The pellets were made by applying a pressure of around 75 kg/cm^2. FTIR spectra of the 13 mm diameter pellets were recorded using the Jasco 4100-model. Uranium distribution in the PEGMP-membrane samples was studied by Energy Dispersive X-ray Fluorescence (EDXRF). The EDXRF measurements were carried out using an EX 3600-M spectrometer, Jordon valley AR Ltd. (Migdal Haemek, Israel). This EDXRF spectrometer has a 50W Rh-anode X-ray tube, an assembly of 6 filters (Cu, Fe, Mo, Rh, Sn and Ti), a Ge secondary target and a Si(Li) detector with a 12.5 μm thick beryllium window(energy range of 1–40 keV, resolution 139 eV at 5.9 keV of Mn K_α). The elements present in the samples were identified with their characteristic peaks. The surface morphology of the membrane was imaged using a scanning electron microscope (SEM) (VEGA MV2300T/40, Tescan, CZ). In order to avoid the charging effect on thesamples during SEM measurements, a thin gold layer of 200Åwas deposited on the samples by thermal evaporation using a tungsten filament at a base pressure of 2 × 10^{-6} Torr.

2.3. U(VI) Uptake in membrane

The uptake studies of U(VI) in membrane from seawater were carried out using ^{233}U radiotracer. The amount of ^{233}U spiked in the aqueous samples was 9.54 μg/ml. This amount of ^{233}U was taken to obtain sufficient α-scintillation counts (≈10,000 cpm) in 50 μl sample of aqueous feed added to the liquid scintillation cocktail. In order to keep the pH of seawater unaltered, the known volume of ^{233}U radiotracer solution was dried under the IR lamp, and 100 mg/ml $NaHCO_3$ solution was added to prevent the precipitation of uranium from seawater. The uptake of U(VI) in the membrane sample (2 × 1 cm) was monitored by liquid scintillation counting of samples (50–100 μl) of feed solution (15 ml) taken before and after equilibration with the membrane. The uptake of U(VI) in the membrane was obtained from following equation:

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

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

The U(VI) loading capacity of membrane was measured by drying fixed volume of the solution containing known concentration of uranyl nitrate ($^{\text{nat}}UO_2(NO_3)_2$) spiked along with required radioactivity of ^{233}U, and 15 ml of seawater was added to equilibrate the membrane sample of known weight for overnight with a constant stirring. ^{233}U radiotracer sorbed in the membrane samples was obtained from the difference in total radioactivity of ^{233}U in solution and residual radioactivity of ^{233}U in solution left after equilibrating the membrane sample. U(VI) loading capacity of the membrane was calculated from the standard radioactivity comparison method, and knowledge of weight of the membrane sample using following equation:

$$\text{U(VI) uptake capacity (mol/g)} = \frac{(A_{\text{mem}})}{(A_{\text{std}})(w_{\text{mem}})}$$

where A_{mem} is the radioactivity (counts/s) of ^{233}U sorbed in the membrane sample, A_{std} is the radioactivity of ^{233}U (counts/s) of 1 mol of uranium having same proportion of $^{\text{nat}}$U and ^{233}U as used for loading uranium in the membrane, and W_{mem} is the weight of dry membrane sample.

2.4. Interference study

The interference of other metal ions such as V(IV), Fe (III), and Cu(II) towards uranium uptake in PEGMP-membrane and PAO-membrane in seawater condition was studied. The membrane samples of equal weights were equilibrated with 15 ml of well-stirred seawater spiked with uranium (tagged with ^{233}U) and the each metal ion, as mentioned above individually, from their relevant salt solutions followed by drying under IR lamp. The molar concentration of uranium was fixed and that of each metal ions with respect to uranium were varied as 1:200, 1:1000, 1:2000 and 1:10000 at mole/mole ratio. The uptake of U(VI) in the membrane sample (2 × 1 cm) was monitored by liquid scintillation counting of samples (50–100 μl) of feed solution taken before and after equilibration with the membrane.

3. Results and discussion

EGMP was anchored in the fibrous membrane by two different routes i.e., electron-beam (EB) and UV-initiator induced grafting. The chemical structures of the EGMP monomer and its complex with UO_2^{2+} ion are shown in Fig. 1. In spite of different methodologies, the amount of EGMP anchored on the membrane was found to be in the range of 170–200 wt.% by both the routes. However, UV-route is expected to be better as UV radiations do not affect the mechanical strength of the base poly(propylene) substrate. The SEM image of final PEGMP-membrane shown in Fig. 2 seem to suggest that the membrane is made up of the fibers having ≈20 μm diameter, and there is a large void space in the fibrous structure. This ensures that membrane would have larger contact area with equilibrating solution to facilitate the uranyl ions covalent bonding with functional groups of the membrane. The water uptake capacity of PEGMP- membrane in seawater was found to be 200 ± 10 wt.%, which is due to large void space in the fibrous structure of the membrane. The FTIR spectra of the membrane samples confirmed the

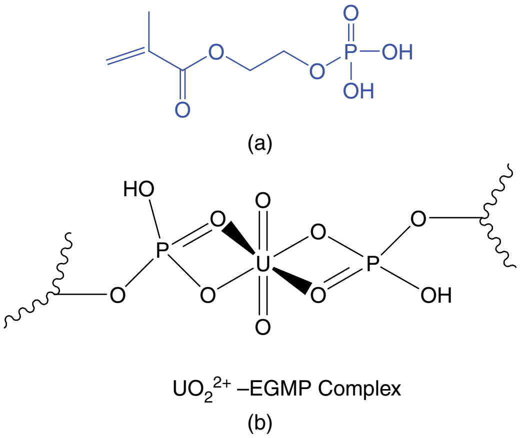

Fig. 1. Chemical structure of ethylene glycol methacrylate phosphate (EGMP) monomer grafted (a) and uranium complex formed (b) in phosphate functionalized fibrous poly(propylene) membrane.

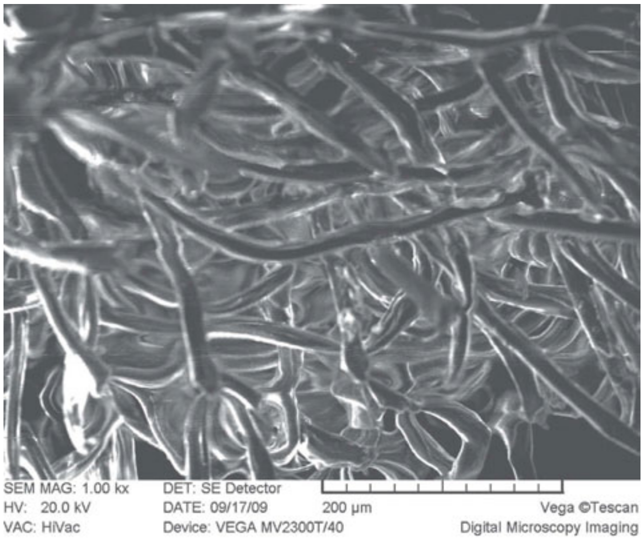

Fig. 2. SEM image of UV-grafted PEGMP membrane.

presence of bands corresponding to P–O–H (≈1000 cm^{-1}, 2400–2200 cm^{-1} and a broad band in the region of 3400–3000 cm^{-1}), associated P=O (1171 cm^{-1} and 1170 cm^{-1}), free P=O (1330 cm^{-1} and 1350 cm^{-1}) and C=O (1715 cm^{-1} and 1720 cm^{-1}). The consistency in anchoring of functional groups in the membrane samples was also studied by EDXRF analysis of uranium loaded samples from same batch as well as different batch. The EDXRF spectra taken from different locations with the membrane samples are shown in Fig. 3. This study indicated that the uranium was distributed in the PEGMP membrane samples within 8–10% variation.

The uptake of uranium in the PEGMP-membrane sample from seawater conditions was studied by spiking solution with known radioactivity of ^{233}U radiotracer. The uptake of uranium species, existing in these equilibrating solutions, in PEGMP-membrane samples was found to be more than 95%. The quantitative desorption (≈98%) of uranium from PEGMP-membrane was found to be possible in equilibration with well-stirred Na_2CO_3 solution (0.5 mol/l) for 10 min. It is important to note that desorption of uranium from PEGMP-membrane with Na_2CO_3 did not require conditioning of the membrane for reuse. However, PAO-membrane required alkali treatment after desorption of uranium with HCl [28,29]. In the present work, the PEGMP-membrane samples were subjected to 10 cycles of sorption-desorption of uranium from well-stirred seawater without any conditioning. Uranium sorption in the PEGMP-membrane remained quantitative (95 ± 4%) in these experiments. The average uranium loading capacity in the PEGMP-membrane samples from seawater was found to be $(1.4 \pm 0.11) \times 10^{-3}$ mol/g. Therefore, the PEGMP-membrane studied in the present work has high uranium loading capacity (0.34 g of U/g of membrane). The calculated functional group density in the PEGMP-membrane having 200 wt.% EGMP grafting is 3.2×10^{-3} mol/g. The comparison of experimental U-loading capacity and calculated functional group density indicates that probably UO_2^{2+} ions formed complex with EGMP groups in

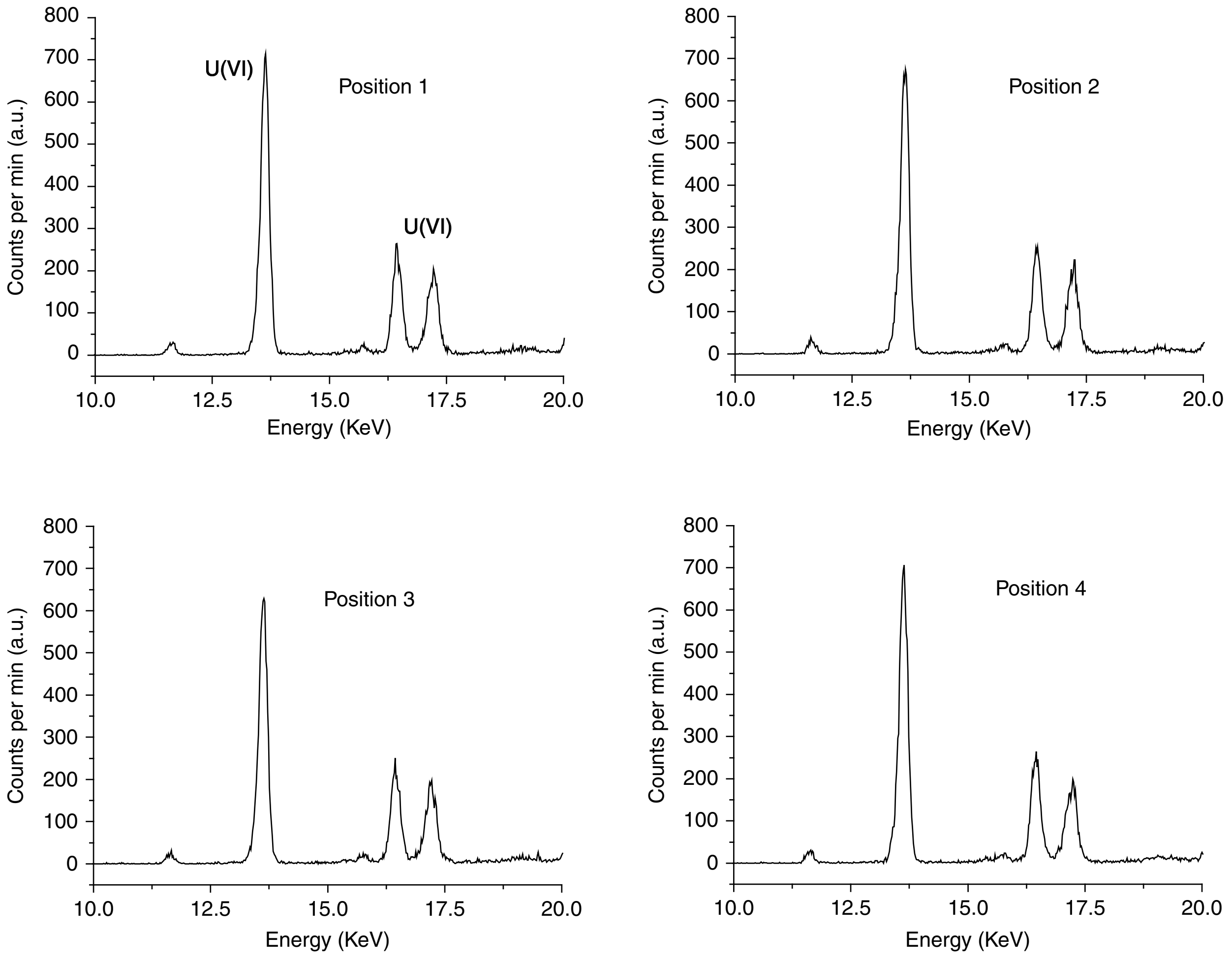

Fig. 3. EDXRF spectra of U(VI) loaded PEGMP membrane showing the distribution of uranium in the membrane at four different locations.

Table 1
Characterization of PEGMP-membrane for uranium preconcentration from seawater

Property	Experimental measurement
Degree of grafting on fibrous poly(propylene)	190 ± 15 wt.%
Functional group density	3.2×10^{-3} mol/g
U(VI) uptake capacity	$(1.4 \pm 0.11) \times 10^{-3}$ mol/g
U to monomer unit (ligand) ratio in uranium complex formed in the membrane	1:2
U(VI) uptake efficiency	95 ± 2%
Water uptake capacity in seawater	200 ± 10 wt.%
Desorption of uranium	0.5 M Na_2CO_3 for 10 min
Reusability	Conditioning is not required, as such it can be used
Stability	Highly stable in acid or base

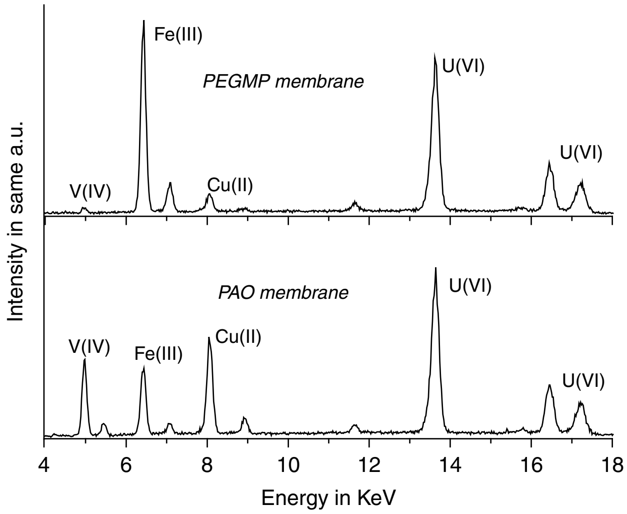

Fig. 4. EDXRF spectra of PEGMP-membrane and PAO-membrane sample after equilibration with well stirred seawater spiked with equi-molar concentration of uranium and other representative ions (Fe(III), V(IV), and Cu(II),) up to saturation level concentrations.

1:2 proportion as shown in Fig. 1b. The summary of the properties of PEGMP-membrane important for uranium preconcentration from seawater is given in Table 1.

In order to test the selectivity of PEGMP-membrane towards uranium, the membrane samples were equilibrated with well-stirred seawater spiked with 10,000 times excess moles of representative ions like Fe(III), V(IV), and Cu(II) than uranium. The concentration of uranium in the feed solution was kept to saturate the membrane sample. It was observed that uptake of uranium (90 ± 3) in the PEGMP-membrane was not affected significantly by the presence of V(IV), Fe(III), and Cu(II) at concentration ratio 1:10000 (mole of uranium to mole of respective metal ions) in the equilibrating solution. However, the presence of V(IV) and Fe(III) in equilibrating solution reduced the uptake of uranium in the PAO-membrane to less than 80%. It is most likely that uranium may not saturate the membrane during its preconcentration from lean aqueous feed like seawater. In such a situation, it is likely that other ions may also be sorbed in the membrane along with uranium. The PAO and EGMP membrane samples were equilibrated with a well stirred seawater spiked with equimolar concentration of uranium and other representative ions (Fe(III), V(IV), and Cu(II)). It was taken care of to keep total concentration of these ions 2–3 times less than that required to saturate the membrane samples. The EDXRF spectra of the ions-loaded PEGMP and PAO membranes samples, equilibrated with well-stirred solutions under similar conditions, are shown in the Fig. 4. It is seen from comparison of EDXRF spectra that only Fe(III) sorbed significantly along with U(VI) in the PEGMP-membrane. Unlike PAO-membrane, V(IV) did not sorb significantly in the PEGMP-membrane. The selectivity experiment using equimolar concentrations of Fe(III) (tagged with ^{59}Fe) and U(VI) (tagged with ^{233}U) showed that PEGMP-membrane was 2.5 time more selective towards uranium as compared to Fe(III). In order to study the replacement of Fe(III) ions held in the PEGMP-membrane with uranium, the ^{59}Fe radiotracer tagged Fe(III) loaded PEGMP-membrane sample was equilibrated with the stirred solution containing 10 times excess of uranium than its sorption capacity. It was observed that UO_2^{2+} ions were able to replace Fe(III) from the EGMP-membrane, but with three time slower rate that in absence of Fe(III). The PAO membrane sample was found to uptake U(VI) along with significant amounts of Fe(III), Cu(II), and V(IV) ions.

4. Conclusions

A new PEGMP-membrane has been developed for uranium recovery from seawater. The PEGMP-membrane offers number of advantages in terms of its preparation, reusability and stability for many repeated cycles, and selective sorption of uranium. The experiments carried out in the present work indicated that uranium could be loaded in the PEGMP-membrane in high amount (0.34 g of U/g of membrane). The uranium from PEGMP-membrane could be quantitatively desorbed in Na_2CO_3 (0.5 M). Interference study also indicated that uranium can be selectively uptaken in presence of other interfering ions in seawater. These studies indicated potential applications of the PEGMP-membrane in uranium preconcentration from seawater.

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