



Poly(ethylene glycol methacrylate phosphate-co-2-acrylamido-2-methyl-1-propane sulfonate) pore-filled substrates for heavy metal ions sorption

T. Vasudevan^a, A.K. Pandey^{b,*}, Sadananda Das^{b,1}, P.K. Pujari^b

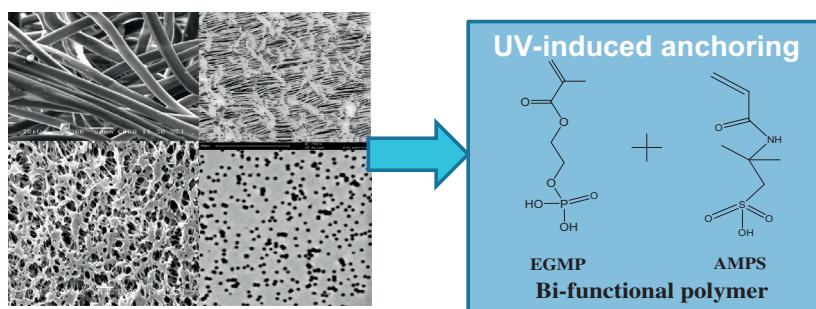
^a Research Reactor Services Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

^b Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, Trombay, India

HIGHLIGHTS

- Bi-functionalized sorbents and membranes were developed.
- UV-induced in situ polymerization in pores of host substrates was carried out.
- Microporous membranes, fibrous substrate and filter papers were functionalized.
- Effects of chemical and physical compositions on metal ions sorption were studied.
- Uranium recovery from seawater using bi-functionalized substrates was promising.

GRAPHICAL ABSTRACT



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ABSTRACT

Bi-functional membranes/sorbents have been prepared by anchoring cross-linked poly(ethylene glycol methacrylate phosphate-co-2-acrylamido-2-methyl-1-propane sulfonate) (poly(EGMP-co-AMPS)) in pores of the microporous substrates by in situ photo-polymerization. Thus prepared materials are found to sorb U(VI) from seawater (98%) as well as from 4 mol L⁻¹ HNO₃ (80%). The poly(EGMP-co-AMPS) (1:1) could be anchored 170 wt.% in grafted fibrous poly(propylene) membrane. This membrane is found to take up 200 wt.% water, and has U(VI) loading capacity 2.9 × 10⁻³ mol g⁻¹. The metal ions sorption kinetics has been found to be dependent not only on physical structure of host substrate but also on proportion of EGMP and AMPS in the guest component poly(EGMP-co-AMPS). The competitive sorption of U(VI) and Fe(III) has suggested that the selectivity of poly(EGMP-co-AMPS) towards U(VI) decreases with increase of AMPS proportion in the polymer, and selectivity is completely lost when AMPS units are more than 4 times with respect to EGMP (phosphate bearing units). However, the kinetics of U(VI) sorption increases with increase of AMPS units in poly(EGMP-co-AMPS). U(VI) sorption efficiency is not affected by the presence of 10,000 times excess of moles of representative ions like Ca, Cu and V in solution. However, Fe(III) compete with U(VI) for sorption in poly(EGMP-co-AMPS) anchored membrane. Desorptions of U(VI), Fe(III) and other ions from the membrane samples are found to be quantitative in equilibration with 0.5 mol L⁻¹ Na₂CO₃, 0.2 mol L⁻¹ EDTA, and 1 mol L⁻¹ HCl, respectively.

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1. Introduction

Functionalized polymeric materials in the form of resins, beads, gels or disks have potential applications as a solid phase sorbent for selective preconcentration and quantification of the target metal ions from multi-components aqueous feed [1–5]. A simple and

* Corresponding author. Tel.: +91 22 25594566; fax: +91 22 25505150/25505151.

E-mail addresses: ashokk@barc.gov.in, memgreek@gmail.com (A.K. Pandey).

¹ Present address: Institut de Chimie Moléculaire de Reims, Université de Reims, France.

reliable method for rapid extraction and spectrophotometric determination of uranium in natural waters has been reported by Shamsipur et al. using octadecyl-bonded silica membrane disks modified with tri-*n*-octylphosphine oxide (TOPO) [6]. The chemically cross-linked acrylamide/sodium acrylate hydrogels have been developed for preconcentration of uranium from aqueous solutions in the pH range [7]. The ligand-grafted biomaterials have been found to be effective for adsorptive separation of uranium from aqueous solution [8–10]. A microcolumn of alumina modified with sodium dodecyl sulfate and 1-(2-pyridylazo)-2-naphthol has been used for preconcentration of uranium from natural water [11]. The direct spectrophotometric determination of uranium complexed with dye in the solid sorbent, called optode or optrode, has also been reported [12–15]. The uranyl ion-imprinted polymer has been grafted on surface of the silica gel particles through covalently surface-bound initiators [16]. The imprinting has been found to enhance selectivity of the sorbent towards uranyl ions over competing metal ions such as Fe³⁺ and Th⁴⁺. However, the most of these sorbents take up uranium efficiently from aqueous solution having pH 3–5. Under seawater conditions, the poly(acrylamidoxime) (AO) based sorbents have been used for the uranium recovery [17–26].

The polymer membranes have potential application for preconcentration of the target species/ions from natural water. The Donnan-membrane technique has been used for measuring free trace cation concentration in natural samples [27,28]. The solid phase micro-extraction related techniques are surface-dependent processes. The stir-membrane extraction is best suited for such applications [29].

The application of membranes for preconcentration of target metal ions is not only dependent on the chemical composition of the membrane but also on its physical architecture. It has been observed that the membrane containing phosphate and sulfonate groups have selectivity of phosphate groups but diffusion of complexing metal ions is faster in the matrix [30]. Alexandratos and Hussain showed that bi-functionality could enhance the complexation kinetics of selective resins [31]. They observed that ion-exchange groups (–SO₃H) on the polymer provide an access mechanism and another ligand groups (phosphinic acid) govern the recognition mechanism for selective preconcentration of the complexing ions. Ion imprinted polymer for Ag(I) has also been prepared using two functional monomers 4-vinyl pyridine and 1-vinyl imidazole [32]. Thus, it will be interesting to study how selectivity and kinetics of metal sorption are influenced by two different functional groups. It is known that heavy metal ions bind with sulfonic acid groups by electrostatic interactions. Therefore, the selectivity of sulfonic groups is dependent upon strength of electrostatic force between ion and sulfonic group, and involves ion-exchange equilibrium [1]. Sulfonic acid groups do not have selectivity and extraction efficiency towards metal ions at higher acidity. Phosphate groups are known to form complex with actinides and lanthanides [33]. It is expected that covalent interactions of heavy metal ions with phosphate groups would provide selectivity, particularly at high acidity.

In present the work, ethylene glycol methacrylate phosphate (EGMP) with or without 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) have been anchored in different host substrates by UV-initiator induced in situ polymerization. The functionalized monomers used in the present work are acrylate based commercially available monomers having phosphate and sulfonate groups, which are easy to polymerize or graft than styrene based monomer. The phosphate group is known for its selectivity towards heavy metal ions. Sulfate is strong acidic group and interacts with ions only by ion-exchange process (electrostatic binding). The poly(EGMP-co-AMPS) has been anchored in highly porous substrates (Whatman filter papers and fibrous poly(propylene)

and different pore-sizes membranes made up of poly(propylene), polycarbonate and poly(tetrafluoroethylene). The choices of these host substrates are based on the fact that the extraction discs and fibrous sorbents have been found to be amenable for application for preconcentration of target metal ions [34], and enhancing the sorption kinetics due to their highly porous structure [35]. These sorbents/membranes have been characterized for their efficacy for preconcentration of uranium and other representative metal ions like Cs(I), Cd(II) and Eu(III) from different aqueous samples. To optimize the chemical composition of poly(EGMP-co-AMPS) in the host substrates, the proportions of EGMP and AMPS have been varied.

2. Experimental

Analytical reagent grade chemicals and de-ionized water (18 MΩ cm⁻¹) purified by Quantum™ from Millipore (Mumbai, India) were used throughout the studies. EGMP, AMPS, methylene-bis-acrylamide (MBA) and α,α'-dimethoxy-α-phenyl-acetophenone (DMPA) were obtained from Sigma–Aldrich (Steinem, Switzerland). Tetrahydrofuran (THF) and N,N'-dimethyl formamide (DMF) were obtained from Merck (India). Radiotracers dissolved in aqueous solutions were obtained either from the Board of Radiation and Isotope Technology, Mumbai, India or produced by neutron irradiation of appropriate target samples in the laboratory. Free-radical polymerization of monomers in the pores of host membranes was carried out in a UV multi-lamps photo reactor procured from Heber Scientific, Chennai, India (model no. HML-SW-MW-LW-888) fitted with eight 8 W mercury UV lamps of wavelength 365 nm (Sankyo Denki, Japan).

The monomer EGMP, cross linker MBA (4–5 mol%) and UV initiator DMPA (1 wt.%) were dissolved in THF and DMF 1:1 mix solvent. AMPS (in different proportions) was first dissolved in water-methanol (1:1) mixed solvent and then added to polymerizing solutions. For in situ polymerization, the host membrane sheets were soaked in polymerizing solution for 2–3 h and excess solution on surface of the membranes were wipe out with Teflon roller. The polymerizing solution filled membrane samples were sandwiched between two transparent polyester sheets to avoid evaporation of solvent. Then these were exposed to 365 nm UV light in a multi-lamps photo reactor for a period of 20 min. The host microporous membranes used were poly(propylene), PTFE, polycarbonate and Whatman filter paper having different pore sizes and porosities. After irradiation in the photo reactor, the membranes/sorbents were washed thoroughly with THF, methanol and distilled water to remove the un-grafted components, and then conditioned with aqueous solution having 0.25 mol L⁻¹ NaCl. The amounts of cross-linked polymer anchored in the membrane samples were determined from the knowledge of weights of membrane sample before (*W_i*) and after in situ polymerization (*W_f*) using the gravimetric relation as given below:

$$\text{Degree of Grafting/Anchoring} = \frac{(W_f - W_i)}{W_i} \times 100$$

The uptake studies of U(VI) in the membranes/sorbents from seawater and aqueous solution containing different concentration of HNO₃ were carried out using ²³³U radiotracer. The amount of ²³³U was taken to obtain sufficient α-scintillation counts (≈5000 cpm) in 50 μL sample of aqueous feed added to the liquid scintillation cocktail. To maintain chemical conditions, ²³³U in the form uranyl nitrate was completely dried under IR lamp by slow evaporation and then required volume of seawater/aqueous solution was added and homogenized by stirring and ultrasonication. The uptake of U(VI) in the membrane sample (2 × 1 cm) was monitored by liquid scintillation counting of samples (50–100 μL) of

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