CHAPTER 4
Studies on Hydrogels: Search for better Chemical Composition of Sorbent for Uranium Recovery from Seawater
There are two key factors that affect the viability of uranium recovery from seawater. These are (1) uranium sorption kinetics, and (2) bio-fouling. This chapter accounts for the studies related to the search for chemical composition of the sorbent that can enhance uranium sorption kinetics significantly, and incorporate Ag nanoparticles in the sorbent having optimized chemical composition to minimize bio-fouling under seawater conditions. The chapter has been divided into two subsections. Section 4A deals with the results on synthesis and characterization of different crosslinked hydrogels and their evaluation with reference to uranium uptake. It also describes the dependence of U(VI) sorption kinetics on the acidity of the co-monomer compositions and that of the feed solution. Section 4B describes the synthesis and characterization of Ag\(^0\)@PEGMP nano-composite and bio-resistivity of this nano-composite sorbent and explores it’s possibility towards uranium uptake from multi-component aqueous feed like seawater.
SECTION 4A

Scanning of Chemical Composition of Hydrogels
4A.1 Background

The chemical composition of the sorbent affects the de-complexation of $[\text{UO}_2(\text{CO}_3)_3]^+$ to $\text{UO}_2^{2+}$, followed by complexation of $\text{UO}_2^{2+}$ with functional groups (fixed-sites). The de-complexation of $[\text{UO}_2(\text{CO}_3)_3]^+$ at the fixed-sites accessible at the surface of sorbent may be the rate determining step in U(VI) sorption from seawater. Since de-complexation of $[\text{UO}_2(\text{CO}_3)_3]^+$ can be catalyzed by $\text{H}^+$-ions, the presence of acidic co-monomer with appropriate $pK_a$ value may enhance the sorption kinetics of U(VI) in the AO-sorbent from seawater [1-3]. The de-complexation of $[\text{UO}_2(\text{CO}_3)_3]^+$ at the surface of AO-sorbent is also expected to enhance the U(VI) sorption kinetics as $[\text{UO}_2(\text{CO}_3)_3]^+$ diffusion would be quite slow in the sorbent matrix as compared to $\text{UO}_2^{2+}$ ions. Zhang et al. have studied the mechanism and kinetics of U(VI)-sorption in a fibrous amidoxime-functionalized polymer matrix at different pH [4-6]. These studies indicated that the sorption of U(VI) in AO-sorbent is an endothermic chemical process, and dependent on the pH of the equilibrating solution.

In the work described in this section, the single or two component hydrogels have been prepared by UV-initiated bulk polymerization of the monomers in a desired proportion with a crosslinker. Two component gels consisting of AO groups along with acidic or basic co-monomer have been prepared to explore the possibility of enhancing U(VI) sorption kinetics from seawater. The single component hydrogels containing ethylene glycol methacrylate phosphate (EGMP) or 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) have been studied to explore the better functionalized hydrogel for U(VI) preconcentration from multi-components lean feed like seawater. The monomers used in the preparation of the two component AO hydrogels are AMPS, acrylic acid (AA), 3-(acrylamido propyl) trimethylammonium chloride (APTAC), methacrylic acid (MAA), and EGMP. These co-monomers are ionic (acidic or basic) and expected to
influence the binding of U(VI) with AO-groups in the hydrogels. N-N-methylene-bis-acrylamide (MBA) and α,α-dimethoxy-α-phenyl acetophenone have been used as the crosslinker and UV-initiator, respectively. All the AO-hydrogels have been conditioned with alkali as described in the literature [7]. These hydrogels have been studied in terms of their water uptake capacity, U(VI) uptake capacity, U(VI)-uptake efficiency in presence of large excess of vanadyl ions, and U(VI) sorption kinetics from seawater spiked with \(^{nat}\text{U}^+, ^{233}\text{U}\). The physical structures of hydrogels have been studied by scanning electron microscope (SEM) with EDAX. The results obtained in these studies indicated that chemical design of the sorbent can be tuned to enhance the sorption kinetics of U(VI) from seawater in the AO-sorbent, and EGMP hydrogel is a promising alternate to AO-sorbents. EGMP hydrogel has been found to sorb U(VI) from the seawater as well as aqueous solutions having high acidity.

4A.2 Preparation of Hydrogels

The hydrogels were prepared by UV induced photo-irradiation in a UV-photoractor. The details of the method of preparation are described in the section of chapter 2.

4A.3 Chemical and Physical Characterizations

The hydrogels were characterized in terms of different parameters as described below:

4A.3.1 FTIR Spectra

The presence of required functional groups in the hydrogels (AO, AO + co­monomer, AMPS, and EGMP) were confirmed by the characteristic bands of functional groups in the FTIR spectra as shown in Figure 4A.1. The conversion of AN (-C≡N) to AO groups (-C(=NOH)NH₂) during amidoximation of the hydrogels were also confirmed from the difference observed in the FTIR spectra recorded before and after treating these with hydroxylamine. In the FTIR spectra of
amidoximated gels, the intensity of band at 2243 cm\(^{-1}\) corresponding to C=N groups reduced significantly. The bands at 1650 cm\(^{-1}\) (C=N stretching vibration), 920 cm\(^{-1}\) (N-O stretching vibration), and multiple peaks broad band at 3000-3600 (N-H, O-H stretching vibrations) were observed in FTIR spectra of the amidoximated hydrogels. Presence of the C=N stretching vibrations in the spectra indicated incomplete conversion of AN to AO groups in the amidoximated gels. The FTIR spectrum of AMPS hydrogel showed the vibration bands of sulfonyl group at 1040 cm\(^{-1}\) (S=O), 1210 and 1380 cm\(^{-1}\) (S=O), 1455 cm\(^{-1}\) (-SO\(_2\)-), amide carbonyl group at 1650 cm\(^{-1}\) (C=O), and a broad band in the region of 3600-3000 cm\(^{-1}\). The FTIR spectra of EGMP gel showed bands corresponding to P-
O-H vibrations at 1070 cm$^{-1}$ and 984 cm$^{-1}$, and HPO$_2^-$ vibration at around 1260 cm$^{-1}$, associated P=O (1170 cm$^{-1}$), free P=O (1380 cm$^{-1}$), C=O (1730 cm$^{-1}$), and a broad band in the region of 3700-3400 cm$^{-1}$.

4A.3.2 Elemental Analysis

The elemental analyses of hydrogels indicated increase in nitrogen content after amidoximation of the hydrogel, corresponding to 75-80 % conversion of -C≡N to -C(=NOH)NH$_2$ group. The presence of co-monomer did not affect the conversion of AN to AO groups during amidoximation. The chemical structures of different AO-hydrogels are shown in the Scheme I. It is seen from the chemical structures that the hydrogels prepared in the present work contain fixed-sites that can form electrostatic as well as covalent bonds with UO$_2^{2+}$ ions. The fixed-sites in the hydrogels may also have significant extent of hydrogen bonding that is not shown in Scheme I for the sake of simplicity in representations of chemical structures of the hydrogels.

The results obtained for various parameters investigated for the hydrogels are given in table 4A.1. From the table, it is observed that the hydrogels swell more in de-ionized water as compared to seawater. The water uptake capacities of AO gels with strong acidic groups (-SO$_3$H) and strong basic groups (-N$^+$-(CH$_3$)$_3$) are higher (300 wt.%) as compared to other hydrogels (=100 wt.%) when these are equilibrated with the seawater. Further, all the gels except AMPS, exhibit similar uptake efficiency for uranium after equilibration with de-ionized or seawater overnight.
Scheme 1 - Chemical structures of different AO-hydrogels: (a) AO+MBA, (b) AO+AA+MBA, (c) AO+MAA+MBA, (d) AO+PSA+MBA, (e) AO+EGMP+MBA and (f) AO+APTAC+MBA.
Table 4A.1 The properties of AO hydrogels studied in the present work.

<table>
<thead>
<tr>
<th>Gel composition (mole %)</th>
<th>Water-uptake capacity (wt.%)</th>
<th>U(VI)-uptake efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>De-ionized water</td>
<td>Seawater</td>
</tr>
<tr>
<td>AO</td>
<td>152</td>
<td>118</td>
</tr>
<tr>
<td>AO+AMPS (60:40)</td>
<td>928</td>
<td>502</td>
</tr>
<tr>
<td>AO+AA (60:40)</td>
<td>168</td>
<td>76</td>
</tr>
<tr>
<td>AO+MAA (60:40)</td>
<td>220</td>
<td>70</td>
</tr>
<tr>
<td>AO+APTAC (60:40)</td>
<td>480</td>
<td>310</td>
</tr>
<tr>
<td>AO+EGMP (60:40)</td>
<td>508</td>
<td>116</td>
</tr>
<tr>
<td>AMPS</td>
<td>1450</td>
<td>520</td>
</tr>
<tr>
<td>EGMP</td>
<td>360</td>
<td>195</td>
</tr>
</tbody>
</table>

4A.3.3 Scanning Electron Microscopy (SEM)

The surface images of the hydrogels obtained by SEM are as shown in Figure 4A.2. From the images, it can be noted that the physical architecture of these hydrogels are quite different. As can be seen from the Figure, the AO hydrogel consists of microclusters. However, AO+MAA hydrogel has a uniform featureless surface. The physical structure of EGMP hydrogel appears to be in between AO and AO+EGMP hydrogels i.e. it has bigger intermingled clusters. However, physical structure of the hydrogel may not affect the U(VI) sorption behavior of the hydrogels as U(VI) sorption in these hydrogels from seawater involves the chemical reaction, which is highly dependent on the chemical composition of the hydrogel.

4A.4 Determination of pKa Values of Co-monomers

The apparent acid dissociation constant pKₐ values of water soluble acidic co-monomers AMPS, AA, and MAA were determined by potentiometric titration with standard NaOH. Apparent pKₐ of a weak acid can be obtained by the equation 4.1 [8].
Figure 4A.2 The SEM images of the EGMP (A), AO (B), and AO+MAA (60:40) hydrogels under different magnification.
\[ pK_a = \text{pH} + \log [HA]/[A^-] \] ..................................(4.1)

where [HA] and [A\(^-\)] are the molar concentrations of the acid and dissociated anion, respectively, at equilibrium. When [A\(^-\)] = [HA], then [A\(^-\)]/[HA] = 1 and log[A\(^-\)]/[HA] = 0. Under this condition, pK\(_a\) will be equal to pH. Typically, 50 mL of 0.01 mol L\(^{-1}\) of the acid monomer were titrated with standard 0.1mol L\(^{-1}\) NaOH. pH meter (model PICO+, LAB INDIA, Mumbai, India) calibrated with buffers 4.0, 7.0 and 10.0 was used to measure the change in pH during titration. Wet burette was used for adding the increments of known weight of NaOH in the beaker containing well-stirred aqueous solution of acidic monomer at 25 °C. The end point was obtained by taking the derivative of the titration curve. The volume of alkali corresponding to the end point was calculated. The apparent pK\(_a\) values were obtained from the pH value corresponding to the half neutralization point.

4A.5 Sorption and Desorption of U(VI) in Hydrogels

The sorption of U(VI) from seawater in the AO hydrogel involves following chemical reaction:

\[ [\text{UO}_2(\text{CO}_3)_3]^{4+} + 4HL \Leftrightarrow [\text{UO}_2(\text{HL})_2] + 3\text{CO}_3^{2-} + 2H^+ \] ..................................(4.2)

where HL denotes the fixed complexing sites in the hydrogel. This chemical reaction proceeds either by direct ligand exchange of U(VI) or de-complexation of [UO\(_2\)(CO\(_3\))\(_3\)]\(^{4+}\) to UO\(_2\)\(^{2+}\), followed by complexation of UO\(_2\)\(^{2+}\) with fixed-sites in the hydrogels. The ligand-exchange / de-complexation of [UO\(_2\)(CO\(_3\))\(_3\)]\(^{4+}\) may be the rate determining step as this anionic U(VI) species has high stability constant under prevailing seawater conditions [9-10]. Since de-complexation of [UO\(_2\)(CO\(_3\))\(_3\)]\(^{4+}\) can be catalyzed by H\(^+\)-ions, the presence of acidic co-monomer like AA and MAA are found to enhance the sorption kinetics of U(VI) in the AO-sorbent from seawater [1-3]. Contrary to de-complexation of [UO\(_2\)(CO\(_3\))\(_3\)]\(^{4+}\), eq. 4.2 seems to suggest that the complexation of UO\(_2\)\(^{2+}\)
with the fixed-sites in hydrogels may be retarded in the presence of $H^+$ ions. The microenvironment around the complexation sites is reported to govern the U(VI) sorption process from seawater [11-14]. Therefore, the AO gels with different acidic groups (-SO$_3$H, -COOH, -P(=O)(OH)$_2$) and strong basic group (-N$^+$-(CH$_3$)$_3$) were prepared to study the possibility of enhancing overall kinetics involved in the sorption of U(VI) from seawater. The U(VI)-uptake efficiency of different hydrogels, measured by equilibrating hydrogels with well-stirred seawater spiked with 1-5 ppm of $^{233}$U, are given in Table 4A.1 earlier. U(VI)-uptake efficiency represents sorption of U(VI) in a hydrogel having excess of binding sites for the U(VI) complexation. It was observed that the AO gels with different acidic and basic co-monomer take up U(VI) from seawater quantitatively (> 90%). It was also observed that AMPS and EGMP hydrogels also take up U(VI) from seawater with 35% and 95% efficiency, respectively. Unlike AO-gels, the desorption of U(VI) from EGMP gels was not possible with 1 mol L$^{-1}$ HCl. The quantitative desorption of U(VI) from EGMP hydrogel could be achieved by equilibrating it with 0.5 mol L$^{-1}$ Na$_2$CO$_3$. The reloading of U(VI) in the EGMP-hydrogel did not require any treatment or conditioning. In case of AO-hydrogels, the reloading of U(VI) was not possible without alkali treatment [7].

The U(VI)-uptake efficiency in AO sorbent as a function of pH was studied by Zhang et al. [4]. It was observed in this study that U(VI) uptake in AO-sorbent was quantitative only in the pH ranging from 4 to 6. The U(VI) uptake efficiency of AO sorbent decreased sharply below pH 4, and there was no uptake of U(VI) below pH=1. In the present work, the uptake efficiency of U(VI) in AO+MAA (60:40) and EGMP hydrogels were studied as a function of acidity in the equilibrating solution. The results thus obtained are shown in Figure 4A.3. As can be seen from this figure, U(VI) uptake in AO+MAA hydrogel is similar to that reported for AO hydrogel, [5] and not quantitative.
from aqueous solution having HNO$_3$ concentration higher than 0.01 mol L$^{-1}$. Unlike AO and AO+MAA hydrogels, the uptake of U(VI) in the EGMP hydrogel is not affected by the concentration of HNO$_3$ as high as 4 mol L$^{-1}$. This means that EGMP hydrogel can not only be used for preconcentration of U(VI) from seawater but also from a variety of aqueous feed.

Figure 4A.3 U(VI) uptake efficiency of AO+MAA (60:40) (X) and EGMP (△) hydrogels as a function of HNO$_3$ concentration in the equilibrating feed solution containing 2-4 μg mL$^{-1}$ $^{233}$U(VI).

4A.6 Comparison of U(VI) Sorption Capacity of Hydrogels

To study the U(VI) loading capacity, the known weights of the hydrogel samples were equilibrated with a well-stirred seawater sample having 10 fold excess of $^{nat}$U(VI) than expected total functional group density in the hydrogel for 24 h. $^{nat}$U(VI) was tagged with $^{233}$U for monitoring the uptake in hydrogel. The saturation uptake of U(VI) (loading
capacity) of the AO, AO+MAA(60:40), and EGMP hydrogels were found to be 670 mg g\(^{-1}\), 493 mg g\(^{-1}\), and 550 mg g\(^{-1}\), respectively. Therefore, these sorbents can be used in adsorptive preconcentration of U(VI) due to their high U(VI) loading capacities. The functional group to U(VI) mole ratio is given in table 4A.2. The AO to U(VI) mole ratio in AO and AO+MAA (60:40) hydrogels were found to be 4.4 and 2.6, respectively. In case of EGMP hydrogel, the EGMP to U(VI) mole ratio is 1.9. The possible modes of

Table 4A.2 Functional group to U(VI) mole ratio in the hydrogels after saturation loading with uranium.

<table>
<thead>
<tr>
<th>Gel composition (mole %)</th>
<th>AO</th>
<th>AO+AMPS (60:40)</th>
<th>AO+AA (60:40)</th>
<th>AO+MAA (60:40)</th>
<th>EGMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functional gr./U(VI) mole ratio</td>
<td>4.4</td>
<td>1.1</td>
<td>1.2</td>
<td>2.6</td>
<td>1.9</td>
</tr>
</tbody>
</table>

UO\(_2^{2+}\) binding in EGMP and AO+MAA (60:40) hydrogel are given in the scheme I. These structures are based on the mole ratio of AO, co-monomer, and U(VI) in the hydrogels, and FTIR of U(VI)-loaded hydrogels. It is interesting to note that the AO/U(VI) ratio changed depending upon the proportions of an acidic co-monomer in the hydrogel. For example, AO/U(VI) ratio were found to be 2.1 and 1.2 in AO+AA hydrogels having 80:20 and 60:40 AO:AA mol %, respectively. Similarly, AO/U(VI) ratio changed from 1.1 to 1.6 on changing the proportion of AO: AMPS from 60:40 to 80:20, respectively. This seems to suggest that U(VI) binding in AO-hydrogels is highly dependent on the nature of co-monomer and its proportion with respect to AO groups. The change in binding of U(VI) in the AO-hydrogel may influence the kinetics involved in chemical reaction shown in eq 4.2 as well as diffusion of U(VI)-species in the sorbent matrix.
4A.7 Effects of Chemical Composition of Hydrogel on Sorption Kinetics

The U(VI)-sorption profiles obtained represent the parameters involved in the transfer of U(VI) from equilibrating solution to hydrogel matrix (complexation reaction kinetics at the interface), and subsequent diffusion of U(VI) in the hydrogel matrix. The equilibration time \( t \) required for the saturation sorption of U(VI) in different hydrogels, obtained from the sorption profiles, are given in Table 4A.3. It is seen that equilibrium time required for the saturation sorption was highest in AO+APTAC hydrogel (720 min), and lowest in AO+MAA (10 min) and EGMP hydrogels (7 min).

Table 4A.3 Equilibrium time for saturation sorption of U(VI) in the hydrogels.

<table>
<thead>
<tr>
<th>Gel composition (mole %)</th>
<th>AO</th>
<th>AO+AMPS (60:40)</th>
<th>AO+AA (60:40)</th>
<th>AO+MAA (60:40)</th>
<th>AO+APTAC (60:40)</th>
<th>EGMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibration time (min.)</td>
<td>25±2</td>
<td>35±2</td>
<td>20±2</td>
<td>10±1</td>
<td>≈ 720</td>
<td>7±2</td>
</tr>
</tbody>
</table>

among the different hydrogels listed in table. The comparison of U(VI) sorption in the EGMP hydrogel and hydrogels having the combination of AO + co-monomer is shown in Figure 4A.4. The slow sorption rate of U(VI) in AO+APTAC hydrogel may be due to sorption of \([\text{UO}_2(\text{CO}_3)_3]^{4+}\) as an ion-pair with fixed-positive sites (quaternary ammonium groups) in the sorbent. Since \([\text{UO}_2(\text{CO}_3)_3]^{4+}\) is quite bulky, the transfer of this U(VI) species from seawater to hydrogel and its subsequent diffusion in the matrix of hydrogel would be quite slow. The lower equilibration time for saturation sorption of U(VI) in AO+MAA and EGMP hydrogel seems to indicate that the acidic groups in the hydrogels enhance the ligand-exchange and/or de-complexation of \([\text{UO}_2(\text{CO}_3)_3]^{4+}\) to \(\text{UO}_2^{2+}\) ions, which forms complex with the fixed-sites in the hydrogels. \(\text{UO}_2^{2+}\) ions would also diffuse faster in the sorbent matrix as compared to bulky \([\text{UO}_2(\text{CO}_3)_3]^{4+}\). Therefore, EGMP and
AO+MAA are better candidates for U(VI) recovery from seawater as compared to other AO based sorbents.

**Figure 4A.4** Comparison of fractional attainment of U(VI)-sorption equilibrium $F(t)$ in AO hydrogels containing 40 mol% of the co-monomer.

**4A.8 Mechanistic Study of U(VI) Sorption**

The kinetic models commonly used for the analyses of sorption profiles are pseudo-first-order, pseudo-second-order, and diffusion model. The details of these models are mentioned in chapter 3. In order to understand the rate determining process in sorption of U(VI) in the AO hydrogels from seawater, the U(VI) sorption profiles of AO-hydrogels having different proportions of an acidic co-monomer were analyzed. The variations of $F(t)$ as a function of square root of equilibration time ($t^{1/2}$) are shown in Figures 4A.5-4A.7. It is seen from these analyses that $F(t)$ varies linearly with $t^{1/2}$ upto 70-80 % attainment of U(VI) sorption equilibrium in all the cases except AO+AA and
AO+AMPS hydrogels having 40:60 proportion of AO to co-monomer. As expected from the diffusion model, Morris-Weber equation,

\[ q_e = K_i \sqrt{t} \]

the slope of linear variation of \( F(t) \) as a function of \( t^{1/2} \) represents the Fickian diffusion. However, it is likely that more than one process may be involved in the U(VI)-sorption in hydrogels, which may switch to rate determining process in the different stages of the sorption process. The analyses of U(VI)-sorption profiles shown in Figures 4A.5-4A.7

Figure 4A.5 Comparison of fractional attainment of U(VI) uptake equilibrium (F(t)) in AO and AO+AA hydrogels from well-stirred seawater spiked with 10 times excess of \(^{233}\)U + natU as a function of square root of equilibrating time \((t^{1/2})\). Symbols \(\Delta, +, \) and \(O\) represent AO, AO+AA (40:60), and AO+AA (60:40), hydrogels respectively.
seem to indicate that the U(VI)-sorption process from seawater is delayed initially (lag time) for 4-11 s in all the hydrogels except those containing strongly acidic co-monomer AMPS up to 60 mol%. After a period of time (lag time), the experimentally measured U(VI)-sorption kinetics follow the trend predicted by eq 4.3. Thus, U(VI)-sorption profiles can be divided into two parts i.e. (i) initial lag representing reaction kinetics at the seawater-hydrogel interface and (ii) linear variation of $F(t)$ with $t^{1/2}$ due to Fickian diffusion.

Figure 4A.6 Comparison of fractional attainment of U(VI) uptake equilibrium ($F(t)$) in hydrogels having different proportions of AO and MAA from well-stirred seawater spiked with 10 times excess of $^{233}U + ^{nat}U$ as a function of square root of equilibrating time ($t^{1/2}$). Symbols Δ, +, and O, represent AO+MAA (60:40), AO+MAA (80:20), and AO+MAA (40:60) hydrogels, respectively.
diffusion of U(VI) in the hydrogel matrix. The slopes of curves $F(t)$ vs. $t^{1/2}$ representing U(VI) diffusion rate constant ($K_i$) in different gels were found to be in the order: EGMP (0.41 min$^{-0.5}$) > AO+MAA (60:40) (0.36 min$^{-0.5}$) > AO+AA (60:40) (0.29 min$^{-0.5}$) > AO (0.24 min$^{-0.5}$) > AO+AMPS (60:40) (0.20 min$^{-0.5}$). The diffusion rate of $\text{UO}_2^{2+}$, formed at surface of the sorbent by de-complexation of $[\text{UO}_2\text{(CO}_3)_3]^{4-}$, in the sorbent is

![Graph showing comparison of fractional attainment of U(VI) uptake equilibrium ($F(t)$) in hydrogels having different proportions of AO and AMPS from well-stirred seawater spiked with 10 times excess of $^{233}\text{U}_4^{\text{nat}}\text{U}$ as a function of square root of equilibrating time ($t^{1/2}$). Symbols $\triangle$, $+$, and $\bigcirc$ represent AO+AMPS (80:20), AO+AMPS (40:60), and AO+AMPS (60:40) hydrogels, respectively.]

Figure 4A.7 Comparison of fractional attainment of U(VI) uptake equilibrium ($F(t)$) in hydrogels having different proportions of AO and AMPS from well-stirred seawater spiked with 10 times excess of $^{233}\text{U}_4^{\text{nat}}\text{U}$ as a function of square root of equilibrating time ($t^{1/2}$). Symbols $\triangle$, $+$, and $\bigcirc$ represent AO+AMPS (80:20), AO+AMPS (40:60), and AO+AMPS (60:40) hydrogels, respectively.

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affected by its physical and chemical interactions with the matrix. Chemical interactions of $\text{UO}_2^{2+}$ with matrix are due to its covalent and electrostatic interactions with the fixed sites (AO and/or acidic functional groups) of hydrogels. The retardation of diffusion mobility of $\text{UO}_2^{2+}$ in the matrices of AO + acid co-monomer hydrogels follows the trend of apparent pK$_a$ values of acid co-monomers i.e. AMPS (2.6) $>$ AA (4.2) $>$ MAA (4.6). This seems to suggest that covalent interactions of $\text{UO}_2^{2+}$ may be same in all AO-hydrogels with acid co-monomer, but electrostatic interactions of $\text{UO}_2^{2+}$ with matrix having strong acid group like $\text{SO}_3^-$ would be higher. As initial lag in U(VI)-sorption profiles represents the reaction kinetics at the seawater-hydrogel interface, the

Figure 4A.8 Analyses of sorption profiles of U(VI) in EGMP and AO+MA (60:40) hydrogels in terms of pseudo-second-order rate eq 4.5. The symbols O and X represent EGMP and AO+MAA (60:40) hydrogels, respectively.
experiments were carried out to measure the sorption profiles of EGMP and AO+MAA (60:40) hydrogels within short span (2-3 min). The choice of these two hydrogels was based on the facts that these showed better kinetics among different hydrogels studied in the present work. $^{233}$U(VI) concentration in seawater was kept at 2 ppm which was not sufficient to saturate the hydrogels. The sorption profiles were analyzed using rate equation of pseudo-first-order (eq 4.4) and pseudo-second-order (eq 4.5) below.

$$
\ln \left( \frac{q_e - q}{q_e} \right) = -K_1 t \\
\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}
$$

As can be seen from Figure 4A.8, the early stages of U(VI) sorption from seawater to EGMP and AO+MAA (60:40) hydrogels follow the pseudo-second-order rate eq 4.5. The analysis of U(VI)-sorption profiles gave the values of pseudo-second-order rate constant $K_2$ as $3.20 \times 10^4$ and $2.94 \times 10^4$ g mol$^{-1}$ min$^{-1}$ for EGMP and AO+MAA hydrogels, respectively. This seems to indicate that the decomplexation of $[\text{UO}_2(\text{CO}_3)_3]^+$ to $\text{UO}_2^{2+}$ in EGMP and AO+MAA hydrogels are comparable.

**4A.9 Selectivity of Hydrogels**

The uptake of U(VI) in EGMP gel was not found to be affected by the presence of large excess of representative ions like $\text{Ca}^{2+}, \text{Cu}^{2+}, \text{Fe}^{3+},$ and $\text{VO}_2^{2+}$. The selectivity of AO, AO+MAA, and EGMP hydrogels towards U(VI) in the presence of vanadyl ions were compared by adding a constant amount of U(VI) and varying the mole ratio of $\text{V(IV)}/\text{U(VI)}$ ions in the seawater, and results are shown in Figure 4A.9. The interference of vanadyl ions was studied as it is known to be a competing ion in U(VI) recovery from seawater. The AO+MAA and EGMP gels were found to have better selectivity towards U(VI) ions in seawater as compared to AO gel, and both gels could tolerate presence of more than 1000 fold excess of the vanadyl ions as can be seen from the Figure 4A.9.
4A.9 Comparison of U(VI) uptake efficiencies of AO, AO+MAA (60:40), and EGMP hydrogels from a well-stirred seawater as a function of V(IV)/U(VI) mol ratio.

4A.10 Conclusions

The study of chemical compositions of the hydrogels indicated that the presence of weak acid co-monomer like MAA with AO enhances the selectivity as well as kinetics of U(VI) sorption from seawater. However, the kinetics of uptake of U(VI) from seawater was found to be highly dependent on the proportion of MAA and AO in the hydrogel. The presence of a strong acid (-SO$_3$H) or strong base (-N'^(CH$_3$)$_3$) as a co-monomer with AO retards the overall kinetics involved in the U(VI) sorption from seawater. It was observed that EGMP hydrogel sorb U(VI) quantitatively from seawater as well as aqueous feed containing high acid concentration. The sorption kinetics of
U(VI) in EGMP hydrogel from a well-stirred seawater was found to be better than AO+MAA (60:40) hydrogel, and follow second order kinetics in both cases. This indicated that EGMP hydrogels can be used for preconcentration of U(VI) not only from seawater but also from a lean acidic waste generated during nuclear fuel processing. The advantages of EGMP-hydrogel would be: (i) one step synthesis using a single monomer, no hydroxylamine and alkali treatment are required, (ii) unlike acrylonitrile, EGMP is neither volatile nor toxic, (iii) EGMP is readily polymerizable, (iv) under identical seawater conditions, the profile of U(VI) sorption kinetics is faster in EGMP hydrogel as compared to AO and AO + acid co-monomer hydrogels, and (v) EGMP hydrogel can be used for preconcentration of U(VI) from the seawater as well as aqueous feed having high acidity.
References


SECTION 4B
Development of Bioreistant Sorbent
4B.1 Background

Polymers are excellent host materials for the nanoparticles (nps) of metals and semiconductors [1-5]. When the nanoparticles are embedded or encapsulated in polymer, the polymer acts as surface capping agent. The formation of polymer-based metal nanocomposites requires interactions between polymer and nps such as electrostatic, hydrogen bond, charge-transfer etc. For any application, the control of particle size and their uniform distribution within the polymer are the key issue for effective performance of the nano-composite. Synthesis of Ag nps in commercially available polymers such as poly(vinyl alcohol) (PVA) [6-8], poly(methylmethacrylic acid) (PMMA) [9], poly(vinylpyrrolidone) (PVP) [8,10,11], polystyrene (PS) [12] etc. has been carried out because of its excellent surface capping ability. In general, these polymers are effective in terminating particle growth due to presence of free electrons in the functional groups of the polymer chain. Availability of free electrons is crucial for better particle stability. Thermal polymerization processes normally lead to instant clustering of the nps during the formation because of high activation energy. The photo-polymerization of the monomers along with slow reduction of metal ions could be a suitable option to generate high quality nano-composites.

Functionalized polymeric sorbents in the forms of resins, beads, gels, or membranes have potential applications in selective preconcentration or separation of target metal ions from multicomponent environmental aqueous samples from ground water and seawater. In many applications, the functionalized sorbents have to be equilibrated with natural samples for a long period of time for preconcentration of the target metal ions from lean aqueous feeds. The long exposure of polymeric sorbents with bio-aggressive feed leads to biofouling of the sorbent, which drastically affects the sorption of the target ions from feed to sorbent matrix. This has been found to be a major
problem in recovery of uranium from seawater [13,14]. Incorporation of antimicrobial nano-materials into sorbents/membranes offers an innovative potential solution to biofouling control [15,16]. Silver ions and its compounds are known to exhibit strong antimicrobial activity towards broad-spectrum bacteria [17]. The antibacterial property of the silver nps in polymeric matrix prevents the adherence and proliferation activities of bacteria at the surface of polymeric materials [18]. The silver nps coordinate to electron-donating groups such as thiols, carboxylates, amides, imidazoles, indoles and hydroxyls inhibiting propagation of microorganisms [17,19]. Ag-containing materials developed so far are polymer thin films and nano-fibers that have been widely used for catheters, dental material, medical devices, implants, and wound and burn dressings [20-24].

4B.2 Synthesis of Nano-composite Sorbent

Table 4B.1 Experimental details and UV-Visible absorption maxima of as-prepared Ag@PEGMP composite films with different extent of Ag loading.

<table>
<thead>
<tr>
<th>Id.</th>
<th>Amount of Ag(^0) (wt.%</th>
<th>Amount of EGMP (g)</th>
<th>Amount of initiator (wt. %)</th>
<th>DMF (mL g(^{-1}))</th>
<th>Reaction duration (h)</th>
<th>(\lambda_{abs.}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-1</td>
<td>0.85</td>
<td>2</td>
<td>2</td>
<td>0.50</td>
<td>3</td>
<td>400</td>
</tr>
<tr>
<td>E-2</td>
<td>1.60</td>
<td>2</td>
<td>2</td>
<td>0.50</td>
<td>3</td>
<td>415</td>
</tr>
<tr>
<td>E-3</td>
<td>3.00</td>
<td>2</td>
<td>2</td>
<td>0.50</td>
<td>3</td>
<td>420</td>
</tr>
<tr>
<td>E-4</td>
<td>0.85</td>
<td>2</td>
<td>2</td>
<td>0.75</td>
<td>3</td>
<td>400</td>
</tr>
<tr>
<td>E-5</td>
<td>1.60</td>
<td>2</td>
<td>2</td>
<td>0.75</td>
<td>3</td>
<td>405</td>
</tr>
<tr>
<td>E-6</td>
<td>3.00</td>
<td>2</td>
<td>2</td>
<td>0.75</td>
<td>3</td>
<td>415</td>
</tr>
<tr>
<td>E-7</td>
<td>1.60</td>
<td>2</td>
<td>0.5</td>
<td>1.00</td>
<td>3</td>
<td>410</td>
</tr>
<tr>
<td>E-8</td>
<td>1.60</td>
<td>2</td>
<td>1</td>
<td>1.00</td>
<td>3</td>
<td>412</td>
</tr>
<tr>
<td>E-9</td>
<td>1.60</td>
<td>2</td>
<td>3</td>
<td>1.00</td>
<td>3</td>
<td>418</td>
</tr>
</tbody>
</table>
The details of the method of preparation are described in chapter 2, section 2.1.3.4. The composition of the self-supported Ag@PEGMP films is given in the table 4B.1. The physical appearances of self-supporting nano-Ag@PEGMP film is shown in figure 4B.1.

![Figure 4B.1 The photograph showing physical appearance of self-supporting Ag@PEGMP nano-composite film.](image)

**4B.2 Results and Discussion**

**4B.2.1 Synthesis of Sorbent Film**

PEGMP has acidic phosphate groups that makes it a cation-exchanger as well as capping agent for Ag nps. PEGMP takes up different metal ions depending on the chemical conditions of the equilibrating aqueous feeds [25]. DMF is known to reduce Ag\(^+\) ions to form Ag nps [26,27]. Ag\(^+\) ions could also be reduced by the phosphate groups of EGMP. In order to clarify this, EGMP monomer was dissolved in AgNO\(_3\)-chloroform solution with continuous stirring. The resulting colorless solution became yellowish in an hour and gradually changed to dark yellow after standing for 48 h. The absorption spectrum of this solution showed absorbance band at 402 nm (as shown from figure 4B.2) that corresponds to surface plasmon resonance (SPR) of Ag nps.
Figure 4B.2 UV-Visible spectra of nano-silver obtained by reduction of silver nitrate by (A) EGMP monomer in chloroform, and (B) PEGMP hydrogel in de-ionized water.

PEGMP gel turned to brown during its equilibration with dilute aqueous solution of AgNO₃ at 70 °C with constant stirring. The aliquot of the brownish solution gave the SPR at 400 nm for nano silver. This seems to indicate that PEGMP itself acts as mild reducing for Ag⁺ ions. The overall mechanism of formation of the Ag@PEGMP is shown in chapter 2.

Figure 4B.3 UV-Visible absorption spectra of as prepared Ag@PEGMP nano-composite with (a) 0.85 wt. % (E-1 & 4), (b) 1.6 wt.% (E-2 & 5) and (c) 3.0 % (E-3 & 6) Ag loading.
The SPR absorption band of 0.85 and 3 wt % Ag\(^0\) loaded nano-composite samples are observed at 400 nm and 415-420 nm, respectively (see figure 4B.3).

The alteration of SPR was also observed on increasing the amount of initiator in polymerizing solution e.g. the absorption band of Ag nps in the nano-composite was shifted from 408 nm for 0.5 wt % initiator to 416 nm for 3 wt % of initiator.

There was no appreciable change in SPR by varying the amount of DMF from 0.5 mL to 1.0 mL under similar experimental conditions (see Table 4B.1 and figure 4B.4). This seems to suggest that high reduction and fast rate of polymerization leads to agglomeration of Ag nps in PEGMP leading to red shifted SPR absorption band.

![Figure 4B.4 UV-Visible absorption spectra of as-prepared Ag@PEGMP nano-composite with 1.0 mL DMF and varied silver loading (a) 0.85 wt.% (E-7), (b) 1.6 wt.% (E-8) and (c) 3.0 % (E-9).](image)

To see the stability of Ag nps in the polymer matrix, the Ag@PEGMP nano-composite sorbent (with 1.6 wt % of Ag\(^0\) loading) was kept in open atmosphere at room temperature. The SPR peak intensity of Ag nps at 405 nm gradually increased over a period of 60 days in air as given in figure 4B.5. The increase in the peak intensity was
due to slow reduction of $\text{Ag}^+$ ions held in ion-exchange sites by phosphate groups of PEGMP itself.

Figure 4B.5 Enhanced SPR during study of stability of 1.6 % Ag loaded film in air, (a) as-prepared (b) after 10 days and (c) 60 days.

4B.2.2 Characterization of Ag@PEGMP

Figure 4B.6 FTIR spectrum of as-prepared Ag @PEGMP nano-composite sorbent with 1.6 wt % of Ag.
FTIR spectra were recorded to understand the chemical composition of the nanocomposites. The FTIR spectrum of nano-Ag@PEGMP is shown in Figure 4B.6. The FTIR spectra shows peaks associated with P=O (1220 cm⁻¹), C=O (1715 cm⁻¹), and P-OH vibrations at ≈ 1045 cm⁻¹, and broad band in the region of 3600 – 3400 cm⁻¹ due to intramolecular O-H stretching vibrations. These frequencies are assigned based on the comparison of FTIR spectra with the characteristic frequencies reported in the literature for these groups [13,28,29]. The band at 670 cm⁻¹ is due to silver nps bonded to the functional groups in the PEGMP matrix.

The amount of Ag as nanoparticles that could be anchored in the self-supported nano-Ag@PEGMP and Ag@PEGMP reinforced with fibrous poly(propylene) were measured by tagging Ag⁺ ions with ¹¹⁰mAg radiotracer as described in chapter 2. The γ-radioactivity of ¹¹⁰mAg radiotracer in Ag@PEGMP nano-composite was correlated with amount of Ag as described in the experimental section. This radiotracer study indicated that 5±1 wt. % of Ag as nanoparticles were anchored in the PEGMP matrix of film. The size of Ag nanoparticles in Ag@PEGMP nano-composite film with 1.6% silver loading as obtained by the TEM analysis

![Image](image.png)

Figure 4B.7 TEM (A) and particle size distribution profile as obtained by dynamic light scattering (B) of Ag@PEGMP nano-composite sorbent with 1.6 wt % silver loading.
ranges between 5 to 7 nm. TEM micrograph along with the particle size distribution profile as obtained by dynamic light scattering technique of Ag@PEGMP nanocomposite are shown in Figure 4B.7.

4B.2.3 Antibacterial Study

It is important for the sorbents to have better shelf-life and be robust and stable against the environmental degradation. The PEGMP is found to have required selectivity towards uranium under seawater conditions [13]. However, it is likely that prolonged exposure of the PEGMP sorbent in seawater would lead to bio-fouling of the sorbent. The suitability of the Ag@PEGMP film for its use in bioagressive feed was examined by studying the antibacterial property of PEGMP with E.Coli. The study of antibacterial property of the Ag@PEGMP

Figure 4B.8 Study of antibacterial property against E Coli. Flask (a) contained E.Coli solution with the Ag @PEGMP nano-composite, and Flask (b) contained only E.Coli solution.

system was performed by spiking sufficient amount of the bacteria E Coli-2066 in the solution in two flasks, one having the nano-composite sample in the bacterial solution (Figure 4B.8a), and the other with bacterial solution alone (Figure 4B.8b). It is seen that the solution is clear in the presence of Ag@PEGMP nano-composite. However, solution
without nano-composite became turbid. This clearly indicates that the Ag@PEGMP sorbent prevents the growth of bacteria. This would make Ag@PEGMP nano-composite sorbent more effective in bio-aggressive feed.

4B.2.4 Sorption of U(VI) in Nano-composite Under Seawater Conditions

In order to study the stability of Ag@PEGMP nano-composite sorbent under seawater conditions, the sorbent sample was equilibrated in seawater for overnight. The SPR band of Ag nps in nano-composite was monitored to see the effects of its equilibration in seawater.

![Figure 4B.9 Absorption spectra of Ag@PEGMP nano-composite film (a) before soaking, (b) after soaking and (c) equilibrated seawater.](image)

As can be seen from Figure 4B.9, $\lambda_{\text{max}}$ of SPR peak becomes sharper. However, there was no significant loss of Ag nps as indicated by UV-Vis spectra of equilibrated seawater. The change of SPR band of Ag nps in nano-composite sorbent may be attributed to sorption of the ions from seawater in PEGMP, which may change the conformation of PEGMP chains. As PEGMP holds the Ag nps, the change of PEGMP...
physical structure would alter the optical properties of Ag nps. As uranium forms complex with phosphate units of PEGMP, the nano-composite sorbent samples were equilibrated with seawater spiked with $^{nat}$U(VI).

The comparison of EDXRF spectra of the sorbent samples shown in Figure 4B.10 below, indicates that presence of Ag nps does not affect the U(VI) sorption, and U(VI) also does not displace Ag nps from PEGMP matrix.

![EDXRF spectra](image)

**Figure 4B.10** EDXRF of Ag@PEGMP nano-composite (a) as prepared, (b) after soaking in seawater and (c) after soaking in seawater spiked with $^{nat}$U.

The sorption kinetics of U(VI) in pure PEGMP gel and Ag@PEGMP nano-composite sorbent from well-stirred seawater (15 mL) were studied using $^{233}$U radiotracer. The uptake of $^{233}$U in the samples ($2 \times 1 \text{ cm}^2$) was monitored by $\alpha$-scintillation
counting of 50 μL samples taken from equilibrating solution at regular time intervals as described in chapter 2. The comparison of rates of fractional attainment of U(VI) uptake equilibrium F(t) in the PEGMP and Ag@PEGMP nano-composite samples as a function of equilibration time in well-stirred seawater is shown in Figure 4B.11.

**Figure 4B.11** Uranium (VI) uptake kinetics by PEGMP gel (□), and Ag@PEGMP nano-composite (○) samples equilibrated with well-stirred seawater spiked with $^{233}$U.

This comparison seems to suggest that the U(VI) sorption kinetics is not affected significantly by the presence of Ag nps embedded in PEGMP matrix. The slightly faster kinetics in pure PEGMP gel is due to the fact that it swells higher than the nano-composite sorbent in seawater.
4B.3 Conclusions

The synthesis of Ag nano particles has been described in PEGMP by a simple and easy photochemical transformational route. Formation of Ag/PEGMP nano-composite has been monitored by UV-Visible spectroscopy. The UV-Visible spectra indicate well-defined absorption bands for Ag nanoparticles due to surface plasmon resonance phenomena. The photolytic reduction of AgNO₃ by DMF in PEGMP is considered to be a key step in the formation of such system. The particle diameter of the silver by the current methodology is found to be between 5-10 nm for various preparations. TEM reveals that the nanoparticles are well dispersed in the polymer matrix. The nano-Ag@PEGMP film could be used in bio-aggressive feed like seawater for better uptake of U(VI) as it exhibits antibacterial property. Also, the sorption kinetics of U(VI) is not affected significantly by the presence of Ag nps embedded in PEGMP matrix.
References


