Summary

The polymeric sorbent containing amidoxime chelating functional group is most promising for the recovery of uranium from seawater and has been extensively used by the Japanese group (JERI). However, studies on uranium uptake kinetics and the parameters affecting the uptake kinetics from such a multi-component bio-aggressive feed are not available. Therefore, the scope of the present thesis was to study the chemical aspects of uranium recovery from seawater using poly (amidoxime) (PAO)-sorbent, and develop a new potential sorbent for pre-concentration of uranium from multi-component feed like seawater with fast kinetics without sacrificing selectivity. The thesis is divided into five chapters. Chapter 1 gives the introduction, literature survey and scope of the work. Experimental details of the work are accounted in chapter 2. Chapters 3 to 5 present the results and discussion on the studies carried out to develop and evaluate various sorbents for selective and fast pre-concentration of uranium from multi-component feeds.

Chapter 1 elaborates on the importance of uranium as a future energy source and the seawater as the inexhaustible source of uranium. In this chapter, various chemical separation methods for trace element speciation, solid phase extraction technique using polymer membranes for the pre-concentration of target analytes, the concept of the membrane based techniques and speciation using membrane based methods are described. A brief overview of literature reports on the importance and separation of uranium using different extractants has been presented. The background of requirements for the chelating sorbent to be used for uranium recovery from multi-component feed has also been discussed in this chapter.

General outline about different experimental techniques and instrumentation used in the present work are given in chapter 2. The methods of preparation and purification
of various radiotracers have been described followed by the synthesis and characterization of relevant sorbents like polyamidoxime (PAO), poly(ethylene glycol methacrylate) (PEGMP) along with other polymer gels, grafted fibrous polypropylene (PP) membranes, Ag°@PEGMP nano-composite film, and Ag°@PEGMP nano-composite enforced PP membrane. A brief discussion of the various analytical techniques such as UV-visible absorption spectroscopy, Infrared (IR) spectroscopy, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Energy Dispersive X-ray Fluoroscence (EDXRF), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Neutron Activation Analysis (NAA) etc.) is presented in this chapter. The chapter is concluded with the details of working principles of gamma spectrometry carried out with NaI(Tl) detector and HPGe detector, and liquid scintillation counter employed for alpha radioactivity measurement.

In chapter 3, different chemical parameters (such as, water uptake capacity, U(VI) loading capacity, Na⁺-exchange capacity, self-diffusion coefficient of UO₂²⁺ ions etc.) that determine the kinetics of U(VI) sorption in PAO-sorbent from seawater are discussed. The water uptake capacity, Na⁺-exchange capacity, and uranium loading capacity of PAO-membrane, in seawater conditions were found to be 200±10 wt. %, (3.1±0.2)×10⁻² mol.g⁻¹, and (1.60±0.18)×10⁻³ mol.g⁻¹, respectively. The U(VI)-exchange rate profiles in the PAO-sorbents (fibre and sheet)(S) have been measured using ²³³U radiotracer spiked in the well-stirred seawater/aqueous(aq) solution. The kinetics of U(VI)-exchanges studied involve (H⁺/Na⁺)⇌(UO₂[(CO₃)₂]⁺)ₙ, (UO₂⁺)ₙ⇌(UO₂⁺)ₙ and (UO₂²⁺)ₙ⇌(UO₂²⁺)ₙ systems. The rate profiles of (M⁺)ₙ⇌(M⁺)ₙ isotopic-exchanges were analyzed using an analytical solution of Fick’s second law to obtain the self-diffusion coefficient of UO₂²⁺ ions in PAO-sorbents. The exchange profiles thus obtained seem to suggest that the reaction
kinetics involved in de-complexation of \([\text{UO}_2(\text{CO}_3)_3]^{4+}\) into \(\text{UO}_2^{2+}\), which forms complex with AO-groups, is the rate determining step and kinetics of U(VI) sorption from seawater follows the pseudo-second-order rate equation. The values of self-diffusion coefficient \((D_s)\) of \(\text{UO}_2^{2+}\) in fibrous and sheet PAO sorbents are found to be \(1.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}\) and \(2.3 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}\), respectively. The higher diffusion mobility of \(\text{UO}_2^{2+}\) in the fibrous PAO sorbent is attributed to its higher free volume as observed from the scanning electron micrographs. The self-diffusion coefficient of \(\text{Sr}^{2+}\) was also measured as it has comparable self-diffusion coefficient as that of \(\text{UO}_2^{2+}\) in water, but expected to have different chemical interactions with AO groups in the sorbent. The lower value of \(D_s\) for \(\text{UO}_2^{2+}\) than that for \(\text{Sr}^{2+}\) in the fibrous membrane could be attributed to stronger (covalent + electrostatic) binding of \(\text{UO}_2^{2+}\) with AO groups as compared to \(\text{Sr}^{2+}\) (electrostatic).

As PAO sorbents were found to have inherently slow uptake kinetics of uranium from seawater, search for new chemical structures has been explored in Chapter 4. This chapter is divided into two subsections. In section 4A, screening of functionalized hydrogels and emergence of PEGMP as a new potential sorbent for uranium has been extensively studied. This section also describes the dependence of U(VI) sorption kinetics on the pKa of different acidic co-monomers. The mechanism of sorption of U(VI) in the hydrogels were also studied to understand the factor that controls the U(VI) sorption. In section 4B, the bio-resistivity of \(\text{Ag}^0@\text{PEGMP}\) nano-composite film and \(\text{Ag}^0@\) polypropylene reinforced PEGMP matrices is described. This section also explores the utility of this nano-composite sorbent for uranium uptake from bio-aggressive multi-component aqueous feeds.

The hydrogels can be anchored within pores of a robust microporous host membrane, which provides a containment and mechanical strength to the hydrogel and mitigates the impact of osmotic forces. To understand the appropriate chemistry of
hydrogel (the guest component), PEGMP was anchored in the polypropylene fibrous membrane. Evolution of PEGMP membrane for pre-concentration of uranium from seawater and other acidic aqueous media has been investigated in Chapter 5. PEGMP membrane has been characterized in terms of its physical and chemical architectures including uranium uptake efficiency from seawater and acidic aqueous solutions (HNO₃/HCl/H₂SO₄/H₃PO₄), uranium sorption kinetics, self-diffusion coefficient of UO₂²⁺ ions, and its selectivity towards uranium in sorption-desorption process. The uranium sorption kinetics in the PEGMP membrane was found to be five times faster than that in the PAO membrane. The PEGMP membrane was studied for practical analytical applications in leach liquors of rock samples, uranium process stream and seawater by EDXRF, ICP-AES, UV-spectrophotometry and neutron activation analysis (NAA). Although the PEGMP membrane showed good selectivity towards uranium, Fe(III) was also sorbed in the membrane in case of lack of saturation by uranium. Therefore, a selective uranium desorption scheme was developed by sequential equilibrations of loaded membrane with HCl, Na₂CO₃, and EDTA, for selective desorption of Cu(II), U(VI), and Fe(III), respectively.