“STUDY OF RECOVERY OF HEAVY METAL IONS FROM SEAWATER BY NOVEL ADSORBENTS”

by

TL PRASAD

(HBNI Enrollment No.ENGG01200704015)

Bhabha Atomic Research Centre Mumbai

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Under the guidance of
Prof D Sathiyamoorthy & Prof PK Tewari

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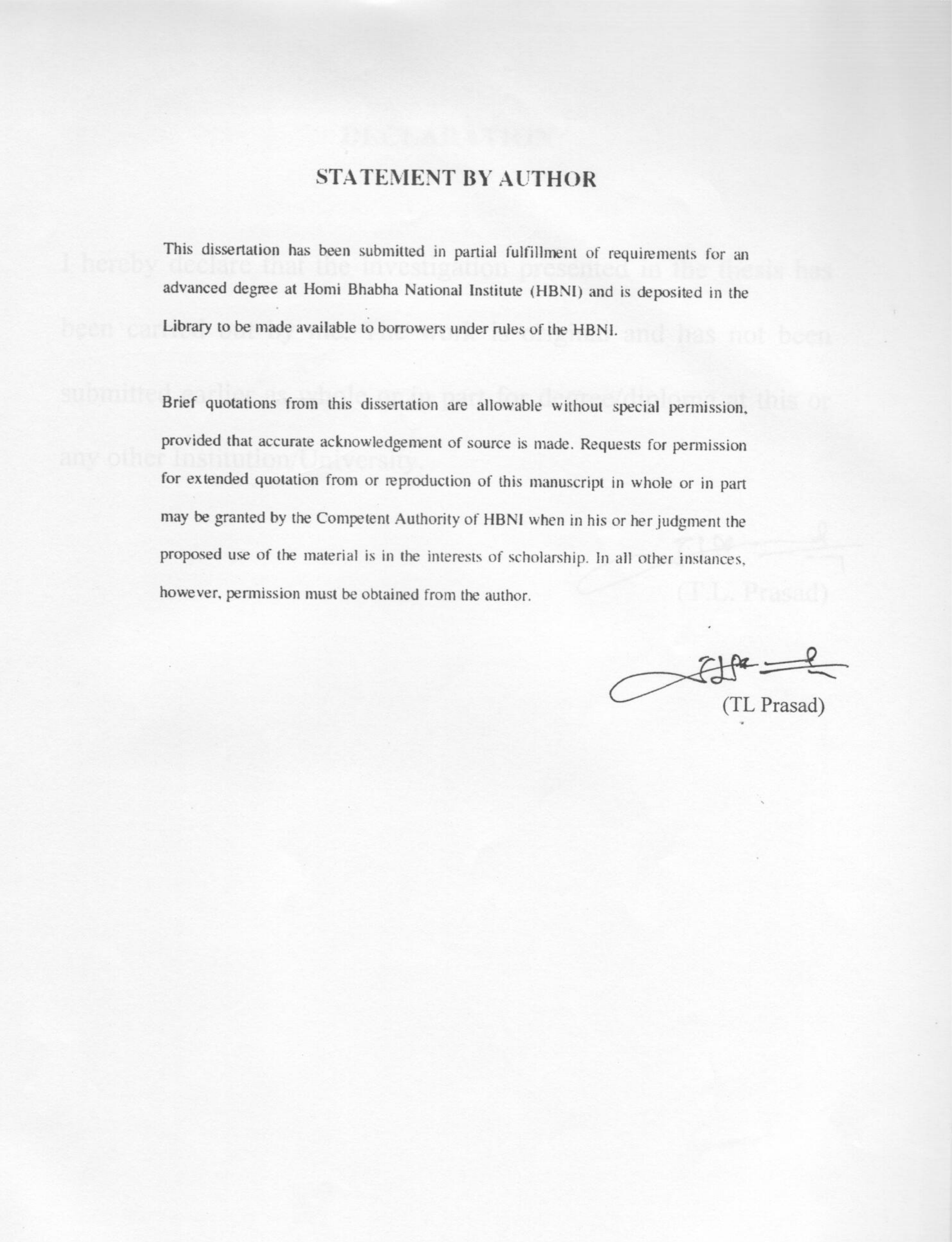

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DECLARATION

I hereby declare that the investigation presented in the thesis has been carried out by me. The work is original and has not been submitted earlier as whole or in part for degree/diploma at this or any other Institution/University.

(T.L. Prasad)

"Research is to see what everybody else has seen and to think what nobody else has thought"

DEDICATIONS

I dedicate this thesis to my

Grand mother

&

Parents

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CONTENTS

“Study of Recovery of Heavy Metal Ions from Seawater by Novel Adsorbents “

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Synopsis

Selective separation of valuable heavy metals from lean sources such as seawater/brine is an area of considerable interest for recovering these metals from the vast secondary resources. Various novel techniques are being attempted by researchers for efficient and economical way of recovering these metals [1]. General reagents or sorbents such as bi-functional ion selective polymer supported reagents; biosorbents; functionalised organic ceramic sorbents; polymeric ligand exchangers; molecular imprinting polymers; solvent impregnated resins and grafted sorbents are some of the suggested choices [2-6]. The concentration of uranium in seawater is at least three orders of magnitude less than the conventional primary resources, which are fast depleting. Hence a method, which evolved in the recent past, is the use of adsorbent for recovery of uranium from seawater. And the adsorbent should have superior property with respect to selective adsorption and regeneration. "Radiation grafting on polymers" facilitates for imparting of superior properties onto polymeric adsorbents [7-10]. The parametric sensitivity analysis of such radiation grafting and the use of resultant polymeric adsorbent for recovering the uranium are investigated in this thesis [11]. Grafting is used in situations where the requirements for bulk and surface properties cannot be readily created by using single polymeric material [12-14]. Radiation grafting has made it possible to create a material whose bulk is made of one polymer type but with a surface of another polymer type. A chemical bond is formed between the grafted moiety and the bulk material. During irradiation of polymers free radicals are produced in the material without the use of chemicals. Any amount of functional groups can be introduced to the trunk polymer fiber by selecting proper type of irradiation and grafting conditions. Electron beam irradiation eliminates the sensitivity of catalysts to temperature. An efficient grafting technique needs to be developed to reduce the manufacturing cost of radiation grafted polymeric adsorbents. Higher selectivity and more efficient adsorption properties can be imparted with proper selection of ligand and by controlling the functionality of grafted chains. Considering a large number of parameters and variables in radiation grafting, results have been reported in this research work [15]. Studies on radiation grafting polymerization of monomers to monofilament fibers and systematic evaluation of grafting conditions for an optimum grafting yield have been reported, with a view for recovery of heavy metals such as uranium and vanadium. In this thesis, each aspect of radiation grafting and application stages to establish metal pick up characteristics have been presented for variety of polymeric substrate materials.

Chapter-1: Introduction

Oceans are potential secondary sources for uranium and other valuable heavy metals, as it contains around eighty elements of periodic table. Some of the elements are either very scarce on land or very expensive. Uranium is also one among them. With its lean but clean resource, oceans can serve as constant potential source of uranium and other valuable heavy metals for a long run. India with a large coast-line and favorable tropical climate for most part of the year has a large stake in exploiting the valuable elements locked in seawater. The co-operative R&D efforts on fundamental research and engineering studies are the solution to sustainable and economical recovery of uranium from seawater. **Chapter-1** provides an overview of the "Recovery of heavy metals from Seawater/Brine" and development & application of radiation grafted sorbents for the same. The motivation and objectives of area of research are detailed in this chapter.

Motivation for the area of research:

In the last century uranium has universally gained acceptance as primary energy source. Currently, it caters to approximately 17% of the electricity generation globally. Uranium has been projected as the main workhorse of future when the fossil energy reserves dwindle by the middle of 21st century and hence it is going to be important member of the energy family. The terrestrial distribution of uranium ore occurrence is grossly uneven. With a large coastline, India, Japan, Korea and a few other nations have a larger stake in exploiting 4.5 billion tones of uranium locked in seawater [1]. Compared to terrestrial mineralisations, seawater is practically an inexhaustible resource for uranium [2, 3]. Uranium in seawater mainly exists as tricarbonyl complex of uranyl and tricarbonate as tetravalent anionic form. The structure of uranyl complex is as shown in Fig. 1.

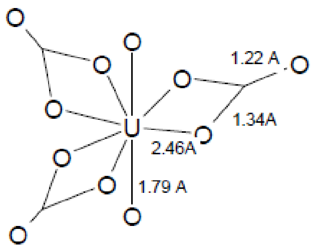

Fig. 1 Structure of uranyl complex in seawater conditions

The proposed research work was undertaken to employ the radiation grafting aspects for polymeric adsorbent synthesis and analyse the same for study of recovery of heavy metals such as uranium from seawater

Chapter-2: Literature Survey and State of Processes and Technology in Uranium Extraction from Seawater

Over the past four decades, theory and application of adsorbents and ion exchange have greatly advanced and touched almost every industrial sector. Nevertheless, the field is still to be explored, in terms of both synthesis of novel materials and application opportunities in new areas. Selective separation of valuable metals from lean sources such as seawater and their possible recovery is an area of considerable interest. Novel techniques/materials being targets of researchers are: bifunctional ion selective polymer supported reagents, biosorbents, functionalised organo-ceramic adsorbents, polymeric ligand exchangers, molecular imprinting techniques (MIPs), solvent impregnated resins (SIRs) and grafted adsorbents. Literature survey given in this chapter encompasses the state of the art development in this area. **Chapter-2** reviews the literature of various sorbents and techniques for heavy metal separation in general and the current status of processes and technology in various Labs/countries especially with respect to radiation grafting aspects.

Chapter-3: Various Recovery Processes for Uranium and Other Valuables

This chapter describes the possible various recovery processes with their limitations and emphasise the need for development of radiation grafted sorbents. These include, in particular, ion-exchange, solvent extraction, foam separation, co-precipitation, biological separation and adsorption.

Chapter-4: Basic Process Mechanism and Thermodynamic Aspects

This chapter describes the basic process mechanism for sorbent synthesis and thermodynamic aspects of metal pick up from seawater. Extraction occurs when interaction potential energy equals to the work done to bring to the sorbed state. The minimal energy to extract one mole of Uranium from seawater can be calculated by assuming reversible process and variation of entropy created by the concentration process.

Chapter-5: Radiation Processing by Electron Beam Technology

The radiation processing by electron beam technology has been adopted in our work for developing polymeric adsorbents through the process of radiation grafting. The electron beam equipment and technology have been matured from a little known technology in the mid 1950's to a mature, reliable process system of choice for many processes today. Radiation processing by electron beam technology is discussed in this chapter**.**

Chapter-6: Modern Analytical Techniques Adopted

Quality assurance for solid and liquid samples is an important aspect of analysis and hence modern analytical techniques adopted are described in **Chapter-6** briefly, especially highlighting the nuclear analytical techniques for uranium analysis. This chapter highlights the sorbent characterisation techniques for characterization of substrate samples and grafted samples. Nuclear analytical techniques were adopted for liquid sample analysis.

Chapter-7: Description of the Experiments & Results

This chapter provides Experimental methods and materials used. This chapter also deals with the characterization of radiation grafted adsorbents and their metal pick up characteristics. **Chapter-7** gives description of the experiments and in-field trials carried out. The effect of various parameters with respect to sorbent synthesis and their metal pick up characteristics are described. The salient experimental results are as follows:

Radiation grafting has been studied using electron beam energies of both 2MeV and 1.25 MeV. Characteristics of radiation grafted polymeric substrates of four types such as poly ethylene (PE); poly propylene (PP); poly styrene (PS) and Poly Tetra Fluro Ethylene (PTFE) have been carried out and the results are shown in Table 1. The quality assurance for grafting extent was done gravimetrically using the equation:

$Grafting\% = ((W_g - W_i) / W_i) \times 100$

Where W_i, W_g are the weights of the substrate polymer sample before and after grafting.

Post irradiation grafting technique has given better grafting yields for PP and PE substrates.

Table-1 Radiation Grafting Characteristics of four types of polymeric substrates

Sl.No	**Polymer type**	**Grafting technique**	**Dose (kGy)**	**Irradiation atmosphere**	**Reaction Mixture**	**Grafting yield at 60 ºC (%)**
1	Polystyrene	Post irradiation with Electron Beam (EB)	200	air	70:30 ACN:DMF	2
2	PTFE	Post irradiation with EB	200	air	70:30 ACN:DMF	5
3	Polyethylene	Post irradiation with EB	200	air	70:30 ACN:DMF	40
4	Poly propylene	Post irradiation with EB	200	air	70:30 ACN:DMF	79

Five types of commercially available fiber compositions and geometries, thermally bonded non woven fabrics of various GSM (Grammes per Square Meter) were evaluated for their suitability for grafting purposes. Fibres of 1 denier size (0.00000011 kg/m) and circular geometry were used. The cumulative dose of 200 kGy was given to all the samples at the rate of 1 M Rad per pass and subsequently grafting was done at temperature of 60 ºC. The sample size used in experiments was 50mm x 50mm. The observed radiation grafting characteristics of Poly Propylene fibers of various makes are given in Table 2.

Table-2 Characteristics of EB grafted PP fiber

Sl.no	Density of PP substrate sample (GSM)	Initial weight (g)	Final weight (g)	Grafting yield (%)	Avg value	Remarks
1	500	2.6	4.807	84.88	87.73	With PS scrim
		1.2	2.287	90.58		
2	270	1.02	1.912	87.45	77.92	Without scrim
		0.56	0.943	68.39		
3	300	1.07	1.842	72.145	77.48	Without scrim
		0.39	0.713	82.82		
4	500	2.03	4.04	99.21	89.09	With scrim
		0.78	1.396	78.97		
5	500	1.42	2.334	64.37	62.46	With scrim and bicomponent fiber
		0.53	0.851	60.57		
6	500	1.23	1.79	46.01	43.10	With PE scrim and bicomponent fiber
		0.52	0.729	40.19		

Non woven substrates of 300 to 500 GSM with monofilament and bi-filament fiber (80% PP and 20% PE) have given good grafting yields at air retention time of 15 minutes. The type and range of parameters studied are dose; dose rate; air retention time; duration; temperature and different monomer concentrations [11, 15]. The grafting yield with time for different solvent-monomer concentrations ranging 10% to 80% was studied. Grafting levels of up to 150% have been achieved, without degradation in mechanical characteristics of the synthesized sorbent. The optimum monomer concentration, duration and temperature for grafting reactions are 70% acrylonitrile and 30% DMF solvent, 3 hours and 60ºC respectively. The order of rate of grafting reaction on monomer concentration $[M]$ was found to be 0.36. The equation may therefore be represented as $R_g \alpha [M]^{0.36}$ at 60ºC. The fractional order dependence shows that homopolymerisation is not occurring. Physical (300% improvement in surface area); chemical (FTIR: DSC) and mechanical characterization of radiation grafted polymeric adsorbents are reported in this thesis. A reduction of 25 to 30% is observed in case of tensile strength and 30% in case of elongation at break, for the conditions of study range.

No or little attempts have been made for recovery of heavy metals in this range of low concentrations. The knowledge of many important chemical aspects involved in recovery of heavy metals from seawater is inadequate. Data were collected for metal pick up both from lab scale studies and field trials and reported in this thesis. The adsorption isotherm in seawater is difficult to obtain experimentally, as much longer time is required to attain equilibrium. Information in the very low concentration range, in the parts per billion, is extremely difficult to obtain. It is the information in this low concentration range that is needed for practical applications. Single parameter models were used to analyse using Freundlich and Langmuir isotherms. The values of constants indicate favorable conditions for adsorption. Freundlich isotherm model is fairly satisfactory empirical isotherm and can be used for non ideal sorption that involves heterogeneous adsorption. The Freundlick isotherm predicts that the adsorption of metal ion on the sorbent increases as long as there is an increase in the metal ion concentration. As the value of 1/n < 1, it indicates favorable adsorption. The model parameters for Langmuir and Freundlich isotherms are shown in Table-3.

Table-3 Model parameters for sorption isotherms

Sl. No	**Parameters**	**Values of Regression analysis**	**Values of model parameters**	**Remarks**
I	Langmuir isotherm $\frac{c_e}{q_e} = \frac{1}{q_m k_l} + \frac{c_e}{q_m}$			$R^2 = 0.7816$
1	slope	0.0296	LI constant $K_I = 0.5778$	
2	intercept	0.0513	Q_m = 19.993 ppb ; Separation factor $K_L = 0.2$	
II	Freundlich isotherm $q_e = K_f c_e^{\frac{1}{n}}$			$R^2 = 0.9722$
1	slope	0.6635	Intensity of adsorption, n = 1.50715	
2	intercept	1.2704	$K_f = 3.56227$	

Present thesis gives results related to key performance indicator such as uranium pick up rate as influenced by submergence duration; fouling factors; initial concentration and grafting levels. Appropriate kinetic models have been attempted to fit the observed data and analysed for uranium and vanadium elements from seawater/brine. The pseudo first and second order Lagergren rate equation plots are as shown below. Pseudo first order equation fits well for the interactions of uranium onto the radiation grafted sorbent [16]. The Lagergren rate equation plot and parameters are shown in Fig 2 and Table-4 respectively.

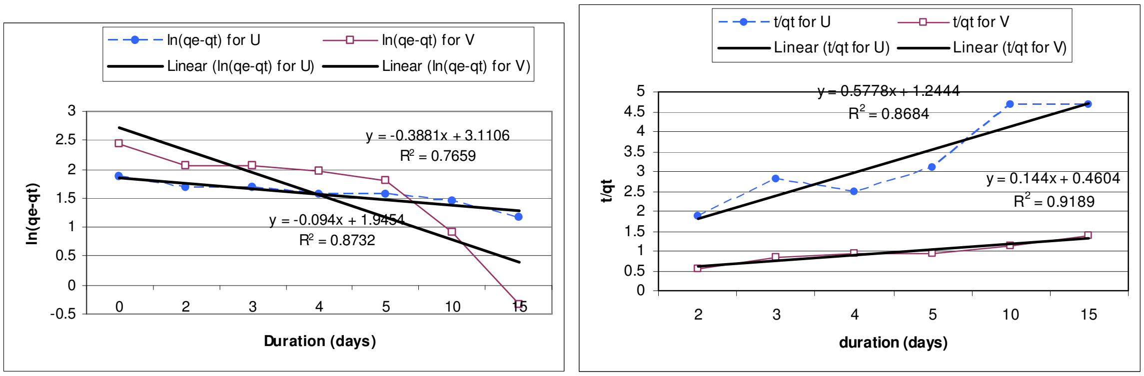

Fig. 2 Lagergren rate equation plots

Table-4 Lagergren rate equation parameters for sorption kinetics

	For first order kinetics $\frac{dq_t}{dt}=k_{ad}\left(q_e-q_t\right)$					**For second order kinetics** $\frac{dq_t}{dt}=k\left(q_e-q_t\right)^2$				
	Slope (k_{ad})	intercept ($\ln q_e$)	qe mg/kg of PAO)	k_{ad} (1/day)	R^2	slope ($1/q_e$)	intercept ($1/kq_e$^2)	R^2	k(kg/mg-day)	q_e
for U	0.094	1.9454	6.9964	0.094	0.8732	0.5778	1.2444	0.8684	0.268	1.73
for V	0.3881	3.1106	22.435	0.3881	0.7659	0.144	0.4604	0.9189	0.045	6.94

In order to establish Differential elution studies for uranium and vanadium, field trials were carried out in Arabian seawaters at Trombay estuary and also using desalination effluents of SWRO (Sea Water Reverse Osmosis) Kalpakkam using radiation grafted adsorbent of size 50mmx50mm size. Differential elution studies on uranium pick up were carried out using 0.5M HCl solution at 60deg.C and 4 hour duration. Vanadium and uranium pick up rates from desalination effluents and high seas are evaluated.

Desalination effluents have given vanadium pick up of up to 1200 ppb with 5M HCl solution. Uranium pick up rate observed was 1g/kg of adsorbent for submergence period of 12 days. The fouling factors observed for radiation grafted polymeric sorbents for various seawater conditions were also evaluated. The radiation grafted sorbent material developed and radiation grafting systems designed have given most optimum uranium pick up compared to any other materials reported in India under actual field trials.

Chapter-8: Conclusions and Future work

Various adsorbents including synthetic polymers, inorganic materials and bio polymers have been tested for uranium recovery from seawater. To date, the specially indigenized organic adsorbent PolyacryloAmidOxime (PAO) has shown promising results for recovery of uranium and other heavy metals from seawater. Pumped circulation schemes which were inherently riddled with negative electricity gain were abandoned. By harnessing tidal energy innovatively the advantage of positive energy gain ratio has been achieved. Feasibility studies on various sizes of pilot scales will help in optimization of process design parameters of adsorbent synthesis and improving the yield of recovered uranium.

- Economical recovery of uranium is a challenge in view of lean nature of resource and bio-aggressive nature of multi-component feed.
- EB radiation grafted sorbents has offered advantages of easy preparation; reusability; sorption kinetics and selective desorption of uranium and vanadium.
- The grafting levels of up to 130% to 150% have been achieved without much degradation of mechanical properties.
- Metal pick up characteristics have been established and CF of order 1000 has been observed from initial concentration of 3.3 ppb on pilot scale. CF of order 30000 has been observed for lab scale studies.
- The adsorption kinetics is likely to follow a pseudo-first order model suggesting complex nature of the adsorption of uranyl ions. Both liquid-film mass transfer and intra-particle diffusion play important role in uranium transport from seawater to the porous adsorbent.

- The three order of improvement in concentration factors for uranium has been achieved by repeated A-S-E cycles.
- Radiation grafting for synthesis of metal chelate embedded polymeric adsorbents is one of the important industrial application of ionizing radiations in future.
- The sorbent material developed and radiation grafting systems designed have given most optimum uranium pick up compared to any other materials reported in India under actual field trials.
- The repeated usability of sorbent is established both on lab scale and bench scale and given satisfactory performance for 5 to 6 A-S-E cycles.
- The alpha spectrum profile shows U234 and U238 in the activity ratio of 1:1.03, the ratio observed for natural uranium in the environment

The Table showing the comparison of salient features of adsorbent synthesized using radiation technique by various research groups is presented in the thesis. The major benefit of this work is improved process technology to augment the Uranium supplies through viable and sustainable secondary sources such as seawater.

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1. Prasad TL., Tewari PK., Sathiyamoorthy D., "Recovery of uranium from reject streams of Desalination plants" was presented at Eighteenth annual conference of Indian Nuclear Society held at Nuclear Fuel Complex Hyderabad during November 21-24, 2007.
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Certificate and cash award was given during inaugural session of CHEMCON-2011 held at MS Ramaiah Institute of Technology Bangalore

Citations received for the research work

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- The following citing publication has been published:

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- How Amidoximate Binds the Uranyl Cation Sinisa Vukovic, Lori A. Watson, Sung Ok Kang, Radu Custelcean, and Benjamin P. Hay Inorganic Chemistry 51:3855-3859 (2012) http://pubs.acs.org/doi/abs/10.1021/ic300062s

- The following citing publication has been published:
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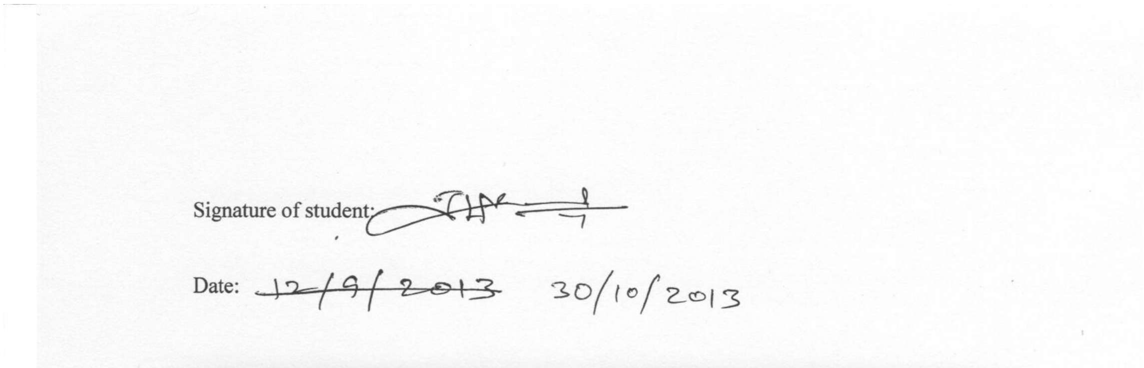
- Adsorption of the uranyl ions on an amidoxime-based polyethylene nonwoven fabric prepared by pre-irradiation induced emulsion graft polymerization Xiyan Liu, Hanzhou Liu, Hongjuan Ma, Changqing Cao, Ming Yu, Ziqiang Wang, Bo Deng, Min Wang, and Jingye Li Industrial & Engineering Chemistry Research 0 http://pubs.acs.org/doi/abs/10.1021/ie301965g



Signature of student:

Date: ~~12/9/2013~~ 30/10/2013

S.no.	Name	Designation	Signature	Date
1.	Prof. S. Banerjee	Chairman		
2.	Prof. P.K. Tewari	Convenor/Guide		
3.	Prof. G.K. Dey	Member		
4.	Prof. S.B. Roy	Member		
5.	Prof. N.K. Maheswari	Member		

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List of symbols and nomenclature

W_i	Weights of the substrate polymer sample before grafting.
W_g	Weights of the substrate polymer sample after grafting.
kGy	Kilo gray
Rad	Radiation absorbed dose
$[M]$	monomer concentration
R_g	Rate of radiation grafting
K_I	Langmuir Isotherm constant
c_e	Equillibrium concentration
q_e	Equillibrium adsorption capacity
q_m	Maximum adsorption capacity
n	Intensity of adsorption
K_f	Freundlich Isotherm constant
(q_e)	Concentration at equillibrium
q_t	Concentration at any time t
k	Second order Lagergren rate constant
k_{ad}	First order Lagergren rate constant

M	Molar concentration
ppb	Parts per billion
ppm	Parts per million
A-S-E	Alkalination – Submergence – Elution
PAO	Polyacrylo amidoxime
k	boltzmann constant
ΔS	Entropy
Ŋ	Avogadro constant
C	concentration factor
Q	Energy to extract to mole of uranium
NPP	Nuclear Power Plants
CJ	Cirus Jetty
A&N	Andoman & Nicobar islands
SWRO	Sea Water Reverse Osmosis

Chapter-1

Introduction

Oceans are potential secondary sources for uranium and other valuable heavy metals, as it contains around eighty elements of periodic table. Some of the elements are either very scarce on land or very expensive. Uranium is also one among them. With its lean but clean resource, oceans can serve as constant potential source of uranium and other valuable heavy metals for a long run. India with a large coast-line and favorable tropical climate for most part of the year has a large stake in exploiting the valuable elements locked in seawater. Around 5000 tonnes of uranium is being added to the sea every year naturally. The scientific and technological challenges in extracting uranium from seawater are lying in finding a process technology and recovery system design that gives a net positive energy balance in terms of usable energy produced from the recovered uranium and the cost of its production. This was identified as one of the thrust areas of research for harvesting uranium from alternative secondary resources, during DAE Collective Vision held in 2004. The co-operative R&D efforts on fundamental research and engineering studies are the solution to sustainable and economical recovery of uranium from seawater.

1.1 Motivation for the area of research:

In the last century uranium has been universally gained acceptance as primary energy source. Currently it caters to approximately 17% of the electricity generation globally. Uranium has been projected as the main workhorse of future when the fossil energy reserves dwindle by the middle of 21st century and hence it is going to be important member of the energy family. The terrestrial distribution of uranium ore occurrence is grossly uneven. With a large coastline, India, Japan, Korea and a few other nations have a larger stake in exploiting 4.5 billion tones of uranium locked in seawater [1]. Compared to terrestrial mineralisations, seawater is practically an inexhaustible resource for uranium [2, 3]. Uranium in seawater mainly exists as tricarbonyl complex of uranyl and tricarbonate as tetravalent anionic form. The structure of uranyl complex is as shown in Fig. 1.

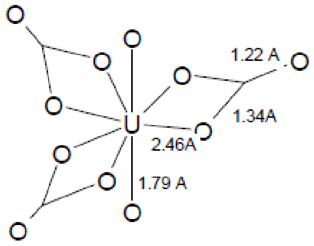


Fig. 1 Structure of uranyl complex in seawater conditions

Seawater contains both cationic and anionic metal ions in different proportions. The typical composition of metals and other ions are as shown in Table 1 below:

Table 1 Metal ion composition of Seawater

	Cations (ppm)		**Anions (ppm)**	
Major Components	Na^+	10,500	Cl^-	19000
	Mg^{2+}	1350	SO_4^{2-}	2650
	Ca^{2+}	400	HCO_3^-	140
	K^+	380	Br^-	65
	Sr^{2+}	133	F^-	1.3
			H_3BO_3	260
	Li^+	0.17	I^-	0.06
	Rb^+	0.12	MoO_4^{2-} (as Mo)	0.01
	Cs^+	0.0005		
Minor Components	Ba^{2+}	0.03	$VO_2(OH)_3^{2-}$ (as V)	0.002
	Zn^{2+}	0.01	PO_4^{3-}	0.07
	Fe^{3+}	0.01		
	Cu^{2+}	0.003		
	Mn^{2+}	0.002		
	In^{3+}	0.02		
	Ge^{4+}	0.00007		
	U^{6+}	as	$UO_2(CO_3)_3^{4-}$	0.00334

The proposed research work was undertaken to employ the radiation grafting aspects for polymeric adsorbent synthesis and analyse the same for study of recovery of heavy metals such as uranium from seawater

1.2 Objective of the thesis:

This research work deals with the issues and the novel processes/sorbents being developed for the recovery of heavy metals from seawater by harnessing the **Tidal Wave Power** using electron beam grafted amidoxime as a super specialty adsorbent by post irradiation grafting technique [4, 5 and 6]. The parametric sensitivity analysis has been done to see the effect of variable parameters on key performance indicators. The Table-2 shows the comparison of salient features of adsorbent systems being used/suggested by various research groups.

Table 2 Adsorbent types and process systems used by various researchers since 1980

Sl.no	**Researcher**	**Shape of sorbent**	**Mode of adsorbent bed**	**Mode of seawater transport**
1	Best, 1980	bead	fixed	Pump
2	Driscoll, 1983	cloth	fixed	Pump
3	Kanno, 1983	bead	fluidised	Pump
4	Koske et al, 1983	bead	loop	Pump
5	Bitte et al, 1983	bead	fluidised	Current
6	Forberg et al 1983	bead	fixed	Wave
7	Suzuki et al, 1985	bead	fluidised	Pump
8	Chihara et al 1987	bead	fluidised	Current
9	Suzuki et al 1987	bead	fluidised	Wave
6	Okazaki et al, 1988	bead	fixed	Current
7	Hirai et al 1988	bead	fixed	Current
8	Nobukawa et al 1989	fiber	fixed	Current
11	Nakamura 1989	bead	loop	Current
14	Toshiya Takeda et al 1991	fiber	fixed	pump
15	Present study 2012	fiber	Leaflet, floating with Seawater	Tidal wave (for seawater) ; Gravity flow (for brine)

The engineering flow sheet is being developed for a scale up facility with an output of about 100 g/yr uranium based on present research work and other parametric studies. As a part of research work, development studies at lab scale and other engineering scale studies have been carried out using radiation grafted adsorbents and optimized the equipment, material and other operating parameters. Lab scale and as well as in-field trials have been carried out at multiple locations and data obtained was correlated and analysed w.r.t various factors such as uranium pick up rate, dirt fouling, bio fouling, submergence durations, temperature, concentration, advection of water body, tidal movements etc. The overall process flow sheet for <u>recovery part</u> contains mainly three steps i.e Adsorbent synthesis; Submergence into sea; Elution of valuables from adsorbent. The optimisation of A-S-E (Alkalination – Submergence – Elution) cycle of process flow sheet is very important. The standardization of the process for the scale up designs required for future commercial plants is a critical aspect needing deeper understanding of the parameters involved and has been addressed as part of the research work. It is planned to simulate a model of the process parameters using the data collected through especially designed experiments as future work. The major benefit of this work is improved process technology to augment the Uranium supplies through viable and sustainable secondary sources such as seawater. The proposed work also gives energy credits to nuclear desalination and nuclear power plants by recovering uranium present in brine/seawater reject streams. The Technology development work will generate experience for handling and automation of the various systems associated with the uranium recovery plant and data for fine-tuning the process design. It will further provide a field investigation pilot plant support to the R&D programme for harnessing oceans for uranium and other scarce materials like Vanadium, Rubidium, and Cesium etc.

1.3 Outline of the thesis:

The thesis is structured in eight chapters. **Chapter-1** provides an overview of the "Recovery of heavy metals from Seawater/Brine" and Development & application of radiation grafted sorbents for the same. The motivation and objectives of area of research are detailed in this chapter. **Chapter-2** reviews the literature of various sorbents and techniques for heavy metal separation in general and the current status of processes and

Technology in various Labs/countries especially w.r.t radiation grafting aspects. **Chapter-3** describes the possible various Recovery Processes with their limitations and emphasis the need for development of radiation grafted sorbents. **Chapter-4** describes the basic process mechanism for sorbent synthesis and thermodynamic aspects of metal pick up from seawater. Radiation processing by electron beam technology is discussed in **Chapter-5**. Quality assurance for solid and liquid samples is an important aspect of analysis and hence modern analytical techniques adopted are described in **Chapter-6** briefly, especially highlighting the Nuclear Analytical techniques for uranium analysis. **Chapter-7** gives description of the experiments and in-field trials carried out. The effect of various parameters w.r.t sorbent synthesis and their metal pick up characteristics are described. Finally the conclusions are summarized and future work recommended in **Chapter-8**.

Chapter-2

Literature Survey and State of Processes and Technology in Uranium Extraction from Seawater

Over the past four decades, theory and application of adsorbents and Ion exchange have greatly advanced and touched almost every industrial sector. Nevertheless, new ground still is broken in this field, in terms of both synthesis of novel materials and application opportunities in new areas. Selective separation of valuable metals from lean sources such as seawater and their possible recovery is an area of considerable interest. Novel techniques/materials being targets of researchers are Bifunctional ion selective polymer supported reagents (IPNs), Biosorbents, Functionalised organo-ceramic adsorbents, Polymeric ligand exchangers, Molecular imprinting techniques (MIPs), Solvent Impregnated Resins (SIRs) and Grafted adsorbents. Literature survey given in this chapter encompasses the state of the art development in this area.

A significant attempt to develop a sorbent for uranium recovery from seawater was reported by Davies et.al [1, 7]. They evaluated several organic and inorganic sorbents and identified that hydrous titanium (IV) oxide is a promising sorbent for uranium heavy metal. Cortina and et al [8] developed Solvent Impregnated Resins (SIR) based on DEHPA and TOPO with macroporus support of Amberlite XAD-2 for better separation of Zn(II)/Cu(II) and Zn(II)/Cd(II) mixtures. Alexandratos and et al [9] developed new SIR by thin membrane coating of phosphonate groups around each bead of polyvinyl benzyl chloride. Membrane coating is anchored to the surface of beads from a 2% aqueous solution of glycidyl methacrylate/bis (acrylamide) in a 75/25 weight ratio. It is found to complex 96% of Cu (II) present. Bonnesen et al [10] prepared quarternary ammonium ligands with low charge to volume ratio by increasing the size of groups on nitrogen. Trihexylamine was immobalised on poly vinyl benzyl chloride beads to give trihexylamine ion ligand, which has a single positive charge associated with very large ligand. Contact studies showed that this resin was selective for TcO-4 (pertechnetate ion). Alexandratos et al [11] developed Interpenetrating Polymer Networks (IPN) as they offer a novel means of preparing bifunctional polymers and probing supported ligand synergistic interactions. Used N-vinylimidazole (VI) and ethyl acrylate (EA) to polymerise within initial network of cross linked polystyrene for studying IPNs where microenvironment of ligand L1 was varied by introducing differing amounts of non binding group B1 within an initial A1 network. Five IPNs with various VI/EA ratios

(100:0; 77:23; 53:47; 27:73; and 0:100) were studied. Polymeric functionality may also be incorporated in membrane morphology by polymer blending. Park et al [12] have prepared a chelating membrane composed of polyvinyl alcohol and poly (N-salicylidene allyl amine) for Co (II) sorption. Cobalt complexed in the membrane to an extent as high as 15% by weight and membrane was found to become too brittle beyond this limit. Aldor et al [13] proposed bio-sorption for removal of toxic heavy metal contaminants from industrial waste water. They combined with metal recovery by a desorption process. Byerkey et al [14] demonstrated a good uranium pick up performance using fresh water algae chlorella regularis and vulggaris. Kabay et al [15] have synthesized cross linked poly(acrylonitrile-co-divinylbenzene) beads (RN-5) by suspension polymerization with 3% hydroxylamine in methane and used in batch wise adsorption of uranyl ions and reported 50% loading after 30 minutes. Highly porous structure was introduced into the cross linked polymer beads using dichloroethane and chloroform as a porogen. They have reported effect of alkaline treatment on chelating resins and significant increase of sorption capacities at elevated temperatures. Anyun Zhang et al [16] studied the adsorption properties of fibrous and polymeric adsorbents provided by Takasaki Research Establishment, Japan Atomic Research Institute using token sizes of 3x4 mm and urnayl solution of 128 ppm and pH of 6. They have used ICP-AES (Atomic Emission spectrometer) for measurement of U^{6+} in solutions. They have reported activation energy of the uranium adsorption reaction as 28.54 kJ/mole. Akira Goto et al [17] used commercial polyacrylonitrile bicomponent fiber of 6 denier for preparing amidoxime fibrous adsorbent and for uranium desorption studies. Reported 10 mg of uranium loaded onto 1 gm of dry fiber using 10 ppm seawater solutions using various eluents. Goto Akira and et al of Kyushu Univ, Fukuoka, Japan studied desorption of uranium from amidoxime fiber adsorbent. An amidoxime fibrous adsorbent is contacted with uranium enriched seawater (10 ppm); about 10 mg of uranium is loaded per 1 g dry fiber. Then the rate and yield of uranium desorption from the fiber are determined with various eluents. Acid solutions are superior to alkali carbonate solutions as eluents. With a 0.1 $mol{\cdot}L^{-1}$ HCl solution, desorption is completed in 2 hours regardless of the presence of uranium in the leaching solution up to 15 ppm ($\approx 6 \times 10^{-5} mol{\cdot}L^{-1}$). Serial operation of the adsorption-desorption cycle four times does not affect desorption efficiency, but the addition of heavy metal ions to the eluent at a level of 1.8 × 10^{-3}mol·L^{-1} significantly decreases desorption efficiency.

Graft polymerization has been successfully achieved with hollow fibers, as it provides highest surface area to volume ratio in a packaged module. Irradiation produces higher concentration of radicals near the pore mouth and not all of the internal surface area is utilized. Kim et al [18] used mixed non woven fabric of poly ethylene and polypropylene and grafted glycidyl methacrylate groups by radiation induced grafting. Subsequent sulfonation of the material created a fairly open structure with sulfonic acid functionality. Konishi et al [19] have used polyethylene hollow fibers and functionalized by radiation grafting using chelating agent IDA (Imino diacetic acid). Tsuneda et al [20] used graft polymerization of glycidyl methacrylate with ethylene diamine to impart chelation groups to the membrane. Someada [21] used Dowex-1x8 and carbonized apricot stone to study the sorption of uranium U^{vi} from seawater in the presence of 0.002% of arsenazo^{III} and 10^{-3} M EDTA. It is found that uranium is completely sorbed by the two sorbents from seawater samples collected from coast of Mediterranean sea and the red sea. Tomomi Kawai et al [22] co grafted the methacrylic acid and 2-hydroxyethyl methacrylate with acrylonitrile onto polyethylene fiber by radiation induced graft polymerization in various ratios for cooperative study of amidoxime adsorbents. Reported uranium adsorption rate of 0.9 g/kg of MAA-cografted AO fiber, for 20 days of contact time at the ocean site. Del-aal et al [23] have used the wood pulp and radiation modified starch in waste water treatment for heavy metal removal. They have reported starch derivatives (polyelectrolyte) containing amide groups as favorable sorbents. The starch possesses unique molecular structure as it has linear as well as branched units and most abundant biopolymer after cellulose and chitosan.

This chapter also documents the status of this research area in various laboratories and other developments in radiation processing. Japan and UK had initiated research study on the topic a few decades back using inorganic adsorbents. The effort was not met with success due to high attrition rates and less pick up rates. Then studies have been done using organic adsorbents. Again Japan is taking lead in analysing various aspects of the process using organic adsorbents. And with the advent of radiation processing techniques, it is possible to synthesize tailor made organic adsorbents by grafting radicals in different configurations. Availability of open literature is less in this area. We are the first group in Department of Atomic Energy (DAE) to demonstrate the process successfully through our actual field trial experiments, along with laboratory studies. **Apart from India, other countries interested in this technology development and year wise progress are as follows:**

First studies on Uranium extraction from seawater started as early as 1953 by Atomic Energy Research Establishment in Harwell, U.K [24] using hydrated titanium dioxide. Vermon F et al of University of Salford UK have reported conceptual design of a plant of 10 kg capacity with 1500 tonnes throughput sea water/hr with an objective to design a 1000 tonnes/year plant. The adsorbent material being suggested that time was hydrated TiO_2 granules and poly hydroxamic acid (PHA) chelating resin.

Extensive efforts have been made by Japan since 1960. Mr. Takanobu Sugo, head of Radiation Processing development laboratory, Dept of Material development of Japan Atomic Energy Research Institute (JAERI) has conducted adsorption tests several times by mooring 12 kg of material in sea and recovered 16 g of Uranium [25] in the year 2000. S. Nakamura et al of Nagaoka university of Technology, Nagaoka, Japan in the year 1996 have carried out recovery of uranium from seawater by ‘Circulating Fluidised Bed Adsorber (CFBA)’ consisting of granular amidoxime resin (AOR) and hydrous titanium oxide granulated with poly acrylonitrile (PAN-HTO) [26]. The experiment had shown a net negative energy balance. Japan has recently taken a patent on the PAO based recovery of uranium from seawater process, which was sealed on 14th December2001. The PAO adsorbent is co grafted on a polyolefin material. The submergence is done in the ‘black current (Kurohito ocean current’) passing close to the shores of the Islands of Japan. They have put up a 330 gms per 3 years of valuable elements extraction plant in 2003. <u>They appear to be close to putting up a commercial plant very soon.</u>

In 1970 at ORNL, studies were done using 10" diameter titanium oxide absorber using tidal flow. They had reported an absorption rate of 240 mg of U/kg of Ti. Cost analysis for a 500 Te/year plant showed a figure of \$300/lb of U. USA has taken fresh initiative in 2002 and proposals are incorporated in the Generation IV Roadmap [27]

Richard from European Atomic Energy Committee reported [27, 28] using a thin flexible permeable sheet type adsorption bed of Ti $(OH)_4$ for recovery of uranium from seawater. The bed is held in position parallel to the sea surface by a central cable, the upper end of which is fixed to a buoy and lower end to an anchor. The bed is lowered by gravity down the cable and upon reaching the deepest point; the bed is folded and pulled up. The lowering – rising cycle is repeated till the bed becomes saturated. Thus in this theoretical study 30 kg of uranium in the form uranyl carbonate was postulated to be recovered from 10,000 m^2 of adsorbent surface area and multiple lowering and raising to a depth of 1000 meters. Koske Peter and Ohlrogge. K had reported about a floating adsorbent based on hydrated TiO_2 for the recovery of uranium. The floating adsorbent were mounted on pontoons and towed by a parent ship to the ocean. The energy balance was found negative taking into account the fuel oil required for ship propulsion.

A project report to recover 100 tonnes of U per year by pumping seawater at $11.5x10^6$ m^3/hr through 200 adsorbent beds each having 320m^2 adsorption surface area was also prepared but it was concluded to be technically not feasible due to negative energy balance.

Investigations have been carried out by FRG using HTO as main adsorber [28]. Due to its insufficient mechanical stability, more attention has been given to polyacrylamidoxime (PAO) adsorbent for last one decade. Elution optimization has been carried out by them using aqueous solutions of sodium bicarbonate and sodium carbonate, which are recycled and provides favorable environmental conditions. Elute concentration being tried using both evaporative concentration and as well as ion exhange. R&D activities in the country, concentrates on floating production plants operating in the open seas.

Investigations have also been carried out in France, Italy, Russia, and Finland and more recently in Korea and Sweden. In Sweden, the feasibility of a floating unit using wave energy is being studied under the sponsorship of National Swedish Board of Technical Development [24, 27, and 29].

Choi, S., H., and et al [30] of Kyungpook National University, Daegu 702-701, South Korea studied the adsorption of uranium ions by resins with amidoxime and amidoxime/carboxyl group prepared by radiation induced polymerization. In order to recover uranium ions from seawater, chelate-type resins with amidoxime and amidoxime/carboxylic acid groups were prepared by radiation-induced polymerization of acrylonitrile (AN) and AN/acrylic acid and by subsequent amidoximation of cyano group of poly(AN), respectively. The adsorption rate of uranium ion by resins with the amidoxime/carboxylic acid group was higher than that of resins with the amidoxime group. The adsorption of uranium ions in artificial seawater to chelate-type resins was also examined.

Toshiya Takeda and et al [31] used poly ethylene hollow fiber packed bed of 0.9 m high for placing in the coast of Pacific Ocean for recovery of uranium from seawater. Continuous flow of seawater at a superficial velocity of 4 cm/sec has given uranium content of 0.97 g of U/kg in the amidoxime hollow fiber. For elution, 1N HCl at flow of 0.0125 cm/sec is used. They have reported the requirement of cross section area of 9.4 sq.m and with 0.9 m height packed bed to produce 10 kg of uranium per annum.

Omichi and et al [32] made amidoxime group containing sorbent using tetrafluoroethylene-ethylene copolymer as substrate. Conditioning of sorbent was done using 2.5% KOH solution before use in column mode. Reported increase in uranium adsorption with flow rate from 0.3 to 1.5 kL/day. Results have shown possibility of evaluation of sorbent at any amount of seawater and adsorbent. Liquid solid ratio has an effect on sorption rate.

Seong-Ho Choi and et al [33] studied graft copolymerisation of various monomer mixtures onto pre irradiated poly ethylene film. The effect of solvents, additives and monomer composition on the grafting yield was investigated. The irradiation was done using gamma ray source and degree of grafting was reported upto 40% only. Beneficial effects of sulphuric acid as additive upto 0.2M in grafting mixture are reported.

Bhuvanesh Gupta and et al [34] have studied graft polymerization of acrylonitrile onto polypropylene monofilament using pre irradiation method using cobalt source. Reported profound influence of the nature of medium of the grafting and the additives over the grafting reaction. Beneficial effect of methylethyl ketone over Dimethylformamide as grafting media is reported. Advantage of partial replacement of DMF with water is reported. Grafting yields of up to 10 to 15% is reported for various conditions.

Chapter-3

Various Recovery Processes for Uranium and other valuables

Out of the 4.58 billion tonnes of uranium present in the upper 100 m or the well-mixed surface layer of the oceans, nearly 2 x 10^9 tonnes should be considered accessible for recovery. Freshwater rivers in the world contribute about 9000 tons per year of uranium to the sea. This uranium if trapped from the feed seawater for the nuclear desalination plant or from the rejected brine, may contribute to the fuel of the nuclear reactor and thus the energy required for desalination processes may be partly met from the uranium recovered from the desalination process. Therefore, it is worthwhile to tap this resource of uranium. There have been several methods of uranium extraction explored during the past four decades [35, 36]. These include, in particular, ion-exchange, solvent extraction, foam separation, co-precipitation, biological separation and adsorption.

3.1. Ion-exchange

This is one of the earliest methods investigated and also highlighted the research work in this area in literature survey of this thesis. However, ordinary ion-exchange resins cannot be used in the extraction of uranium from seawater because of low selectivity. Resins having complexing reagents such as 8-hydroxyquinoline or resorcinol arsenic acid formaldehyde show a very good uptake of uranium. Nonetheless, practical application of these materials is hampered by their fairly rapid deterioration with aging.

3.2. Solvent Extraction

Solvent extraction is widely used in the extraction of metals using specific, chelating, solvating or liquid ion-exchange reagents. Many researchers used organo-phosphoric agents in kerosene, 8-hydroxyquinoline in chloroform or using diethyl ether to extract uranium from seawater. There are several other report of extraction of many of the metals from natural waters using solvent extraction, e.g., using diethyldithiocarbamate and their extraction into acetone-chloroform mixture followed by preconcentration by anion exchange column Dowex1-X8 (chloride form) using sorption solution of tetrahydrofuran, methyl glycol and 6M hydrochloric acid, or by using 8- hydroxyquinoline-chloroform mixture or using di-(2-ethylhexyl)-phosphoric acid in carbon tetrachloride. The major problem with solvent extraction of metals from seawater on large scale is either that it involves complicated procedure, large amount of chemical and volatile solvent requirement or the solvent loss by entrainment and solubility.

3.3. Foam Separation

Surface-active agents can be used in collecting metal ions by foam separation. Lauryl amine (CH_3 $(CH_2)_{11}NH_2$) and alkybenzyl ammonium chloride (CH_3 $(CH_2)_{13}NH_2$ $(CH_2C_6H_5)Cl$), for instance, effect separation of uranium from seawater. A good example of this technique is using the collector surfactant - air system at pH 6.7. The uranium is adsorbed effectively on a positively charged ferric hydroxide collector. Upon addition of anionic surfactant, sodium dodecyl sulfate, and the bubbling of air though the seawater, the colloidal particulates of ferric hydroxide enriched with uranium by adsorption are floated within 2-3 minutes to the surface as a stable froth which is easily removed. The average recovery of uranium by this method is around 82%. However, it is difficult to recover the surface-active agents after use.

3.4. Co-precipitation

Coagulation and co-precipitation methods are reported in the literature by using precipitation agents, $Fe(OH)_3$, $Al(OH)_3$, $Ti(OH)_4$ and $Ca_3(PO4)_2$. However, the long precipitation time that is required makes the process impractical with large volumes of seawater.

3.5. Biological Separation

Living cells have been known to concentrate cations from their aqueous environment. Microbial biomass has been documented to exhibit a selective retention of heavy metal ions. Polikarpov in 1966 pointed out that radio-nuclides present in an aquatic (sea) environment are accumulated by marine micro-organisms through direct adsorption from the water. He indicated that the above property is independent of the life functions of the microbial cells since dead cells exhibited this property as well as or better than live ones, supporting the hypothesis of physical-chemical uranium ions retention mechanism by the microbial cells. The phenomenon of retention of cations from solution by dead microbial cells has been termed “biosorption” . Since it is the chemical composition of the cell wall and other surface materials which are responsible for cation sequestration, cell viability or other metabolic activities that do not interfere with such characteristics, effectively have no impact on biosorption , e.g., cell walls of procaryotes and eucaryotes contain polysaccharides as basic building blocks. The ion exchange properties of natural polysaccharides have been studied in detail and it is a well-established fact that bivalent metal ions exchange with counter ions of the polysaccharides as shown in the following example involving alginic acid,

$2NaAlg^{+} Mz^{+} \leftrightarrow M(Alg)_2 + 2Na^{+}$

Several types of biomasses have been reported to be used for uranium adsorption, e.g., algae, fungi, bacteria and actinomycetes etc. They are found to be active between pH 2.0 to 5.0. Lyophilized biomass shows higher uranium sorption. The maximum loading obtained in the case of *Pseudomonas sp* is 24.5% g (245 mg-U/g dry biomass) dry wt of the biomass at pH 3.5 and for *Talaromyces mersonii* CBS 814.70 it is 323 mg-U/g dry biomass. The adsorption process follows Langmuir adsorption and the equilibrium reaches in 2 min.

3.6. Adsorption

The concentration of uranium in seawater is at least three orders of magnitude more dilute than that in any commercial process for the economic recovery of the metal. This places stringent requirements on the properties of the adsorbent selected for uranium recovery from seawater. There are many adsorbents explored for the extraction of uranium. These are examined in the light of the above mentioned points.

3.6.1. Titanium Oxide (TiO2)

Hydrous titanium oxide is one of the earliest adsorbent explored for uranium extraction from seawater. Various kinds of preparations of hydrous titanium oxide have been reported, they can be roughly classified into three types.

i) Neutralization method: a titanium solution is neutralized by alkali

ii) Urea method: Urea is added to a titanium solution and then heated

iii) Thermal decomposition method: a titanium solution is heated and hydrolyzed.

For the urea method in which titanium sulfate is reacted with urea, the maximum uptake capacity of 660 μg of U/g dry adsorber at 25°C has been reported for fine powdered material. Three mechanisms are reported in the literature for the adsorption of $UO_2(CO_3)^{4-}$ by titanium oxide. According to the first mechanism, the uranyl moiety is retained on titanium oxide surrounded by two $CO_3^{\ 2-}$ and two TiO ligands.

According to the third mechanism the uranyl ion does not adsorb on the titanium hydroxide particle like an ion-exchange process, but rather it is more likely that the uranyl ion forms an insoluble compound with dissolved titanium hydroxide which has solubility of 100 ppb, which then precipitates out on the titanium hydroxide particles. This is consistent with the fact that the uranium is found only on the outer surface of the titanium hydroxide particles. For the elution of the adsorbed uranium, acids such as hydrochloric acid and sulfuric acid and solutions of carbonates as ammonium carbonate, sodium carbonate and sodium bicarbonate can be used. However, it is reported that the solution of uranium on granulated hydrous titanium oxide adsorbents with relatively concentrated acid cause granule breakage due to gas evolution and dissolution of adsorbent. The rate of elution by acid (e.g., 0.2N HCl) is slower than that by using carbonate. With 1N ammonium carbonate it needs 48 hrs for eluting more than 90% of the adsorbed uranium at room temperature.

3.6.2 Activated Carbon

Activated carbon has been reported to be very effective in adsorbing uranium from seawater to the tune of 500 μg/g of carbon. However, the adsorption rate of a particular activated carbon can vary dramatically, depending upon the original carbon source material used: the pyrolysis method and the activation method. There are varieties of sources of carbonaceous materials which can be used for making of activated carbon, e.g., walnut shells, coconut shells, paper mill wastes, wood chips and bark or some variety of coals, etc. However, the amount of activated carbon requirement for uranium recovery from seawater is so large that the primary feed-stocks will have to be the more plentifully available coal. The advantage of activated carbon is in the elution process, where carbon will not dissolve in the more concentrated eluents. The second method of recovery would be to burn the carbon in a conventional coal fired turbine or gasify, leaving an ash which is highly concentrated uranium ore. This eliminates the requirement of the massive amount of eluents and its purification process as required by hydrous titanium oxide system. It is also reported that the adsorbed uranium, in a concentration of one pound per ton of activated carbon, will be capable of supplying approximately, 10 times more thermal energy (after isotope enrichment) for a nuclear power plant than would be available from the combustion of the activated carbon.

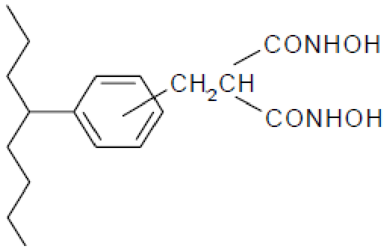
3.6.3 Galena, (PbS)

Galena is reported to be a better adsorbent compared to hydrous titanium oxide. The adsorption capacity of reagent grade galena is around 1100 µg/g PbS as compared to adsorption capacity of hydrated titanium oxide of 600 µg/g of TiO2. The adsorption performance of the galena is not affected by repeated use as it is regenerated by use of dilute hydrochloric acid. The palletized galena lumps have been studied for their adsorption behavior, they did not show degradation in performance till the particle size was about 0.4 mm, above which it decreased with increase of the average diameter of the galena particle. This indicates that the exterior of the galena particle is important for adsorption and the penetration depth is around 0.4 mm.

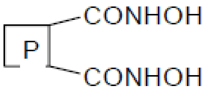
3.7. Use of polymers

3.7.1. Hydroxamic Acid Chelating Polymers

Micro and macroporous polymers having dihydroxamic acid groups as shown below are studied for uranium uptake. By the introduction of N, N-dimetholacrylamide into the dihydroxamic acid polymer, the rate of adsorption for uranium from sea water is reported to increase significantly. The separation of uranium after elution from transition metal ions is thus a possibility.



Polymer with Dihydroxamic Acid Groups



Polyhydroxamic Acid Groups Containing Polymer

3.7.2. Methacryloylamidoglutamic Acid polymer

The incorporation of amino acids and/or polyamino acid in to a polymer matrix has certain advantages since the amino acids are very reactive with different substances including metal ions and biomolecules. The higher flexibility and durability of these metal-chelating ligands as well as significantly lower material and manufacturing costs are also very promising for applications. Methacryloylamidoglutamic acid functionalized poly (2-hydroxyethyl methacrylate) beds have been studied for uranium recovery. The polymer has shown adsorption capacity of ~20000 µg/g of dry polymer at uranium concentration of 100 mg/l. The equilibrium is reached within 100 min at pH 7 and the elution of the uranyl ion takes 10 min with 98% recovery. The adsorption elution cycle does not show much degradation and the adsorption capacity is maintained at 96% level at the 50th cycle. However, this polymer has not been studied under seawater condition and in the presence of other competitive ions; it would thus be interesting to investigate the performance of this polymer under these conditions.

3.7.3. Amidoxime Containing Polymer

The high affinity of the uranyl-carbonate complex towards the polyamidoxime drew attention for the possible recovery of uranium from seawater in the 70's and has gained importance in recent years. Adsorbent containing amidoxime groups were initially prepared from commercial acrylic fibers by reacting with hydroxylamine in methanol. Later the amidoxime polymer was made in the form of hollow fibre form by radiation-induced graft polymerization of acrylonitrile onto a polyethylene/polypropylene hollow fibre, followed by chemical conversion of the produced cyano group to an amidoxime group. The procedure to be followed is the post irradiation grafting acrylonitrile onto polypropylene fiber in dimethyl formamide (DMF) solvent (AN-DMF; 70:30) at 60 °C (%grafting, 125%). Subsequently, this grafted co-polymer is reacted with hydroxyl amine hydrochloride to form (methanol: water; 1:1) at 60 °C for 8 hours to finally get amidoximated {$-C(NH_2)=NOH$) nitrile group. The amidoximation efficiency is ~75-80%. The uranium complexes with amidoxime in the manner shown in other section of this thesis. The chelating functional group can undergo isomerisation as shown below. Based on the isomeric changes the adsorption mechanisms are different acidic conditions resulting in forming different complexes. One of the acceptable reversible equilibrium is as follows. However, a non reversible equilibrium was found to exist in basic solutions when the adsorbent was treated with NaOH solution. The adsorbed uranium can be easily eluted by reducing the pH below 1 where the following reaction takes place and the resulting in the cation formation that does not bind uranium. It is reported that the structural changes in the amidoxime chelating functional group in aqueous solution are complicated. Since the variable structure of the amidoxime functional group at different acidities is not clear, it is difficult to arrive at the specific composition of the amidoxime-U (VI) complexes, although 1:2 complex is generally accepted by researchers 1:1, 1:3

and 1:4 complexes are also reported. This may be important when the seawater is treated with acid to get rid of carbonates in the desalination process, e.g., in reverse osmosis process, the structure of the complex at that acidity is important in order to obtain the maximum adsorption capacity of the adsorbent. The actual adsorption capacity could be far lower, e.g., for the formation of 1:2, 1:3 or 1:4 complexes it will be decided by the probability of finding 2, 3 or 4 amidoxime groups in a right stereochemistry in the vicinity of the uranyl ion and this probability may decrease rapidly with increase in ligand number of the complex. The stereochemistry of the polymer chain in the highly saline condition is of great importance in deciding the capacity of the adsorbent. The second reason for lower uranium capacity could be the simultaneous selectivity of the adsorbent to barium as well as vanadium. A typical adsorption capacity of the polymer in the actual field condition is around 2-3 g/kg (3000 μg/g) of adsorbent. This is far better than the other adsorbents. The adsorption time to collect the 3 g U/kg-A is about 30 days, using a braid type adsorbent. The uranium collected using polyhydroximic acid in India using sheet type adsorbents over a period of 15 days was reported to be 0.61 g-U/kg-A. There are recent reports from Japan of considering adsorption capacity to about 2 g-U/kg-A for 60 days of marooning time.

Chapter-4

Basic process mechanism and thermodynamic aspects

4.1 Process Mechanism:

During seventies and eighties the initial investigations on the possibilities of recovery of uranium from seawater have been done using inorganic adsorbents [36, 37]. Promising Inorganic adsorbents that have attracted the attention of researchers on this topic in the past are given in the Table 3:

Table 3 Uranium loading - Inorganic adsorbents

	Inorganic adsorbents	***U-Loading*** µg/g
1	Hydrous zirconium oxide	13
2	Hydrous tin oxide	17
3	Silica Titania gel	27
4	Hydrous lanthanum oxide	38
5	Hydrous iron (III) oxide	60
6	Hydrous aluminum oxide	61
7	Hydrous titanium oxide (after > 60 days storage)	200
8	Zinc carbonate	540
9	Hydrous titanium oxide (freshly precipitated)	1550
10	Bentonite and titanic acid	--

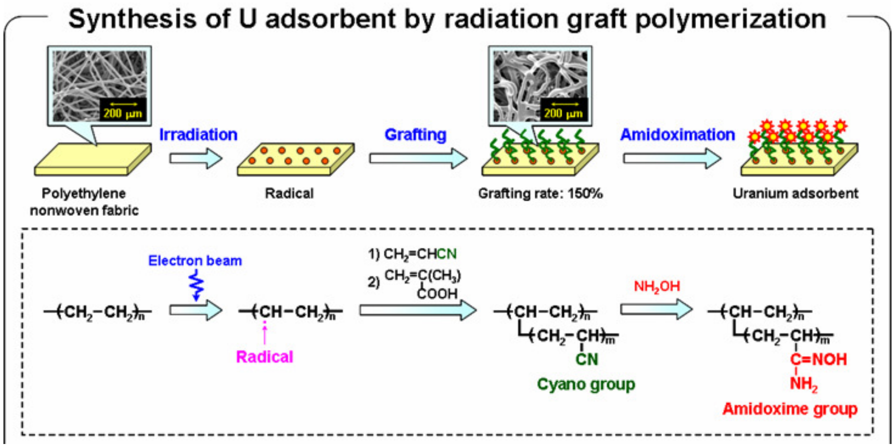
The above listed inorganic adsorbents suffer the limitations of adsorption rate and insufficient mechanical stability.

Extensive investigations are being carried out in currently on organic adsorbents in a more focused manner. Uranium loadings of various organic adsorbents of interest identified so far by various research groups around the world are listed in Table 4.

Table 4 Uranium loading - Organic adsorbents

	Organic adsorbents	***U-Loading*** µg/g
1	Polystyrene acetylene phosphoric acid	24
2	Formaldehyde copolymer	45
3	Poly glyco tri amino phenol	45
4	PTO	50
5	Macrocyclic hexacarboxylic acid	70
6	Hyphan on cellulose	80
7	Oxamidoxime terephtalic acid	240
8	Macrocycloimide resin	930
9	Resorcinol arsenic acid	1112
10	Poly Acrylamid Oxime (PAO)	3600
11	Calixarenes	2000-123,000
12	Bioactive mass	--

The Polyacrylo Amid Oxime (PAO) has been picked up as the best bet for our studies. This organic adsorbent preferentially extracts heavy metal ions by chelating process. A non-woven polypropylene fibre substrate is irradiated with electron beam to create grafting sites on the polymer chain as shown in Fig. 2. The substrate is then treated with acryl polymer to achieve grafting of the cyano group on those sites. In the next step the cyano group of the acryl polymer is reacted with hydroxylamine to convert them into amidoxime groups.



Three standard methods of grafting developed were Mutual grafting (simultaneous) method; Pre irradiation (consecutive) method and Peroxide methods. We have used combination of these methods and developed post irradiation grafting technique to increase the radiation yields. Free radicals have been chosen almost exclusively as the reactive intermediates. Heterogeneous process consists of backbone polymer in solid form such as fiber and the grafting monomer in liquid form. Here the polymer is irradiated in the presence of air to produce mainly hydro peroxides. These polymer oxides, which are often quite stable, can be decomposed in contact with monomer to produce graft copolymers. The reaction can be written as

$$P_A \xrightarrow{O_2} P_AO_2^* \longrightarrow P_AOOH \xrightarrow{heat} P_AO^* + {}^*OH$$

$$P_AO^* + M_B \longrightarrow P_AOM_B^* \text{ (graft copolymer)}$$

$$^*OH + M_B \longrightarrow HOM_B^* \text{ (homo polymer)}$$

In this method, the necessity of inert gas blanket is not required. Here advantage of both trapped radicals and peroxides can be used to initiate the grafting. Solvents are used to increase the monomer diffusion and enhance the efficiency and uniformity of the grafting.

These amidoxime groups trap the loosely bonded uranyl ion from the uranyl tricarbonate present in the ionic form i.e. $UO_2 (CO_3)_3^{4-}$ in seawater. The adsorption mechanism [36] as per stoichiometric conditions is as given in the Fig. 3.

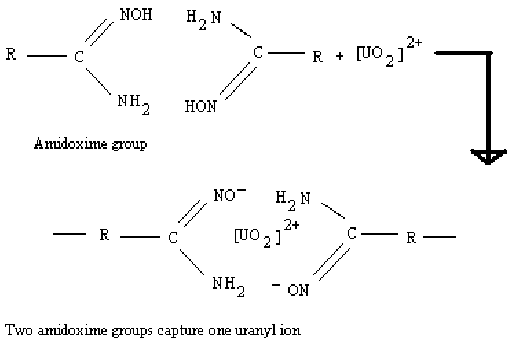


Fig. 3 Adsorption mechanism of uranyl metal ion

For every two molecules of polyacrylamidoxime (PAO) one uranium atom is captured. Thus theoretically PAO should have an extraction capability of 3.6 kg U/kg PAO.

4.2 Thermodynamic aspects of separation:

The minimal energy to extract one mole of Uranium from seawater can be calculated by assuming reversible process and variation of entropy created by the concentration process i.e. mixture entropy. Extraction occurs when interaction potential energy equal to the work done to bring to the sorbed state.

$S = k \log N$ where S – Entropy and k – boltzmann constant

$\Delta S = k\, Ŋ \log C$ where Ŋ – Avogadro constant and C – concentration factor

Energy to extract, $Q = T\, \Delta S$

$= T * (k\, Ŋ \log C)$

$= (298) * (1.38*10^{-23} *6*10^{23} * \ln (1/3*10^{-9})$

$= 48$ kJ/mole

Chapter-5

Radiation Processing by Electron beam Technology

In recent years, radiation processing has emerged as an alternative to conventional technologies such as thermal and chemical processing. The commercial applications of radiation processing by electron beam technology for almost five decades include: Food industry for pasteurization and shelf life extension of foods; Medical field for sterilization; Electrical industry for cross linking of cables; Effluent treatment for waste management; Rheology modification of plastics. The radiation processing source may be an electron beam (EB) accelerator, which is machine source of radiation or a radioactive source such as Cobalt-60. However, EB accelerators rather than radioactive source are generally used for commercial radiation modification of polymers since the dose rate is much higher and more efficient movement of the product in front of the radiation source is usually possible. Two electrically generated sources of radiation are accelerated electrons and photons from high intensity UV lamps. Accelerated electrons can penetrate matter and stopped only by mass and where as UV light can affect only the surface. The frequency and wave lengths of various electromagnetic radiations are as shown in table 5 below.

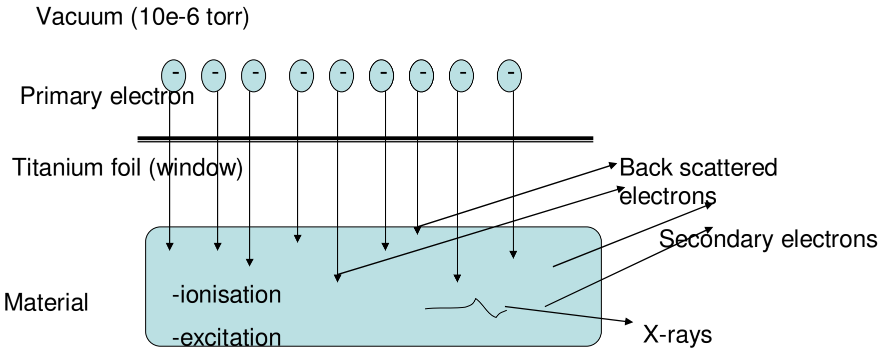
Table 5 Frequency and wavelengths of various electromagnetic radiations

Sl.no	**Radiation**	**Wave length (µm)**	**Frequency (Hz)**	**Remarks**
1	Infrared	$1\text{-}10^{2}$	$10^{15}\text{-}10^{12}$	
2	Ultraviolet	$10^{2}\text{-}1$	$10^{17}\text{-}10^{15}$	Surface effects; lower cost; radiant power ranges from 0.1 to 64 w/cm
3	Microwave	$10^{3}\text{-}10^{5}$	$10^{12}\text{-}10^{10}$	
4	Electron beam	$10^{-7}\text{-}10^{-4}$	$10^{21}\text{-}10^{18}$	Penetration effects; higher cost

In principle, fast electrons are generated at a high vacuum by a heated cathode. The electrons emitted from cathode are then accelerated in an electrostatic field applied between cathode and anode. The electrons leave vacuum chamber if their energy is high enough to penetrate 15-20 µm thick titanium window of accelerator. Number of electrons per second emitted from the cathode is called electron beam current and measured in mA

(1mA = 6.25x10 ^{15} electrons per sec). Product of acceleration voltage and electron beam current is Electron beam power and expressed as kW (1kW = 10 mAx100 kV). Electrons as charged particles transfer their energy to the material is shown in Fig. 4.

Fig 4 The process of generation of reactive species



When electrons of energies in the range of 5 to 10 eV penetrate solids and liquids, they generate ions, radicals and excited molecules. The ionization results from inelastic collisions between fast electrons and the medium and, in the process, the electrons lose energy. Depth of penetration of the electron and their energy are empirically related by $R_G = 4.57\ E_0^{\ 1.75}$ where R_G is Grun range in μm and E_0 is the electron energy in keV. Radiation processing of monomers and polymers by electron beam, such as polymerization, cross linking, grafting and degradation of polymers is induced by different chemically reactive species. Three primary events of the process of interaction of high energy electrons with organic matter are:

1. Ionisation: In this event the fast electron transfers its energy to the bonding electron in the absorbing material and the electron is knocked out. The ionized moleculte dissociates into a free radical and radical ion.

   $$AB \longrightarrow AB^{+} + e^{-}$$

   $$AB^{+} \longrightarrow A^{0} + B^{0+}$$

2. Excitation: Excitation moves an electron from the ground state to the excited state. The excited molecule eventually dissociates into free radicals

$$AB \longrightarrow AB^{*}$$

$$AB^{*} \longrightarrow A^{*} + B^{*}$$

3. Capture of electrons: This process is also ionization. Electrons with still lower energy can be captured by molecules. The resulting ion can dissociate into a free radical and a radical ion.

$$AB + e^{-} \longrightarrow AB^{-}$$

$$AB^{-} \longrightarrow A^{0} + B^{0}$$

The radiation processing by electron beam technology has been adopted in our work for developing polymeric adsorbents through the process of radiation grafting. The electron beam equipment and technology have been matured from a little known technology in the mid 1950's to a mature, reliable process system of choice for many processes today. The penetration and machine production capacity for a given application tends to be very industry specific. The segregation of electron beam equipment based on terminal energy and type of equipment are as shown in table 6.

Table 6 Segregation of electron beam equipments

Sl.no	Energy range	Technical features	Typical applications	Remarks
1	0.15 MeV to 0.3 MeV	Non scanned beams; Beam width of 1 to 3M; Beam currents of mA to 2A;	Curing of coatings on wood panels, floor coverings, magnetic media, printing inks;	Oil filled or gas filled power supplies
2	0.45 MeV to 0.75 MeV	Scanned beams; Beam widths 0.5 to 1.8M; Beam currents of 25 mA to 250 mA;	Curing of coating; cross linking of plastic sheeting and tubing; polymerization of liquid and semi liquid emulsions;	do
3	1 Mev to 4.4 MeV	Scanned beams; Beam widths of 0.5 to 1.8M; Units are characterized by beam power than beam current; Beam powers of 25 kW to 150 kW;	Cross linking of thicker cross sections; polymer rheology; sterilization of medical products	Gas filled power supplies

4	5 MeV to 10 MeV	Scanned beam linacs; Scan widths of 0.5 to 1.8M; Pulsed out put devices; Beam power from 25 kW to 350 kW;	High penetration range; Gem stone enhancement; Polymer rheology; Cross linking of thick sections; Shelf life extension of foods and fruits;	

The critical application information needed to develop process specifications for a new application are the process target speed, dose, depth of penetration into the product required; dose uniformity; The dose is given by the formula below:

$D = K \times (I/A) \times T$ where D is dose in kGy; K is empirically drived and units are kGy-kg/mA-min; I is current density in mA/kg; T is exposure time in min

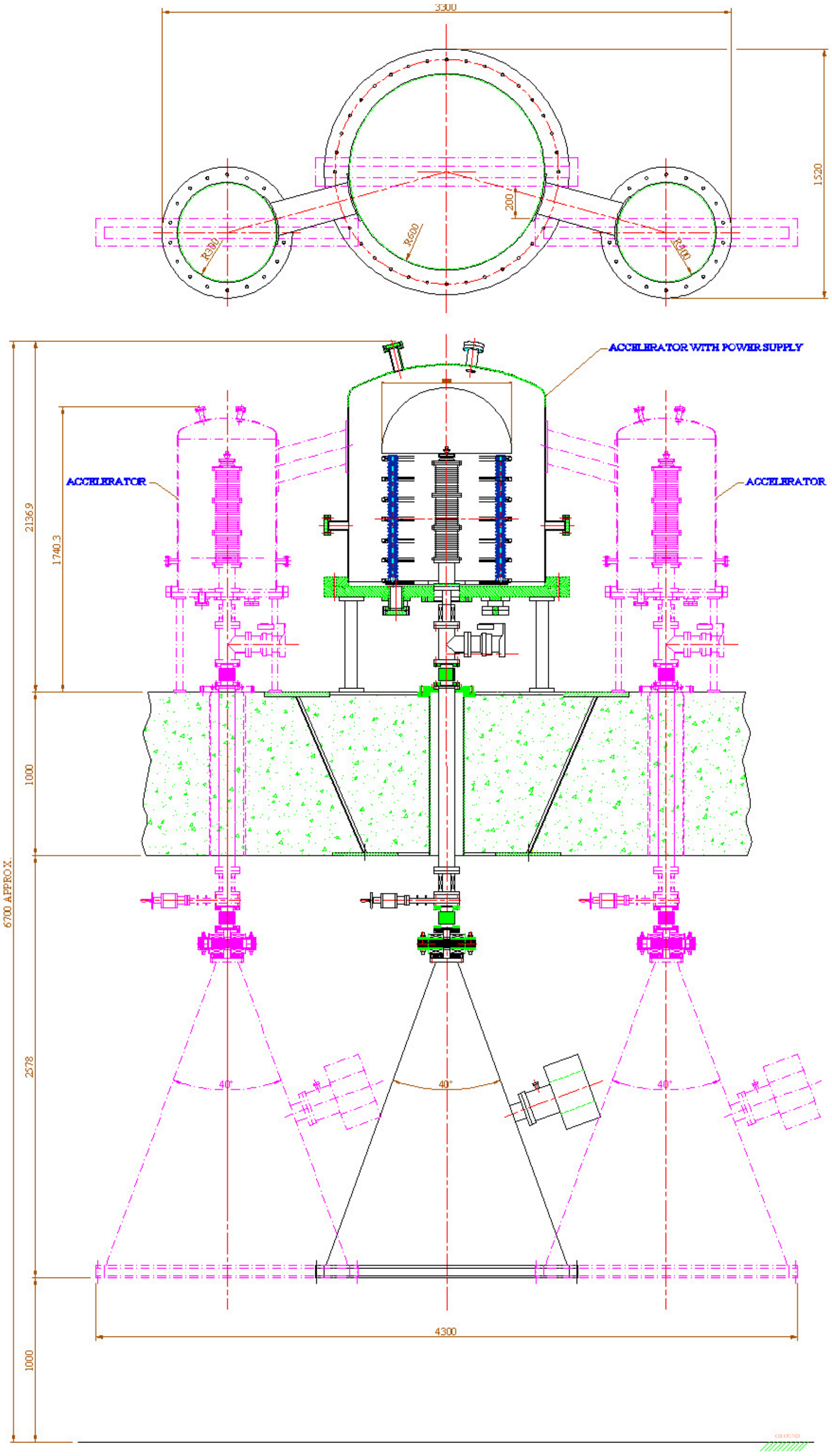
EB processing offers a number of important advantages over chemical processing, as follows:

1. Improved properties: EB processing can provide improvement and enhancement of the material properties, which may not be achievable by chemical processing. The processing can be used for wide range of polymers.
2. Processing advantages: Compared to the chemical processing that induces the same type of reaction, EB processing induces direct electron to electron interactions. In the cases of cross linking and curing, volatile chemicals can be avoided and there are no residues or by-products. There is no need for strict control of temperature and moisture and reactions can complete immediately after processing. The processing is higly controllable, reproducible and precise.
3. Economic advantages: EB processing require capital investment for the accelerator and it offers potentially lower processing costs as a result of higher efficiency and output.
4. Environmental advantages: Materials treated with radiation processing can contain lower or no volatile organic components. The process may require less or

no toxic additives and enhance the purity of the product. It can be carried out at lower temperature and pressure which saves energy.

The typical Specifications of the Accelerator system is shown in Fig. 5 and typical system details to irradiate PP sheets required for uranium recovery from sea water are as shown below:

1. Operating voltage range of the HV generator : 500 to 700kV.
2. Maximum current of the HV generator : 200 mA @ 500 kV
3. Maximum power of the HV generator : 100 kW
4. Number of beam lines for Accelerator : Three.
5. Energy rating of accelerator : 500 to 700 keV
6. Maximum beam current on each beam line : 65 mA
7. Beam scanning width : 1.5m.
8. Number of extraction windows : Three.
9. Three Scan horns will be properly positioned for the irradiation of 4m wide PP sheets.
10. Speed of the sheet on the conveyor under the beam : 10 m/min.
11. At this speed, 4m wide and four million metre long PP sheet can be irradiated with round the clock operation of the accelerator for 280 days in a year to give a dose of 200 kGy.



SCHEMATIC DIAGRAM OF ACCELERATOR SYSTEM
FOR PP SHEET IRRADIATION

D.C. ACCELERATOR LAB

Chapter-6

Modern Analytical Techniques adopted

6.1 Sorbent Characterisation Techniques : For characterization of substrate samples and grafted samples, various modern analytical techniques were adopted. The brief details and other salient features of the same are:

6.1.1 DSC and DTA – TGA Analysis :

All materials store energy in the form of thermal movement. This movement is different in different types of materials. The amount of stored energy changes whenever the state of the system is changed. Every change must be accompanied by an input or output energy – usually in the form of heat. The magnitude of heat capacity depends on the nature of molecular movement in the particular material. It is large when many modes of movement are activated and small when they are frozen. Thus heat capacity is small for glassy and crystalline polymers and large for visco-elastic materials. It changes more or less abruptly at the glass transition temperature. By flow of heat in or out of the system, other processes such as melting, crystallization, vaporization and chemical reactions such as polymerization and decomposition are also occur. So amount of heat entering the sample provides information on its properties. Thermo analytical techniques such as DSC and TGA are designed to measure this heat. A sample of known weight is sealed in a pan and heated at the rate of 10 ° C per minute. A temperature sensor is used for a feedback control of heater to achieve a strictly constant temperature increase rate of. The electrical current is measured precisely and it provides (after proper correction for the heating of pan and other parts of the instrument) a record of the heat capacity of sample as a function of temperature. A purge gas of nitrogen is applied to sample placed in DSC cell to perform the study in an inert atmosphere. Effect of oxidation may be studied by using an air or oxygen atmosphere. The technique of DSC used for samples is limited to temperature below 300 ºC. It is sensitive pieces of modern equipment having the capability to measure heat flows of the order of microwatts. Every physical change or chemical change is accompanied by change of enthalpy, which can be measured by DSC. DSC curves are used solely for “fingerprint” comparison with sets of reference curves generated for each change of parameters in grafting process. The area under the endotherm is related to the value of enthalpy change for the thermal events occurred.

Differential thermal analysis is an older and simpler version of DSC. In this technique, the sample and a reference material (alumina) are placed side by side within a metal block that is heated at uniform rate. Two thermocouples are placed within sample and reference and the difference between the signals is measured. Generally the sample with the larger heat capacity will lag behind in temperature. The difference will suddenly change whenever any transition takes place within sample (no transition occurs in reference). The information provided by DTA is qualitatively similar to that observed from DSC, but difficult to interpret quantitatively.

6.1.2 FTIR analysis :

Infrared spectra result from transition between quantized vibrational energy states. Molecular vibrations range from simple coupled motion of two atoms of a diatomic molecule to the much more complex motion of each atom in a large polyfunctional molecule. Every molecule has slightly different vibrational modes from all other molecules. Thus infrared spectrum of a given molecule is unique and can be used to identify that molecule. Beer's law is the fundamental law of quantitative spectroscopy. Fourier Transform Infra Red spectrometry led to considerable improvement in both quality and the interpretation of IR spectra. In infrared spectroscopy, the absorption of radiation is caused by molecular vibrations. Extensive study of model compounds has shown that a given chemical group (eg. $-CH_3, -OH, -NH_2, > C = O$) is characterized by an absorption band in some region of the spectrum that is typical for this particular group. The exact position of the band within its region provides information about the molecular vicinity of the vibrating group. A particular vibration is active in the infrared absorption only when it is accompanied by a change (vibration) in the dipole moment of the molecule. They must vibrate in the same direction as the electric vector of photon to be absorbed. The typical frequencies of characteristic groups of interest are as tabulated in Table 7.

Table 7 Typical frequencies of characteristic groups of interest

Characteristic group	**Frequency (1/cm)**		**Remarks**
	PAN	**AO-PAN**	
ν (NH2), ν (OH)	-	3100-3600	ν =Stretching vibration
ν (CH2)	2950	2950	
ν (C≡N)	2260	2260	
ν (C=O)	1750	1740	
ν (C=N)		1670	
λ (NH2)		1610	λ = Scissors vibration
λ (CH2)	1460	1460	
λ (CH)	1380	1380	
ν (C-O-C)	1250	1250	
ν (C-O)	1080	1080	
δ (C-N)		1000-1150	δ = Bending vibration
ν (N-O)		920-940	
ν (C-CN)	780	780	

6.2 Sample Analysis Techniques:

6.2.1 ICP-MS method of analysis:

Mass spectrometry is one of the most important analytical techniques used for determination of elemental concentration in trace and ultra trace range due to its

i. very high sensitivity
ii. low detection limits
iii. very small sample volumes (< 1 mmol)
iv. linearity
v. resolving power capable of distinguishing various isotopic form for molecules of molecular masses upto ~ 4000 Da

It is based on physical properties of atomic nucleus. The number of protons determines the chemical properties and the place in periodic table. The masses of neutron, proton and electron are 1.67E-27 kg; 1.67262E-27 kg and 9.10739E-31 kg respectively. Twenty elements are mono isotopic; 21 elements have two stable isotopes. Seven relatively light elements have three stable isotopes. The isotopic composition of elements is demonstrated in the mass spectrum, which is 2D representation of measured ion intensities in dependence of mass to charge ratio (m/z). The MS spectrum records the relative abundance of ions as function of m/z.

6.2.2 Anodic Splitting voltametry:

Estimation of uranium in the samples was also done using alpha spectrometry as follows. The sources were prepared by electrodeposition on a 2.5 cm dia stainless steel planchette in ammonium sulphate–sulphuric acid medium at pH 2.2, for 2h – 3h. A constant voltage of 6V was applied and the current flowing through the circuit was 300 mA. At the end of electro deposition, before switching off the current, few drops of ammonia were added to the plating solution, to neutralize the H^+ ions formed. The source planchette was washed with alcohol and heated directly on the flame till it is red hot. The sample source is measured using a Passivated Implanted Planar Silicon ((PIPS, Type IPC) detector. The active surface area of the detector is ~ 450 mm^2, depletion thickness 100 µm, efficiency of the system ~15% and resolution 40 keV at 5.15 MeV $^{239+240}$Pu alpha energy. The detector is coupled to a 4 K multi-channel pulse height analyzer (Model HPD, 4K MCA). The distance between the stainless-steel planchette and the detector surface was kept 5 mm. Each of these samples was counted for 24 h. A typical alpha spectrum of uranium isotopes in sea water is shown in this thesis report.

6.2.3 Solid State Nuclear fission track Detection analysis:

Here the uranium target with the track detector placed on it, is exposed to neutron flux. Polyester pieces of 2x2 cm^2 are used as nuclear track detectors for registration of fission fragment tracks. In SSNTD, fission track registration is found to be much more sensitive compared to alpha track registration due to low alpha specific activity of uranium and high thermal neutron fission cross section.

Solid State Nuclear Track detectors (SSNTDs) are insulating solids both naturally occurring and man-made. There are several types of these detectors including inorganic crystals, glasses and plastics. When a heavily ionising charged particle (alpha, fission fragment, etc) passes through such insulating solids, it leaves a narrow trail of damage about 50 Å in diameter along its path. This is called 'Latent Track' as it cannot be seen with the naked eye. It is possible to view this latent track with an electron microscope. The exact nature of the physical and chemical changes occurring at the damage site depends on the charge (Z) and velocity ($\beta = \nu/c$, where ν is the particle velocity and c is the velocity of light) of the particle, on the chemical structure of the detector material and also on the environmental conditions like temperature and pressure. These latent tracks can be enlarged / developed so that they can be viewed under an optical microscope by etching with some chemicals such as sodium hydroxide and hydrofluoric acid.

The Pneumatic Carrier facility of Dhruva was standardized for the estimation of uranium in uranyl nitrate solution samples in ppb range by using solid state nuclear track detection method [38, 39]. For this purpose, uranyl nitrate solutions in the concentration range ~10-1000 ppb were prepared from uranium SRM standard. The standard uranium solutions taken in polypropylene tubes along with the Lexan track detectors inside them were irradiated in the Pneumatic Carrier Facility (PCF) of Dhruva, research reactor at BARC Mumbai for 1 min. A blank of 2M HNO_3 was also irradiated along with the uranium solutions. The irradiated detectors were then etched in 6N NaOH at 60 ^{o} C for 1 hr to reveal fission tracks. The fission tracks were counted under an optical microscope to get track density. A linear curve obtained between the track density and uranium concentration indicates the possibility of using this facility for the estimation of uranium in ppb range by track method. It has been found that this facility can be used for the uranium estimation upto 5 ppb for 1 min irradiation time. The detection limit of uranium can be further lowered if the irradiation time is increased. The standardized method was then applied to the feed and elutes samples for uranium estimation. For the U estimation in the feed and elute samples, a U standard was always irradiated along with the samples and the U concentration was calculated with respect to the standard. The track density obtained by scanning a small representative detector area is related to concentration C (g/cc) of the element by equation

$T_d = \frac{K_{wet} CXN\sigma\varphi t}{A}$ where K_{wet} is defined as the track registration efficiency in solution and is expressed in cm; φ is the neutron flux in reactor and σ is the thermal neutron cross section. When simultaneous irradiation of a standard and sample is carried out, then only track densities and concentrations of standard and sample come into picture as shown in equation below:

$$\frac{T_{d(sample)}}{T_{d(s\tan dard)}} = \frac{C_{sample}}{C_{s\tan dard}}$$

The above method makes error independent arising due to small variations in the flux. The PCF facility of Dhruva was standardized for the estimation of uranium in uranyl nitrate solution in ppb levels using SSNTD for the first time [38]. The standardized methods were then applied to the feed and elute samples of RUSWapp facility, routinely generated from Desalination Division for uranium estimation.

6.2.4 Neutron Activation Analysis technique:

This technique is based on irradiation of a sample with neutrons available from nuclear reactors and subsequent measurement of the induced radioactivity (β, γ) for determination of the concentration of an element [40, 41]. Neutron fluxes in the range of 10^{11} to 10^{15} $cm^{-2}.s^{-1}$ are used. In NAA, the steps involved are: (i) Sampling (ii) Preparation of actual sample reference material (SRM) and control sample reference material (CRM) (iii) Preparation of the standards or single comparator (iv) Irradiation of samples and comparator in a reactor (v) Radioactive assay by high resolution γ-ray spectrometry (vi) Gamma spectra analysis for peak areas (vii) Evaluation of detection efficiency (for k_o method) (viii) Calculation of elemental concentrations and (ix) Interpretation of the results.

The k_o–NAA method uses simultaneous irradiation of sample and a neutron flux monitor such as gold and the use of a composite nuclear constant called k_o . The k_o factor is defined as

$$k_0 = \frac{M^* \theta \sigma_0 \gamma}{M \theta^* \sigma_0{}^* \gamma^*}$$

Where σ_0 is the (n, γ) cross section for thermal neutrons; θ – is the abundance of the isotope of interest; M – is the average atomic mass of the element; γ – is the absolute gamma-ray abundance; The symbol * refers to the corresponding parameters of comparator (Au^{197}). The concentration of element is calculated using

$$C(\mu g / g) = \frac{\dfrac{N_p / LT}{S.D.C.W}}{\left[\dfrac{N_p / LT}{S.D.C.w}\right]^*} \frac{1}{k_0} \frac{f + Q_0(\alpha)^*}{f + Q_0(\alpha)} \frac{\varepsilon^*}{\varepsilon}$$

Where N_p - is the net counts; W and w - are masses of sample and single comparator; f- is sub cadmium to epi-thermal neutron flux ratio; α - is epi-thermal neutron flux ratio; ε - is efficiency of the detector; k_0 , Q_0 - are two nuclear constants; $S(=1-e^{\lambda t})$ - is the Saturation factor; $D(=e^{-\lambda t_d})$ - is the Decay factor; $C(=(1-e^{-\lambda * CL/\lambda * LT}))$ - is the Correction factor; CL – clock time of counting; LT – live time of counting ; λ - is decay constant (s^{-1}); t_d – is decay period; t – is the duration irradiation

Instrumental NAA (INAA) is a very good technique to analyze solid samples with lower mass range [9-10]. INAA is an isotope specific technique for simultaneous multielement determination in diverse matrices. It experiences negligible matrix effect and needs small sample size (50-100 mg) for analysis. In the present work, solid adsorbents (PAO) used for extraction of uranium from seawater were analyzed for U estimation. Three sets of **solid** samples (before and after elution) were analyzed by INAA using neutron irradiation at Apsara reactor at a neutron flux of $5x10^{11}$ $cm^{-2}.s^{-1}$ and radioactive assay by high resolution gamma ray spectrometry. Samples of about 100 mg mass and U-standards were packed in polythene and were irradiated for 7 hours in Apsara reactor. Radioactive assay of the daughter products of ^{239}U (^{239}Np, 2.27d, 106, 228 and 277 keV) were done by high-resolution gamma ray spectrometry using a 40% HPGe detector. Peak areas were determined by peak-fit software PHAST developed by Electronics Division, BARC. The relative method of INAA was used for calculation of concentration of heavy metal, the expression which is given below.

$$m_{x,\,sample} = m_{x,\,std} \cdot \frac{cps_{x,\,sample}}{cps_{x,\,std}} \cdot \frac{D_{std}}{D_{sample}}$$

Where $m_{x,\,std}$ and $m_{x,\,sample}$ are the masses of element, $cps_{x.sample}, cps_{x.std}$ are count rates and D_{std} and D_{sample} are decay factors of activation products of standard and sample respectively.

Chapter-7

Description of the Experiments & Results

7.1 Experimental methods and materials used:

7.1.1 *Sample Preparation:*

Sample tokens of various sizes ranging from 25mm x 25mm to 100mm x 100mm were cut from substrate sheets of various makes as per the requirement. Samples were washed with methanol to remove surface impurities and then dried in oven at 50 deg. C. For each reference samples, the IR transmission spectra were taken along with initial weights.

7.1.2 *Substrate materials used:*

Five types of commercially available fiber compositions and geometries were evaluated for their suitability for grafting purposes. Mono and Multi component fibers consisting of Polypropylene, Polyethylene and Polyester materials were short listed for experiments. The non-woven fabric substrate materials available in the market as detailed in Table 8 were characterized by Differential Scanning Calorimetry (DSC) and TGA methods at 3 different laboratories. DSC gives energy change of the various samples during transformation and TGA gives weight loss w.r.t temperature.

Table 8 Details of non-woven substrate materials used

Parameter	**Make-1**	**Make -2**	**Make -3**	**Make-4**	**Make-5**
Fiber Φ in micron	2-10	2-5	1-2	2-5	2-5
Thickness in g/m^2	270	300	500	500	500
nominal Bulk thickness	1.5 mm	1.5 mm	2 mm	2 mm	2 mm
Reinforcement Scrim	none	none	PP	PP	PP
Composition	PP/PE 80:20	PP	PP	PP/PE 80:20	PP/PE/Polyester 80:10:10
Cross section of fiber	Circular	Circular	Circular	Circular	Circular

7.1.3 Reagents:

Most of the reagents used are analytical grade for lab scale studies and commercial grade for bench scale studies. The chemicals used without any further purification. Uranyl nitrate solutions at different concentrations required for lab scale studies were prepared by a stock solution of concentration 500 ppb using low TDS water of desalination plants. Natural seawater of TDS ranging from 35000 to 55000 ppm was also used for studies. Caustic flakes were used for pH adjustment of oximation and alkalination solutions. Dilute Hydrochloric acid and sodium hydroxide solutions are used for varying the pH of the feed solutions of lab and bench scale studies.

7.1.4 *Adsorption procedure and measurement:*

The tokens of various sizes were weighed and equilibrated with solution with occasional shaking at room temperatures. The amount of uranium adsorbed q_t with novel sorbent was calculated as follows:

$$q_t = \frac{(c_o - c_t)*V}{M_a}$$

Where c_o, c_t are the concentrations in feed solutions at initial and at any time respectively; V is volume of solution ; M_a is weight of sorbent; The concentrations are measured using methods highlighted in chapter-5.

The concentration factor is another parameter used for quality assessment. It is calculated as follows:

$CF = \frac{C_e}{C_f}$ where C_e, C_f are concentrations of elute and feed solutions in ppb as measured by methods mentioned chapter-6.

7.1.5 *Irradiation:*

Irradiation of substrate sheets was carried out using departmentally available and as well as private electron beam centre facilities. Table 9 gives the details of various accelerator facilities and beam features used for experimental work

Table 9 Electron Beam features of various electron beam facilities

Sl.no	Location	Beam Energy	Beam Power	Current	Type	Remarks
1	BRIT Vashi	1.8 MeV	20 kW	1.06 mA	DC accelerator; single cavity	
3	EBC Khargahr	10 MeV	10 MW	100 mA	Industrial RF linac accelerator	
4	Private EBC facilities	1.25 MeV				

7.1.6 *Grafting procedure*:

Grafting reaction was carried out using a post irradiation technique i.e. sheets were irradiated prior to immersing them in grafting solution. The Electron beam irradiated substrate sheets were immersed in solution mixture of acrylonitrile and DMF in 70:30 ratios at 60º C for 3 hours. Subsequently the cross linked cyano groups were substituted with amidoxime groups. The quality assurance for grafting extent was done gravimetrically using the equation:

$$Grafting\% = ((W_g - W_i)/W_i) \times 100$$

Where W_i, W_g are the weights of the sample before and after grafting.

7.1.7 *Initial experimental campaigns*:

<u>Trombay estuary</u>:

First trails were carried out on lab scale at Trombay estuary to establish the process and material parameters under actual marine conditions. The mooring of adsorbent tokens were done as per the details shown in Fig. 6.

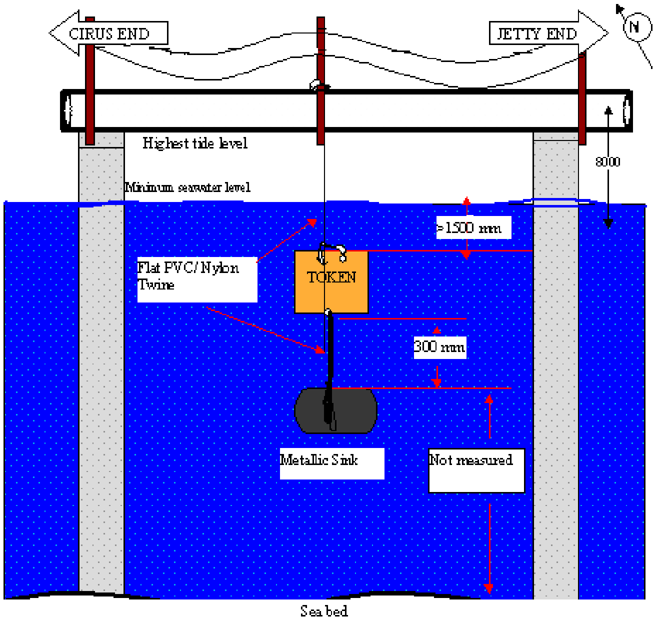


Fig. 6 Mooring arrangements for sorbent tokens at CIRUS jetty

<u>Experiments at Seawater intake and outfall canals of Nuclear Power Plants</u>:

The Nuclear Power plant at Tarapur India site was characterized to arrive at an optimum submergence period based on fouling factor assessment. The tokens were made from PP fiber aggregated by mechanical bonding into a felt of similar specifications as per Trombay experiments. The size of each token was 150x150x2 mm.

<u>Experiments at East coast line of India</u>:

<u>Andaman and Nicobar Islands</u>:

In-field trails were carried out on bench scale at seawaters of Andaman and Indian Ocean to establish the metal sorption characteristics and as well as process and material parameters under actual marine conditions. The mooring of adsorbent tokens were done as per the details mentioned elsewhere. Short listing of sites out of 541 islands that A&N has been done with the co-operation from UT administration and coast guard. Seven sites were selected and reached along with their officers. Indira point is the southern most tip of our country protruding into the Indian Ocean. It is 6.7 ° N of equator. The sizes of tokens used were 100x100x2 mm.

7.2 Manufacture of adsorbent on a suitable & optimised Substrate:

During lab-scale experiments, many types of fiber cross sections and geometry were evaluated for their efficacy for grafting purposes. Polyester and polypropylene fiber materials were shortlisted for further experiments. Finally experiments are done using polypropylene fiber of 1.5 denier cross section as stem material in non-woven felt form. Electron Beam Radiation induced grafting of acrylonitrile on the stem fibre was carried out at ILU-6 and other EB centres to optimize the parameters for maximized % grafting. The solution viscosity and temperature were also found to be important factors during conversion of grafted acrylonitrile into amidoxime.

7.2.1 Characterisation studies:

The type and nature of substrate materials plays a role in both achieving higher grafting levels and as well as in influencing the metal complex formation. Functional groups may be attached to the substrate through various surface chemistries. The micro environment created around the ligand is an additional factor in ionic selectivity. The elucidation of the mechanism by which the supporting matrix influences complex formation may enable new and more efficient methods of metal separation. Various characterization methods are being followed to study the morphology, chemical characteristics, physical characteristics and mechanical characteristics. The details are as follows:

Radiation characteristics of various polymeric substrates:

In our studies, we have used non woven thermally bonded materials as substrate materials. Non woven materials are porous media consisting of fibers or filaments oriented mainly in the x,y directions according to the method of fabric production. The fiber size and filament type has significant influence on the geometrical, hydraulic and mechanical properties of the fabric. The pore size distribution of nonwovens is particularly important in respect of transport phenomena within the structure. Four types of polymers polystyrene, poly tetra fluoro ethylene, polyethylene, and polypropylene were used as sample substrates to investigate radiation grafting characteristics of polyolefin. Among the samples tried, polystyrene shows most radiation resistant since absorbed energy converts into heat by aromatic rings. Radiation processing is limited and radiation yield of radicals is limited than in other polymers. Three radicals can be produced - two are formed on abstraction of hydrogen and one created via addition of hydrogen to aromatic ring. In case of PP, the dominant product is 3rd order alkyl radical that undergoes oxidation. Formed peroxy radicals are very stable. PE is also radiation resistant polymer, but ionising radiation induces residual radicals in crystalline phase. The alkyl, allyl and polyenyl radicals are produced. The Fig. 7 shows the radiation grafting yields observed for various substrate polymers.

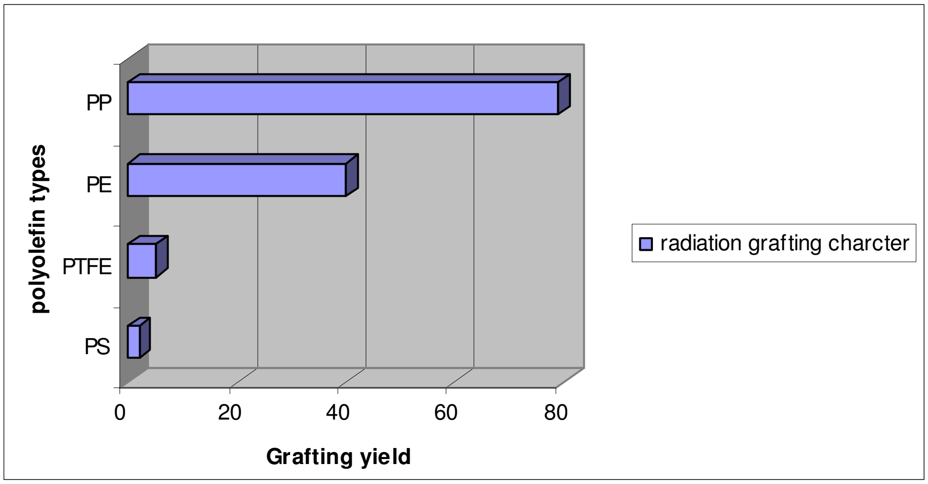


Fig 7 Radiation characteristics of various polymeric substrates

Scanning Thermo analysis:

Five types of commercially available fiber compositions and geometries were evaluated for their suitability for grafting purposes. Mono and Multi component fibers consisting of Polypropylene, Polyethylene and Polyester materials were short listed for experiments. The non-woven fabric substrate materials available in the market as detailed in Table 10 were characterized by Differential Scanning Calorimetry (DSC) and TGA methods at 3 different laboratories. DSC gives energy change of the various samples during transformation and TGA gives weight loss w.r.t temperature.

The chemical characterization of various substrate materials was carried out using scanning thermo analytical tehchniques such as Differential Scanning Calorimetry (DSC). The tempertature difference between substrate sample and non reactive reference is determined as function of tempertarue. The sample energy change during transformation is directly compared. The results of DSC endothermic peaks as reported by three independent laboratories for the five types of substrate materials are shown in Fig. 8.

Table 10 Non woven substrate materials investigated

Parameter	**Type-1**	**Type -2**	**Type -3**	**Type-4**	**Type-5**
Fiber Φ in micron	2-10	2-5	1-2	2-5	2-5
Thickness in g/m^2	270	300	500	500	500
nominal Bulk thickness	1.5 mm	1.5 mm	2 mm	2 mm	2 mm
Reinforcement Scrim	none	none	PP	PP	PP
Composition	PP/PE 80:20	PP	PP	PP/PE 80:20	PP/PE/Polyester 80:10:10
Cross section of fiber	Circular	Circular	Circular	Circular	Circular

PP= Poly Propylene; PE=Poly Ethylene;

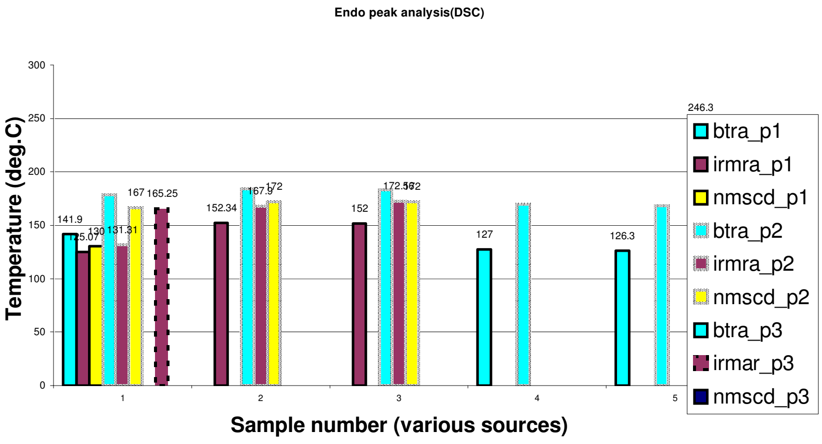


Fig. 8 DSC endo thermic peaks

Studies related to thermally bonded non woven porous polypropylene fiber sheet substrate characterization was carried out on various samples having different gsm, as it is an important engineering parameter in selection of suitable substrate base. Fig 9 and Fig 10 shows the DSC thermo grams having endothermic peaks at temperatures 166deg.C and 171 deg.C for 300 and 500 gsm respectively corresponding to Tm of poly propylene of 160 to 175 deg.C.

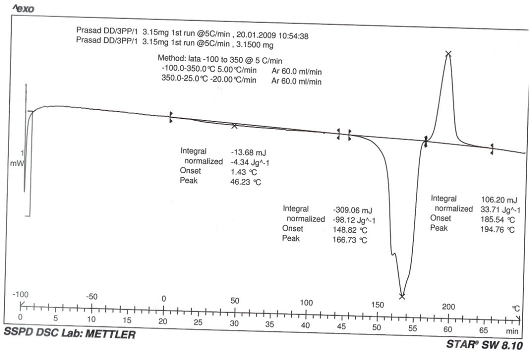


Fig 9 DSC thermogram of 300 gsm substrate sheet

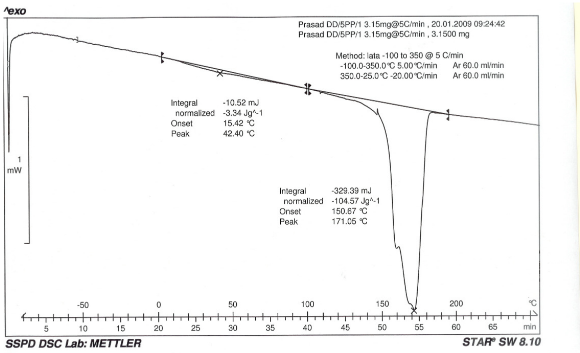


Fig 10 DSC thermogram of 500 gsm

Table 11 and Table 12 shows the calculations for actual surface area and apparent porosity of fibers considered.

Table 11 Surface area of poly propylene fibre substrate

sl.no	**Parameter**	**Rounded value**	**units**	**Computed value**	**Remarks**
1	Size of fiber	1.0000	denier		
1.1	Denier	1.0000	g/9000 yards		
		2.8000	ug/inch		
		0.0001	g/mt		
1.2	Substrate weight	300.0000	g		
1.3	Length of fibre	3000000.0000	mts	3000000	
1.4	Density of fibre	910.0000	kg/cu.mt		
1.5	Volume of substrate	0.0003	cu.mt	0.00032967	
1.6	Diameter	0.0000	mts	1.07075E-05	
		0.0107	mm	0.010707459	
1.7	Actual Surface area available	100.0000	sq.mt	100.8642652	
		0.3360	sq.mt/g	0.336214217	

Table 12 Apparent porosity of poly propylene fibre substrate

sl.no	Parameter	Rounded value	units	Computed value	Remarks
1	Apparent thickness of fibre	1.0000	mm		
2	Substrate weight	300.0000	g/sq.mt		
3	Bulk density	910.0000	kg/cu.mt		
4	Actual thickness	0.2700	mm	0.32967033	
5	Apparent weight/mm	910.0000	g/sq.mt	910	
6	Apparent porosity	70.0000	%	67.03296703	

In addition to chemical characterization, the substrate samples of various makes were studied for radiation characterization. The assessment of various above substrate materials for radiation grafting was carried out and the results are as tabulated below in Table 13.

Table 13 Radiation Grafting Analysis PP sample substrates of various types

Type of PP substrate sample	Initial weight (g)	Final weight (g)	% Grafting	Avg Value	Remarks
Type 1	1.02	1.912	87.45		270 GSM
	0.56	0.943	68.39	77.92	
Type 2	1.07	1.842	72.14		300 GSM
	0.39	0.713	82.82	77.48	
Type 3	2.03	4.04	99.21		500 GSM with scrim
	0.78	1.396	78.97	89.09	
Type 4	1.42	2.304	64.36		500 GSM with PP scrim with bicomp
	0.53	0.851	60.566	62.46	
Type 5	1.23	1.796	46.01		500 GSM with PE scrim with bicomp
	0.52	0.729	40.19	43.10	

Differential Scanning Calorimetry of grafted sheets: Scanning thermo analytical techniques are being used for characterizing the changes occurred in samples. The thermograms were taken for control and grafted sheets to observe the changes occurred due to grafting. Fig 11 shows the DSC thermograms of oximated substrate sheet. Endothermic peak occurred at reduced temperature of 149 deg.C compare to control samples shown above due to formation of cyano groups. Overall comparative DSC characteristics of control samples, grafted samples and oximated samples are as shown in Fig. 12.

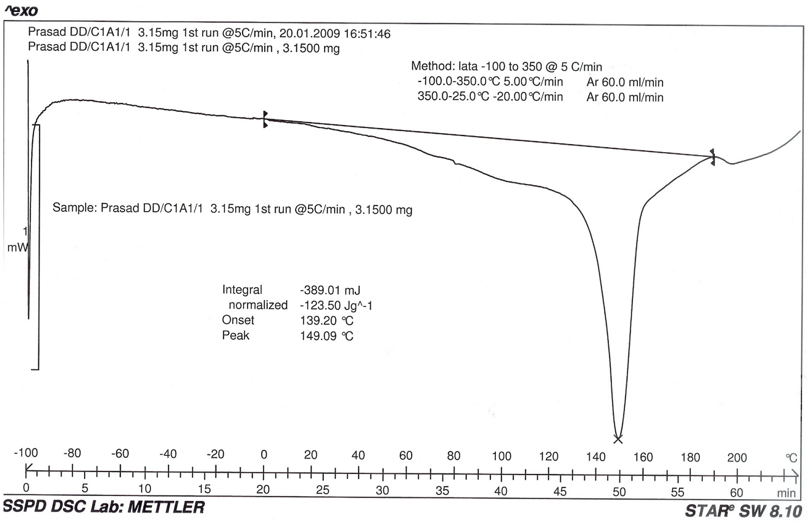


Fig.11 DSC thermogram of 300 gsm oximated substrate sheet

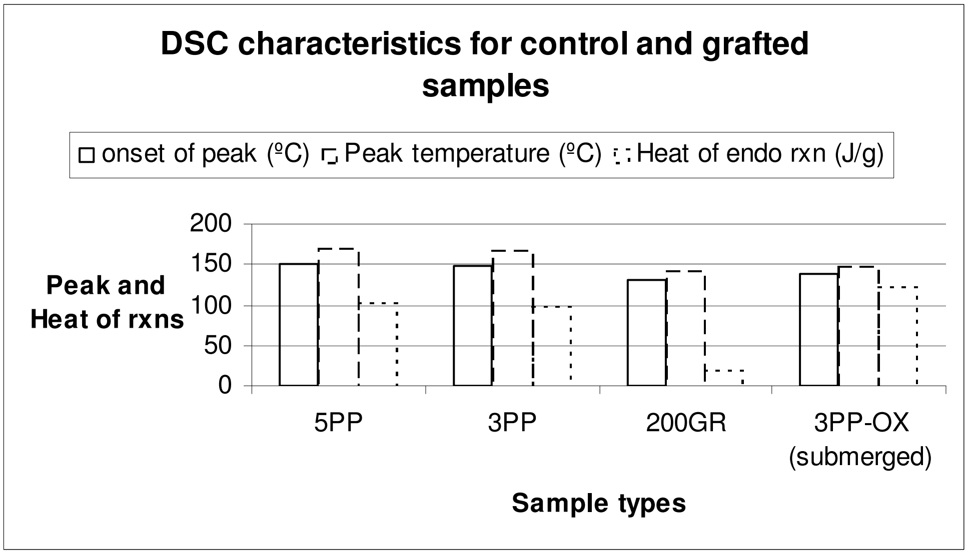


Fig 12 DSC characteristics of ungrafted, grafted and oximated samples

Optical micrograph characteristics of grafted substrates:

The changes occurred due to irradiation, grafting and oximation are followed by optical micrographs and scanning electron microscope for the purpose of characterization of changes in structure and morphology. Fig. 13 shows changes both in texture and diameter of the fibers.

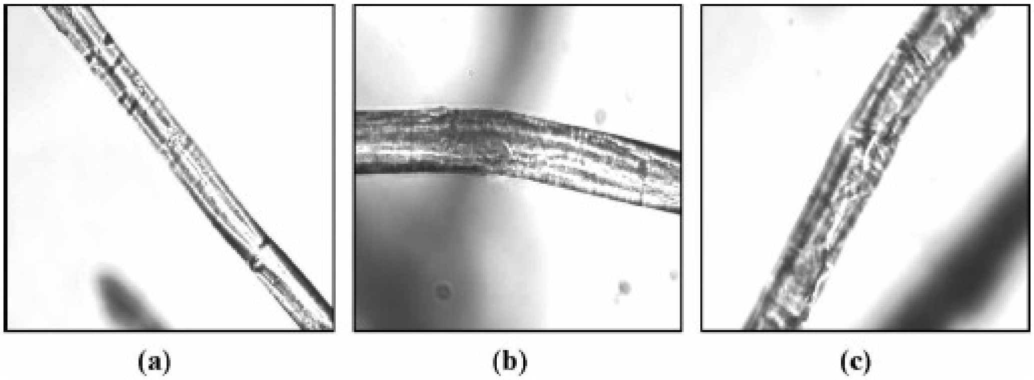


Fig 13 Optical micrograph of a) fiber b) PAN grafted fiber c) PAO fiber

The scanning electron microscopy images of EB radiation grafted amidoxime sorbent are shown in Fig. 14 at different scales. These scanning electron microscopy images also showed swelling of fibre and changes in diameter after the introduction of grafted polymer chain.

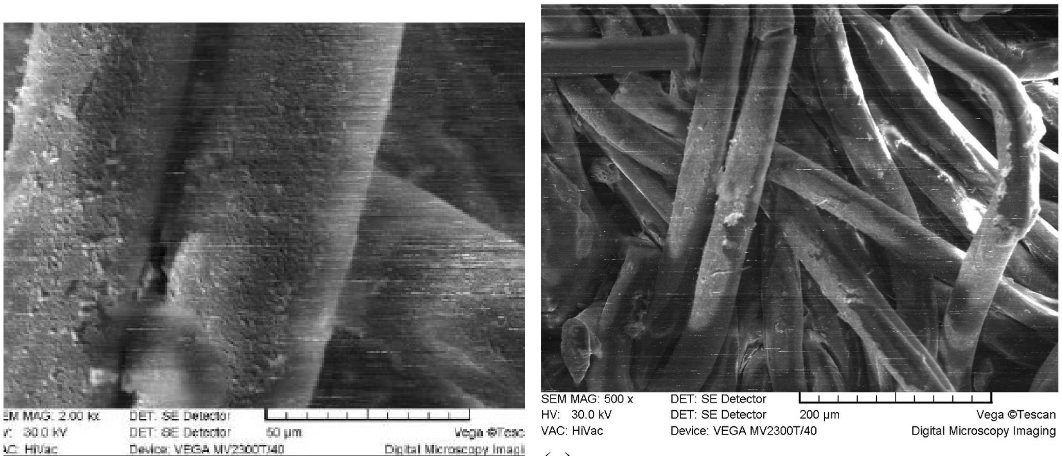


Fig 14 SEM image of sorbent a) 200X b) 500 X

Physical characteristics of grafted substrates:

Adsorption and Ion exchange processes are influenced by diffusion of metal ions, surface interaction mechanism and presence of surface functional groups on sorbents. Hence surface area and pore volume are determined by gas adsorption method. The characteristics of radiation grafted and chemical grafted sorbents are as shown in Fig. 15. For comparison purpose, the value of surface area (63.3 sq.m/g) reported for chemical grafted bisorbent [42], made of tamarind fruit shell is also presented, along with radiation grafted sorbent. Radiation grafting has given good improvement of surface area of upto 300% for differently radiation grafted sorbents.

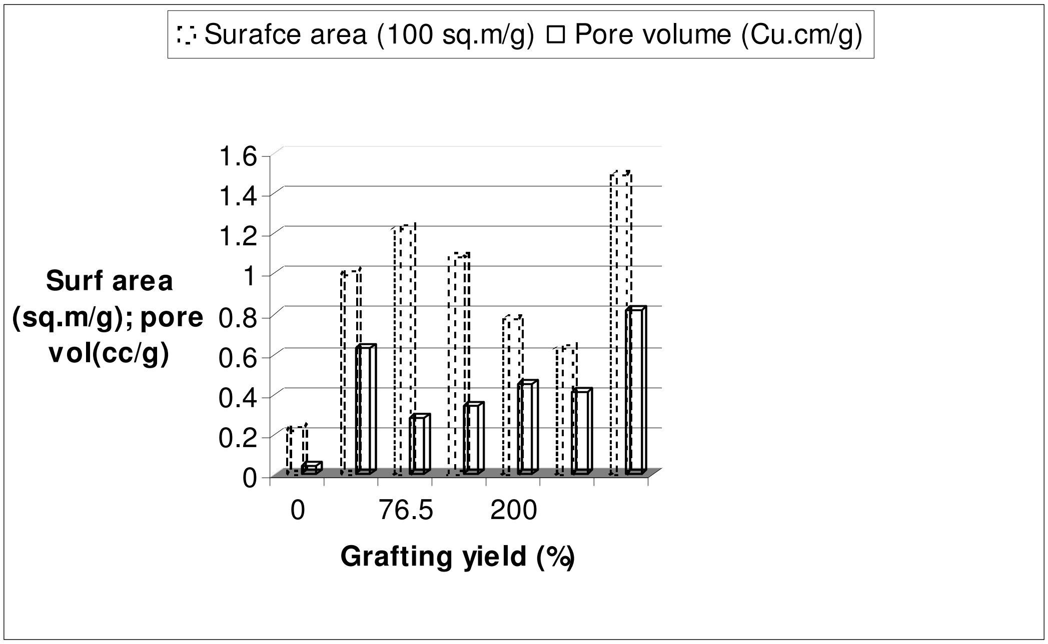


Fig 15 Physical characteristics of radiation grafted sorbents

Contact anagles are important macroscopic parameters characterising surface wettability. Grafting of hydrophilic layer as the surface of hydrophobic matrices ought to result in lowering of contact angle values as compared to ungrafted samples. The Fig. 16 shows the trends observed. But decrease in the values upon grafting is relatively small. Further it is planned to see effect of other hydrophilic additives.

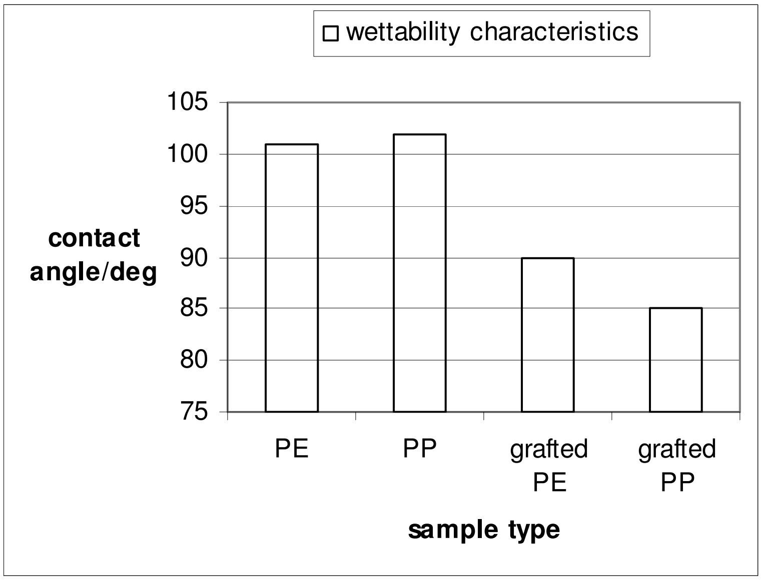


Fig 16 wettability characteristics of grafted sorbents

<u>FTIR scans of grafted sheets:</u>

The FTIR spectra were taken for control and grafted sheets to verify the grafting. A FT-IR spectroscopy study shows the extent of modification through change in characteristic peak intensities as listed in Table 7. Fig 17 shows the formation of cyano groups.The sharp absorbance band at ~2200 cm^{-1} is very characteristic of C≡N, the cyano groups. The depletion of these groups during oximation supports the idea that conversion of C≡N groups to H_2N-C=NOH groups almost completed.

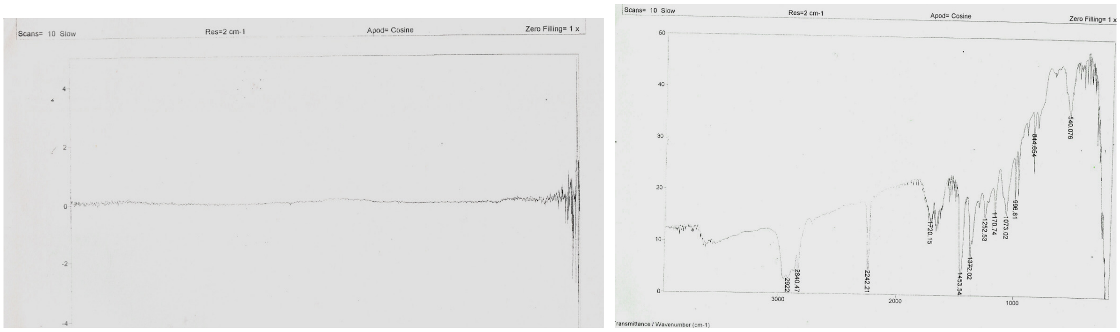


Fig 17 FTIR scans of grafted sheets

7.2.2 Parametric studies for synthesis of radiation grafted sorbents:

Effect of Cumulative dose on Radiation grafting at 10kgy:

Fig. 18 shows the grafting yields as a function of the cumulative dose at a dose rate of 10 kGy/pass in air and reaction was carried out at 60 deg.C for 3 hours. The yields are increased with the dose upto 200 kGy and then leveling off is observed.

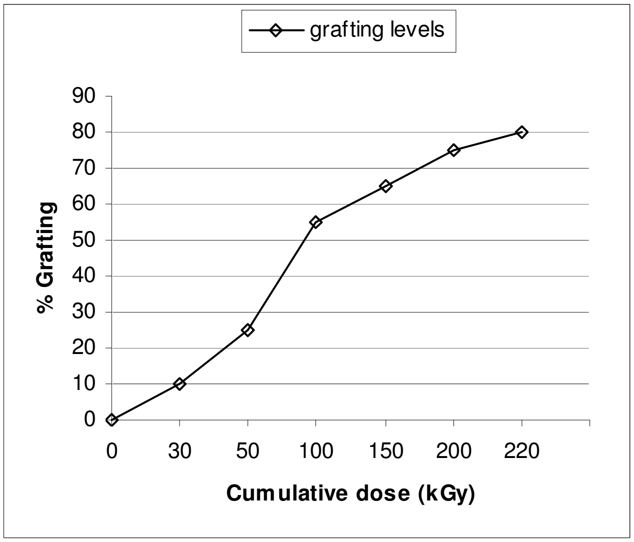


Fig 18 Effect of dose on radiation grafting

Effect of Solvent concentration on Radiation grafting:

Fig. 19 shows the grafting yields as function of different proportions of acrylonitrile to DMF. The presence of DMF is beneficial up to 30% (v/v). As long as solvent is present in the grafting reaction, PAN grafted PP layers swell in the medium and regulate the monomer diffusion through the swollen layer to the grafting sites. At lower concentrations of solvent or in its absence, the lower level of grafting yield is noticed. This is because the acrylonitrile is a non solvent for PAN chains and diminishes the swelling of the grafted mono/bi filament fibers. It is therefore, instantaneous swelling of the grafted fibers that aids in grafting at a specific monomer solvent composition. B. Gupta and et al [34] reported similar trends in the grafting reaction and reported maxima at 20% solvent in monomer solvent mixture.

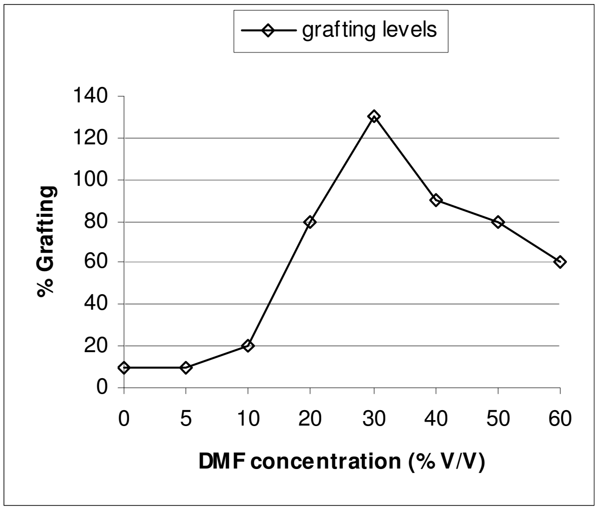


Fig 19 Effect of solvent concentration on radiation grafting

Effect of Solvent & co solvent system on Grafting yield:

Solvent and co-solvent sytems helps in improving the grafting yields. Figure shows the effect of different solvents and solvent&co-solvent systems on grafting yield and conversion of cyano groups to oxime groups. It shows that higher grafting yield can be achieved in co-solvent system than single solvent systems. Some co-solvent systems were tried to see the effect on oximation yields and easy of grafting. The presence of co-solvent system is beneficial as seen in Fig 20.

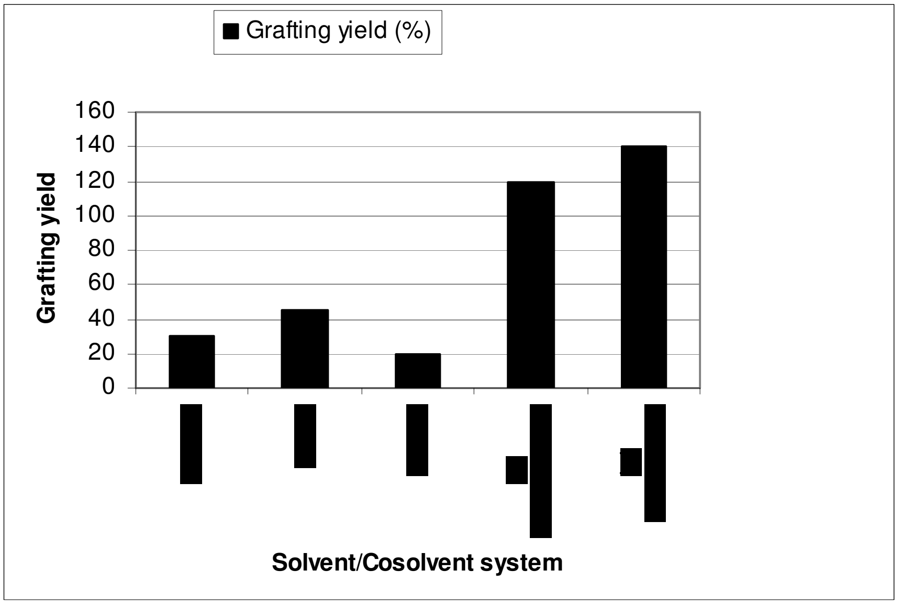


Fig 20 Effect of solvent & co solvent on radiation grafting

Effect of Duration on Grafting yield :

Figure 21 shows the grafting yield as function of reaction time. It gradually increases with reaction time and then leveling off are observed after four hours. The post irradiation grafting is a typical chemical reaction involving radicals. Intention of this investigation was to see the effect of reaction duration for grafting. Figure 21 shows the grafting yields as a function of the grafting duration at cumulative dose of 20 MRad at a dose rate of 10 kGy/pass in air. The yields are increased till duration of three hours and then it plateaus. The rise in concentration values of acrylonitrile vapors in operating area were also monitored and are as shown in figure.

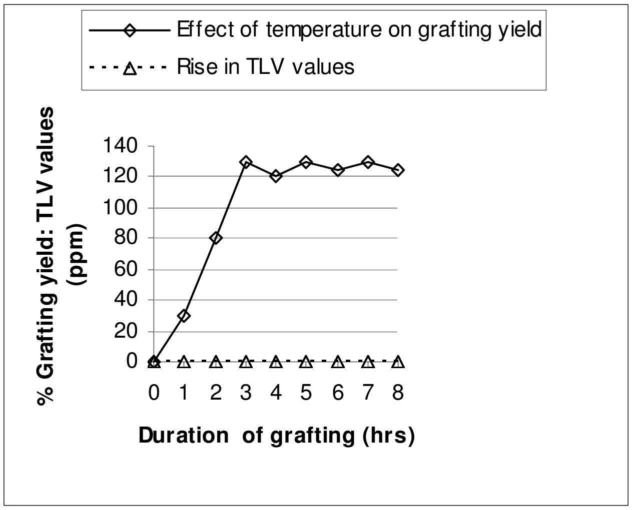


Fig 21 Effect of duration on grafting yield

Effect of retention time in air on Radiation grafting at 10kgy:

The post irradiation grafting can be carried out by two different ways. Intention of this investigation was to see the effect of type of free radicals and amount of free radicals available for grafting. Radiation grafting is simillar to oxidation phenomena and free radical are used to initiate and continue with grafting process. Formation peroxides on substrate surface supports the grafting process. Air atmosphere has given better levels of grafting at a temperature of 55 to 60 deg.C. Maximum grafting achieved in nitrogen atmosphere is only upto 25%. In air atmoshere, it helps formation trapped free radicals and these can be used by doing grafting at higher temperature. Figure 22 below shows the grafting yields as a function of the retention time in air at cumulative dose at a dose rate of 10 kGy/pass in air and reaction was carried out at 60 deg.C for 3 hours. The yields are increased with the retention time upto 15 minutes and then drooping off is observed. Here the back bone polymer is irradiated in the presence of air and mainly hydro peroxide radicals are produced. These polymer oxides which are often stable can be decomposed in contact with monomer to produce graft copolymers. It avoids the necessity of using inert gas blanket, which is required during pre irradiation grafting method. The graph shows radicals build up and then leveling off. It is best, if possible to design the process and reactor system, so that comparatively plateau concentration is used rather than build up period. Investigations are carried out to get details on this aspect of radiation grafting reactor systems.

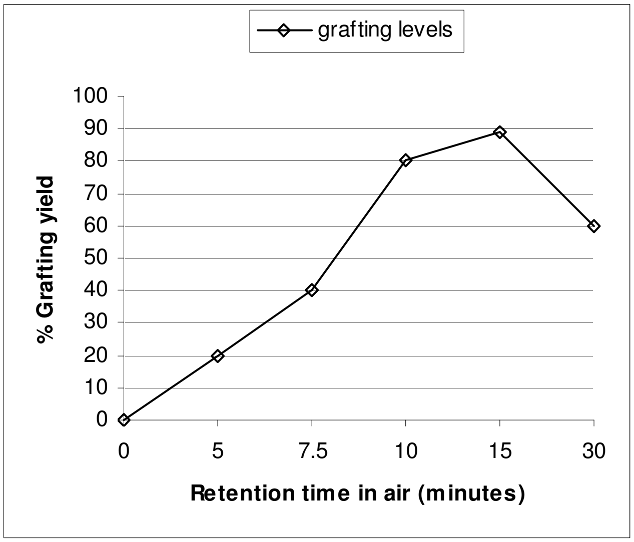


Fig 22 Effect of retention time in air

Effect of different atmospheres on radiation grafting:

Figure 23 shows the effect of different atmosphere maintained for achieving grafting levels. It shows that peroxy radicals plays important role in getting good grafting levels. Few more studies are planned using different energy beams also. Radiation grafting solid liquid reaction and is similar to oxidation phenomena and free radical are used to initiate and continue with grafting process. Formation peroxides on substrate surface supports the grafting process. Air atmosphere has given better levels of grafting at a temperature of 55 to 60 deg.C. Maximum grafting achieved in nitrogen atmosphere is only upto 25%. In air atmosphere, it helps formation both trapped free radicals and peroxy radicals. These can be used by doing grafting at higher temperature.

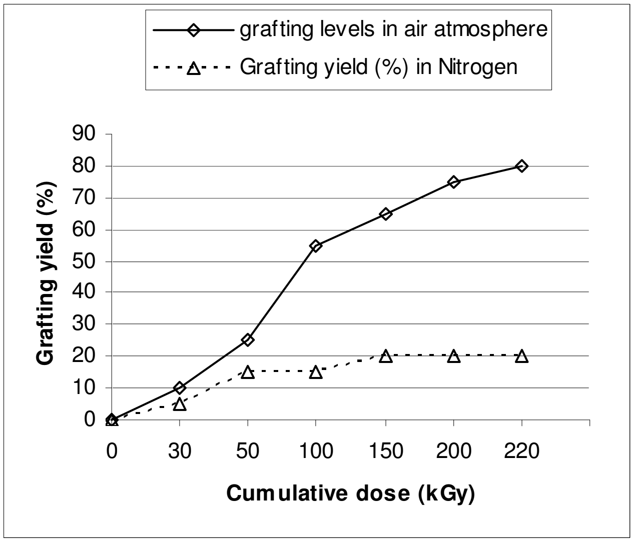


Fig 23 Effect of different atmospheres on radiation grafting

Effect of temperature on radiation grafting:

Post irradiation grafting is typical chemical reaction involving radicals. The intention of this investigation is t see the effect of temperature for grafting. Figure 24 shows the grafting yields as a function of the grafting temperature at a cumulative dose of 200 kGy at a dose rate of 10 kGy/pass in air. The reaction was carried out for three hours. The yields are increased until the boiling temperature of the media is reached. The graph also shows the threshold limit values (TLV) for acrylonitrile vapors measured at breathing levels in the operating area. For safe operation, the temperatures are established accordingly for regular pilot scale operations.

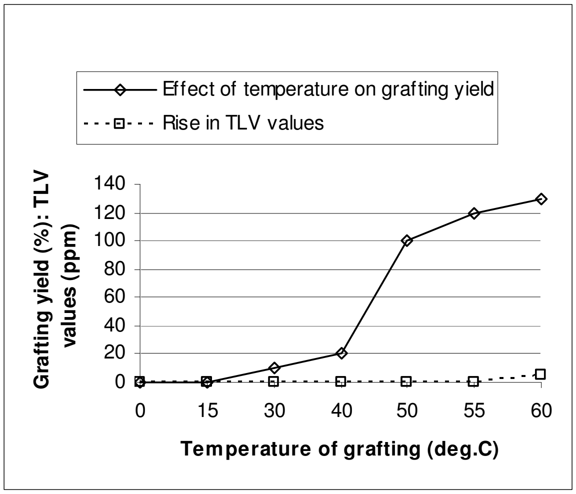


Fig 24 Effect of temperature on radiation grafting

Effect of radiation dose on radiation grafing of PP sheets (diff energy beams) :

The trends in figure 25 shows effect of cumulative dose on grafting yields at a dose rate of 1Mrad/pass in case of 2 MeV energy beam and at a dose rate of 1MRad/minute in case of 1.25 MeV energy beam. The yields are increased with the dose upto 20 Mrad and then leveling off is observed.

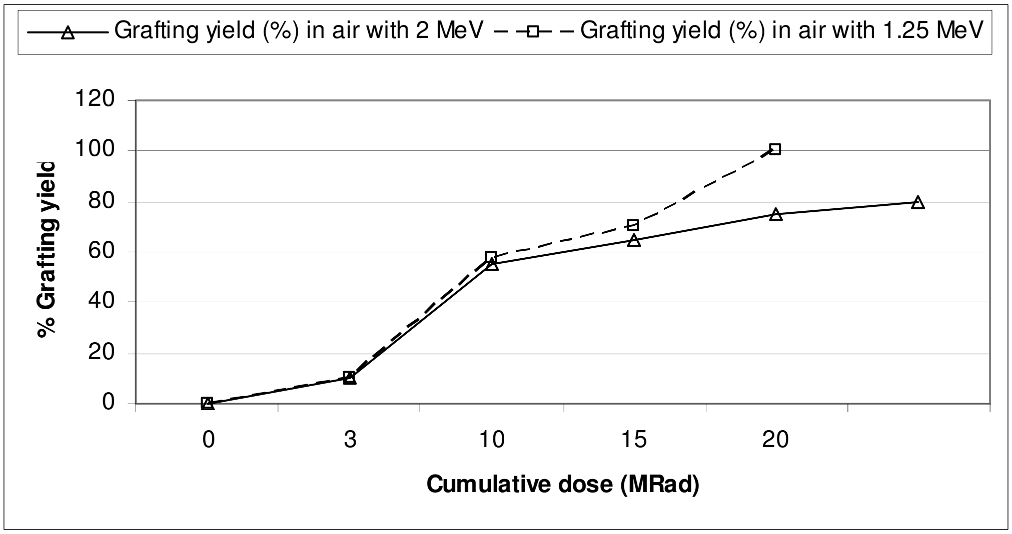


Fig 25 Effect of radiation dose on grafting using different energy beams

7.3 Metal Pick Up characterization studies of radiation grafted sorbents :

7.3.1 Lab scale studies: The metal pick up characterization of radiation grafted sorbents was carried out under lab scale to see effect of various parameters. The details are as follows:

Effect of % of grafting levels on heavy metal sorption

The effect of grafting levels on the removal of heavy metals such as uranium was studied using differently grafted sorbents in the range of 0 to 150%. The % uptake found to increase with increasing grafting levels as shown in figure 26. Between 80% and above the % uptake ncrements observed are less steep. Initial investigations concludes that 80% and above grafting levels gives sufficient removal efficiency and a scope for further improvement.

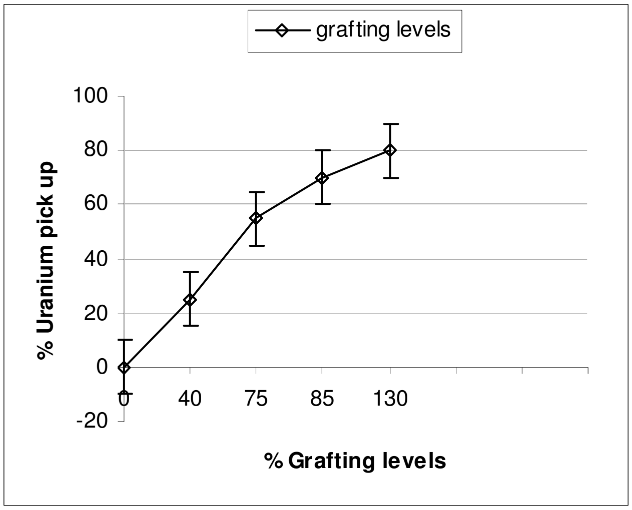


Fig 26 Effect of grafting levels on uranium pick up

Effect of dissolved salts on heavy metal sorption:

Due to seasonal changes in seawater conditions, the TDS (total dissolved salts) varies and hence it is interesting to see the effect of this parameter under lab scale conditions. The objective of this investigation is to see effect of dissolved salts on sorption characteristics of grafted adsorbents. The salts of sodium in the range of 0.1 to 1M and calcium in the range of 0.01 to 0.1M are studied. The results as shown figure 27 below reveal variation of 75 to 80% pick up only in the study range. Presence of these salts has not affected the sorption characteristics. Basically oxime groups are weak acid in character and hence less affinity for alkali metals. In the present study, it is seen that the amidoxime group possess a very high adsorptivity for uranyl ions which is scarcely affected by the co-existence of other alkali metals at pH of around 8. Slight variation can be related to the change in diffusion layer around the surface of grafted sorbents.

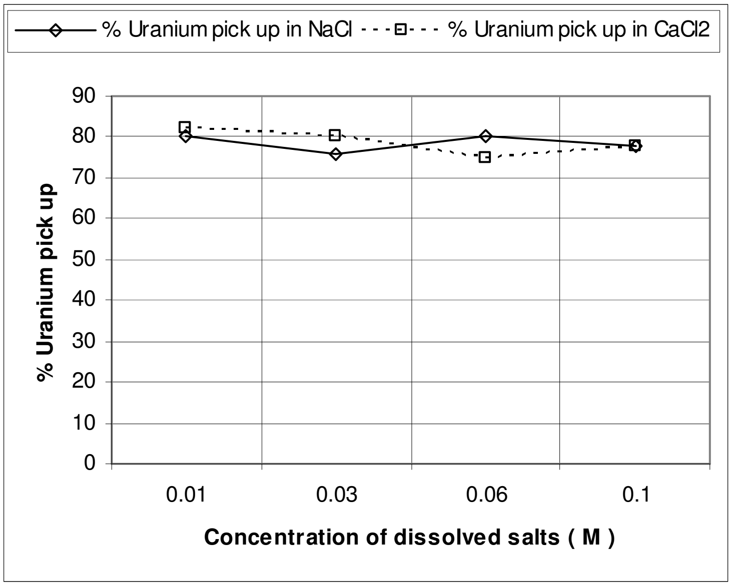


Fig 27 Effect of dissolved salts on heavy metal sorption

Effect of initial concentration of uranium on metal pick up of MCEPs:

The influence of the concentration of uranyl nitrate in the ranges of ppb on the adsorption capacity of uranium was studied using 0.2031 g of PAO. The adsorption capacity increases rapidly with concentration as shown in figure 28. The trends are as reported by Zhang and et al [16]. The concentration ranges used by other researchers are in the range of ppm. The uptake is function of initial concentration and kinetics varies accordingly.

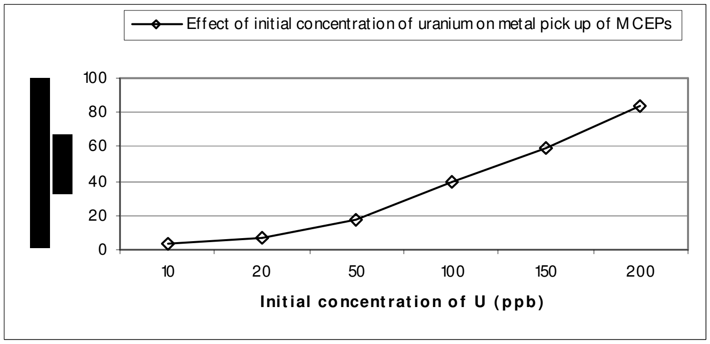


Fig 28 Effect of initial concentration on heavy metal pick up

Modeling of adsorption phenomena by Freundlich isotherms:

This study is aimed to investigate the adsorption behavior of uranyl ion onto radiation grafted adsorbents. Adsorption isotherms are curves which relate the amount of adsorbate adsorbed per unit mass of adsorbent to the amount of unabsorbed adsorbate remaining in the solution at equilibrium. Single parameter models were used to analyse using Freundlich and Langmuir isotherms.

Langmuir postulated that the adsorption equillibrium was the result of two rate processes, equal in magnitude but opposite in directions. They are the rate of adsorption (proportional to solute pressure or the concentration and the available free surface area) and rate of desorption (varies directly with the fractional surface coverage). The langmuir isotherm is based on the assumption that intermolecular forces decrease rapidly with distance and consequently predicts the existence of monolayer adsorption. It also assumes all sorption sites are identical and energetically equivalent. The Langmuir model is given by the following equation.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

By linearising the model equation we get,

$$\frac{c_e}{q_e} = \frac{1}{q_m K_L} + \frac{c_e}{q_m}$$

The essential features of langmuir isotherm can be expressed in terms of dimensionless separation factor or equillibrium parameter $K_L = (1/(1+K_l C_o))$ where C_o is initial concentration (mg/l); K_l is LI constant (1/mg); The parameter K_L indicates the shape of isotherm and nature of process [$K_L>1$: unfavourable; $K_L=1$: Linear; $0<K_L<1$ favourable; $K_L=0$: Irreversible;].

Freundlich isotherm model is fairly satisfactory empirical isotherm and can be used for non ideal sorption that involves heterogeneous adsorption. The Freundlich isotherm predicts that the adsorption of metal ion on the sorbent increase so long as there is an increase in the metal ion concentration. The FI model is given by following equation.

It is very difficult to get isotherms for seawater as much longer time is required to achieve equilibrium. Figure 29 and 30 shows the model based on Langmuir isotherm(LI) and Freundlich isotherm (FI) respectively. The values of constants indicate favorable conditions for adsorption as shown by figure 30.

$$q_e = K_F C_e^{1/n}$$

By linearising the model equation we get

$$\log q_e = \log K_f + {}^{1}\!/_{n} \log c_e$$

It is very difficult to get isotherms for seawater as much longer time is required to achieve equilibrium. Figure 29 and 30 shows the model based on Langmuir isotherm(LI) and Freundlich isotherm (FI) respectively. The values of constants indicate favorable conditions for adsorption as shown by figure 30. As the value of 1/n < 1, it indicates favorable adsorption.

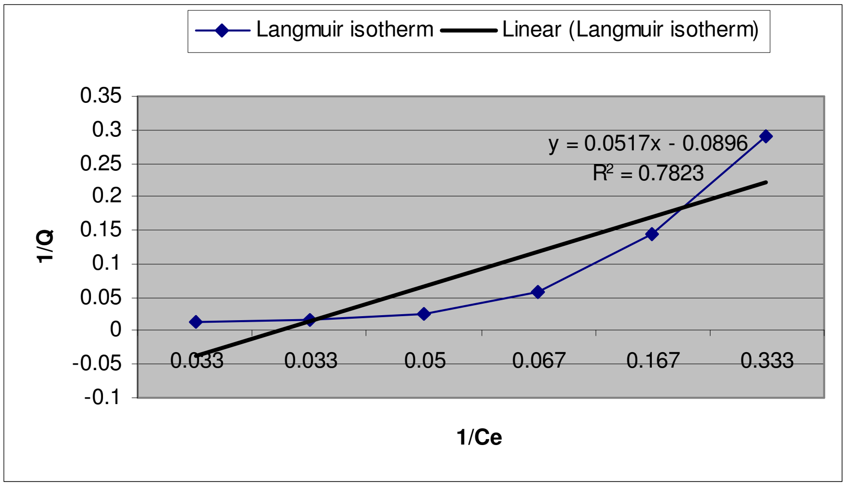


Fig 29 Modelling adsorption isotherm by LI

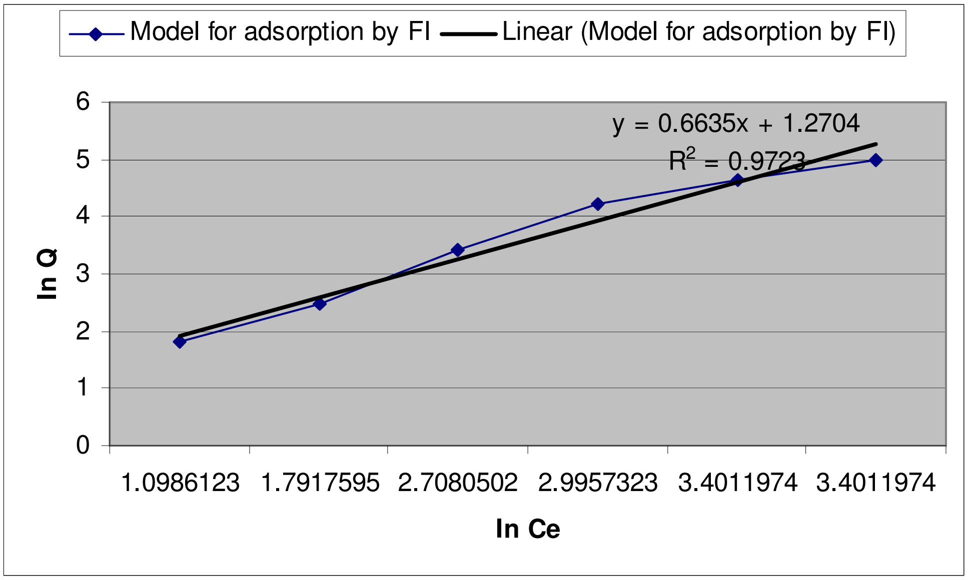


Fig 30 Modelling adsorption isotherm by FI

7.3.2 In filed bench scale studies:

The metal pick up characterization of radiation grafted sorbents were carried out under different locations by In-field bench scale trials to see effect of various parameters. The details are as follows:

<u>Effect of contact time in seawater at Cirus jetty on concentration factors</u>:

The recovery of uranium from sea water is important in the field of energy production. The main problem is the low concentration of uranium and vanadium in the presence of other dissolved salts. Contact time plays important role due to this consideration. The purpose of this investigation is to see the effect of contact time on concentration factors achievable for seawater and also to get some measure of the relative performance of sorbent in kinetic terms. The adsorption profile was obtained in terms of concentration factors is as shown in figure 31. The figure shows sorption occurs after certain threshold value and then increases with time till saturation value is obtained. The similar trends were reported by Saito and et al [43]. The data shows threshold value of 50 hrs for uranium. This long time may be related to more hindrances to complex diffusion for final immobalisation. Afterwards it facilitates formation of donor-acceptor complexes between amidoxime groups and the polar sites of the sorbent.

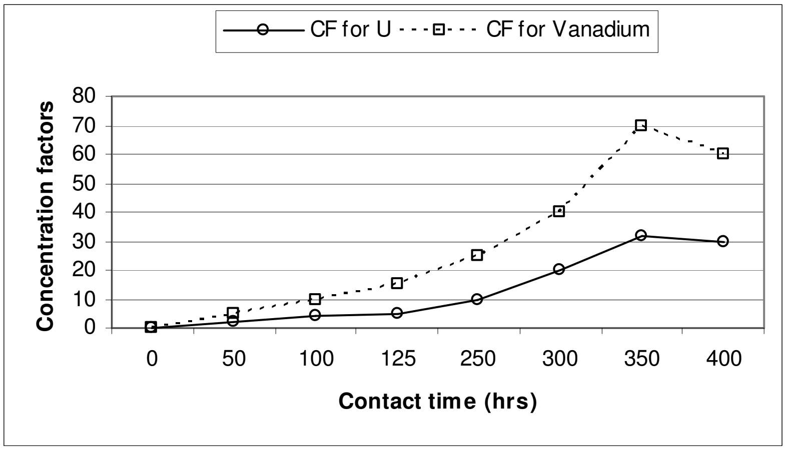


Fig 31 Effect of contact time on concentration factors at CIRUS jetty

Effect of contact time on concentration factors from desalination effluents:

Contact time plays important role and the purpose of this investigation is to see the effect of contact time on concentration factors achievable for desalination effluents and also to get some measure of the relative performance of sorbent in kinetic terms. The adsorption profile was obtained in terms of concentration factors. The figure 32 shows that sorption after certain threshold value and then increases with time till saturation value is obtained. Similar trends were observed by Saito and et al [43]. The data shows threshold value of 4 to 5 days for uranium. This long time may be related to more hindrances to complex diffusion for final immobalisation. Afterwards it facilitates formation of donor-acceptor complexes between amidoxime groups and the polar sites of the sorbent.

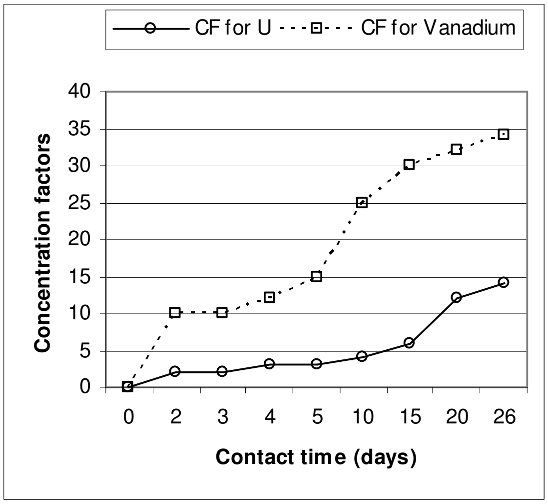


Fig 32 Effect of contact time on concentration factors for desalination effluents

Modeling of diffusion mechanism in Sea conditions of CIRUS jetty:

Adsorption kinetics is usually controlled by different mechanisms. Most limiting are diffusion mechanisms. Initial curved portion is attributed to rapid external diffusion or boundary layer diffusion and surface adsorption and the linear portion is (a gradual adsorption stage) is due to intra-particle type of diffusion. This is followed by plateau to equilibrium where the intra-particle diffusion starts to decrease due to low concentration in solution as well as fewer available bonding sites. Weber and Morris model helps in characterisation of intra-particular diffusion using the specific sorption 'q' and square root of time as q = Kid * sqrt(t) where 'q' is amount of adsorbed per unit mass of adsorbent at time t and Kid is intra-particle diffusion rate constant. The plot of mass of heavy metals adsorbed per unit mass of adsorbent v/s sqrt(t) shown in figure 33 and 34 respectively of cirus jetty and desalination effluents. The plots below shows deviation of straight lines from the origin. So intra-particle transport is not the rate limiting step. The process may be controlled by reaction kinetics and complex formation at the internal binding sites. Weber Morris parameters for various regressions are as shown in table 8 below. The rate constant for V is higher than Uranium.

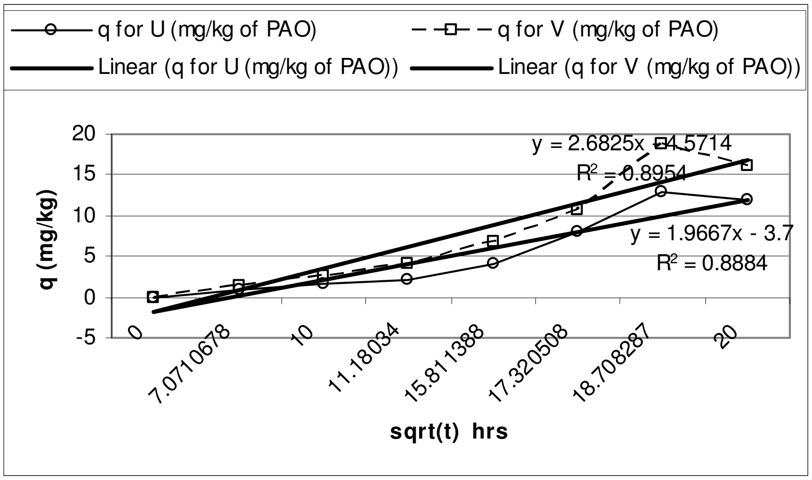


Fig 33 Modeling of diffusion mechanism for seawater conditions

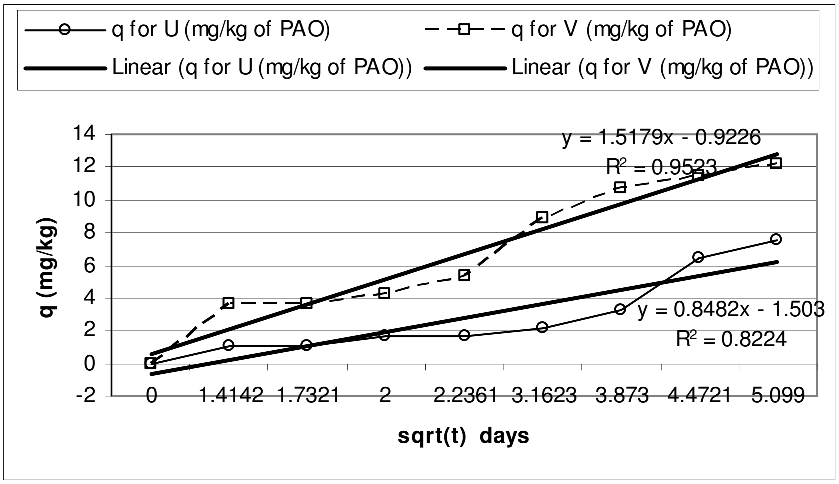


Fig 34 Modeling of diffusion mechanism for desalination effluent conditions

Table 14 Rate constants observed for various conditions

Conditions	**Heavy metal**	**K_d with out intercept**	**Correlation coefficient**	**K_d with intercept**	**R^2**
CIRUS jetty	U	1.317	.7651	1.9667	.8884
	V	1.875	.7854	2.6825	.8954
NDDP kalpakkam	U	.6109	.7409	.8482	.8224
	V	1.3722	.9412	1.5179	.9523

Andaman & Nicobar Islands:

Out of large Indian coastal line, Andamans and Lakshadweep Islands are locations in which good depths are available near shore lines and seawater is having extremely low turbidity coupled with good turbulence and advection of water body.

Seven sites out of 541 islands available were short listed in the A & N Islands. Plain as well as PAO loaded tokens were placed in position and later retrieved after different submergence periods. Seawater samples are also collected and analysed for uranium content and analytical results (reported by various labs by different techniques) are as shown in Table 15. Assistance from Union Territory Administration and Coast Guard

Services was obtained for acquaintance with local marine topography, weather and ocean current patterns over the years and movement logistics. The summary of the observations recorded are shown in Table 16. The submergence period was varied from ten days to thirty days. Even after 28 days of submergence the Great Nicobar sites were found to be the cleanest with respect to all the sites investigated so far. A total of ~200 µg of Uranium was collected from two sites. Specific loadings up to 160 µg /g of sorbent in 25 days are observed. Three independent labs Viz. ACD, HPD and EAD of Bhabha Atomic Research Centre Trombay India have given the confirmation on uranium collection though there is a sizeable difference in the results.

Table 15 Analysis of seawater samples from A&N islands at Eastern coastal line of India

Sl.no	**Sample code**	**Uranium (ppb)**		**Remarks**
		Lab-1 Alpha-spectrometry technique (IDD/BARC)	Lab-2 Anodic splitting voltametry technique (EAD/BARC)	
1	CI-1		1.78	CG jetty portblair
2	PB-1	2.31+/-0.37	2.74	Pigeon bay island
3	TB-1	3.07+/-0.40	2.34	Trinket bay
4	SB-1	3.15+/-.41	2.27	Singha bay
5	BI-1	2.62+/-0.36	1.87	Barren island
6	IP-1		2.15	Inidra point
7	HT-1		2.16	

Table 16 Metal pick up studies at Indian Eastern coastal line

Sl.no	**Parameter**	**Sample-1 Port Blair CG jetty (Andaman)**	**Sample-2 Indira point (Nicobar)**
1	Substrate size (mm)	50x50x2	50x50x2
2	% Grafting	110	110
3	Alkalination	2 hrs using 5% NaOH	2 hrs using 5% NaOH
4	Submergence period (hrs)	550	570
5	Elution with 0.5M HCl	4 hrs at 60 deg.C	4 hrs at 60 deg.C
	Elute Analysis		
1	Uranium (ppm)	0.7	2.1
2	Uranium (mg)	.08	.12
3	Total uranium collection (mg)	0.2	

<u>Differential elution studies</u>:

Field trials were also carried out in Arabian seawaters at Trombay estuary in addition to desalination effluents of SWRO kalpakkam. The tokens were made from PP fiber aggregated by mechanical bonding into a felt of similar specifications as per other experiments. Differential elution Studies on Uranium pick up were also carried out. Figure 35 and 36 shows the vanadium and uranium pick up rates w.r.t desalination effluents and high seas respectively. The graph in figure 11 shows vanadium pick up for four samples and the average value observed. Desalination effluents have given vanadium pick up of up to 1200 ppb.

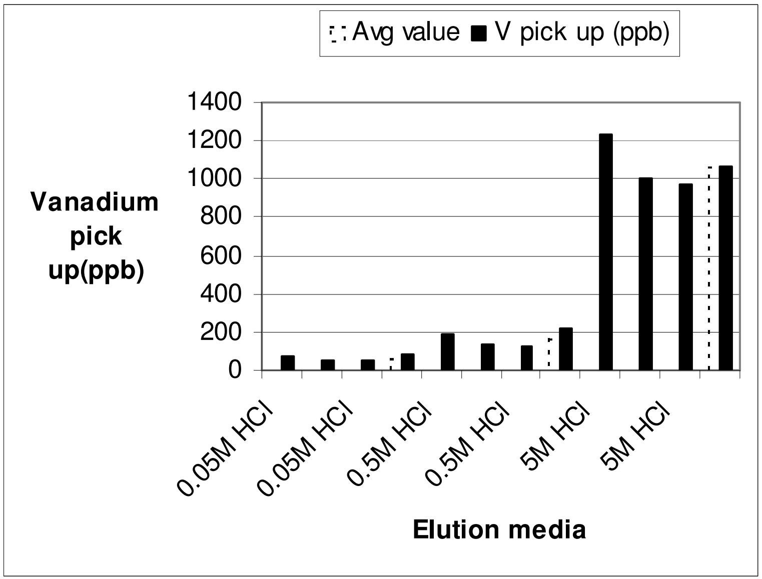


Fig 35 Differential elution studies for desalination effluents

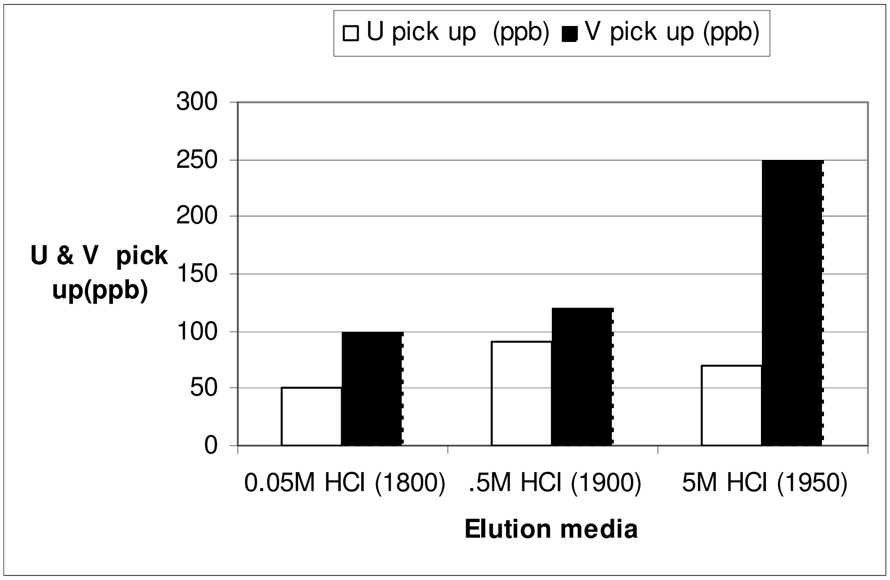


Fig 36 Differential elution studies for desalination effluents

Repeated usability under different A-S-E cycles:

The repeated usability of radiation grafted sorbent is very important aspect to optimise techno economic feasibility. The objective of this study is to evaluate pick up sorbent for various Alkalination-Submergence-Elution (A-S-E) cycles. The values observed under different ASE cycles are shown in figure-1 below. The data shows both for lab scale (LS) and pilot scale (PS) studies. The concentrated elute by evaporation is also plotted in terms of Concentration factors (CF). The uptake remains unaffected for 4-6 cycles. The samples are analysed using Nuclear analytical techniques for uranium and as well as ICP-MS methods for vanadium. Studies for further improvements are underway.

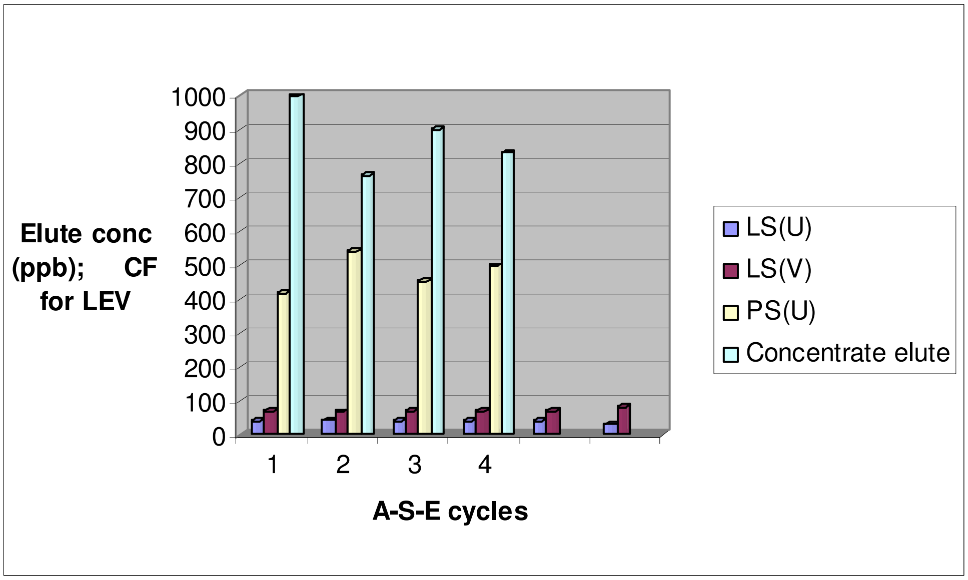


Fig 37 Repeated usability of radiation grafted sorbents

<u>Fouling factors assessment of various submergence conditions:</u>

The seawater is bio aggressive multi component feed. The feed solution conditions and fouling conditions has effect on the adsorptive properties of MCEP for uranyl ions. In case of uranium recovery from seawater, the functional groups existing on the surface layer are occupied by various kinds of metal ions and are quickly covered with dirt and bio growth. The fouling factor assessment was carried out at various locations both on bench scale and pilot scale levels and observations as shown in figure 38. The recovery of heavy metals depends on diffusion in bulk, in film and intra particle type of diffusion and as well as chemical reaction steps. The fouling factors observed for nuclear power plants and desalination plant conditions are lower than seawater conditions at high seas. The submergence period of beyond 12 to 13 days is not favorable for trombay estuary conditions due to more bio fouling and dirt fouling conditions.

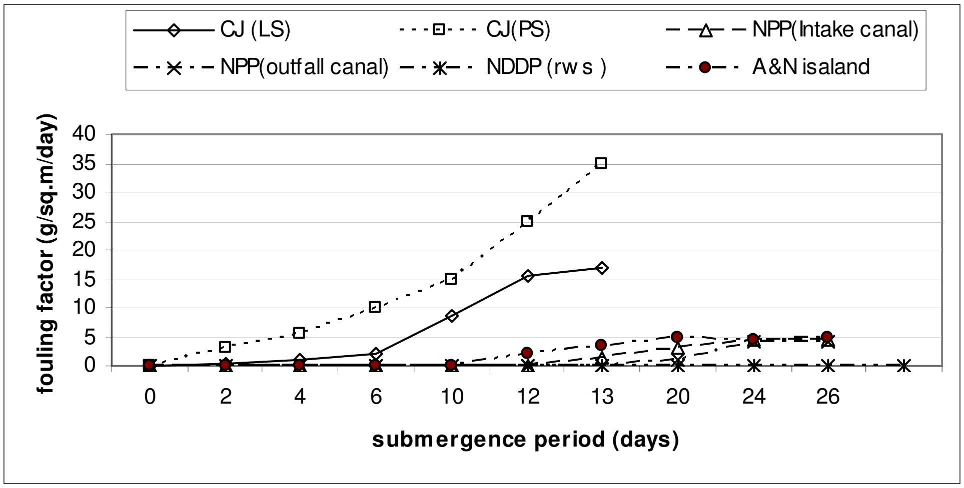


Fig 38 Fouling factor assessment for various in-field trials

Isotopic composition of recovered uranium from seawater:

The recovery of uranium from sea water is important in the field of energy production. The main problem is the low concentration of uranium and vanadium in the presence of other dissolved salts. The purpose of this investigation is to see the isotopic composition of recovered uranium heavy metal from seawater and also to get some measure of the relative purity compared to land resource. Additional information regarding the isotopic composition of uranium present in the precipitate samples was obtained by alpha spectrometry technique. The alpha spectrum profile is as shown in figure 39. It showed ^{234}U and ^{238}U in the activity ratio of 1: 1.03 i.e. the ratio observed for natural uranium in the environment.

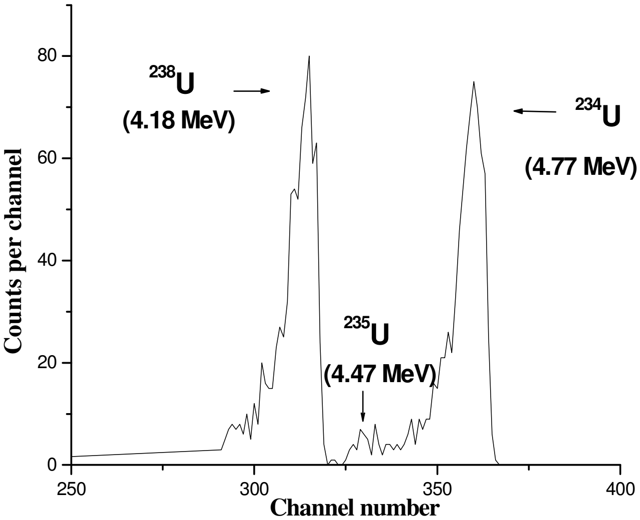


Fig 39 Alpha spectrum of recovered uranium from seawater

Chapter-8

Conclusions and Future work

8.1 Conclusions:

Various adsorbents including synthetic polymers, inorganic materials and bio polymers have been tested for uranium recovery from seawater. To date, the specially indigenized organic adsorbent PAO has shown promising results for recovery of uranium and other heavy metals from seawater. Pumped circulation schemes which were inherently riddled with negative electricity gain were abandoned. By harnessing tidal energy innovatively the advantage of positive energy gain ratio has been achieved. Feasibility studies on various sizes of pilot scales will help in optimization of process design parameters of adsorbent synthesis and improving the yield of recovered uranium.

- The adsorption kinetics is likely to follow a pseudo-second order model suggesting complex nature of the adsorption of uranyl ions. Both liquid-film mass transfer and intraparticle diffusion play important role in uranium transport from seawater to the porous adsorbent.
- Economical recovery of uranium is a challenge in view of lean nature of resource and bio-aggressive nature of multi-component feed.
- EB radiation grafted sorbents has offered advantages of easy preparation; reusability; sorption kinetics and selective desorption of uranium and vanadium.
- The three order of improvement in concentration factors for uranium has been achieved by repeated A-S-E cycles.
- Radiation grafting for synthesis of metal chelate embedded polymeric adsorbents is one of the important industrial application of ionizing radiations in future.
- The grafting levels of up to 130% to 150% have been achieved without much degradation of mechanical properties.
- Metal pick up characteristics established and CF of order 1000 is observed from initial concentration of 3.3 ppb on pilot scale. CF of order 30000 is observed for lab scale studies.
- The sorbent material developed and radiation grafting systems designed have given most optimum uranium pick up compared to any other materials reported in India under actual field trials.

- The repeated usability of sorbent is established both on lab scale and bench scale and given satisfactory performance for 5 to 6 A-S-E cycles.
- The alpha spectrum profile shows U234 and U238 in the activity ratio of 1:1.03, the ratio observed for natural uranium in the environment

The table 17 shows the comparison of salient features of adsorbent synthesized using radiation technique by various research groups.

Table 17 Comparison of Salient features of Radiation grafting levels reported by various researchers

Sl. no	**Researcher**	**Substrate types**	**Radiation source/ Dose**	**Grafting media**	**Degree of grafting**	**Remarks**
1	MH Rao and KN Rao India (1979)	PP	Co-60	AAc	40%	Surface modification of textiles
2	Omichi H and et al JAERI (1986)	PTFE- ethylene copolymer	Dynamitron (model IEA 3000-25-2)/ 10MRad	AAc-ACN	NA	Separation
3	Stannet et al Research Traingle institute (1990)	PVC	EB/ 5xe05 rad	Styrene	323%	Studies on rad grafting
3	Toshiya Takeda and et al; Univ of Tokyo T sugo and et al JAERI (1991)	Porous PE hollow fiber	EB	ACN	125%	Do
4	Song-Ho choi and et al South Korea (2000)	PE of 70 micron thickness; 20 x 50 mm size	Co-60/ 30 kGy		30%	Do
5	B Gupta and et al IIT Delhi (2006)	Monofilament PP of IPCL make 760 gpd	900 curie/ 0.27 kGy/hr	80% CAN & 20% DMF	10%	Bio medical applications
6	Our study	Mono filament and Bi-filament PP fibers; 300 to 500 GSM	EB of 2 & 1.25 MeV/ 200kGy	70% CAN & 30% dMF	130% (LS) 150% (BS)	Recovery of U from sea brine

The table 18 shows the comparison of salient features of metal pick up of radiation grafted adsorbent synthesized using radiation technique by various research groups for different submergence periods and flow velocties.

Table 18 Comparison of Salient features of metal pick up by various researchers

Sl.no	**Researcher**	**Bed length (cm)**	**Superficial velocity (cm/s)**	**Contact period (days)**	**Adsorption rate (g of U/kg)**
1	Astheimer et al (1983)	44	0.29-1.36	10	0.19
2	Omichi et al (1986)	50	0.044-0.44	10	0.14
3	GIRIS (1980)	0.3	0.34	10	1.8
4	Uezu et al (1988)	30	0.125-1	10	0.11
5	Saito et al (1988)	30	0.25-1	10	0.26
6	Saito et al (1990)	3	1	10	0.24
7	Toshiya Takeda et al (1991)	90	4	10	0.51
8	Our study	Leaflet size of 100 cm	Tide wave of 3M	12	0.6 to 1

Thus Uranium recovery from seawater has been brought very close to the economic exploitation point by concerted efforts. This progress in the technology development is extra ordinary even when viewed in comparison to the achievements of the global stalwart i.e. Japan in this technology. Very soon harvesting uranium from seawater should be comparable to the current mining costs and will create no eco-hassles in the surroundings.

8.2 Future work:

The research and development efforts on uranium uptake technology given good progress and some additional future perspectives are

8.2.1 Other valuable elements are present in seawater in potentially attractive concentrations and there is future perspectives as viable co-products.

8.2.2 Mixed matrix adsorbents combining useful features from both polymeric and inorganic materials could be a promising approach for uranium recovery. Various parameters such as pH, temperature, physico-chemical properties of adsorbent and flow rate of seawater affect adsorption kinetics; thermodynamics as well as transport rates.

8.2.3 Parallel developments are required on co-grafting to develop more hydrophilic materials and for special fiber development to have different surface morphology with higher unit surface area per unit mass of substrate.

8.2.4 Studies to improve grafting levels further without compromising mechanical characteristics of the substrate materials and controlling the viscosity of the grafting media.

8.2.5 Studies to improve the physical structure of the sorbent, at achieved grafting levels in the studies

8.2.6 Studies to improve hydrophilicity by co-grafting hydrophilic co-monomers and thereby enhance the metal pick up rates by catalyzing decomplexation of uranyl carbonate by hydrogen ions.

8.2.7 Bio-fouling is major issue to increase the submergence duration in bio aggressive feed like seawater. Studies to improve the bio-fouling factors and enhance the submergence duration at various sites

8.2.8 Studies to use fibres in rope form to enhance the grafting levels and pick up rates by facilitating covalent bonding of uranyl ions with functional groups.

8.2.9 Surface engineering of polymers by other techniques such as plasma techniques for enhancing the free radical generation rate.

8.2.10 Establish effective and non destructive regeneration methods. Studies on Fractional elution of alkali metals such as Lithium, which is of interest to DT fuelled fusion reactors.

8.2.11 High adsorption capacity can be achieved by enhanced physicochemical properties (i.e surface area, pore volume, pore size and high ligand density) Studies to increase the porous structure by using dichloroethane and chloroform as a porogen and introducing into the radiation grafted polymers.

8.2.12 To improve anti-bifouling properties of adsorbents by incorporating silver nano-particles, as this is beneficial in extracting uranium from seawater and minimize biofouling of adsorbent in the ocean environment

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Annexure 1

Publicatons in peer reviewed journals and awards related to Doctoral research

AN ENGINEERING SCALE STUDY ON RADIATION GRAFTING OF POLYMERIC ADSORBENTS FOR RECOVERY OF HEAVY METAL IONS FROM SEAWATER

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The ocean contains around eighty elements of the periodic table and uranium is also one among them, with a uniform concentration of 3.3 ppb and a relative abundance factor of 23. With a large coastline, India has a large stake in exploiting the 4 billion tonnes of uranium locked in seawater. The development of radiation grafting techniques, which are useful in incorporating the required functional groups, has led to more efficient adsorbent preparations in various geometrical configurations. Separation based on a polymeric adsorbent is becoming an increasingly popular technique for the extraction of trace heavy metals from seawater. Radiation grafting has provided definite advantages over chemical grafting. Studies related to thermally bonded non woven porous polypropylene fiber sheet substrate characterization and parameters to incorporate specific groups such as acrylonitrile (AN) into polymer back bones have been investigated. The grafted polyacrylonitrile chains were chemically modified to convert acrylonitrile group into an amidoxime group, a chelating group responsible for heavy metal uptake from seawater/brine. The present work has been undertaken to concentrate heavy metal ions from lean solutions from constant potential sources only. A scheme was designed and developed for investigation of the recovery of heavy metal ions such as uranium and vanadium from seawater.

KEYWORDS : Radiation Grafting, Uranium, Seawater; Non Woven Substrate, Engineering Scale Study

1. INTRODUCTION

The oean is the limitless reservoir of dissolved heavy metals in a well defined chemical environment [1,2]. Methods to extract these metals such as co precipitation, adsorption, ion floatation, solvent extraction have been suggested in the literature. An adsorption process using a suitable adsorbent seems to be a prominent method. During the seventies and eighties the possibilities of recovery of uranium from seawater were explored using inorganic adsorbents. The inorganic adsorbents have limitations on adsorption rate and have poor mechanical stability under marine conditions; as a result, investigations met with little success [3,4]. Numerous investigations have been carried out on organic adsorbents and have shown good uranium loadings [4-7]. Radiation grafting is an easy and highly efficient procedure for modifying the properties of polymeric substrates of synthetic as well as natural origin and offers some unique advantages over the conventional chemical grafting method [3,5,8].

A method based on ion exchange and in-situ chelating and extraction for the recovery of U and other heavy metals from seawater is proposed. The objective of this study is to investigate the selectivity of polymeric adsorbents for the extraction of valuable heavy metal ions directly from seawater under actual marine conditions. In-field demonstration experiments were carried out on the western coastline of India and as well as in intake and outfall canals of a nuclear power plant. The results are presented in this paper. The new extraction technology appears promising for exploring alternative sources of uranium such as seawater/brine [9-11]. These studies have focused on the synthesis of the Polyacrylonitrile amidoxime (PAO) class of chelating agents for possible metal extraction and optimization of the parameters for the same. The substrates were chosen because of their flexibility, commercial availability, and general applicability. Field trials have been carried out at multiple locations and data obtained is correlated and analysed w.r.t various factors such as uranium pick up rate, dirt fouling, bio fouling, submergence durations, temperature, concentration, advection of water body, tidal movements, etc. The post irradiation grafting technique is used to graft required functional groups to backbone polymers. A large number of parameters and variables are involved in radiation grafting and the effects of dose, dose rate, reaction duration, and co-solvent systems have been investigated in this study.

2. EXPERIMENTAL

2.1 Irradiation

Irradiations of substrate sheets were carried out using departmentally available 20 kW ILU-6 accelerators at beam energy of 1.8 MeV and beam current of 1.06 mA and using variable conveyor speed.

2.2 Grafting Procedure

Grafting reaction was carried out using a post irradiation technique, i.e. sheets were irradiated prior to immersing them in grafting solution. Electron beam irradiated substrate sheets were immersed in solution mixture of acrylonitrile and DMF at 60 ºC for three hours. Subsequently, the cross linked cyano groups were substituted with amidoxime groups. The quality assurance for grafting extent was done gravimetrically using the equation:

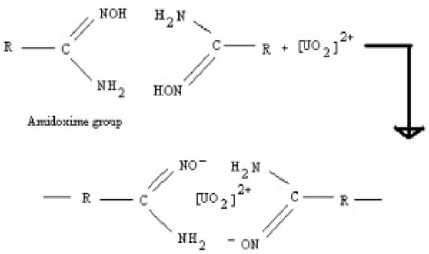
$$Grafting\% = ((W_g - W_i)/W_i)\ 100$$

where W_i, W_g are the weights of the sample before and after grafting.

2.3 Manufacture of Adsorbent on a Suitable & Optimized Substrate

During lab-scale experiments, many types of fiber cross sections and geometry were evaluated for their efficacy for grafting purposes. Polyester and polypropylene fiber materials were short listed for further experiments. Finally, experiments were done using polypropylene fiber of 1.5 denier cross section as stem material in non-woven felt form. Electron Beam Radiation induced grafting of acrylonitrile on the stem fiber was carried out to optimize the parameters for maximized grafting yields. The solution viscosity and temperature were also found to be important factors during conversion of grafted acrylonitrile into amidoxime. Conversion of grafted acrylonitrile into amidoxime was done. The PAO thus synthesized was conditioned with alkaline treatment to impart hydrophylicity and enhance adsorption characteristics. PAO was synthesized on the substrate as shown in Figure 1.

The adsorption mechanism as per stoichiometric conditions is as given in Figure 2. For every two molecules



Two amidoxime groups capture one uranyl ion

Fig. 2. Adsorption Mechanism of Metal Ions

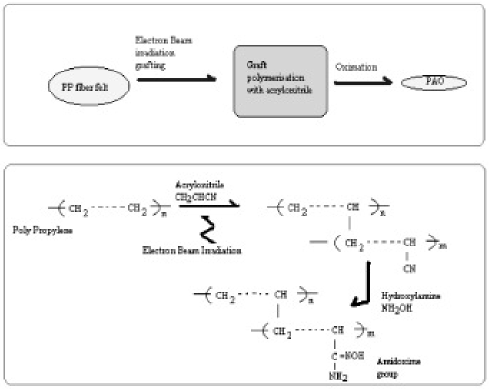


Fig. 1. Synthesis of Novel Adsorbent

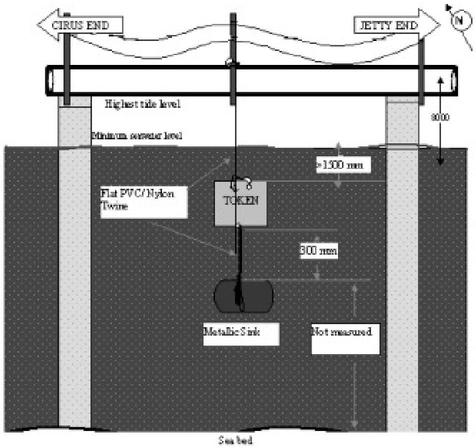


Fig. 3. Mooring Set up Details at CIRUS Jetty

of polyacrylamidoxime (PAO) one uranium atom is captured. Thus theoretically PAO should have an extraction capability of 3600 g U/kg of PAO [11].

2.4 Initial Experimental Campaigns

2.4.1 Trombay Estuary

First trails were carried out at lab scale at the Trombay estuary to establish the process and material parameters under actual marine conditions. The mooring of adsorbent tokens was done as per the details shown in Figure 3.

2.4.2 Experiments at Seawater Intake and Outfall Canals of Nuclear Power Plants

The Nuclear Power plant at Tarapur India was characterized to arrive at an optimum submergence period based on fouling factor assessment. The tokens were made from PP fiber aggregated by mechanical bonding into a felt of similar specifications as per the Trombay experiments. The size of each token was 150 × 150 × 2 mm.

3. RESULTS AND DISCUSSIONS

3.1 Characterization and Optimization of Substrate Sheets

3.1.1 FTIR Scans of Grafted Sheets

The FTIR spectra were taken for control and grafted substrate sheets to verify the grafting. An FT-IR spectroscopy study shows the extent of modification through change in characteristic peak intensities as listed in Table 1. Figure 4 shows the formation of cyano groups. The sharp absorbance band at ~2200 cm^{-1} is characteristic of $C\equiv N$, the cyano groups. The depletion of these groups during oximation supports the idea that conversion of $C\equiv N$ groups to $H_2N\text{-}C\text{=}NOH$ groups was almost completed.

3.1.2 Substrate Development

Five types of commercially available fiber compositions and geometries were evaluated for their suitability for grafting purposes. Mono and Multi component fibers

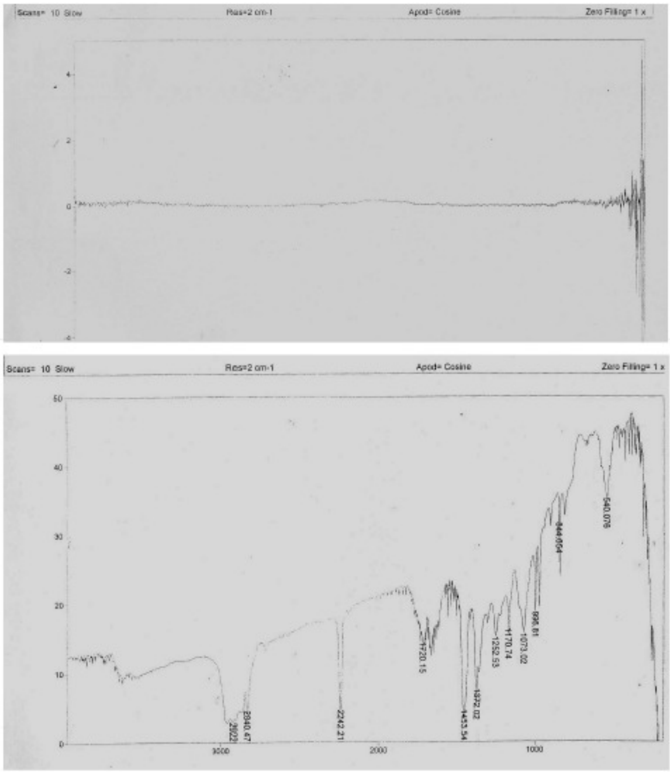


Fig. 4. FTIR Spectra of Non Irradiated Substrate Sheet and EB Irradiated Sheet

Table 1. The IR Frequency Bands of Characteristic Groups

Characteristic group	Frequency (1/cm)		Remarks
	PAN	AO-PAN	
ν (NH2), ν (OH)	-	3100-3600	ν =Stretching vibration
ν (CH2)	2950	2950	
ν (C≡N)	2260	2260	
ν (C=O)	1750	1740	
ν (C=N)		1670	
λ (NH2)		1610	λ = Scissors vibration
λ (CH2)	1460	1460	
λ (CH)	1380	1380	
ν (C-O-C)	1250	1250	
ν (C-O)	1080	1080	
δ (C-N)		1000-1150	δ = Bending vibration
ν (N-O)		920-940	
ν (C-CN)	780	780	

consisting of Polypropylene, Polyethylene, and Polyester materials were short listed for experiments. The non-woven fabric substrate materials available in the market, as detailed in Table 2, were characterized by Differential Scanning Calorimetry (DSC) and TGA methods at three different laboratories. DSC gives energy change of the various samples during transformation and TGA gives weight loss w.r.t temperature.

The chemical characterization of various substrate materials was carried out using scanning thermo analytical techniques such as Differential Scanning Calorimetry (DSC). The temperature difference between substrate sample and non reactive reference was determined as a function of temperature. The sample energy change during transformation was directly compared. The results of DSC endothermic peaks as reported by three independent laboratories for the five substrate materials are shown in Figure 5.

In addition to chemical characterization, the substrate samples of various makes were studied for radiation characterization. The assessment of various of the above substrate materials for radiation grafting was carried out and the results are as tabulated in Table 3.

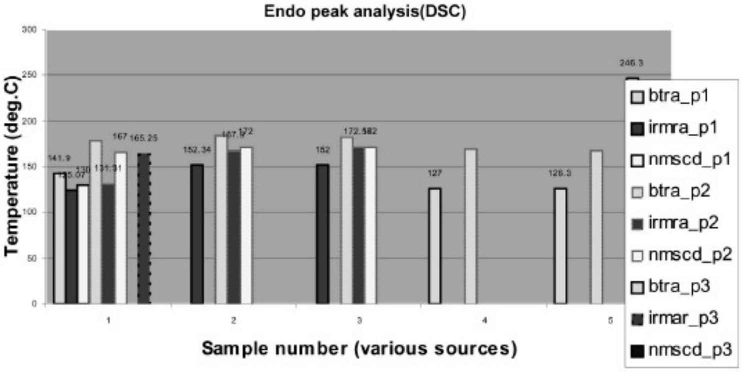


Fig. 5. Chemical Characterization of Substrate Sheets of Various Makes

Table 2. Substrate Materials Investigated

Parameter	Make-1	Make -2	Make -3	Make-4	Make-5
Fiber ∅ in micron	2-10	2-5	1-2	2-5	2-5
Thickness in g/m²	270	300	500	500	500
Nominal Bulk thickness	1.5 mm	1.5 mm	2 mm	2 mm	2 mm
Reinforcement Scrim	none	none	PP	PP	PP
Composition	PP/PE 80:20	PP	PP	PP/PE 80:20	PP/PE/Polyester 80:10:10
Cross section of fiber	Circular	Circular	Circular	Circular	Circular

PP= Poly Propylene, PE=Poly Ethylene

Table 3. Grafting Analysis PP Sample Substrates of Various Makes

PP substrate sample	I.W (g)	F.W (g)	% Grafting	Av. Value	Remarks
Old (1999)	2.6	4.807	84.88		
	1.2	2.287	90.58	87.73	500 gsm/scrim
Make-1	1.02	1.912	87.45098		
	.56	.943	68.39	77.92192	270 gsm
Make-2	1.07	1.842	72.14953		
	.39	.713	82.82051	77.48502	300 gsm
Make-3	2.03	4.044	99.21182		
	.78	1.396	78.97436	89.09309	500 gsm/scrim
Make-4	1.42	2.334	64.3662		
	.53	.851	60.56604	62.46612	500 gsm/scrim/bicomp
Make-5	1.23	1.796	46.01626		
	.52	.729	40.19231	43.10428	500 gsm/PEscrim/bicomp

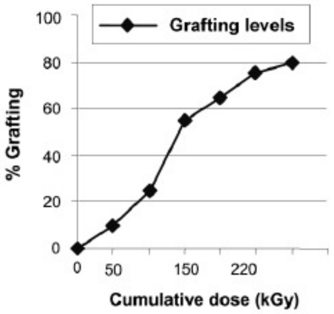


Fig. 6. Effect of Radiation Dose on Grafting Levels
(10kGy/pass)

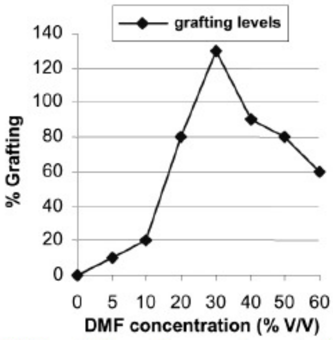


Fig. 7. Effect of Solvent Concentration on Grafting Levels
(at 55 °C)

3.2 Parametric Studies of Irradiation & Grafting of PP Sheets

3.2.1 The effect of Cumulative Dose on Radiation Grafting

Radiation induced processing is dependent both on cumulative dose and dose rates. Figure 6 shows the grafting yields as a function of the cumulative dose at a dose rate of 10 kGy/pass in air; reaction was carried out at 60 °C for three hours. The yields are increased with the dose up to 200 kGy and then leveling off is observed.

3.2.2 Effect of Solvent Concentration on Radiation Grafting

Phase separation occurs due to polymerization of acrylonitrile (AN) to poly-AN in pure acrylonitrile; this hinders further propagation of poly-AN on backbone polymer. Presence of solvent such as dimethyl formamide (DMF) reduces phase separation as poly-AN is soluble. Figure 7 shows the grafting yields as function of different proportions of acrylonitrile to DMF. Optimum solution viscosity is also an important factor to achieve higher grafting yield. The presence of DMF is beneficial up to 30% (v/v).

3.2.3 Effect of Oximation Duration on Grafting Yield

Figure 8 shows the grafting yield as function of reaction time. Yield gradually increases with reaction time and then leveling off is observed after four hours.

3.2.4 Effect of Solvent & Co Solvent System on Grafting Yield

Conversion of cyano groups to amidoxime groups is

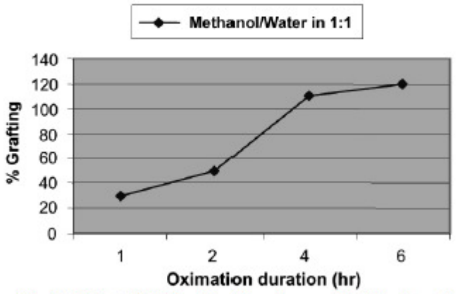


Fig. 8. Effect of Oximation Duration on Grafting Levels (*at* 55 °C)

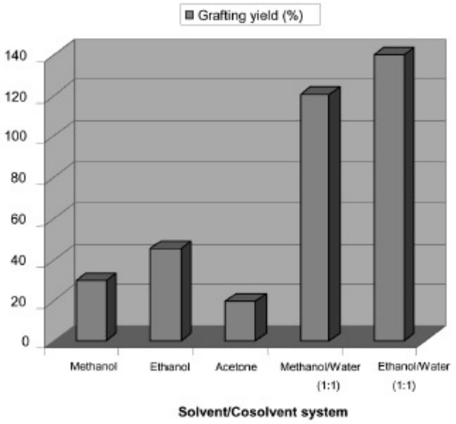


Fig. 9. Effect of Co-solvent Systems on Grafting Levels (*at* 55 °C)

Table 4. Campaigns 1 and 2 at Trombay Estuary

Parameter	Campaign-1	Campaign-2
Substrate mm	75 × 70 × 2	75 × 70 × 2
% Grafting	130%	130%
Alkalination	2-4 hrs	2-4 hrs
Submergence	260 hrs	260 hrs
Elution	2 hrs	2 hrs
Analysis of elute µg/ml		
Vanadium	0.06 to 0.2	0.02 to 1.5
Uranium	ND	0.35 to 0.93
Uranium collected µg/gm of PAO	ND	75.97

Table 5. Campaigns 3 and 4 at Trombay Estuary

Parameter	Campaign-3	Campaign-4
Substrate size mm	150 × 150 × 2	150 × 150 × 2
% Grafting	100%	100%
Alkalination	4 hrs	4 hrs
Submergence	400 hrs	366 hrs
Elution	2 hrs	2 hrs
Analysis of elute µg/ml		
Vanadium	0.5 to 3.3	0.61 to 0.87
Uranium	0.22 to 0.65	0.09 to 0.67
Uranium collected µg/gm of PAO	112 max	62
Total	800µg	

facilitated by presence of co-solvent systems. Some co-solvent systems were tried to see their effect on oximation yields and ease of grafting. The presence of suitable co-solvent system is beneficial, as seen in Figure 9. Alcohol and water systems at 1:1 volume basis have given better yields.

3.3 In Field Experimental Trials

3.3.1 At Trombay Estuary

Initial experimental campaigns were carried out on bench scale to establish the process and material parameters under actual marine conditions. The summary of the observations recorded are shown in Table 4 and Table 5. Corrosion, bio-fouling, and their combined effect on the adsorption kinetics and mechanical properties of the materials used in the suspension assembly and the substrate were studied and their compatibilities vis a vis seawater and temperature & concentration of process chemicals used were established. The submergence period was varied from ten days to fifteen days. The optimum period was observed to be around twelve days, beyond which bio-growth is greater and thereby mass transfer of heavy metals drops [12].

3.3.2 At Nuclear Power Plants

Experiments are also carried out at Tarapur Atomic Power Station Seawater intake and outfall canals. A study of fouling factor assessment was done. The Tarapur site was characterized to arrive at an optimum submergence period. The tokens were made from PP fiber aggregated by mechanical bonding into a felt of similar specifications as per Trombay experiments. The results are given below in Table 6. Studies of uranium pick up were also carried out. The observations and results are tabulated in Table 7.

Relatively less bio fouling was observed here compared

Table 6. Fouling Factor Assessment at TAPS 1&2 Seawater Intake & Outfall Canals

Sample no	Location	Sub mergence (hrs)	Fouling (gms)	% Loading	Remarks
Token-1	Discharge canal	330	5.737	30	Avg. ff for the token 2,3&4 = 4.15 g/sq.m/day
Token-2	-do-	330	3.658	16.9	
Token-3	-do-	570	3.061	16.9	
Token-4	-do-	570	4.719	17.9	
Token-5	Intake canal	330	2.872	21.8	Avg. ff for token 5,6&7 = 4.43 g/sq.m/day
Token-6	-do-	330	3.748	20.6	
Token-7	-do-	570	3.589	28.7	
Token-8	-do-	570	5.061	40.3	

Table 7. Uranium Pick-up Assessment at TAPS 1&2 Seawater Intake & Outfall Canals

Parameter	**Sample OX-1**	**Sample OX-2**	**Sample OX-3**	**Sample OX-4**
Substrate mm	85 × 159 × 2	93 × 162 × 2	90 × 163 × 2	90 × 163 ×2
% Grafting	105	105	105	105
Alkalination	2 hrs	2 hrs	2 hrs	2 hrs
Submergence	330 hrs Discharge canal	570 hrs Discharge canal	330 hrs Intake canal	570 hrs Intake canal
Elution	4 hrs at 60 °C	4 hrs at 60 °C	4 hrs at 60° C	4 hrs at 60 °C
Analysis of elute (ppm)				
Vanadium	1.4	Not analysed	1.4	Not analysed
Uranium	1.8	4.85	1.3	3.92
Total collection	**1.8 mg**			

to the Trombay estuary. The submergence periods of up to twenty days were done here before onset of bio-growth on the adsorbent tokens. Fouling factors of up to 4.43 g/m^2/day were observed for the submergence periods considered. Based on average value of uranium pick up rates, an improvement of 30% was observed for discharge canal compared to intake canal.

3.4 Pilot Scale Production of Adsorbent Sheets

Based on the initial success of extracting about 800 μg of uranium by harnessing the tidal wave using electron beam grafted amidoxime as adsorbent, a Process flow sheet for scaled up facility to extract 100gU/year has been developed. The process flow scheme and set up details for production of adsorbent sheets of size 1m by 1m is as shown in Figure 10. The material of construction used for reactor systems during initial pilot scale trials is polypropylene. The production capacity of scaled up facility is two adsorbent sheets per day. Inherent safety of grafting reactors has been achieved with deep bed designs, which render less surface area for evaporation and suppresses the vapor formation. The major unit processes are: Electron-Beam Irradiation of the substrate; Grafting of acrylonitrile; Dissolving of excess monomer & drying; Oximation; Alkalination; Submergence in sea; Retrieval from sea; Defouling; Elution and Conversion to yellow cake.

Substrate materials of adequate strength and quality were selected based on chemical and radiation characterization of various makes used during bench scale trials. The properties of substrate material are as shown in Table 8. The reduction in bursting strength after grafting is about 40%. Performance studies of the grafted sheets in assembled condition are being carried out.

4. CONCLUSIONS

Radiation grafted polymeric adsorbents are synthesized at bench scale and some of the parameters, such as dose, dose rate, and duration were established. The metal sorption characteristics were evaluated through bench scale field trials. Grafting levels of up to 130% were achieved during bench scale studies. Infield trials have shown optimum submergence period of twelve days for the prevailing

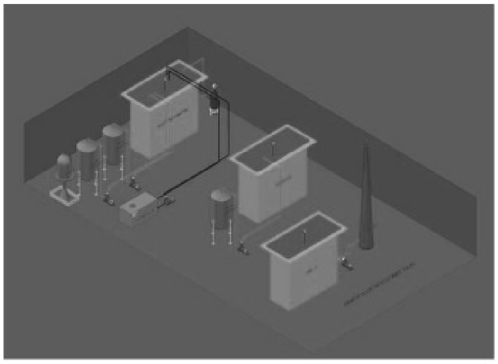


Fig. 10. Pilot Scale Facility for Synthesis of Adsorbent Sheets

Table 8. Properties of Substrate Material for Pilot Scale Udies

Sl.no	Parameter	Description
1	Material	Polypropylene (PP)
2	Form	Non woven thermal bonded fabric
3	Width	1000 mm
4	Length	1000 mm
5	Bulk thickness	1.8 mm
6	Weight	300 gsm
7	Fiber size	1 denier
8	Air permeability	250 L/dm^2/min/20mm WC
9	Bursting pressure	30 kg/cm^2
10	Service temperature	95 ℃
11	Specific surface area	0.33 m^2/g

conditions of the western coastline of India and submergence period of twenty days for outfall canals of nuclear power plants. Fouling factors of up to 4.43 g/m^2/day were observed for the submergence periods studied for Intake/outfall canals of Nuclear power plant. We demonstrated the successful grafting of adsorbent sheets of a larger size of 1m by 1m in the pilot scale facility with uniform grafting levels. The specially indigenized organic adsorbent has shown promising results for recovery of uranium and vanadium from seawater.

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Parametric Studies on Radiation Grafting of Polymeric Sorbents for Recovery of Heavy Metals from Seawater

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Uranium and vanadium are valuable trace metals in seawater. The economic viability of recovery of these metals depends on development of efficient sorbents. The radiation induced graft polymerization technique was adopted in this study to prepare metal chelate embedded polymers in sheet form in order to investigate the recovery the heavy metals from seawater, using different nonwoven substrate materials. In order to obtain more direct information on the grafting levels, the parametric studies to see the influence of cumulative dose, retention time in air, surrounding atmosphere, and reaction temperature on grafting yields were investigated using different electron beam energies. The grafted sorbents were verified by infrared spectroscopic measurements, and thermal properties were analyzed by scanning calorimetric methods. Metal sorption characteristics for uranium and vanadium were evaluated through in-field trials at seawaters of the Andaman and Nicobar Islands, Indian Ocean, and Arabian Sea along Indian coastal lines.

1. Introduction

Researchers are taking renewed interest in the development of technology for extraction of valuable species from solids or solutions of ultralow concentrations.[1−10] Also there is a need to remove trace contaminants during environmental remediation. The viability of such a process depends largely on the technology employed, which needs to be highly selective and energy efficient in order to compensate for the ultralow concentrations of valuable species. Recent advances in synthesis of novel adsorbents and ion exchange materials are causing a paradigm shift in separation science. The current trend in research and development studies shows that at present, "radiation grafting on polymers" is developing in the direction of polymeric adsorbents as one of the key areas of application. Grafting polymerization is a valuable method for the modification of chemical and physical properties of polymeric surfaces. Ionizing irradiations,[11] ultraviolet,[11] ozone,[12] plasma,[9] and chemical initiators are some of useful methods for grafting polymerization. Grafting is used in situations where the requirements for bulk and surface properties cannot be readily provided using a single polymeric material. Radiation grafting has made it possible to construct a material whose bulk is made of one polymer type but whose surface is made of a different polymer type.[11−22] A chemical bond is formed between the grafted moiety and the material. Radiation provides a highly advantageous means of grafting.[9,12] Free radicals are produced in the irradiated substrate material without the use of chemical initiators. Also electron beam irradiation eliminates the concern over the sensitivity of reaction catalysts to temperature. More efficient grafting techniques need to be developed to reduce the manufacturing cost of radiation grafted polymeric adsorbents. Higher selectivity and more efficient adsorption properties can be imparted with proper selection of ligands and controlling the functionality of grafted chains.

Considering the large numbers of parameters and variables involved in radiation grafting, some more results have been reported here in addition to the results reported earlier.[9,10] No or little attempts have been made in separation technology, for this range of lean concentrations. In this study, the effect of parameters such as cumulative dose, retention time, surrounding atmosphere, reaction temperature, and duration were investigated to obtain information on the grafting yields, using different electron beam energies of 2 and 1.25 MeV. The other objective of this study is to investigate the selectivity of metal chelate embedded polymers (MCEP) for the extraction of valuable heavy metals such as uranium and vanadium directly from seawater under actual marine conditions. The results of in-field bench scale demonstration experiments that were carried out at seawaters of the Andaman and Nicobar Islands, Indian Ocean, and Arabian Sea along Indian coastal lines[2,9] are also presented in this paper. Differential elution studies that were carried out in order to study the desorption behavior of heavy metals from the sorbents are also presented. The investigations for uranium pick up studies on an engineering scale and as well as repeated usability of sorbent sheets have also been carried out.

2. Experimental Section

2.1. Reagents. Most of the reagents used are analytical grade for lab-scale studies and commercial grade (Numex chemicals Mumbai India) for bench-scale studies. The supplied chemicals are used without any further purification. Uranyl nitrate (Merck Mumbai India) solutions at different concentrations required for lab-scale studies were prepared by a stock solution of concentration 500 ppb using low total dissolved solids (TDS) water of desalination plants. Caustic flakes were used for pH adjustment of oximation and alkalination solutions.

2.2. Irradiation. Irradiation of substrate sheets was carried out using linear accelerators under the following conditions:

For ILU-6 accelerators

Beam energy = 2.0 MeV, current = 1.06 mA, and variable conveyor speed

For DC accelerators

Beam energy = 1.25 MeV, current = 1.0 mA, and variable roller speed

2.3. Grafting Procedure. A grafting reaction was carried out using a post irradiation technique i.e. sheets were irradiated prior to immersing them in grafting solution. The electron beam

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Table 1. Surface Area of Polypropylene Fiber Substrate

sl no.	parameter	rounded value	units	computed value
1	size of fiber	1.0000	denier	
2	denier	1.0000	g/9000 yd	
		2.8000	μg/in.	
		0.0001	g/m	
3	substrate weight	300.0000	g	
4	length of fiber	3000000.0000	m	3000000
5	density of fiber	910.0000	kg/m^3	
6	volume of substrate	0.0003	m^3	0.00032967
7	diameter	0.0000107	m	1.07075×10^{-5}
		0.0107	mm	0.010707459
8	actual surface area available	100.0000	m^2	100.8642652
		0.3360	m^2/g	0.336214217

Table 2. Apparent Porosity of Polypropylene Fiber Substrate

sl no.	parameter	rounded value	units	computed value
1	apparent thickness of fiber	1.0000	mm	
2	substrate weight	300.0000	g/m^2	
3	bulk density	910.0000	kg/m^3	
4	actual thickness	0.2700	mm	0.32967033
5	apparent weight/mm	910.0000	g/m^2	910
6	apparent porosity	70.0000	%	67.03296703

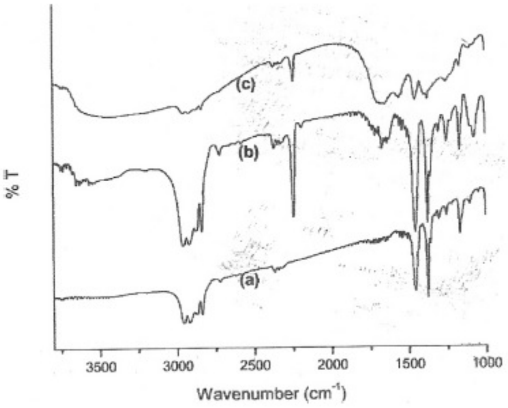

Figure 1. FTIR for control (a), grafted (b), and oximated (c) samples.

irradiated substrate sheets were immersed in a solution mixture of acrylonitrile and dimethylformamide (DMF) in 70:30 ratios at 55−60 °C for 3 to 4 h. Subsequently, the cross-linked cyano groups were substituted with amidoxime groups. The quality assurance for grafting extent was done gravimetrically using the equation:

$$\text{grafting } \% = ((W_g - W_i)/W_i) \times 100$$

Where W_i, W_g are the weights of the sample before and after grafting.

2.4. Manufacture of Adsorbent on a Suitable and Optimized Substrate. During lab-scale experiments, many types of fiber cross sections and geometry were evaluated for their efficacy for grafting purposes. Bifilament polypropylene (PP) fiber materials of 300 and 500 g/m^2 (grams per square meter: GSM) were short-listed for further experiments. The calculated values of surface area and porosity for the substrate materials considered are shown in Tables 1 and 2 below. Finally experiments are done using polypropylene fiber of a 1.5 denier cross section as stem material in nonwoven felt form (Supreme non wovens Mumbai India). Electron beam radiation induced grafting of acrylonitrile on the stem fiber was carried out using different energy beams to optimize the parameters for maximized grafting yields.

2.5. In-field Experimental Campaigns. 2.5.1. Andaman and Nicobar Islands. In-field trails were carried out on the bench scale at the seawaters of the Andaman and Indian Oceans to establish the metal sorption characteristics and as well as process and material parameters under actual marine conditions. The mooring of adsorbent tokens was done as per details mentioned elsewhere.[9] Short-listing of sites out of 541 islands in the Andaman and Nicobar Islands (AN) has been done with the cooperation from the UT administration and coast guard. Seven sites were selected and reached along with their officers. Indira point is the southern-most tip of our country protruding into the Indian Ocean. It is 6.7° N of the equator. The sizes of tokens used were 100 mm × 100 mm × 2 mm.

2.5.2. Trombay Estuary. In-field experiments were also carried out on the lab scale at the Trombay estuary to establish the process and material parameters under actual marine conditions. A study on the differential/fractional elution of heavy metals of interest was also carried out. The mooring of adsorbent tokens was done as per the details mentioned in our previous paper.[10]

3. Results And Discussions

3.1. Characterization and Optimization of Substrate Sheets for Radiation Grafting. The type and nature of substrate materials plays a role in both achieving higher grafting yields and influencing the metal complex formation. Functional groups may be attached to the substrate through various surface chemistries. The microenvironment created around the ligand is an additional factor in ionic selectivity. The elucidation of the mechanism by which the supporting matrix influences complex formation may enable new and more efficient methods of metal separation. Various characterization methods are being followed, and the details are as follows:

3.1.1. FTIR Scans of Grafted Sheets. The Fourier transform infrared (FTIR) spectra were taken using an FTIR-8400S Shimadzu for control and grafted substrate sheets to verify the grafting. An FTIR spectroscopy study shows the extent of modification through change in characteristic peak intensities. Figure 1 shows the spectrum for control, grafted and oximated samples, and the formation of cyano groups. The sharp absorbance band at around ~2200 cm^{-1} is characteristic of C≡N, the cyano groups. The depletion of these groups during oximation supports the idea that conversion of C≡N groups to $H_2N-C=NOH$ groups almost completed.

3.1.2. DSC Analysis. The chemical characterization of various substrate materials was carried out using scanning thermoanalytical techniques such as differential scanning calorimetry (DSC). Scanning thermoanalytical techniques are being used for characterizing the changes occurring in samples. The thermograms were taken for control and grafted sheets to observe the changes occurring due to grafting. The temperature difference between substrate sample and nonreactive reference is determined as a function of temperature. The sample energy change during transformation is directly compared. Figure 2 given below shows the DSC thermograms of control, grafted, and oximated substrate sheets. DSC thermograms having endothermic peaks at temperatures of 166 and 171 °C were observed for 300 and 500 GSM, respectively, corresponding to the T_m of polypropylene, 160−175 °C.

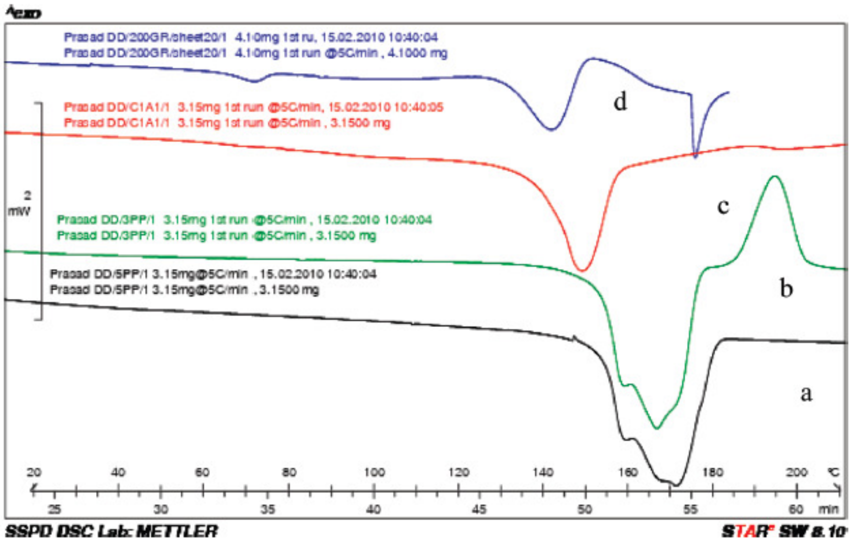

Figure 2. DSC for (a) control sample (500 GSM); (b) control sample (300 GSM); (c) oximated sample; (d) grafted sample.

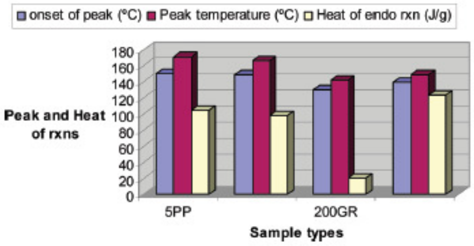

Figure 3. DSC characteristics for control, grafted, and oximated samples.

Endothermic peak occurred at reduced temperature of 149 °C compared to control samples shown above due to formation of cyano groups. Overall comparative DSC characteristics of control samples, grafted samples, and oximated samples are as shown in Figure 3 below.

3.2. Parametric Studies on Irradiation and Grafting of PP Sheets. 3.2.1. Effect of Radiation Dose and Atmosphere on Radiation Grafting of PP Sheets. The postirradiation grafting can be carried out in two different ways. The intention of this investigation was to see the effect of type of free radicals and amount of free radicals available for grafting. The formation of peroxides on the substrate surface supports the grafting process. The air atmosphere has given better levels of grafting at temperatures between 55 and 60 °C. Figure 4 shows the grafting yields observed in different atmosphere as a function of cumulative dose. The maximum grafting achieved in a nitrogen atmosphere is only up to 25%. In an air atmosphere, the formation of trapped free radicals is helped, and these can be used for carrying out grafting at higher temperatures. This shows that peroxy radicals play an important role in achieving good grafting levels.

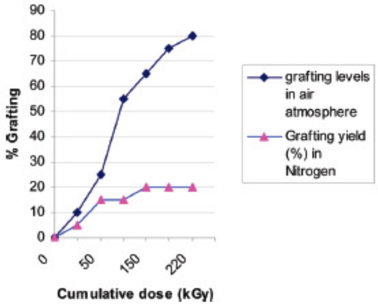

Figure 4. Effect of radiation dose and atmosphere on radiation grafting of PP sheets.

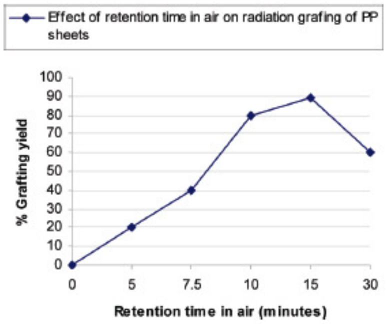

Figure 5. Effect of retention time in air on radiation grafting of PP sheets.

3.2.2. Effect of Retention Time in Air on Radiation Grafting of PP Sheets. Radiation grafting is similar to oxidation phenomena, and free radicals are used to initiate and continue with the grafting polymerization process. The formation of peroxides on the substrate surface supports the grafting process. An air atmosphere has given better levels of grafting at temperatures between 55 and 60 °C. Figure 5 below shows the grafting yields as a function of the retention time in air at a cumulative dose of 200 kilo Gray (kGy) at a dose rate of 10

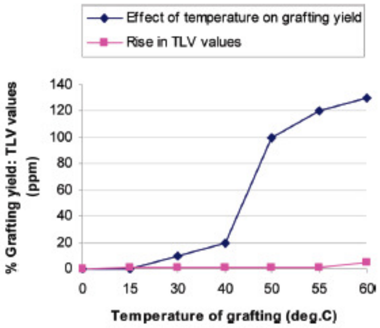

Figure 6. Effect of temperature on radiation grafing yields of PP sheets.

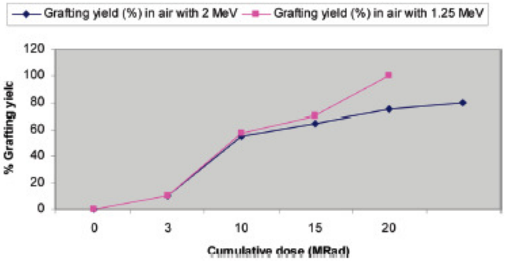

Figure 7. Effect of cumulative dose on grafting yields.

kGy/pass in air, and the reaction was carried out at 60 °C for 3 h. The yields are increased with the retention time up to 15 min, and then, a drop off is observed. After a certain retention time, losses of free radicals are expected due to recombinant phenomena. A few more studies are being planned using different energy beams also.

3.2.2. Effect of Temperature on Radiation Grafting Levels of PP Sheets. Postirradiation grafting is a typical chemical reaction involving radicals. The intention of this investigation was to see the effect of temperature for grafting. Figure 6 below shows the grafting yields as a function of the grafting temperature at a cumulative dose of 200 kGy at a dose rate of 10 kGy/pass in air. The reaction was carried out for 3 h. The yields are increased until the boiling temperature of the media is reached. The graph also shows the rise in threshold limit values (TLV) for acrylonitrile vapors, measured at breathing levels in the operating area. For safe operation, temperatures are established accordingly for regular pilot scale operations.

3.2.3. Effect of Cumulative Dose on Radiation Grafting. Figure 7 shows the grafting yields as a function of the cumulative dose. Experiments were carried out in an air atmosphere, and the reaction was carried out at 60 °C for 3 h. The trends shows the effect of cumulative dose on grafting yields at a dose rate of 10 kGy/pass in the case of 2 MeV energy beam and at a dose rate of 10 kGy/min in the case of 1.25 MeV energy beam. As shown by trend lines, the yields are increased with dose up to 200 kGy. Furthermore, some more studies are being planned using different energy beams to see the change in mechanical properties with respect to (wrt) different cumulative doses.

3.3. In-field Experimental Trials. Experimental campaigns were carried out on the bench scale to establish the process and material parameters under actual marine conditions. Corrosion, biofouling, and their combined effect on the adsorption kinetics and mechanical properties of the materials used in the suspension or contactor assembly and the substrate were studied. And, their compatibilities with seawater and temperature and concentration of process chemicals used were established. Fractional elution studies were done to investigate the differential desorption behavior of heavy metals such as uranium and vanadium.

3.3.1. At the Andaman and Nicobar Islands. Out of the large Indian coastal line, the Andamans and Lakshadweep Islands are locations in which good depths are available near shore lines and seawater has extremely low turbidity coupled with good turbulence and advection of the water body.

Seven sites out of 541 islands available were short-listed in the AN. Plain as well as polyacrylamid oxime (PAO) loaded tokens were placed in position and later retrieved after different submergence periods. Seawater samples from different locations are also collected and analyzed for uranium content and analytical results (reported by various laboratories using different techniques) are as shown in Table 3. Assistance from Union Territory Administration and Coast Guard Services was obtained for acquaintance with local marine topography, weather, and ocean current patterns over the years and movement logistics. The summary of the observations recorded are shown in Table 4. The submergence period was varied up to 30 days. Even after 28 days of submergence, the Great Nicobar sites were found to be the cleanest with respect to all the sites investigated so far. A total of ~200 μg of uranium was collected from two sites. Specific loadings up to 160 μg/g of sorbent in 25 days are observed. Four independent laboratories, viz. ACD, HPD, RChD, and EAD of Bhabha Atomic Research Centre, Trombay, India, have given confirmation of the uranium collection, though there is a sizable difference in the results.[23]

3.3.2. At Trombay Estuary. Experiments were also carried out in Arabian seawaters at the Trombay estuary along the western coast line of India. The site was characterized to arrive at an optimum submergence period. The tokens were made from PP fiber aggregated by mechanical bonding into a felt of similar specifications as that of other experiments. Differential elution studies on uranium pick up were also carried out. The results are given below in Table 5 and Figure 8. Relatively more biofouling was observed here compared to at the AN. The

Table 3. Analysis of Seawater Samples from AN at the Eastern Coastal Line of India

		uranium (ppb)		
sl no.	sample code	lab-1 alpha-spectrometry technique (IDD/BARC)	lab-2 anodic splitting voltametry technique (EAD/BARC)	remarks
1	CI-1		1.78	CG jetty Port Blair
2	PB-1	2.31 ± 0.37	2.74	Pigeon bay island
3	TB-1	3.07 ± 0.40	2.34	Trinket bay
4	SB-1	3.15 ± .41	2.27	Singha bay
5	BI-1	2.62 ± 0.36	1.87	Barren island
6	IP-1		2.15	Inidra point
7	HT-1		2.16	

Table 4. Metal Pick up Studies at Indian Eastern Coastal Line

sl no.	parameter	sample-1 Port Blair CG jetty (Andaman)	sample-2 Indira point (Nicobar)
1	substrate size (mm)	50 × 50 × 2	50 × 50 × 2
2	% grafting	110	110
3	alkalination	2 h using 5% NaOH	2 h using 5% NaOH
4	submergence period (h)	550	570
5	elution with 0.5 M HCl	4 h at 60 °C	4 h at 60 °C
	elute analysis		
1	uranium (ppm)	0.7	2.1
2	uranium (mg)	0.08	0.12
3	total uranium collection (mg)	0.2	

Table 5. Differential Elution Studies for Uranium and Vanadium Recovery from the Trombay Esturary

token no	location	duration (d)	wt of tokens taken for elution (g)	elute media (M HCl)	elute volume (mL)	V pick up (ppb)	U pick up (ppb)	remarks
A1	cirus jetty	15	100	0.05	1800	100	50	analysis by ACD
A1	cirus jetty	15	94.69	0.5	1900	120	90	do[a]
A1	cirus jetty	15	88	5	1950	250	70	do[a]

[a] do = as above.

submergence periods, up to 12 d, could be done here before the onset of biogrowth on the adsorbent tokens.

The fouling factors observed at the AN and Trombay estuary were 5 and 35 g/m^2·d, respectively. On the basis of the average value of uranium pick up rates, good improvement of metal pick up by an order of magnitude was observed for the AN compared to the Trombay estuary. This may be attributed to the high diffusion mobility conditions existing there due to the reduction in dirt fouling and biofouling. Also there is better accessibility of $[UO_2(CO_3)_3]^{4-}$ to a large number of binding sites and thereby better complexation of UO_2^{2+} with amidoxime groups. Both mass transfer and chemical reactions play a role in controlling mechanisms of adsorption processes.

3.4. Engineering Scale Studies on Radiation Grafted Adsorbent Sheets. On the basis of the success of extracting uranium in micro- and milligram levels by harnessing the tidal wave using electron beam radiation grafted amidoxime as an adsorbent, the process flowsheet for a scaled up facility to extract 100 g uranium/y has been developed. The process flow scheme and setup details for production of adsorbent sheets of size 1 m × 1 m were given in our earlier reports.[2,10] The substrate materials of adequate strength and quality were selected based on chemical and radiation characterization of various makes of substrate sheets used during bench scale trials. The reduction in bursting strength after grafting is about 40% for 300 GSM substrate sheets. Radiation grafted polymeric sorbents of size 1 m × 1 m were produced using substrate sheets of 300 GSM, and the grafting levels observed are as shown in Table 6 below. Grafting is done using electron beam energy of 2 MeV and to a total dose of 200 kGy. Performance studies in assembled conditions are being carried out by loading the radiation grafted sheets into the contactor assembly, specially designed for the purpose. The mooring facility for engineering-scale studies is as shown in Figure 9 below. Ten sheets of 1 m × 1 m are loaded into each of contactor assembly, and submergence is carried out for a duration of 13 d at the Trombay estuary. The uranium pick up rate observed is calculated, and the results are as shown in Table 7 below. The repeated usability of MCEP (metal chelate embedded polymers) is a very important aspect to optimize technoeconomic feasibility. The objective of this study is to evaluate sorbent capacity for various alkalination−submergence−elution (ASE) cycles. The values observed under different ASE cycles are shown in Figure 10. The sorbent capacity remains unaffected for 4−5 cycles. Studies for further improvements are underway.

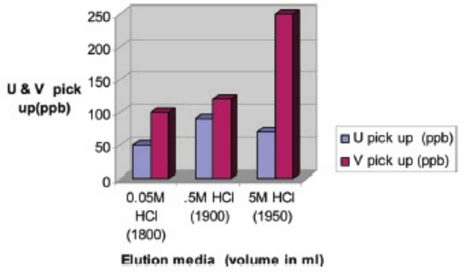

Figure 8. Differential elution studies for uranium and vanadium recovery from the Trombay esturary.

Table 6. Engineering-Scale Studies on Radiation Grafting (size 1 m × 1 m)

sheet no.	temperature (°C)	heating duration (min)	grafting %
PP-1	60	180	14.29
PP-2	60	180	6.70
PP-3	60	180	21.42
PP-4	60	180	21.42
PP-5	60	180	46.67
PP-6	60	180	73.33
PP-7	60	180	40.00
PP-8	60	180	93.75
PP-9	60	180	56.25
PP-10	60	180	112.5

4. Conclusions

The parametric studies to see the influence of cumulative dose, retention time, surrounding atmosphere, and reaction temperature were established to obtain information on the grafting yields, using different electron beam energies of 2 and 1.2 MeV. The selectivity of MCEP's for the extraction of uranium and vanadium directly from seawater under actual marine conditions were confirmed by in-field bench scale

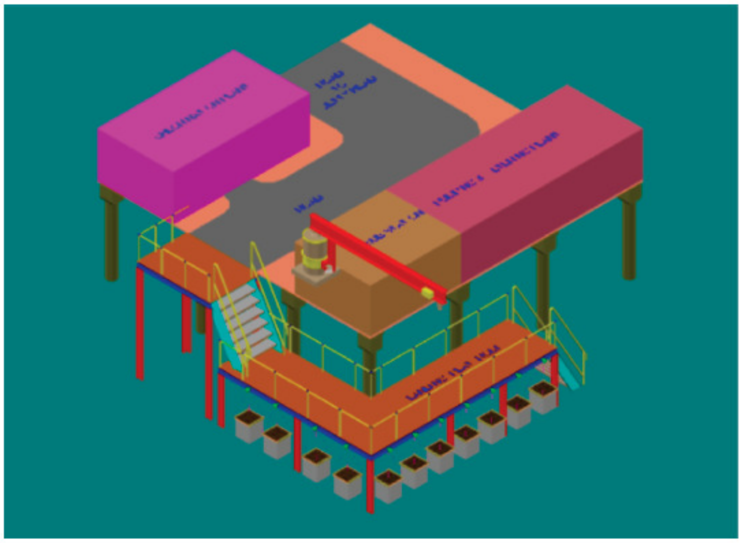

Figure 9. Submergence facility at Trombay estuary for pilot-scale studies.

Table 7. Uranium Sorption Capacity Observed for Engineering-Scale Studies at Trombay Estuary

sl no.	parameter	value	unit	remarks
1	initial weight of 10 sheets	3.24	kg	10 sheets per contactor assembly
2	weight of grafted sheets	6.26	kg	
3	% of grafting	93.21		
4	weight of PAO at 50% conversion	1.51	kg	
5	concentration of uranium in elute	511	μg/L	
6	volume of elute	1800	L	
7	total uranium in elute	0.9198	g	
8	uranium pick up rate	0.6091	g/kg	
		0.112	g/kg	value observed for lab-scale studies

demonstration experiments that were carried out in Andaman seawater and the Indian Ocean of the Andaman and Nicobar Islands and as well as Arabian seawaters of the Trombay estuary. Differential elution studies confirmed the desorption behavior of heavy metals from the metal chelate embeded polymers. Grafting yields of up to 110% were achieved during bench-scale studies on a substrate sheet of 300 GSM and of size 1 m × 1 m. In-field trials have shown an optimum submergence period of 12 d for the prevailing conditions of the western coastline of India and a submergence period of 28 d for the AN. Engineering-scale studies have given improved pick up rates compared to lab-scale studies, and the repeated usability of sorbent sheets established for 4−5 ASE cycles. The specially indigenized metal chelate embedded polymers with amidoxime groups have been found chemically suitable for recovery and separation of heavy metals from seawater.

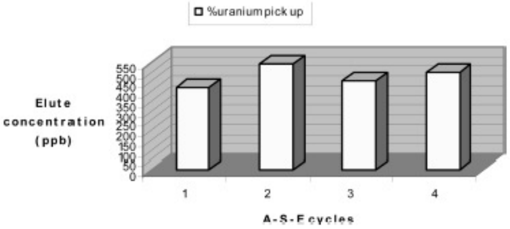

Figure 10. Studies on repeated usability of radiation grafted sorbents at Trombay estuary.

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Sorption kinetic studies using metal chelate embedded polymers for recovery of heavy metals from desalination effluents

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Abstract: The heavy metals, such as uranium and vanadium, are some of the valuable metals in desalination effluents. Metal Chelate Embedded Polymers (MCEP) in leaflet form were prepared using the post-irradiation induced graft polymerisation technique, with different non-woven thermally bonded fibrous substrate materials. The novel sorbents, synthesised by using accelerator energy beams of 1.25 MeV and 2 MeV, were characterised for their radiation, chemical and mechanical characteristics. The novel sorbent was evaluated under different parametric conditions, in order to study the influence of grafting levels, initial concentration, dissolved solids and contact time. The standard isotherm and diffusion models were fitted to the experimental sorption data and model parameters were evaluated. The sorption characteristics of MCEP for recovery of heavy metals such as uranium and vanadium from desalination effluents were investigated.

Keywords: electron beam accelerator; nuclear desalination plant effluents; seawater; radiation grafting; metal chelate embedded polymers; uranium; vanadium.

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1 Introduction

Desalination effluents are moderately electrolytic solutions and contain different metal ions. The ratio of product water recovery to input seawater entering the battery limits of the plants varies from 12% to 35% depending on the desalination technique adopted. During the desalination process, the reject water streams get concentrated and rich in sensible heat (in thermal desalination processes) as well. There is a good scope for recovery of metals such as uranium, vanadium, rubidium, cobalt, etc. Researchers are taking renewed interest in the development of technology for extraction of valuable species from seawater/brine which is of ultra low concentrations (Egawa et al., 1990; El-Naggar et al., 1993; Kabay and Egawa, 1993; Abbasi and Streat, 1994; Ghafourian et al., 1998; Choi and Nho, 2000; Prasad, 2006; Someda, 2006; Prasad, 2009; Prasad et al., 2009). The concentration change of uranium in desalination effluents is only about 1.4×10^{-8} mol/litre to 2.1×10^{-8} mol/litre depending on the type of desalination plant. Uranium and vanadium principally exist in the form of $UO_2(CO_3)_3^{4-}$ and $VO_2(OH)_3^{2-}$, respectively and are anionic coordination compounds with high solubility. Even though the concentration of uranium is low, the total annual amount of uranium in various effluents of typical Indian facilities is as shown in Table 1.

The viability of such a process depends largely on the technology employed, which needs to be highly selective and energy efficient in order to compensate for the ultra low concentrations of valuable species. 'Radiation grafting on polymers' is developing in the direction of polymeric adsorbents, as one of the key area of application. Radiation grafting has made it possible to construct a material whose bulk is made of one polymer type but whose surface is made of a different polymer type (Guthrie and Kotov, 1989; Gawish et al., 1992; Fujimoto et al., 1993; Kostov and Atanassov, 1993; Nho et al., 1993;

Pansare et al., 1994; Kubota, 1995; Chaplin et al., 1996; Sahiner et al., 1999; Hui et al., 2004; Caykara et al., 2007; Contreras-Garcia et al., 2008). A chemical bond is formed between the grafted moiety and the material. Radiation provides highly advantageous means of grafting (Fujimoto et al., 1993; Prasad, 2009). Free radicals are produced in the irradiated material without the use of chemical initiators. Also Electron Beam (EB) irradiation eliminates the concern over the sensitivity of reaction catalysts to temperature. More efficient grafting techniques needs to be developed to reduce the manufacturing cost of radiation grafted polymeric adsorbents. Higher selectivity and more efficient adsorption properties can be imparted with proper selection of ligands and controlling the functionality of grafted chains. In this study, radiation grafting is investigated further, using different electron energy beams of 1.25 MeV and 2 MeV and various non-woven thermally bonded substrate materials.

Table 1 Uranium potential in various facilities

Type of plant facility	*Seawater intake/condenser cooling water (m^3/h)*	*Uranium potential (kg/yr)*
Madras Atomic Power station Unit 1 & 2	22,600	~600
Tarapur Atomic Power Station Unit 1 & 2	85,000	~2200
Tarapur Atomic Power Station Unit 3 & 4	230,000	~6000
Kudankulam		
Atomic Power Station unit 1 & 2	360,000	~11,800
MED –MVC desalination	1000	~25
Nuclear Demonstration Desalination Plant Kalpakkam	2000	~50

In India feasibility studies for large-scale desalination plants are being carried out by many public and private enterprises to meet the future needs. The desalination plants currently under operation and planned in the country have reject streams with potential of about 1 tonne uranium per year in them. Few attempts have been made in this range of concentrations. Field trials and other sorption kinetic studies have been carried out using metal chelate embedded polymers for the purpose of developing the concept of Coupling of Recovery of Uranium from Desalination plant Effluents (CRUDE) for value addition. Differential elution studies were also carried out to study the desorption behaviour of heavy metals from the sorbent. The results are presented in respect of both desalination effluents and seawater as well.

2 Materials and methods

2.1 Reagents

Most of the reagents used were analytical grade for lab-scale studies and commercial grade for bench-scale studies. The chemicals were used without any further purification. Uranyl nitrate solutions of different concentrations required for lab-scale studies were prepared by a stock solution of concentration 500 ppb using low TDS water of desalination plants. Caustic flakes were used for pH adjustment of oximation and alkalination solutions.

2.2 Irradiation

Irradiation of substrate sheets was carried out using electron beam accelerators under the following conditions:

For ILU-6 accelerators:

Beam energy = 2.0 MeV, current = 1.06 mA and variable conveyor speed.

For DC accelerator:

Beam energy = 1.25 MeV, current = 1.0 mA and variable roller speed.

2.3 Grafting procedure

Grafting reaction was carried out using a post-irradiation grafting technique, i.e. sheets were irradiated prior to immersing them in grafting solution. The electron beam irradiated substrate sheets were immersed in solution mixture of acrylonitrile and DMF in 70:30 ratio at 55 to 60°C for 3 to 4 hours. Subsequently the cross-linked cyano groups were substituted with amidoxime groups. The quality assurance for grafting yield was done gravimetrically using the equation:

$$\text{Grafting\%} = ((W_g - W_i)/W_i) \times 100$$

where W_i, W_g are the weights of the sample before and after grafting.

2.4 Manufacture of adsorbent on a suitable and optimised substrate

During lab-scale experiments, many types of fibre geometry and GSM (grams per square metre) were evaluated for their efficacy for radiation grafting purposes. Bifilament Polypropylene fibre materials of 300 GSM and 500 GSM were shortlisted for further experiments. Finally experiments were done using bifilament polypropylene fibre of 1.5 denier cross-section as stem material in non-woven felt form. Electron beam radiation induced grafting of acrylonitrile on the stem fibre was carried out using various accelerators to optimise the parameters for maximised grafting yields.

2.5 Bench-scale experimental campaigns

2.5.1 Nuclear Desalination Demonstration Plant (NDDP) Kalpakkam

In-field trails were carried out on bench scale at SWRO (Sea Water Reverse Osmosis of capacity 1.8 MLD) reject streams of Nuclear Demonstration Desalination Plant (NDDP the hybrid plant of capacity 6.3 MLD) Kalpakkam, India, to establish the metal sorption characteristics as well as process and material parameters under actual field conditions. The mooring of adsorbent tokens were done as per the details mentioned elsewhere (Prasad, 2009). The sizes of tokens used were $100 \times 100 \times 2\ \text{mm}^3$.

2.5.2 Trombay estuary

Trial runs were also carried out on lab scale at Trombay estuary to establish the differential/ fractional elution of heavy metals under actual marine conditions. The mooring of adsorbent tokens were done as per the details mentioned in our earlier paper (Prasad et al., 2009).

3 Results and discussions

3.1 Characterisation and optimisation of substrate sheets

The type and nature of substrate plays a role in both achieving higher grafting levels and influencing the metal complex formation during sorption process. The substrate material consists of non-woven materials which are porous media consisting of fibres or filaments oriented mainly in the x, y directions according to the method of fabrication. The pore size distribution of non-woven materials is particularly important in respect of transport phenomena within the structure. Functional groups may be attached to the substrate through various surface chemistries. The micro environment created around the ligand is an additional factor in ionic selectivity. In our studies four types of polymer fibres such as polystyrene (PS), polytetrafluoroethylene (PTFE), polyethylene (PE) and polypropylene (PP) were considered to investigate the radiation grafting characteristics. The observed results are as shown in Table 2. PS and PTFE showed most radiation resistant since absorbed energy was converted into heat by aromatic rings. Radiation yield of radicals is limited. In PE and PP the alkyl radicals are formed and undergo oxidation. And formed peroxy radicals are very stable. PP has given favourable grafting yields and considered for further work.

Table 2 Radiation characteristics of various substrate polymer fibres

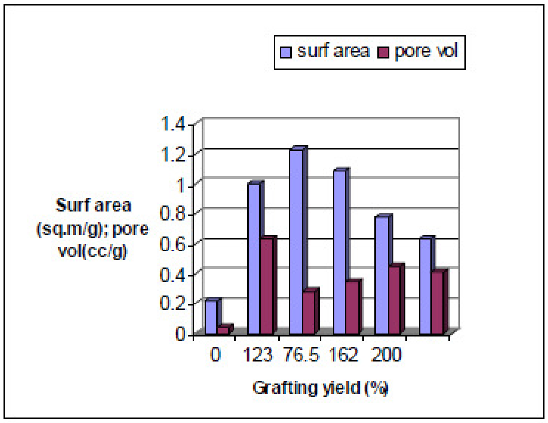
S.No.	*Polymer type*	*Grafting technique*	*Dose (kGy)*	*Size of tokens (mm × mm)*	*Irradiation atmosphere*	*Solution*	*Grafting yield (%)*
1	Polystyrene	Post-irradiation with EB	200	50x50	air	70:30 CAN:DMF	2
2	PTFE	do	do	do	do	do	5
3	Polyethylene	do	do	do	do	do	40
4	Polypropylene	do	do	do	do	do	79

The physical, chemical and mechanical characterisations of the novel radiation grafted sorbents were carried out using modern techniques. The chemical characterisation using FTIR spectroscopy and Differential Scanning Calorimetry (DSC) were as reported in our earlier paper (Prasad et al., 2010). The physical and mechanical characterisations are as presented in following sections.

3.1.1 Physical characterisation of grafted sheets

Adsorption and ion exchange processes are influenced by diffusion of metal ions, surface interaction mechanism and presence of surface functional groups on sorbent. Hence surface area (100 × m^2/g) and pore volume (cm^3/g) are estimated by gas adsorption method. The characteristics of radiation grafted and chemical grafted sorbents are as shown in Figure 1. For comparison purpose, the value of surface area (63.3 m^2/g) reported for chemical grafted biosorbent, made of tamarind fruit shell is also presented, along with radiation grafted sorbent. Radiation grafting has given good improvement of surface area of up to 300% for differently radiation grafted (0–200%) sorbents compare to control non grafted sample.

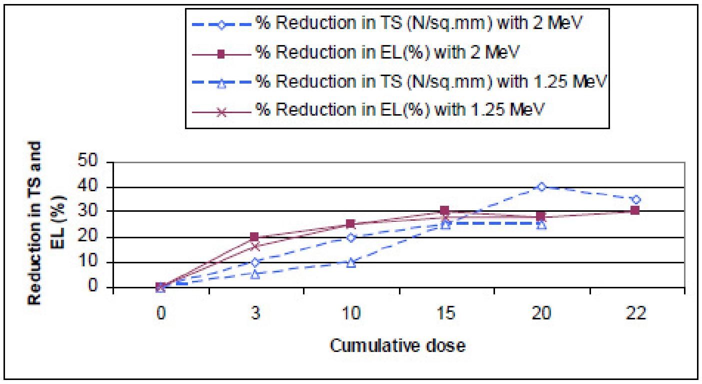
Figure 1 Surface area and pore volume of radiation grafted sorbents (see online version for colours)



3.1.2 *Mechanical characterisation of grafted sheets*

During multiple Alkalination-Submergence-Elution (A-S-E) cycles, it is important to maintain the mechanical strength of grafted sheets. Characterisation of grafted sheets in respect of mechanical properties such as tensile strength and elongation at break were carried out. Figure 2 shows the mechanical property degradation with respect to cumulative dose. The trends show effect of cumulative dose on mechanical properties of substrate and grafted tokens at a dose rate of 10 kGy/pass in case of 2 MeV energy beam and at a dose rate of 10 kGy/minute in case of 1.25 MeV energy beam. The yields are increased with the dose upto 200 kGy and then levelling off is observed. A reduction of 25–40% is observed in case of tensile strength and 30% in case of elongation at break, for the conditions of study range.

Figure 2 Mechanical characterisation of grafted sheets (see online version for colours)

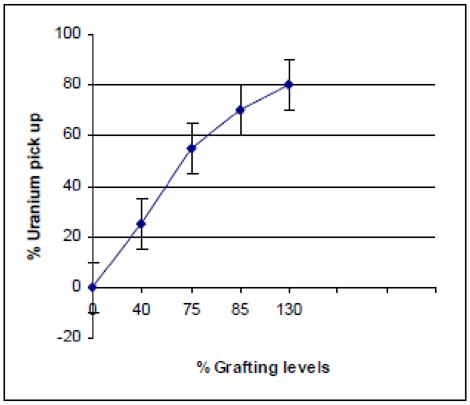


3.2 Parametric studies on sorption characteristics of MCEPs

3.2.1 Effect of grafting levels on heavy metal uptake

The effect of grafting levels on the removal of heavy metals such as uranium was studied using differently radiation grafted sorbents in the range of 0–150%. The percentage uptake found to increase with increasing grafting levels as shown in Figure 3. Between 80% and above the percentage uptake increments observed are less steep. Initial investigations concludes that 80% and above grafting levels give sufficient removal efficiency. Studies are underway for further improvement.

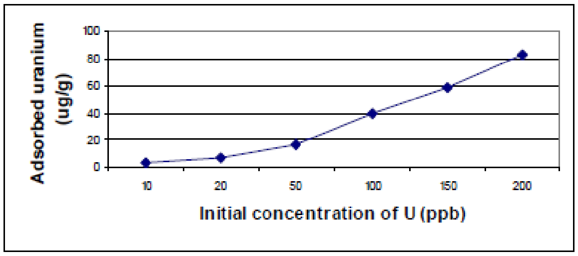
Figure 3 Effect of grafting levels on heavy metal uptake (see online version for colours)



3.2.2 Effect of initial concentration of uranium on metal pick up of MCEPs

The influence of the concentration of uranyl nitrate in the ranges of ppb on the adsorption capacity of uranium was studied using 0.2031 g of Polyacrylo Amide Oxime (PAO) sorbent. The adsorption capacity increases rapidly with concentration as shown in Figure 4. Similar trend was reported by Zhang et al. (2003). The concentration ranges used by other researchers are in the range of ppm. The uptake is function of initial concentration and kinetics vary accordingly.

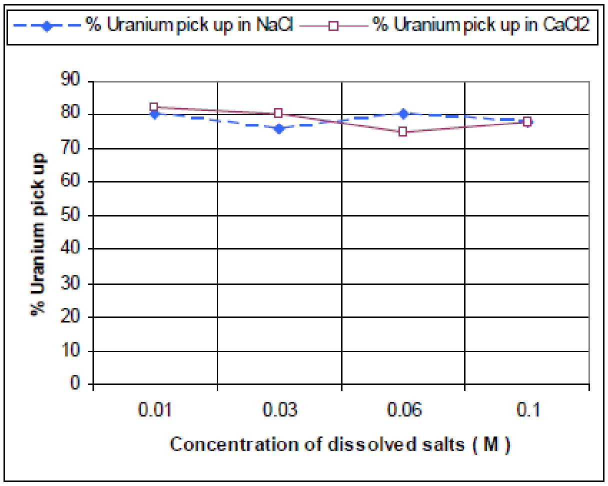
Figure 4 Effect of initial concentration on heavy metal uptake (see online version for colours)



3.2.3 Effect of dissolved solids on heavy metal sorption

Due to seasonal changes in seawater conditions, the TDS (Total Dissolved Salts) varies and hence it is interesting to see the effect of this parameter under lab-scale conditions. The objective of this investigation is to see effect of dissolved salts on sorption characteristics of radiation grafted adsorbents. The salts of sodium in the range of 0.1–1 M and calcium in the range of 0.01–0.1 M were studied. The results shown in Figure 5 reveal variation of 75–80% pick up only in the study range. Presence of these salts has not affected the sorption characteristics. Slight variation can be attributed to the change in diffusion layer around the surface of grafted sorbents.

Figure 5 Effect of dissolved salts on heavy metal uptake (see online version for colours)



3.2.4 Modelling of adsorption phenomena by single parameter isotherms

This study is aimed to investigate the adsorption behaviour of uranyl ion onto radiation grafted adsorbents. Adsorption isotherms are curves which relate the amount of adsorbate adsorbed per unit mass of adsorbent to the amount of unabsorbed adsorbate remaining in the solution at equilibrium. It is very difficult to get isotherms for seawater as much longer time is required to achieve equilibrium. Single parameter models such as Langmuir and Freundlich isotherms were used to analyse sorption phenomena. The correlation coefficients observed were 0.7816 and 0.9722 respectively. The values of constants indicate favourable conditions for adsorption. Freundlich isotherm model is fairly satisfactory empirical isotherm and can be used for non-ideal sorption that involves heterogeneous adsorption. Figure 6 shows the experimental data fitted as per Freundlich isotherm. The Freundlich isotherm predicts that the adsorption of metal ion on the sorbent increase so long as there is an increase in the metal ion concentration. The model parameters for Langmuir and Freundlich isotherms are as shown in Table 3 below. As the value of $1/n < 1$, it indicates favourable adsorption.

Figure 6 Modelling of experimental data using single parameter isotherm (see online version for colours)

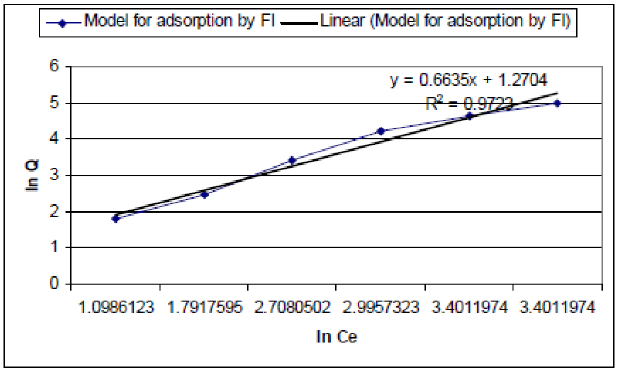


Table 3 Isotherm model parameters

S.No.	*Parameters*	*Values of regression analysis*	*Values of model parameters*	*Remarks*
Langmuir isotherm				$R^2 = 0.7816$
1	slope	0.0296	KI = 0.5778	
2	intercept	0.0513	Q_m = 19.993 ppb; KL = 0.2	
Freundlich isotherm				$R^2 = 0.9722$
1	slope	0.6635	Intensity of adsorption, $n = 1.50715$	
2	intercept	1.2704	$K_f = 3.56227$	

3.3 In-field bench-scale experimental trials

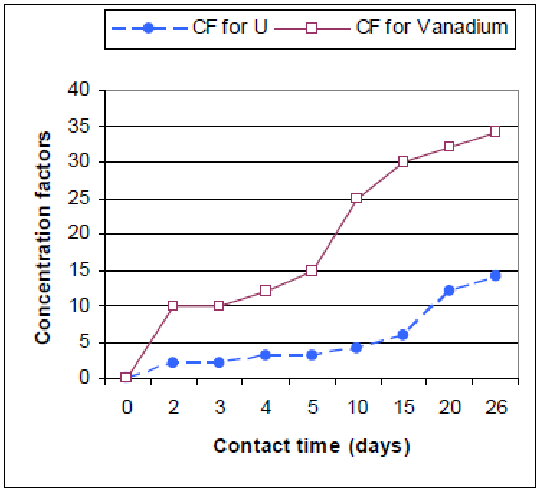
Experimental campaigns were carried out on bench scale to establish the kinetic parameters under actual brine stream and as well as marine conditions. Fractional elution studies were also done to investigate the differential desorption behaviour of heavy metals.

3.3.1 At Nuclear Desalination Demonstration Plant, Kalpakkam

3.3.1.1 Effect of contact time on concentration factors from desalination effluents

The recovery of uranium from sea water is important in the field of energy production. The main problem is the low concentration of uranium and vanadium in the presence of other dissolved salts. Contact time plays important role due to this consideration. The purpose of this investigation is to see the effect of contact time on concentration factors achievable for desalination effluents and also to get some measure of the relative performance of sorbent in kinetic terms. The adsorption profile was obtained in terms of concentration factors. The concentration factors are calculated as ratio of concentration of heavy metal in eluted solution to concentration of heavy metal in seawater/brine. Figure 7 shows that sorption after certain threshold value and then increases with time till saturation value is obtained. Similar trends were observed by Saito et al. (2000). The data shows threshold value of 4–5 days for uranium. This long time may be related to more hindrances to complex diffusion for final immobilisation. Afterwards it facilitates formation of donor-acceptor complexes between metal ions and amidoxime groups and the polar sites of the sorbent.

Figure 7 Effect of contact time on heavy metal uptake in terms of concentration factors (see online version for colours)



3.3.1.2 *Modelling of diffusion mechanism and sorption kinetics*

Adsorption kinetics is usually controlled by different mechanisms. Most limiting are diffusion mechanisms. Initial curved portion is attributed to rapid external diffusion or boundary layer diffusion and surface adsorption and the linear portion is (a gradual adsorption stage) is due to intra particle type of diffusion. This is followed by plateau to equilibrium where the intra particle diffusion starts to decrease due to low concentration in solution as well as fewer available bonding sites. Weber and Morris model helps in characterisation of intra particle diffusion using the specific sorption q and square root of time as $q = K_{id} \times sqrt(t)$ where q is amount of adsorbed per unit mass of adsorbent at time t and K_{id} is the intraparticle diffusion rate constant. Figure 8 is a plot of mass of heavy metals adsorbed per unit mass of adsorbent versus *sqrt*(t) and shows deviation of straight lines from the origin. So intraparticle transport is not the rate-limiting step. The process may be controlled by reaction kinetics and complex formation at the internal binding sites. Weber Morris parameters for various regressions are as shown in Table 4. The rate constant for vanadium is higher than that for uranium.

Figure 8 Modelling of diffusion mechanism for desalination effluents (see online version for colours)

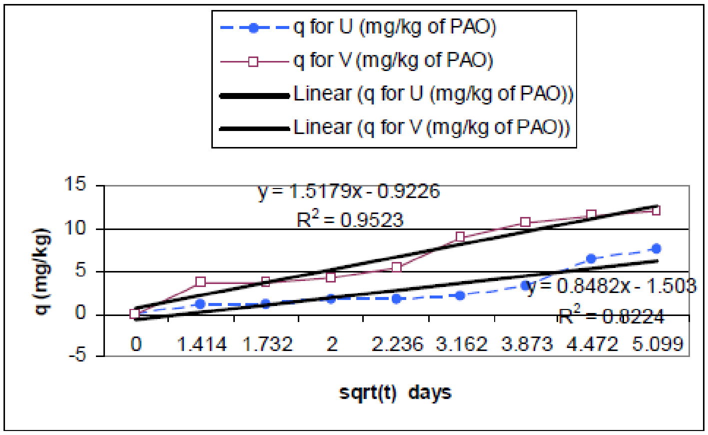


Table 4 Weber Morris parameters for diffusion model

Location/Conditions	*Heavy metal*	*K_d without inter cept*	*Correlation coefficient*	*K_d with intercept*	*Correlation coefficient*
NDDP Kalpakkam	Uranium	0.6109	0.7409	0.8482	0.8224
	Vanadium	1.3722	0.9412	1.5179	0.9523

The order of sorbate and sorbent interactions can be described by using various kinetic models. In case of sorption preceded by diffusion through a boundary, the kinetics in most cases follows pseudo first-order rate equation of Lagergren. The integrated rate law after applying initial conditions $q_t = 0$ at $t = 0$ is $\ln(q_e - q_t) = \ln(q_e) - (k_{ad}) \times t$. The q_t and q_e are amount sorbed at time t and at equilibrium respectively. The plot of $\ln(q_e - q_t)$ versus t gives straight line for first-order kinetics. In order to determine the order and rate of radiation grafted sorbent, tokens of size 100 mm × 100 mm were submerged into reject brine sump of NDDP plant effluents. To identify the suitability of rate equation, the second-order rate equation is also applied for the present data and the plots of t/q_t versus t are drawn for uranium and vanadium sorption. The pseudo first- and second-order Lagergren rate equation plots are as shown in Figures 9 and 10, respectively. So pseudo first-order equation better explains the interactions of uranium onto the radiation grafted sorbent. The Lagergren rate equation parameters are as shown in Table 5.

Figure 9 Lagergren first-order rate model for sorption in desalination effluents (see online version for colours)

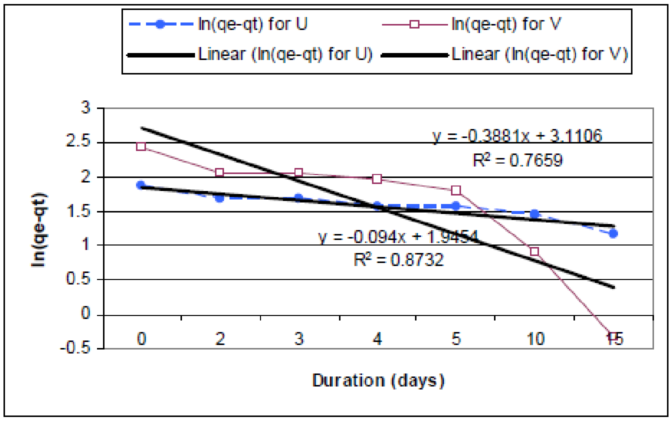


Figure 10 Lagergren second-order rate model for sorption in desalination effluents (see online version for colours)

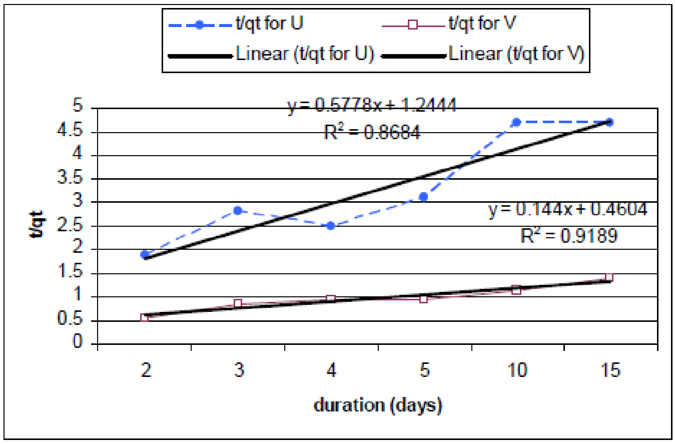


Table 5 Lagergren rate equation parameters for sorption kinetics

	For first-order kinetics					*For second-order kinetics*				
	Slope (k_{ad})	*Intercept ($\ln q_e$)*	*q_e (mg/kg of PAO)*	*k_{ad} (1/day)*	*R^2*	*Slope ($1/q_e$)*	*Intercept ($1/kq_e^2$)*	*R^2*	*k (kg/mg/day)*	*q_e*
for U	0.094	1.9454	6.9964	0.094	0.8732	0.5778	1.2444	0.8684	0.268	1.73
for V	0.3881	3.1106	22.435	0.3881	0.7659	0.144	0.4604	0.9189	0.045	6.94

3.3.2 Differential elution studies

Field trials were also carried out in Arabian seawaters at Trombay estuary in addition to desalination effluents of SWRO Kalpakkam. The tokens were made from PP fibre aggregated by mechanical bonding into a felt of similar specifications as per other experiments. Differential elution studies on uranium pickup were also carried out. Figures 11 and 12 show the vanadium and uranium pickup rates w.r.t. desalination effluents and high seas respectively. The graph in Figure 11 shows vanadium pickup for four samples and the average value observed. Desalination effluents have given vanadium pickup of up to 1200 ppb.

Figure 11 Differential elution studies on desalination effluents of NDDP Kalpakkam (see online version for colours)

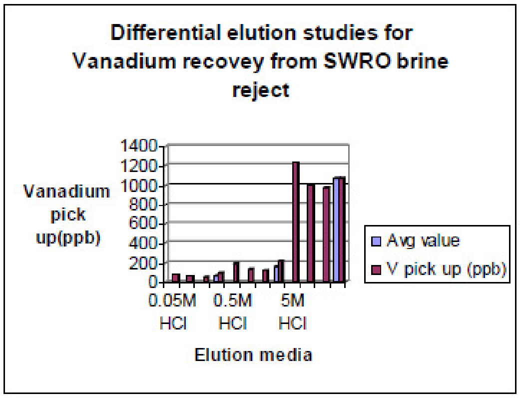
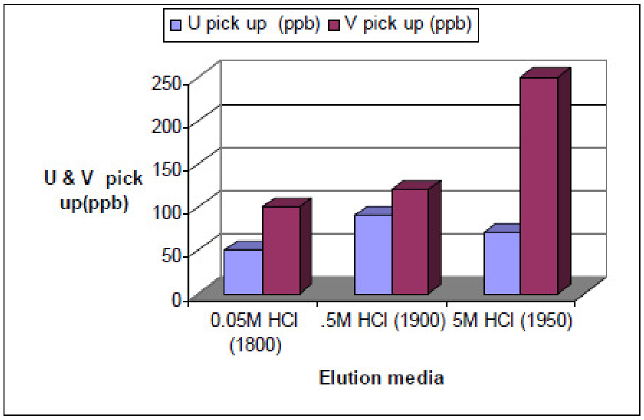


Figure 12 Differential elution studies with high seas at Trombay estuary (see online version for colours)



3.4 Coupling of Recovery of Uranium and other valuables from Desalination Effluents (CRUDE) of desalination plants

Based on the success of extracting uranium in microgram (µg), milligram (mg) and gram (g) levels by harnessing the tidal wave as well as flow streams of desalination effluents, using electron beam grafted amidoxime as adsorbent, the conceptual process scheme for scaled up facility CRUDE to extract 3 kg of uranium per annum has been developed. The substrate material of adequate strength and quality were selected based on chemical and radiation characterisation of various makes used during bench-scale trials (Prasad et al., 2010). The details for 'compact and pressure drop free' Contactor Assembly (CA) of size 4 m × 4 m × 1 m have been worked out to house 480 grafted sorbent sheets. The typical process design details of project CRUDE are as shown in Table 6.

Table 6 Typical process design details for Project CRUDE

S.No.	*Item details*	*Quantity*	*Conceptual details*
1	Radiation grafted PAO sorbent	3 tonnes	Loading factor of 0.1 g/kg PAO/cycle
2	Stem material	5 tonnes	300 GSM non-woven sheets
3	No of contactor assemblies	30	16 modules of 1 × 1 × 1 m^3 in one CA
4	No of units to be handled per day	3	
5	Life of substrate	20 cycles	
6	Total cycle time	20 days	Around 15 days of submergence in mooring canals

4 Conclusions

The parametric studies to see the influence of grafting levels, initial concentration, dissolved solids and contact time were established to obtain information on the metal pickup of metal chelate embedded polymeric sorbents. Sorbents, prepared using different electron energy beams of 2 MeV and 1.25 MeV, were characterised w.r.t. tensile strength and elongation at break. The model parameters evaluated by fitting the observed data to standard isotherm models favours adsorption. The selectivity of MCEPs for the extraction of uranium and vanadium in presence of other heavy metals, directly from desalination effluents under actual field conditions, was confirmed by in-field bench-scale demonstration experiments that were carried out at NDDP Kalpakkam India. Differential elution studies confirmed desorption behaviour of heavy metals from the metal chelate embedded polymers both for desalination effluents and as well as seawater conditions. Coupling of uranium recovery with desalination plants gives added advantage of faster kinetics and bare minimum fouling factors for the mass transfer coefficient. As the need of fresh water will increase in future, larger capacity desalination plants will get pressed into service and the coupling for additional value recovery from reject streams will become more feasible as well as desirable.

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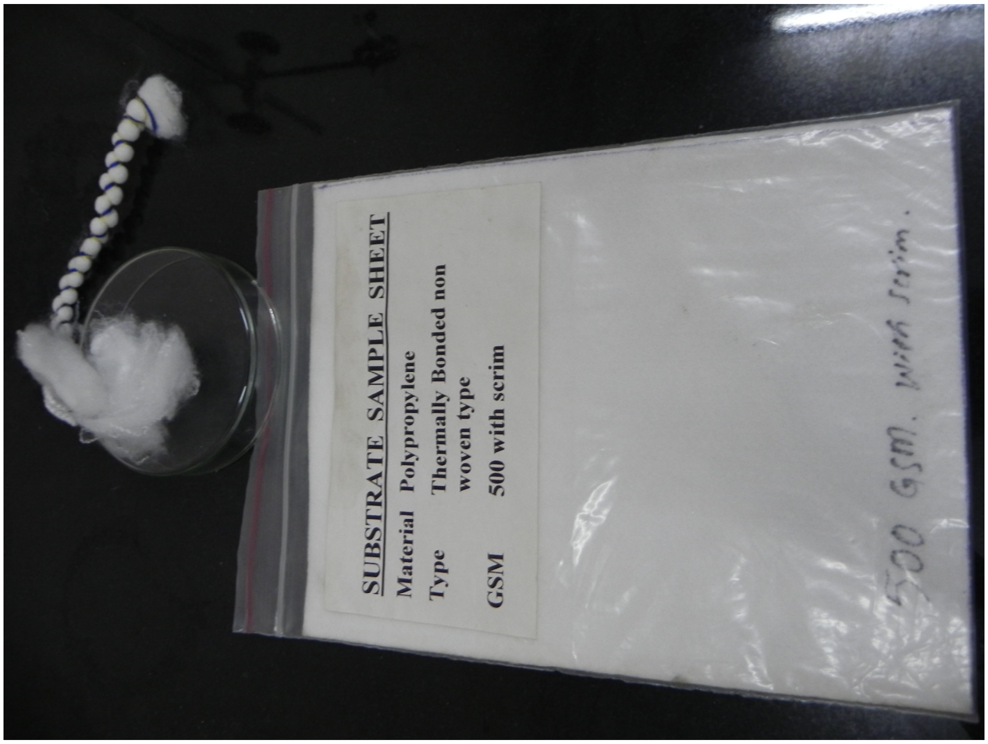
Annexure 2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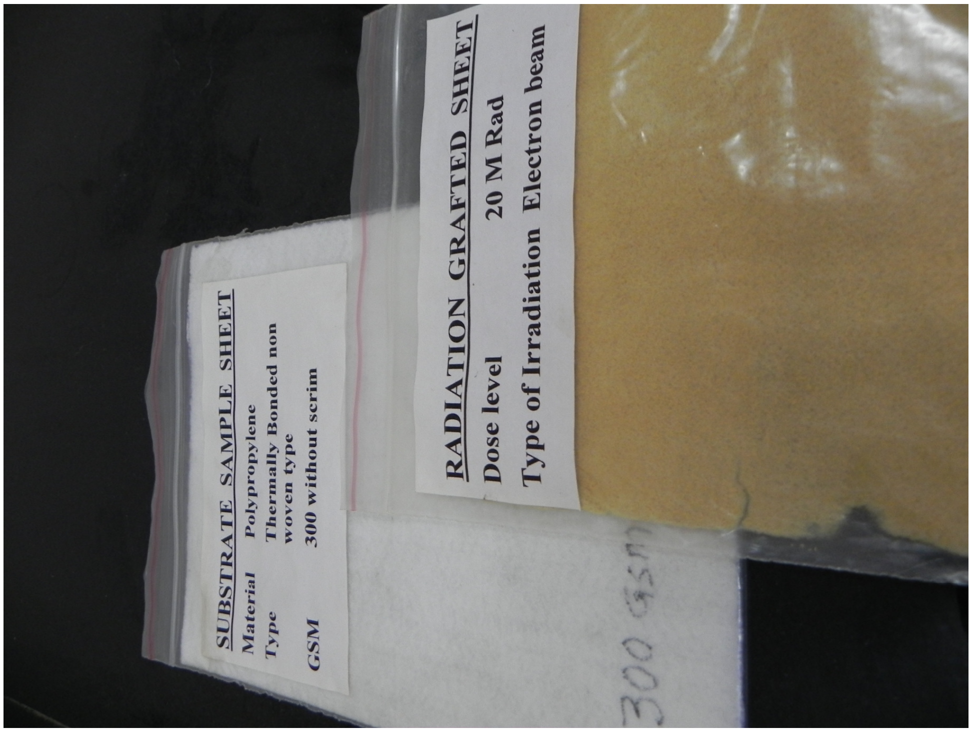
500 GSM. with scrim.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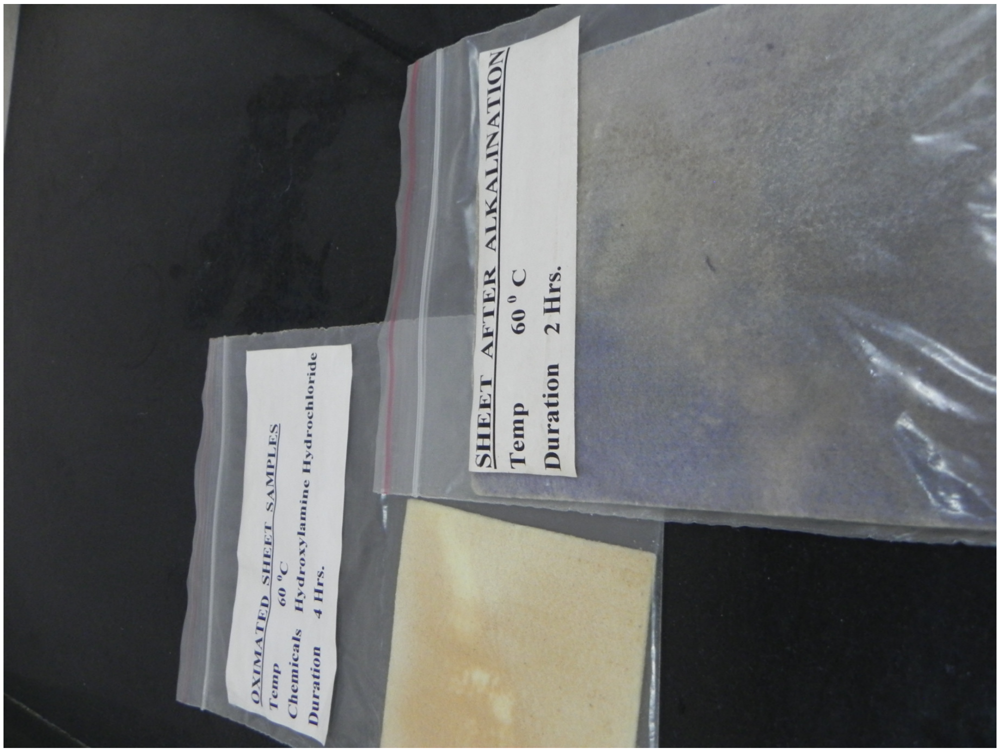
RADIATION GRAFTED SHEET
Dose level 20 M Rad
Type of Irradiation Electron beam
300 GSM


OXIMATED SHEET SAMPLES
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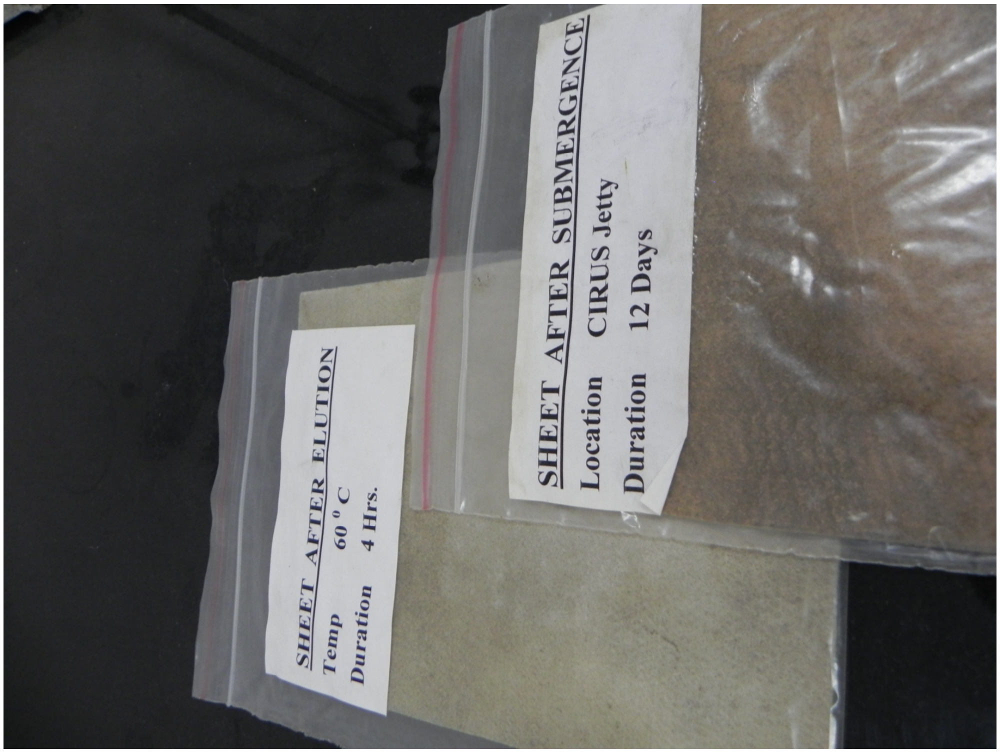
Chemicals Hydroxylamine Hydrochloride
Duration 4 Hrs.
SHEET AFTER ALKALINATION
Temp 60 ^{0} C
Duration 2 Hrs.


SHEET AFTER ELUTION
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SHEET AFTER SUBMERGENCE
Location CIRUS Jetty
Duration 12 Days


R/C1A1/F1
499 PPb
ER/C1A1/F4
970 PPb
DD/LEV
3280 PPb

Annexure-3

1. Singh, K., Chetan Shah., Charu Dwivedi., Manamohan Kumar., Bajaj, P.N., "Study of uranium adsorption using amidoximated polyacrylonitrile encapsulated macroporous beads" Journal of Applied Polymer Science 2012 DOI: 10.1002/APP37684

2. The following citing publication has been published:

   How Amidoximate Binds the Uranyl Cation

   Sinisa Vukovic, Lori A. Watson, Sung Ok Kang, Radu Custelcean, and Benjamin P. Hay

   Inorganic Chemistry 51:3855-3859 (2012)
   http://pubs.acs.org/doi/abs/10.1021/ic300062s

3. The following citing publication has been published:

   Adsorption of the uranyl ions on an amidoxime-based polyethylene nonwoven fabric prepared by pre-irradiation induced emulsion graft polymerization

   Xiyan Liu, Hanzhou Liu, Hongjuan Ma, Changqing Cao, Ming Yu, Ziqiang Wang, Bo Deng, Min Wang, and Jingye Li

   Industrial & Engineering Chemistry Research 0
   http://pubs.acs.org/doi/abs/10.1021/ie301965g

4. The following citing publication has been published:

   Recovery of Uranium from Seawater: A Review of Current Status and Future Research Needs

   Jungseung Kim, Costas Tsouris, Richard T. Mayes, Yatsandra Oyola, Tomonori Saito, Christopher J. Janke, Sheng Dai, Erich Schneider, Darshan Sachde

   Separation Science and Technology 48(3):367 (2013)
   http://dx.doi.org/10.1080/01496395.2012.712599