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 °C 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

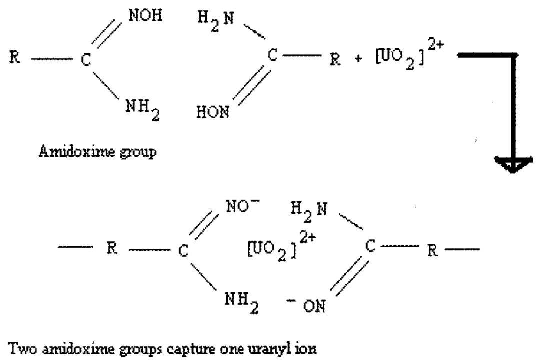

Fig. 2. Adsorption Mechanism of Metal Ions

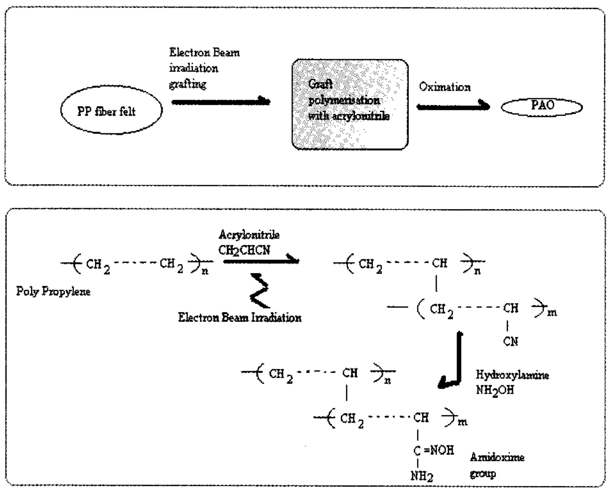

Fig. 1. Synthesis of Novel Adsorbent

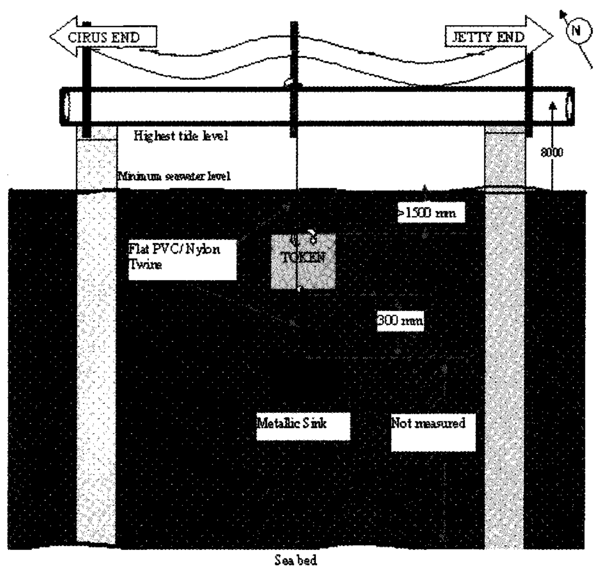

Fig. 3. Mooring Set up Details at CIRUS Jetty

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≡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 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

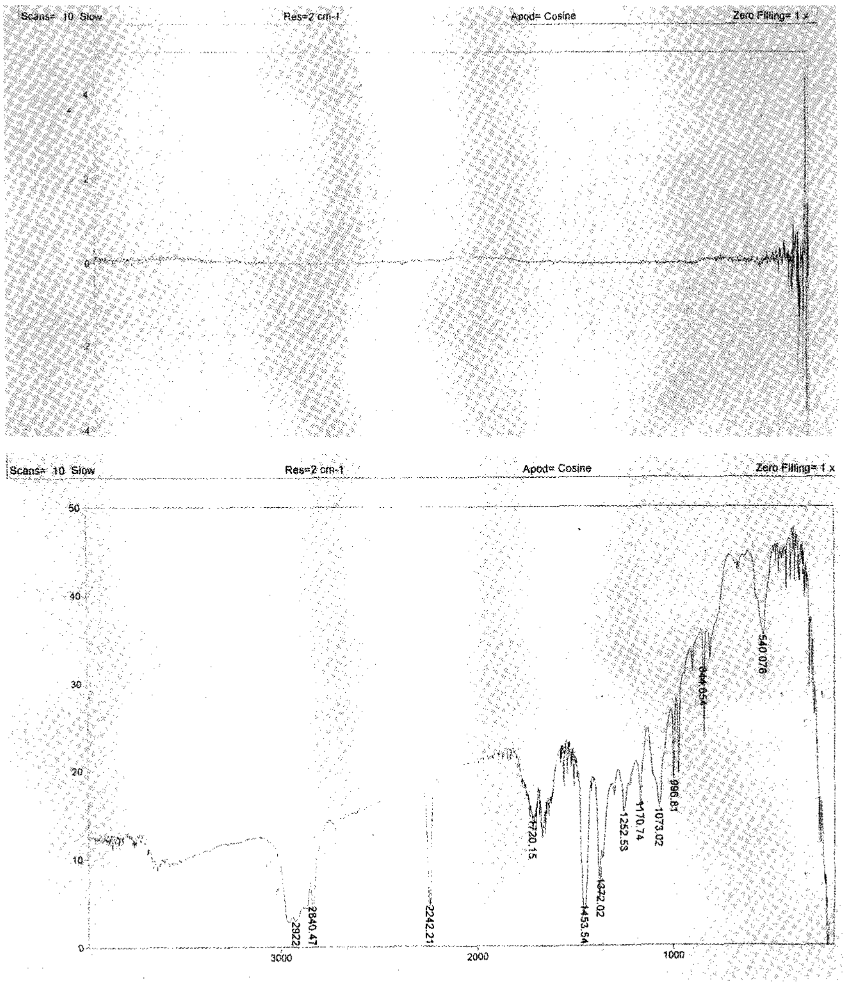

Fig. 4. FTIR Spectra of Non Irradiated Substrate Sheet and EB Irradiated Sheet

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.

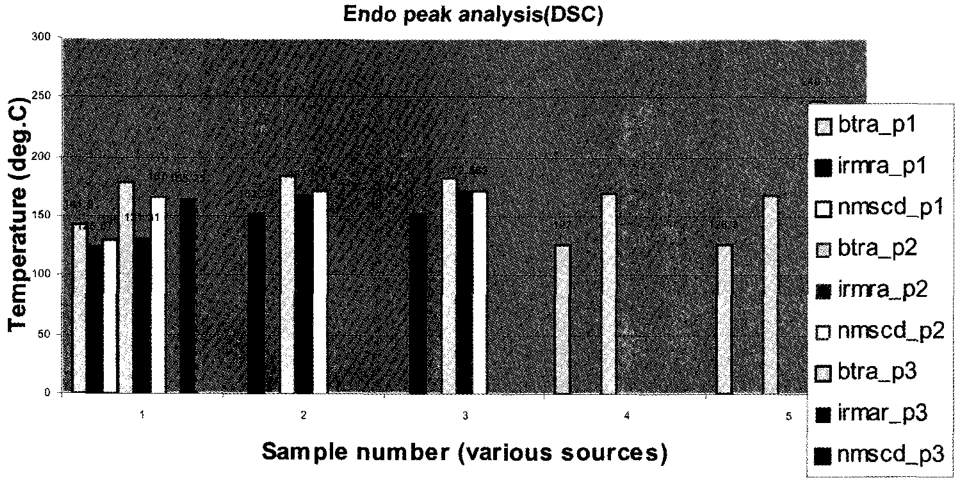

Fig. 5. Chemical Characterization of Substrate Sheets of Various Makes

Table 2. Substrate Materials Investigated

Parameter	Make-1	Make -2	Make -3	Make-4	Make-5
Fiber 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

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

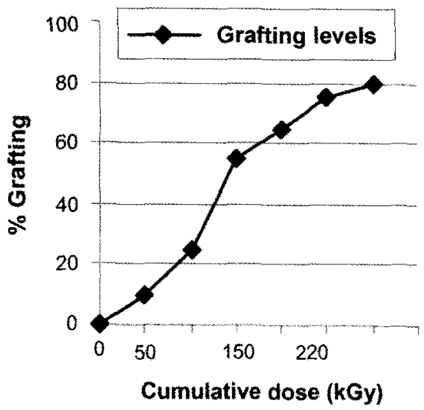

Fig. 6. Effect of Radiation Dose on Grafting Levels (*10kGy/pass*)

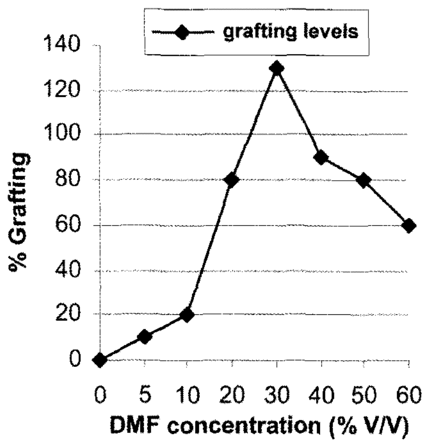

Fig. 7. Effect of Solvent Concentration on Grafting Levels (*at* 55 °C)

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

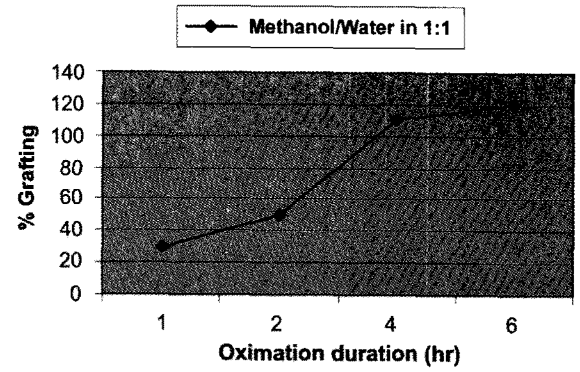

Fig. 8. Effect of Oximation Duration on Grafting Levels (*at* 55 °C)

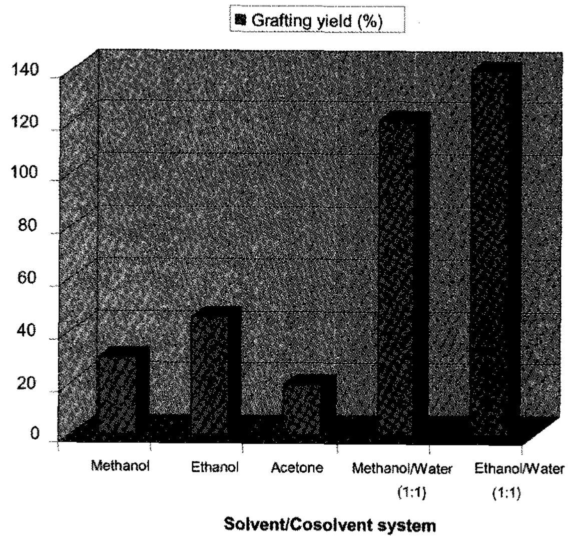

Fig. 9. Effect of Co-solvent Systems on Grafting Levels (*at* 55 °C)

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

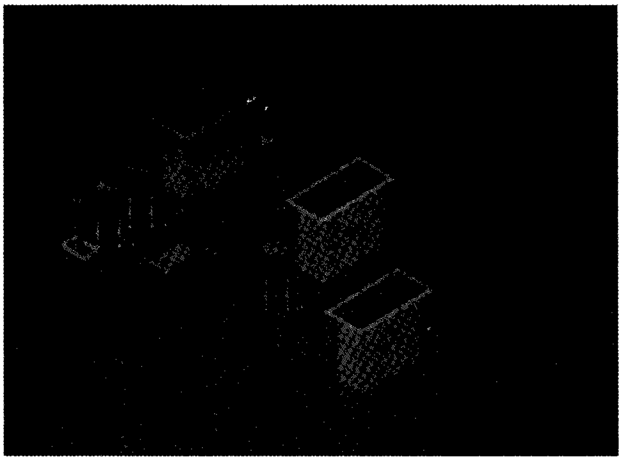

Fig. 10. Pilot Scale Facility for Synthesis of Adsorbent Sheets

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 °C
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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