Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Electron Beam Grafted Polymer Adsorbent for Removal of Heavy Metal Ion from Aqueous Solution

Virendra Kumar[a]; Y. K. Bhardwaj[a]; K. A. Dubey[a]; C. V. Chaudhari[a]; N. K. Goel[a]; Jayashree Biswal[a]; S. Sabharwal[a]; K. Tirumalesh[b]
[a] Radiation Technology Development Section, Trombay, Mumbai, India [b] Isotope Application Division Bhabha Atomic Research Centre, Trombay, Mumbai, India

To cite this Article Kumar, Virendra , Bhardwaj, Y. K. , Dubey, K. A. , Chaudhari, C. V. , Goel, N. K. , Biswal, Jayashree , Sabharwal, S. and Tirumalesh, K.(2006) 'Electron Beam Grafted Polymer Adsorbent for Removal of Heavy Metal Ion from Aqueous Solution', Separation Science and Technology, 41: 14, 3123 — 3139

To link to this Article: DOI: 10.1080/01496390600851673

URL: http://dx.doi.org/10.1080/01496390600851673

Separation Science and Technology, 41: 3123–3139, 2006

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390600851673

Electron Beam Grafted Polymer Adsorbent for Removal of Heavy Metal Ion from Aqueous Solution

Virendra Kumar, Y. K. Bhardwaj, K. A. Dubey,
C. V. Chaudhari, N. K. Goel, Jayashree Biswal,
and S. Sabharwal
Radiation Technology Development Section, Trombay, Mumbai, India

K. Tirumalesh
Isotope Application Division Bhabha Atomic Research Centre,
Trombay, Mumbai, India

Abstract: An electron beam grafted adsorbent was synthesized by post irradiation grafting of acrylonitrile (AN) on to a non-woven thermally bonded polypropylene (PP) sheet using 2 MeV electron beam accelerator. The grafted poly(acrylonitrile) chains were chemically modified to convert a nitrile group to an amidoxime (AMO) group, a chelating group responsible for metal ion uptake from an aqueous solution. The effect of various experimental variables viz. dose, dose rate, temperature, and solvent composition on the grafting extent was investigated. PP grafted with the amidoxime group (AMO-g-PP) was tested for its suitability as an adsorbent for removal of heavy metal ions such as Co^{2+}, Ni^{2+}, Mn^{2+}, and Cd^{2+} from aqueous solution. Langmuir and Freundlich adsorption models were used to investigate the type of adsorption of these ions. The adsorption capacities of the adsorbent for the metal ions were found to follow the order $Cd^{2+} > Co^{2+} > Ni^{2+} > Mn^{2+}$. The kinetics of adsorption of these ions indicated that the rate of adsorption of Cd^{2+} was faster than that of other ions studied.

Keywords: Electron beam, irradiation, grafting amidoxime, adsorption

Received 17 January 2006, Accepted 23 April 2006

Address correspondence to Y. K. Bhardwaj, Radiation Technology Development Section, Trombay, Mumbai-400085, India. Tel: + 91-022-25590175; Fax: +91-022-25505151; E-mail: ykbhard@magnum.barc.ernet.in, ykbhardwaj2001@yahoo.co.in

INTRODUCTION

Graft polymerization is an easy and efficient technique for modifying base polymers as it results in the superposition of properties of the backbone and the pendent grafted chains. Grafting can be initiated conventionally using a suitable redox system (1) or using radiation (2). Radiation grafting is an easy and highly efficient procedure for modifying the properties of polymeric substrates of synthetic as well as natural origin (3) and offers some unique advantages over the conventional chemical grafting method (4). Radiation grafted copolymer matrices have been suggested as suitable devices for controlled drug delivery (5), enhancing biocompatibility (6), increasing adhesion (7), concentration purposes (8), separation purpose (9), and wastewater treatment (10). At present, the focus has been on the utilization of grafted matrices for removal of heavy and toxic metal ions from wastewater (11). Many groups have reported synthesis of several types of ion exchange matrices by grafting monomers like acrylic acid, methacrylic acids on easily available backbones like polyethylene and PP (12–14). A radiation grafting technique has also been used to synthesize chelating membranes for separation purposes. The amidoxime group of amidoxime grafted PP (15, 16) and of copolymers (17–20) have been shown to form stable complex with heavy metal ions like uranium, vanadium, cadmium, copper. Grafted membranes have shown high selectivity for uranium and have been used for the uptake of uranium from seawater (18, 21, 22).

In the present work, a post irradiation-grafting method was used to synthesize a chelating membrane amidoxime grafted polypropylene (AMO-g-PP) by initially grafting AN on to readily available, cheap, commercial grade, thermally bonded non-woven PP cloth using high-energy electron beam ionizing radiation. The −CN group of AN were then chemically treated to convert −CN to an amidoxime group. These amidoximated matrices were investigated for their ability to uptake heavy metal ions from aqueous samples.

EXPERIMENTAL

Material

A non-woven, thermally bonded polypropylene (PP) matrix was obtained from a local supplier M/s NK Filter Fabric, Mumbai, INDIA with properties given in Table 1 was used for grafting purpose. Commercial grade AN from M/s IPCL India and dimethyl formamide (DMF) from M/s SD Fine chemicals, Mumbai were used. Hydroxylamine hydrochloride, salts $Cd(NO_3) \cdot 4H_2O$, $MnCl_2 \cdot 4H_2O$, $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, methanol, and other chemicals were of AnalaR grade and used as received. ICP standard from Merck were used to calibrate the ion exchange column. N_2 gas purity >99% from M/s Bharat Gas, India was used. Nanopure water from Millipore was used for all experiments.

Table 1. Details of the non-woven polypropylene sheet used for grafting

Property	Value
Weight	525 g/m^2
Thickness	2.7 mm
Breaking strength	90 Kgf (for 20 cm × 5 cm strip size)
Busting strength	30–35 Kg/cm^2
Operable temperature	90°C
Air permeability	280 ($lit/dm^2/min$)

Radiation Grafting of AN

Electron beam irradiation of PP sheets was carried out using an industrial 2 MeV, 20 kW ILU-6 accelerator (Budker Institute of Nuclear Physics, Russia) under the following conditions: energy = 1.8 MeV, current = 10 mA and variable conveyor speed. Grafting was carried out using a post irradiation technique i.e. sheets were irradiated prior to immersing them in grafting solution. The grafting extent was estimated gravimetrically using the relation 1:

$$\%\text{Grafting} = \frac{\text{Weight after grafting} - \text{Initial weight}}{\text{Initial weight}} \times 100 \qquad (1)$$

Amidoximation of AN Grafted Films

The CN groups of AN grafted sheet were converted to the chelating group amidoxime by treating the AN-g-PP matrix with aqueous methanolic solution (H_2O:Methanol; 1:1) of hydroxylamine hydrochloride of suitable concentration at elevated temperature in a water bath for sufficient time near neutral pH. The amidoximated sample was then washed several times with an aqueous methanolic solution. The amidoximation extent of CN was estimated using a copper estimation method (23). There was a conversion of 60–65% after 3 hours of chemical treatment and no significant change in % conversion was observed for treatment for longer times. The amidoximated matrix was treated with 2.5%(w/v) aqueous KOH for a few hours prior to using them for metal ion uptake studies.

RESULTS AND DISCUSSION

The ungrafted, grafted, and amidoximated PP matrix was characterized by FTIR and optical microscopy in order to confirm the changes brought about by grafting and amidoximation in the base matrix.

Fourier transformed infrared spectroscopy (FTIR) measurements were performed on a FTIR spectrophotometer FT/IR-660 from JASCO, JAPAN. The samples were thoroughly ground at liquid nitrogen temperature and mixed with KBr. The mixture was compressed to prepare a disc for FTIR analysis. FTIR spectra were recorded in the range from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} and averaged over 25 scans.

The absorption peaks corresponding to 2970, 2870, 1460, 1376 cm^{-1} wavenumber were characteristic of $-CH_3$ and CH_2 groups in FTIR spectrum of PP as shown in Fig. 1. The acrylonitrile (AN) grafted sheet showed a visible color change to yellow color from the initial white color and the grafted $-C{\equiv}N$ was confirmed by a sharp absorbtion peak at 2240 cm^{-1} wave number of FTIR spectrum. The amidoximation of $-C{\equiv}N$ lead to visible color change from yellow to pink/red and also to a broad absorption peak corresponding to $-NH_2$ (3400 cm^{-1}) and $>C{=}N<$ (1560 cm^{-1}) in the FTIR spectrum.

Optical micrographs shown in Fig. 2 illustrate the morphology of the PP, AN-g-PP, and AMO-g-PP fibers. It can be clearly seen that the diameter as well as the texture of the PP fiber changed with grafting and amidoximation.

The extent of radiation grafting depends not only on the characteristic and type of backbone polymer and the monomer to be grafted but also on other experimental variables like dose, dose rate, temperature, ambience of

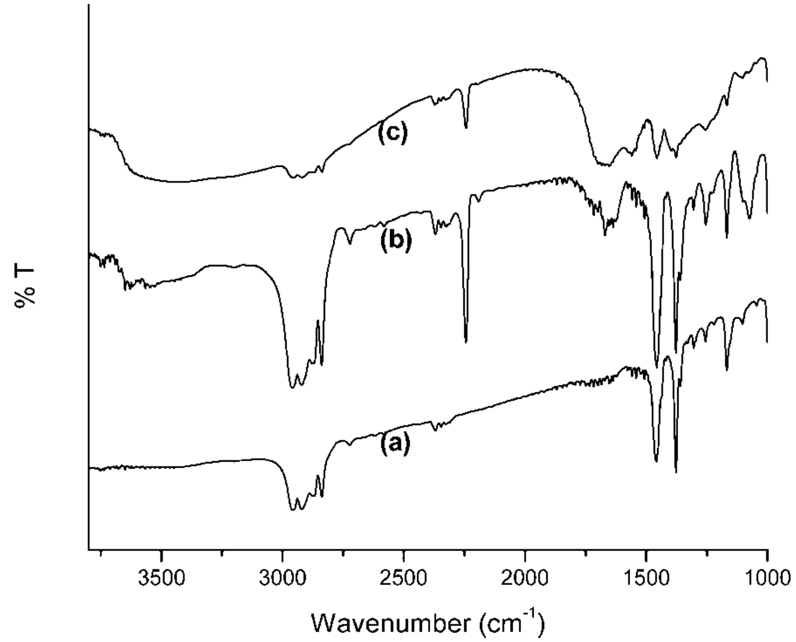


Figure 1. FTIR spectra of (a) PP (b) AN-g-PP, (c) AMO-g-PP.

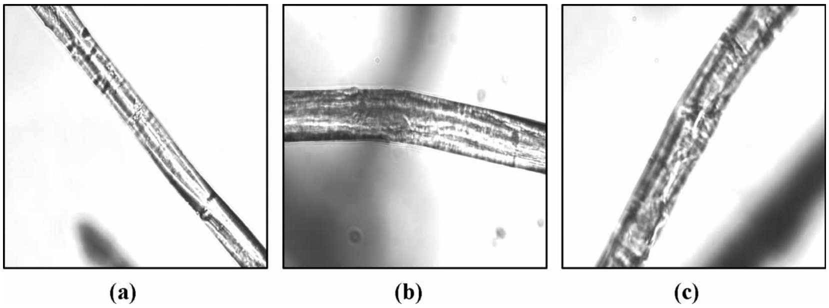

(a) (b) (c)

Figure 2. Optical micrograph of (a) PP (b) AN-g-PP, and (c) AMO-g-PP, (Magnification = 400).

grafting and the composition of the grafting solution (24, 25). Therefore, detailed experiments to study the effect of these parameters were carried out. The results of these studies are detailed below.

Preparation of Grafted PP Matrix

Effect of Irradiation Ambience on Grafting

In order to study the effect of irradiation ambience two sets of PP samples, one packed in N_2 filled PE bags and other as such under open air conditions were irradiated at room temperatures for 200 kGy and plunged into deaerated AN at 50°C. Figure 3 clearly shows that the extent of grafting was much higher for PP samples irradiated under aerated conditions. Higher grafting yields for samples irradiated under aerated conditions indicate the role of peroxides and hydroperoxides radicals formed in grafting reaction as described for other grafting systems (26). For samples irradiated under N_2 atmosphere, the radicals generated on irradiation recombine after some time, thus very few radicals are available for grafting to take place. On the other hand, the radicals formed under aerated conditions react with oxygen to form stable peroxy/hydroperoxy radicals which decompose at elevated temperatures to generate sites for grafting of AN as shown in Scheme 1.

Effect of Dose and Dose Rate

Figure 4 shows grafting yields as a function of the radiation dose when the substrate was irradiated at a rate of 10 kGy/pass in air and grafting was carried out at 50°C in pure deaerated AN. The profile shows that grafting levels increased with the dose up to a dose of 200 kGy and thereafter no significant effect was seen on the extent of grafting. It is well known that radiation induced processes are not only a function of total radiation dose

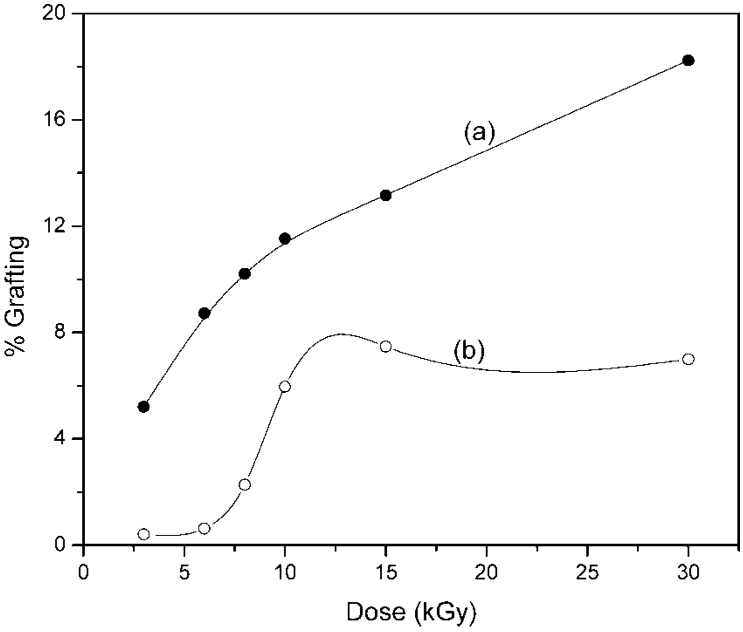
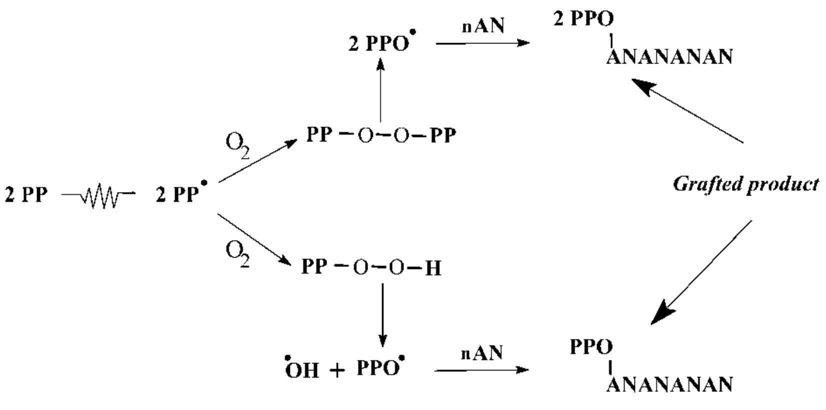


Figure 3. Effect of ambience of irradiation on grafting. Dose rate = 10 kGy/Pass.

but also of the dose rate at which the total dose is imparted (27) therefore the grafting extent was also studied at different dose rates. In order to study the effect of dose rate on grafting extent PP sheet were irradiated at various dose rates for a total dose of 200 kGy and grafted under the same conditions. Inset Fig. 4 shows the result of these studies. As can be seen in the figure,



Scheme 1. Generation of peroxy/hydroperoxy species and grafting in aerated condition.

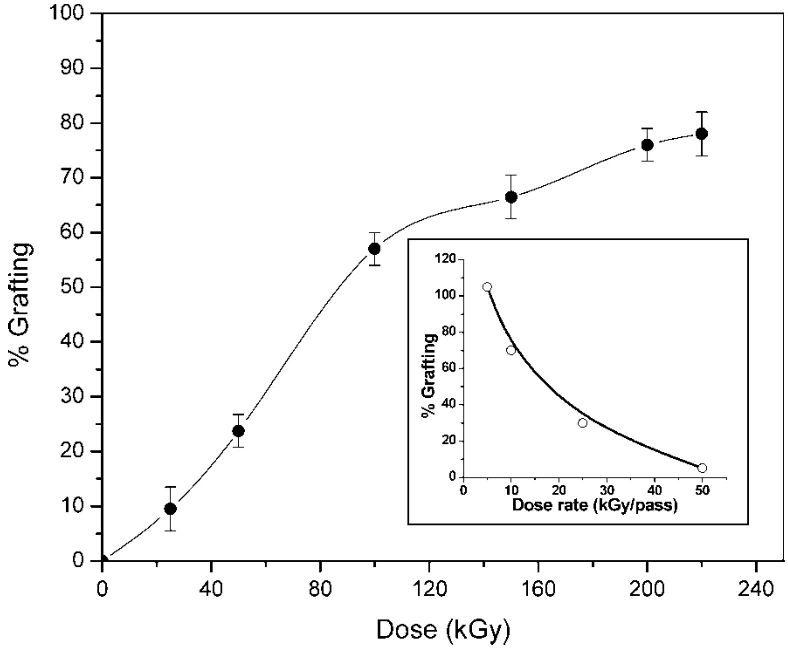


Figure 4. Effect of dose on grafting extent at a dose rate of 10 kGy/Pass. Inset: Extent of grafting at different dose rates for total dose of 200 kGy.

grafting yields decreased with an increase in the dose rate. It seems for a porous PP ($T_g = -20°C$) matrix, the recombination of the radicals generated takes place very efficiently at room temperature at which the sheets were irradiated. At higher dose rates, as more radicals are generated in close vicinity, the recombination is more probable leaving less radicals for peroxy/hydroperoxy radical formation and the latter for grafting. At low dose rates, most of the radicals generated are converted to peroxy/hydroperoxy radicals which are later available for grafting as shown in equations below.

$$\mathrm{PP} + \mathrm{O_2} \longrightarrow \text{peroxides (low dose rate)} \tag{2a}$$

$$2\,\mathrm{PP} \longrightarrow \text{recombination (high dose rate)} \tag{2b}$$

Effect of Solvent Dimethyl Formamide (DMF) on Grafting

Polymerization of AN to polyAN in pure AN causes phase separation of polymer as the polymer formed is not soluble in its own monomer (28). The phase separation may hinder further propagation of grafted polyAN developed on backbone PP matrix because the polyAN chain tends to go from an extended state to a closed globular state due to AN in its vicinity. The phase separation of polyAN from AN can be reduced by using a suitable solvent like dimethyl formamide (DMF) in which polyAN is soluble (29). Figure 5 shows grafting yields when grafting was carried out in different proportions of AN-DMF. As is clear from the figure, the grafting yield was maximum for the AN-DMF mixture of ratio 70:30 indicating that the presence of DMF results in higher grafting yields. However, a decrease in grafting extents at higher DMF concentration may be assigned to the lower concentration of the monomer AN in the grafting mixture.

Effect of Temperature on Grafting Reaction

The above-mentioned grafting reactions were initially carried out at 50°C. As the grafting reaction as well as the decomposition of peroxide are chemical reactions, change in temperatures may affect the final grafting levels. In order to probe the effect of temperature on grafting, the grafting extent was followed at different temperatures in AN-DMF (70:30) mixture. Figure 6 shows the result of this study. It was seen that the grafting extent increased with the temperature in the temperature range studied. The increase in temperature may enhance the decomposition of peroxides resulting in more radical sites being made available for grafting. The other reason may be that at higher

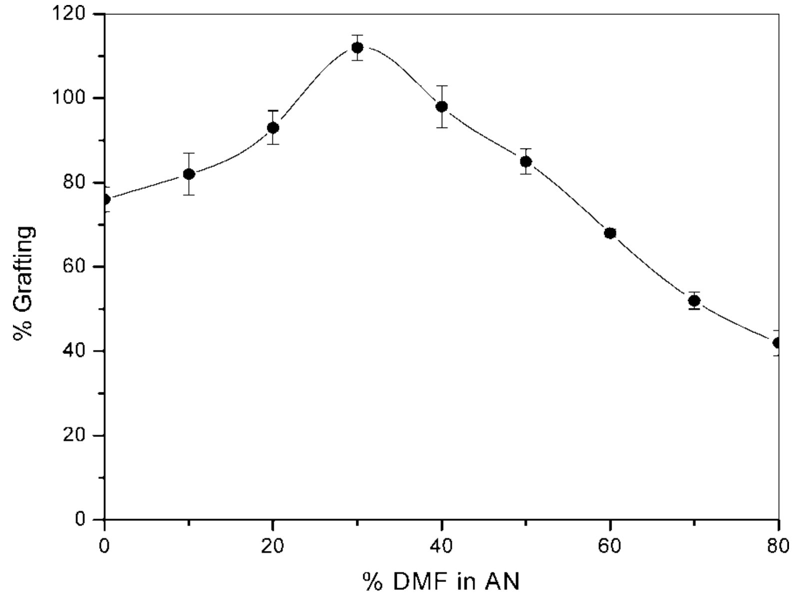


Figure 5. Grafting in AN-DMF mixture. Total dose = 200 kGy, Dose rate = 10 kGy/Pass.

temperatures, the monomer diffusion into the irradiated PP is facilitated thereby contributing to an increase in the grafting extent.

Effect of Reaction Time on Grafting

In order to study the effect of grafting time on final grafting yields, the irradiated sheets were put in grafting solution under the conditions standardized in the above experiments. The sheets were removed from the grafting reactor after different time intervals and monitored for the extent of grafting. The results shown in inset Fig. 6 indicate that the maximum grafting was achieved within 2–3 hours.

Metal Uptake by Grafted Matrix

The metal ion concentration in the aqueous solution was estimated on DIONEX-500 ion chromatograph system (DX-500, Dionex) using a column ion pack CS5 containing 2% crosslinked micro porous divinylbenzene-styrene hydrophobic resin core agglomerated with totally permeable latex particles of polyvinylbenzyl quaternary ammonium salts that cause actual anion exchange. Oxalic acid was used as mobile phase and detection was

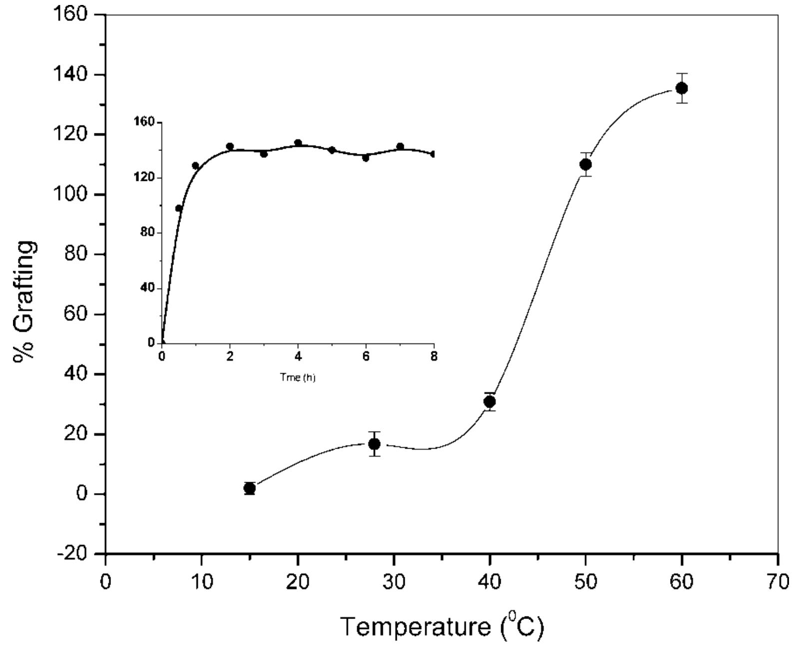


Figure 6. Effect of temperature on grafting in AN:DMF (70:30) solution. Total dose = 200 kGy, Dose rate = 10 kGy/Pass.

done by the absorbance method using (PAR) 4-(2-pyridylazo) resorcinol post column reagent, which has λ_{max} at 520 nm. Sample loop of 25 μL was used.

The equilibrium adsorption study was carried out for metal ions (Co^{2+}, Ni^{2+}, Mn^{2+}, Cd^{2+}) by mixing 0.3 g of AMO-g-PP adsorbent in 25 mL metal ion solution of various known concentrations in 125 mL stoppered conical flasks. The flask containing the metal ion solution and adsorbent were placed in a motorized thermostatic shaker bath and agitated at 25°C for 5 h until an equilibrium was reached. The initial and equilibrium metal ion concentrations of different combinations were measured by an ion chromatograph. These data obtained was used to calculate the adsorption capacity of the adsorbent (Q_e) using equation (3)

$$Q_e = (C_0 - C_e) * V/(m * 1000) \quad (mg/g) \tag{3}$$

Where C_0 and C_e are the initial and equilibrium liquid phase concentration (mg/L) respectively; V is the volume of the metal ion solution used (mL); m is the mass of adsorbent used (g).

The kinetics of adsorption of AMO-g-PP was carried out under similar conditions for a different contact time at 200 ppm ion concentration.

Equilibrium Isotherms

Adsorption isotherms describe how adsorbents interact with adsorbents and are therefore critical for optimizing the use of adsorbents. The correlation between the experimental and the theoretical/empirical models is essential for practical design and operation of adsorption systems. In order to optimize the design of a sorption system to remove heavy metal ions from effluents, it is important to establish the most appropriate correlation from the equilibrium curves. In the present study, adsorption isotherms for metal ions were determined by plotting Q_e as a function of C_e as shown in Fig. 7. The Fig. 7 inset shows Q_e as a function of C_i. It can be seen that the adsorption of metal ions follow the order $Cd^{2+} > Co^{2+} > Ni^{2+} > Mn^{2+}$. The adsorption was analyzed using two adsorption models, namely Langmuir and Freundlich isotherms.

Langmuir Adsorption Isotherms

The Langmuir model is based on the assumption that intermolecular forces decrease rapidly with distance and consequently predicts the existence of monolayer adsorption and secondly, all sorption sites are identical and energetically equivalent (30). The experimental adsorption data for four metal ions on AMO-g-PP adsorbent at 25°C, were analyzed according to the linear form of the Langmuir isotherm (equation (4)).

$$C_e/Q_e = 1/K_L + a_L C_e/K_L \tag{4}$$

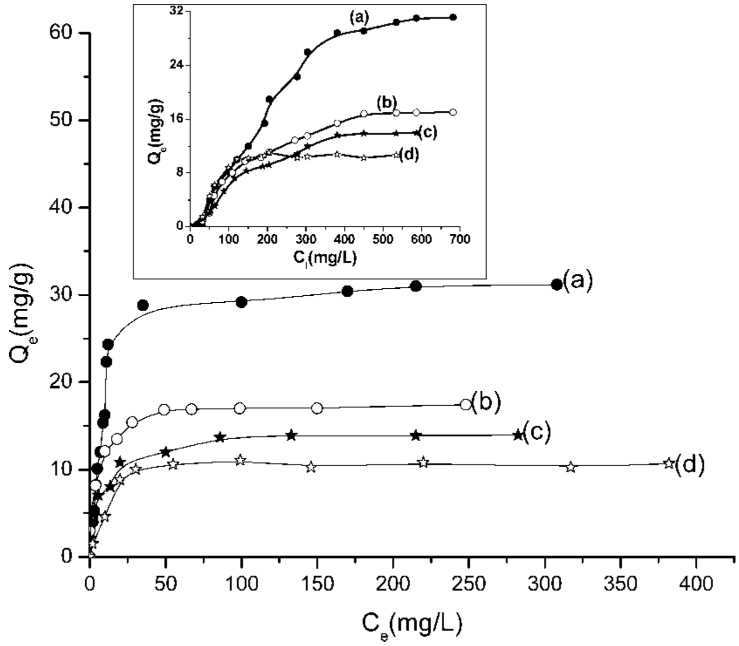


Figure 7. Adsorption isotherm for metal ions (Q_e vs initial metal ion concentration). (a) Cd^{2+}, (b) Co^{2+}, (c) Ni^{2+}, (d) Mn^{2+}. Inset: Q_e vs metal ion concentration after adsorption. (a) Cd^{2+}, (b) Co^{2+}, (c) Ni^{2+}, (d) Mn^{2+}.

where

a_L = Langmuir isotherm constant (L/mg)
K_L = Langmuir equilibrium constant (L/g)
C_e = Equilibrium liquid phase ion concentration (mg/L)
Q_e = Equilibrium solid phase ion concentration (mg/g)
K_L/a_L = Maximum adsorption capacity of the adsorbent (mg/g) or theorical monolayer saturation capacity (q_{max})

Langmuir isotherm linear plots for the adsorption of four metal ions onto AMP-g-PP are shown in Fig. 8, where specific sorption C_e/Q_e was plotted against the equilibrium concentration, C_e for metal ions. Different Langmuir adsorption parameters obtained using Langmuir isotherm plots are given in Table 2. The linearity of isotherms and high correlation coefficient values (>0.99) support the fact that metal-ion adsorbent data closely follows the Langmuir model of sorption over the whole concentration range studied. The theoretical mono-layer saturation capacities (q_{max}) for metal ions calculated from Langmuir isotherm were good agreement with the experimental equilibrium adsorption capacities and also follow the order i.e. $Cd^{2+} > Co^{2+} > Ni^{2+} > Mn^{2+}$.

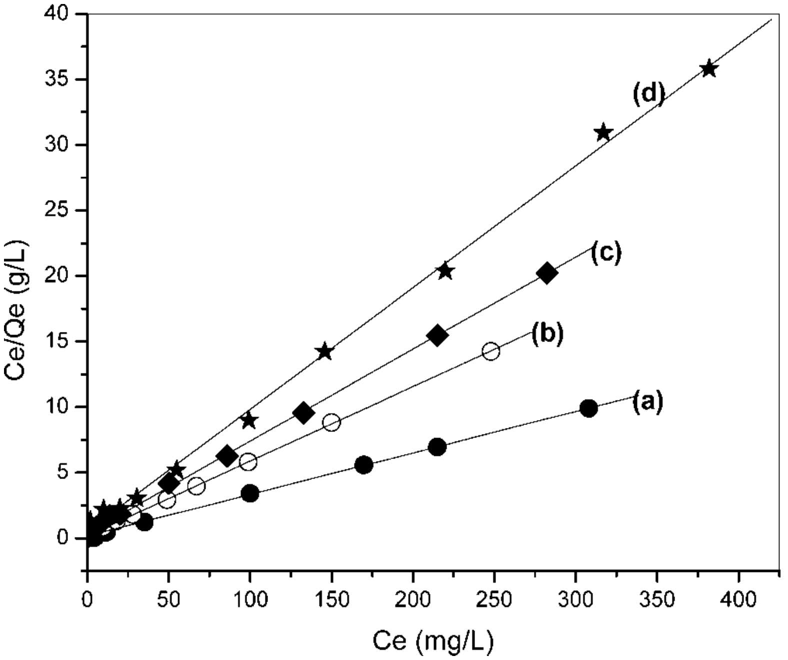


Figure 8. Langmuir adsorption plots of metal ions on AMO-g-PP at 25°C. (a) Cd^{2+}, (b) Co^{2+}, (c) Ni^{2+}, (d) Mn^{2+}.

Freundlich Absorption Isotherms

The Freundlich equation is an empirical equation employed to describe a heterogeneous system (30). The Freundlich isotherm is another form of the Langmuir approach for adsorption on an “amorphous” surface. The Freundlich isotherm describes reversible adsorption and is not restricted to the formation of a monolayer. The Freundlich equation predicts that the adsorption of metal ion on the adsorbent will increase so long as there is an increase in the metal ion concentration. The linear form of the Freundlich

Table 2. Langmuir adsorption parameters of EB grafted AMO-g-PP adsorbent grafting extent ~115% at 25°C

S. no.	Metal ion	K_L(L/g)	a_L (L/mg)	q_{max} (mg/g)	C.F.[a]
1	Cd^{2+}	6.18	0.20	31.58	0.998
2	Co^{2+}	5.88	0.33	17.57	0.999
3	Ni^{2+}	2.72	0.19	14.24	0.999
4	Mn^{2+}	1.91	0.18	10.76	0.998

[a] Correlation coefficient.

equation (equation (5)) was utilized to analyze the adsorption behavior of AMO-g-PP for four metal ions.

$$\log Q_e = \log K_f + (1/n) * \log C_e \tag{5}$$

where

K_f = Freundlich constant (L/g) is the relative indicator of adsorption capacity
n = Freundlich exponent is the indication of favorability of the adsorption process.
The values of $n > 1$ represent favorable adsorption conditions (31)
C_e and Q_e are the same as for the Langmuir equation.

The Freundlich equation treatment of sorption data (shown in Fig. 9) for the metal ions clearly showed a deviation from linearity and instead showed a two segment relationship. When the whole concentration range was divided into two regions (region 1 and region 2), an excellent fit (correlation coefficient values >0.98) to experimental data was obtained. Other groups have also reported similar two segment types of adsorption for adsorption of acid dyes on chitosan (32). Freundlich absorption parameters obtained using the Freundlich equation for lower concentration region are given in Table 3. For all metal ions, the values of $n > 1.0$, indicates the favorable or beneficial

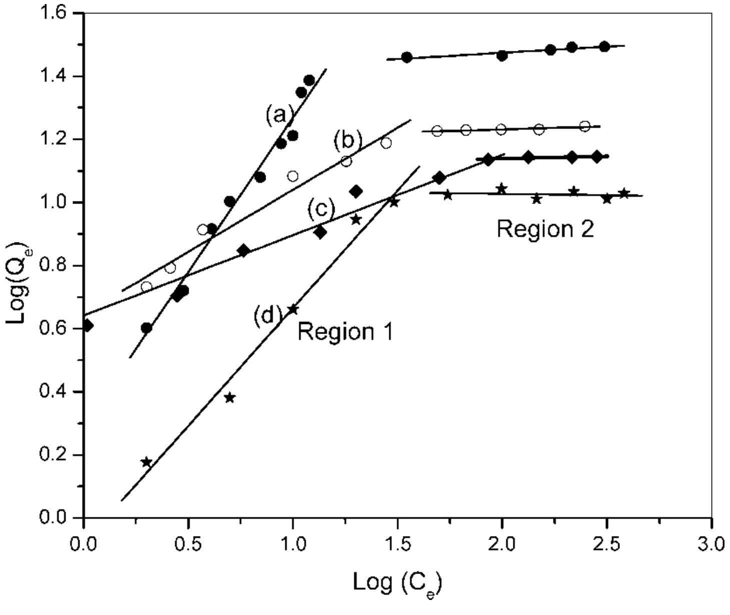


Figure 9. Freundlich adsorption plots of metal ions on AMO-g-PP at 25°C. (a) Cd^{2+}, (b) Co^{2+}, (c) Ni^{2+}, (d) Mn^{2+}.

Table 3. Freundlich adsorption parameters of EB grafted AMO-g-PP adsorbent grafting extent ~115% at 25°C

S. no.	Metal ion	K_f (L/g)	n	[a]C.R. (mg/L)	C.F.[b]
1	Cd^{2+}	1.95	1.24	0–300	0.998
2	Co^{2+}	4.43	2.54	0–215	0.983
3	Ni^{2+}	4.38	3.93	0–250	0.988
4	Mn^{2+}	0.79	1.29	0–150	0.989

[a] Concentration range.
[b] Correlation coefficient.

adsorption process. Comparing the Langmuir and the Freundlich treatment of experimental adsorption data of metal ions (results presented in Table 2, Table 3, and Figs. 8 and 9) clearly indicates that adsorption of metal ions on AMO-g-PP can be better explained by Langmuir adsorption model and hence it can be said that the adsorption of metal ions was more of a homogeneous type.

Adsorption Kinetics

In the kinetic study of adsorption of metal ions on AMO-g-PP, all four ions (Co^{2+}, Ni^{2+}, Mn^{2+}, Cd^{2+}) were tested for adsorption for different contact time with adsorbent under similar conditions. Figure 10 shows the result of adsorption kinetic studies at 25°C. It can be seen that the adsorption rate of theses ions on AMO-g-PP adsorbent was quite fast (i.e. within 30 min of contact time more than 70% of metal ions were removed except Ni^{2+}). The closer look given in Fig. 10 inset at a lower time scale indicates that the order of adsorption rate is $Cd^{2+} > Mn^{2+} > Co^{2+} > Ni^{2+}$. Among the four ions, Cd^{2+} had the highest adsorption rate; within 1 hr more than 90% of the initial 200 ppm Cd^{2+}ions were removed. Meanwhile, Ni^{2+} had the lowest adsorption rate; within 1 hr only upto 70% Ni^{2+} could be removed. It was interesting to see that not only the equilibrium adsorption of the Cd^{2+} ions was highest but also its rate of adsorption was fastest.

Competitive Adsorption of Metal Ions

In order to investigate the competitiveness of the ion adsorption on the AMO-g-PP adsorbent, adsorption of ions was studied from an aqueous solution containing same concentration (100 ppm) of Cd^{2+}, Co^{2+}, Ni^{2+}, and Mn^{2+} ions. After a sufficient time of adsorption, the concentration of ions adsorbed on the grafted matrix was estimated and the results are presented in Fig 11. The equilibrium adsorption from the mixed solution followed the pattern $Cd^{2+} > Ni^{2+} > Mn^{2+} > Co^{2+}$ which was different from that obtained in the case of an individual ion solution where the order was

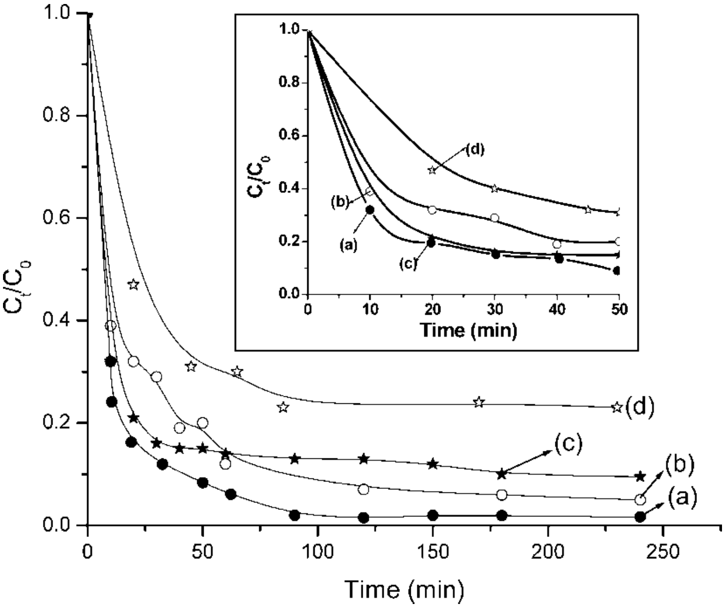


Figure 10. Kinetics of adsorption for metal ions (a) Cd^{2+}, (b) Co^{2+}, (c) Mn^{2+}, (d) Ni^{2+}; initial ion concentration = 200 ppm. (Inset: Adsorption kinetics at lower time scale (a) Cd^{2+}, (b) Co^{2+}, (c) Mn^{2+}, (d) Ni^{2+}).

$Cd^{2+} > Co^{2+} > Ni^{2+} > Mn^{2+}$. These results showed that though the uptake of ions like Cd^{2+} were not affected by the presence of other metal ions but the adsorption of ions like Co^{2+} was affected by the presence of other metal ions in the solution.

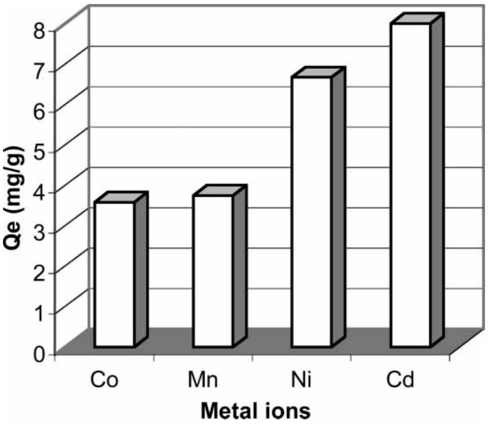


Figure 11. Equilibrium uptake capacity of adsorbent in a mixed ion solution. Initial concentration of each ions = 100 mg/L, grafting yield = 115%, wt. of adsorbent = 0.3 g, volume of solution = 25 mL.

CONCLUSION

The studies indicate that a 2 MeV electron beam accelerator can be conveniently utilized to carry out the grafting of acrylonitrile onto PP sheet by a post irradiation grafting technique. The grafting preferably takes place at the site generated by decomposition of peroxide linkage between the PP chains. Changing the experimental variables like dose, dose rate, temperature of grafting, and composition of grafting solution effectively control the grafting extent. The amidoximated-grafted matrix can be used for the adsorption of metal ions. The adsorption followed the Langmuir adsorption in the concentration range studied. The extent of adsorption of some ions depends on the presence of other ions in the medium.

REFERENCES

1. Fanta, G.F. (1973) *Block and Graft Copolymerization;* Ceresa, R.J. (ed.), Wiley: London; Vol I.
2. Chapiro, A. (1962) *Radiation Chemistry of Polymeric Systems*; John Wiley & Sons: New York.
3. Stanett, V. (1990) Radiation grafting state of the art. *Radiat. Phys. Chem.*, 35: 82.
4. Garnett, J.L. (1979) Grafting. *Radiat. Phys. Chem.*, 14: 79.
5. De Querioz, A.A.A., Vargas, R.R., Higa, O.Z., Barrak, E.R., Bechara, E.J.H., Wladislaw, B., and Marzorti, L. (1999) Graft copolymer with immobilized peroxidase for organic synthesis. *Radiat. Phys. Chem.*, 55: 345.
6. Chon, D., Hoffman, A.S., and Ratner, B.D. (1984) Radiation grafted polymers for biomaterial applications. I. 2-Hydroxyethylmethacrylate: ethyl methacrylate grafting onto low density polyethylene films. *J. Appl. Polym. Sci.*, 29: 2645.
7. Legocka, I., Zimek, Z., Mirkowski, K., and Nowicki, A. (2000) Preliminary study on application of PE filler modified by radiation. *Radiat. Phys. Chem.*, 57: 411.
8. Betz, N., Begue, J., Goncalves, M., Gionnet, K., Deleris, G., and Le Moel, A. (2003) Functionalization of PAA radiation grafted PVDF. *Nucl. Instrum. Meth. Phys. Res. B*, 208: 434.
9. Kumar, V., Bhardwaj, Y.K., Jamdar, S.N., Goel, N.K., and Sabharwal, S. Preparation of anion exchange adsorbent by radiation-induced grafting of vinylbenzyltrimethylammonium chloride onto cotton cellulose and its application for protein adsorption. *J. Appl. Polym. Sci.* (Accepted for publication).
10. Hegazy, E.A., Kamal, H., Maziad, N., and Dessouki, A. (1999) Membranes prepared by radiation grafting of binary monomers for absorption of heavy metal from industrial wastes. *Nucl. Instrum. Meth. Phys. Res. B*, 151: 386.
11. Nasef, M.M. and Hegazy El-Sayed, A. (2004) Preparation and applications of ion-exchange membranes by radiation-induced graft copolymerization of polar monomers onto non polar films. *Prog. Polym. Sci.*, 29: 499.
12. Taher, N.H., Dessouki, A.M., and Khalil, F.H. (1990) Radiation grafting of acrylic acid onto polypropylene films. *Radiat. Phys. Chem.*, 36 (6): 785.
13. Gupta, B. and Chapiro, A. (1989) Preparation of ion exchange membranes by grafting acrylic acid into pre-irradiated polymer films. I: Grafting into polyethylene. *Eur. Polym. J*, 25: 1137.

14. Hegazy, E.S., Abd El-Rehim, H., Khalifa, N., Atwa, S., and Shawky, H. (1997) Anionic/cationic membranes obtained by radiation grafting method for use in waste water treatment. *Polym. Int.*, 43: 321.
15. Saito, K., Hori, T., Furusaki, S., Sugo, T., and Okamoto, J. (1987) Porous amidoxime group containing membrane for the recovery of uranium from sea water. *Ind. Eng. Chem. Res.*, 26: 1977.
16. Sugo, T. (1997) Selective collection of rare elements dissolved in trace amounts in the sea by using polymer adsorbent. *Nippon Kaisui Gakkai-Shi.*, 51 (1): 20.
17. Tamada, M., Seko, N., Katakai, A., Hasegawa, S., Kasai, N., and Sugo, T. (2001) Heavy metal adsorbent synthesized by radiation grafting and its application IAEA TECDOC IAEA-SM-365/73.
18. Suzuki, T., Saito, K., Sugo, T., Ogura, H., and Oguma, K. (2000) Fractional elution and determination of uranium and vanadium adsorbed on amidoxime fiber from seawater. *Analytical Sciences*, 16: 429.
19. Shiraishi, T., Tamada, M., Saito, K., and Sugo, T. (2003) Recovery of cadmium from waste of scallop processing with amidoxime adsorbent synthesized by graft-polymerization. *Radiat. Phys. Chem.*, 66: 43.
20. Ramachandran, V., Kumar, S.C., and Sudarsanan, M. (2001) Preparation, characterization and performance evaluation of styrene-acrylonitrile-amidoxime sorbent for uranium recovery from dilute solutions. *J. Macromol. Sci. Pure Appl. Chem. A*, 38 (11): 1151.
21. Kabay, N., Katakai, A., and Sugo, T. (1995) Preparation of amidoxime-fiber adsorbents by radiation induced grafting. *Radit. Phys. Chem.*, 6 (4–6): 833.
22. Omichi, H., Katakai, A., Sugo, T., and Okamoto, J. (1986) A new type of Amidoxime-group containing adsorbent for the recovery of uranium from seawater. III. Recycle use of adsorbent. *Sep. Sci. Technol.*, 21 (6–7): 563.
23. Okamoto, J., Sugo, T., Kakatai, A., and Omichi, H. (1985) Amidoxime group containing adsorbents for metal ions synthesized by radiation grafting. *J. Appl. Poly. Sci.*, 30: 2967.
24. Chaudhari, C.V., Bhardwaj, Y.K., and Sabharwal, S. (2006) Radiation grafting of methyl methacrylate on radiation crosslinked natural rubber film: Part I: Grafting conditions and grafting yield. *J. Radioanal. Nucl. Chem.*, 267 (1): 113.
25. Kumar, V., Bhardwaj, Y.K., Rawat, K.P., and Sabharwal, S. (2005) Radiation induced grafting of vinylbenzyltrimethylammmonium chloride (VBT) onto cotton fabric and study of its anti-bacterial activities. *Radiat. Phys. Chem.*, 73: 175.
26. Nasef, M., Saidi, H., and Nor, H. (1999) Radition-induced graft copolymerization for preparation of action exchanges membranes: a review. *Nucl. Sci. J. Malaysia*, 17: 27.
27. Woods, R.J. and Pikaev, A.K. (1994) *Applied Radiation Chemistry: Radiation Processing*; Wiley Interscience Publications: New York;
28. Chapiro, A. (1962) *Radiation Chemistry of Polymeric Systems*; John Wiley & Sons: New York;
29. Aldrich chemical catalogue (2005–2006) Pgs. 1896.
30. Ruthven, D.M. (1984) *Principles of Adsorption and Adsorption Process. Wiley: New York.*
31. Baouab, M.H.V., Gauthier, R., Gauthier, H., Chabert, B., and Rammah, M.E.B. (2000) Immobilization of residual dyes onto ino-exchanger cellulosic materials. *J. Appl. Polym. Sci.*, 77: 171.
32. Wong, S.C., Szeta, Y.S., Cheung, W.H., and McKay, G. (2004) Adsorption of acid dyes on chitosan-equilibrium isotherm analysis. *Process Biochemistry*, 39 (6): 695.