Preparation of Toxic Metal Adsorbent by Radiation Induced Grafting of Co-monomers (Acrylic acid/2-hydroxyethyl methacrylate) on Polyethylene Films

N. C. Dafader[1], N. Rahman[1]*, M. R. Hasan[2], M. F. Alam[1]
M. Kabir[2], M. S. Hossen[2]

[1]*Nuclear and Radiation Chemistry Division, Institute of Nuclear Science and Technology*
Atomic Energy Research Establishment, Savar, Dhaka, Bangladesh
[2]*Department of Chemistry, Jahangirnagar University, Savar, Dhaka-1342, Bangladesh*

Abstract

Treatment of industrial heavy metal contaminated waste water prior to its discharge to environment is a contemporary approach. Grafted polymers may work in this purpose as heavy metal adsorbent. A gamma radiation induced grafting process is adopted to graft acrylic acid (AAc) and 2-hydroxyethyl methacrylate (HEMA) co-monomers on polyethylene (PE) in presence of inhibitor (mohr's salt) and solvent (methanol/H_2O). The graft yield was optimized with respect to monomer ratio, monomer concentration and radiation dose. The monomer concentration was varied from 10-20%, radiation dose was varied from 10-30 kGy (10, 15, 20, 25, 30 kGy) and monomer ratio was varied as (HEMA:AAc = 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80, 10:90). Highest graft yield 289% was obtained at 20% monomer concentration, 30 kGy radiation dose and monomer ratio HEMA:AAc = 90:10. The grafted PE films were studied for adsorption of Cu(II) from aqueous solution. Adsorption capacity was studied under different conditions: contact time, grafting percentage, pH and initial metal ion concentration. The adsorption capacity was determined as 39.96 mg/g after 60 minutes contact time at pH 5, initial metal ion concentration 500 ppm and 83 graft percentage.

Keywords: polyethylene, acrylic acid, 2-hydroxyethyl-methacrylate, radiation grafting, heavy metal adsorption

1. Introduction

The rapid development of industries such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper and pesticides industries etc., increases the discharge of toxic heavy metals into the environment as industrial waste waters and heavy metal pollution became one of the most serious environmental problems. Toxic heavy metals of particular concern in treatment of industrial wastewaters include zinc, copper, nickel, mercury, cadmium, lead and chromium. These heavy metals have adverse health effects [1]. Well known environmental destruction cases due to the contamination of heavy metals in aquatic streams are Minamata tragedy (organic mercury poisoning) and Itai-itai disease (cadmium poisoning) in Japan [2]. Hence it is necessary to treat metal contaminated waste water prior to its discharge to the environment. Most commonly used methods for removal of hazardous metal ions from industrial waste water includes precipitation, ion exchange, electrochemical method, activated carbon adsorption etc. But these methods have some disadvantages like high cost, low removal rate or difficulty for regeneration and reuse. Therefore many types of alternative low cost adsorbents have been studied for the adsorption of metal ions from aqueous solutions including sawdust [3], sporopollenin [4, 5], chitosan [6], peat [7], cellulose [8] and clay mineral [9].

Recently many researchers focused attention on grafted polymers as alternative heavy metal adsorbent [10-20]. 'Grafting' is a method by which functional monomers are covalently bonded onto the backbone polymer chain. Graft polymerization allows incorporation of various functions possessed by the grafted monomer to the parent polymer while maintaining the mechanical properties of the parent polymer [21, 22]. Among the different methods for initiating graft copolymerization like ionizing radiation, ultraviolet light, plasma treatment, decomposition of chemical initiators, oxidation of polymers etc, radiation-induced grafting technique is advantageous because of its extensive penetration into the polymer matrix and its rapid and uniform formation of radicals [23].

The excellent mechanical, thermal property and low cost of polyethylene (PE) attracted attention to use this as base polymer to prepare adsorbent. A good number of researchers have studied single or binary monomer grafted polyethylene (PE) film for heavy metal ion adsorption. Study on preparation of synthetic membranes using simultaneous radiation grafting of acrylic acid (AAc) and styrene (Sty) onto polyethylene has been carried out and the affinity of these membranes toward the adsorption or chelation with metal ions have been investigated by Hegazy et. al., 1999 [24]. The possibility of practical use of ion-exchange membranes prepared by gamma-radiation grafting of acrylonitrile (AN) and vinyl acetate (VAc) onto polyethylene in waste-water treatment were examined by Hegazy et. al., 2001 [25]. Graft copolymers were prepared by radiation grafting of acrylic acid onto polyethylene followed by chemical treatments and the selectivity of the prepared membranes towards the adsorption of different metals from a simulated waste solution has been studied by Hegazy et. al., 1999 [26]. Radiation graft copolymerization of styrene /maleic anhydride (Sty /MAn) comonomer onto low density polyethylene (LDPE) membrane was studied and the affinity of the treated grafted films to recover metal ions was studied by Abd El-Rehim et. al., 2000 [27].

Present study focuses on preparation a new adsorbent by grafting of binary monomers acrylic acid (AAc) and 2-

*Corresponding author: naziabaec@gmail.com

hydroxyethyl-methacrylate (HEMA) on polyethylene (PE) films and its application as Cu(II) recovery agent. A gamma radiation induced grafting process is adopted and the graft yield was optimized with respect to monomer ratio, monomer concentration and radiation dose. The AAc and HEMA grafted PE films has been used to adsorb Cu(II) ion from aqueous solution. Adsorption capacity was studied under different conditions: contact time, grafting percentage, pH and initial metal ion concentration.

2. Materials and Methods

2.1 Materials and Reagents

Polyethylene (PE) films (thickness 0.04 mm) were collected from Chakbazar, Dhaka, Bangladesh. These films were cut into small pieces (10×1 cm^2), washed with acetone, and dried in oven before use. Monomers HEMA, (Merck, Germany) and AAc (Guangdong Guanghua, China) were used. Methanol and Acetone were obtained from Merck, Germany. Mohr`s salt was supplied by BDH, England. $CuS0_4.5H_2O$ (Merck, Germany) was used for metal adsorption study. All reagents were analytical grade.

2.2 *Instrument and Apparatus*

The grafted PE films were characterized by FTIR (ATR) spectrophotometer (8400S Shimadzu Japan) in the range 700- 4000 cm^{-1} (resolution 4 cm^{-1}, number of scans: 20 times). The metal-ion concentrations in the solutions were analyzed by absorption spectro-photometer (AA-6800) of SHIMADGU Japan. The radiation source used for grafting experiment was Co-60 gamma ray. It is a 90 kCi Cobalt-60 Batch Type Panoramic Irradiator (Board of Radiation and Isotope Technology (BRIT) India). Activity was 68.63 kCi and dose rate was 13.7 kGy/h.

2.3 Grafting of AAc and HEMA onto the PE films by gamma radiation

The dry PE films weighing $W_{pristine}$ were taken into test tubes containing 0.4% Mohr's salt $[(NH_4)_2Fe(SO_4)_2.6H_2O]$ as inhibitor and acrylic acid (AAc) and 2-hydroxyethyl methacrylate (HEMA) as monomer and methanol:H_2O (96:4) as solvent. The monomer concentration was varied from 10% to 20% (10, 20 %) and monomer ratio was varied as (HEMA: AAc = 90:10, 80:20, 70: 30, 60: 40, 50:50, 40:60, 30:70, 20: 80, 10: 90). The contents of the test tubes were then irradiated with different doses (5, 10, 15, 20, 25, 30 kGy) with Co-60 gamma source. Irradiated PE films are washed with methanol for 1 hour to remove the homopolymers. Then the films were dried to constant weight in an oven at 50°C for 12 hours and were weighed (*$W_{grafted}$*). The graft yield was determined by the percent increase in the weight as follows:

$$\text{Graft Yield (\%)} = (W_{grafted} - W_{pristine})/W_{pristine}\times100 \quad (1)$$

2.4 Metal Ion Adsorption by the Grafted PE Film

The grafted PE films were soaked into the 20 ml aqueous solutions of Cu(II) at room temperature (25°C). The adsorption process was carried out at different pH, percentage of grafting, contact time and initial metal ion concentration. pH of the solutions were adjusted using HCl and NaOH solution. The metal-ion concentrations of the solutions before and after adsorption were analyzed by atomic absorption spectrophotometer. The metal ion uptake capacity of the film was calculated as follows:

$$Q = V(C_1-C_2)/W \quad (2)$$

where Q is the adsorption amount (mg/g), W the weight of the film (g), V the volume of solution (L), and C_1 and C_2 are the concentrations (mg/L) of metal ion before and after adsorption respectively.

2.5 Desorption of Metal Ions

The desorption of Cu(II) ions from the adsorbent films were carried out by the treatment with 2M aqueous solution of HCl for 30 min. The percent desorption was calculated using the following equation:

$$\text{Percent desorption} = (\text{Ions desorbed (mg)}/\text{Ions adsorbed (mg)}) \times 100. \quad (3)$$

3. Results and disscussion

Gamma radiation induced grafting of 2-hydroxyethyl methacrylate (HEMA)/acrylic acid (AAc) on PE films was carried out. The grafting of AAc/HEMA monomers on PE films was characterized by FTIR Spectrophotometer. Polyethylene may be considered as an infinite chain of CH_2 groups, therefore the characteristic features of the IR spectrum of PE film (Fig. 1) are it's C-H stretching and C-H deformation vibrations. C-H asymmetric and symmetric stretching vibrations are observed at 2916 and 2848 cm^{-1} respectively. C-H bending, wagging and rocking deformation of CH_2 group are observed at 1465, 1369 and 721 cm^{-1} respectively. The observed bands are in satisfactory agreement with the results obtained by previous workers [28]. In the spectrum of grafted PE film (Fig. 2), new peaks appear at 1718 cm^{-1} assigned to -C=O group of AAc and HEMA, 1153 cm^{-1} (corresponds to C-O-C bond) indicating ester group of HEMA. Broad peak around 3500 cm^{-1} represents the -OH group of HEMA and AAc. Peak at 1074 cm^{-1} is for C-O(H) bond of HEMA and AAc [29]. Again the peak at 1578 cm^{-1} indicates -C=O asymmetric stretching of carboxylate anion of AAc [30]. These peaks provide evidence of successful grafting of AAc and HEMA on PE film.

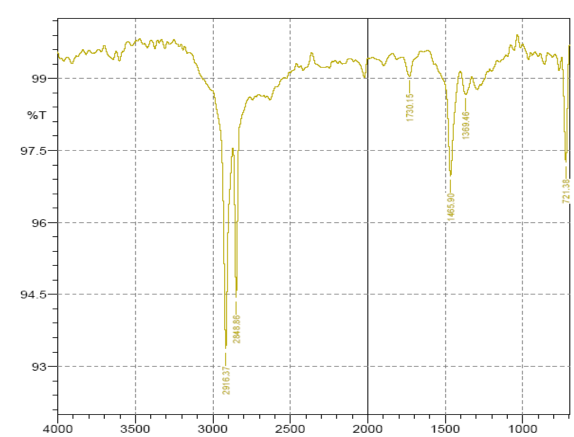

Fig. 1: IR spectrum of PE film

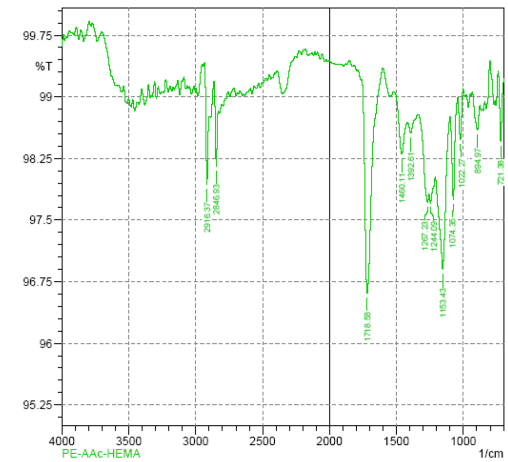

Fig. 2: IR spectrum of grafted PE film

The grafting process was studied under different monomer concentration, radiation dose and monomer ratio. Fig. 3 shows the effect of monomer concentration and radiation dose on graft yield. From the figure it can be found that the graft yield increased with increasing monomer concentration. The graft yield was 19% and 83% for 10 and 20 wt% of HEMA/AAc concentration respectively at 30kGy radiation dose. The increase of monomer concentration might have caused increased interaction between monomers and the polymer backbone. A noticeable homo-polymer was observed with increase of monomer concentration beyond 20%. In the lower dose region graft yield increased linearly and showed saturation at higher doses. This saturation feature could be due to an increase in the hindrance of the monomer permeation during the gamma-ray irradiation due to the growing and extending mass of grafted monomers on the PE surface.

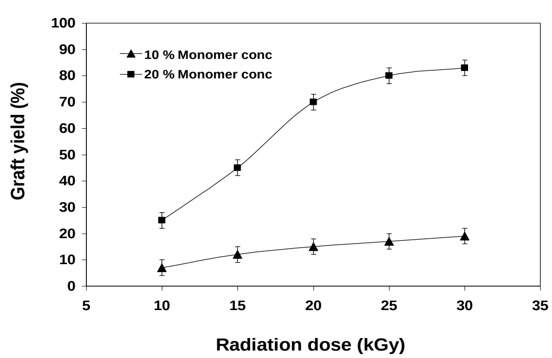

Fig. 3: Grafting of HEMA/AAc co-monomer on PE films at different monomer concentration as a function of radiation dose [HEMA: AAc = 1 : 1, Conc. of Mohr's salt: 0.4%, solvent: 96 % methanol]

Fig. 4 represents the effect of monomer ratio on graft yield. It can be observed that with increased amount of HAMA in the monomer mixture the graft yield increases linearly. These results indicate that HEMA is grafted more easily on PE films than AAc.

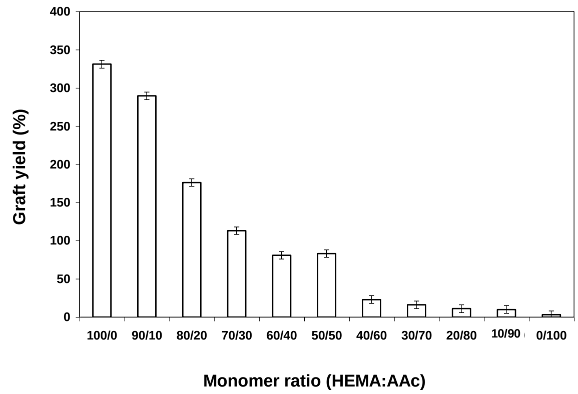

Fig. 4: Grafting of HEMA/AAc co-monomer on PE films at different monomer ratio [20% monomer concentration, 30 kGy radiation dose, Conc. of Mohr's salt: 0.4%, solvent: 96% methanol]

Fig. 5 shows the effect of monomer ratio on graft yield and metal adsorption. It was found that although graft yield increases linearly with increase of amount of HEMA in the monomer mixture, the adsorption capacity was highest for HEMA:AAc = 50/50. The result indicate that HEMA was grafted relatively easily on PE film than AAc, on the other hand AAc adsorbs Cu(II) relatively easily than HEMA. These results indicate the advantage of use of binary monomers than one single monomer. It can be explained as follows: when only AAc is used then graft yield is very low, therefore metal adsorption was very low, when we add HEMA (10-50%) to AAc, the grafting of HEMA and also grafting of AAc increases. Such synergistic effect of one monomer on another monomer is reported in previous study [31]. But when we add HEMA more than 50% it increases grafting of HEMA than AAc, therefore metal adsorption decreases. The rest of the adsorption study was done with HEMA/AAc = 50/50 monomer ratio.

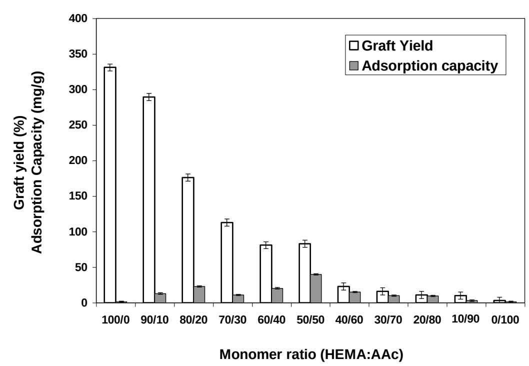

Fig. 5: Change of graft yield and adsorption capacity with monomer ratio [at 20% monomer concentration, 30 kGy radiation dose, Conc. of Mohr's salt: 0.4%, solvent: 96% methanol]

The effects of the graft yield on the adsorption capacities of metal ions have been investigated in the grafting range 15–83%. The results are shown in Fig. 6. The adsorption capacity of Cu(II) ions increased with the increase of graft yield, then almost leveled off after 83% graft yield, reaching 39.96 mg/g of saturation adsorption values, similar trend is reported in previous studies [32–35]. This increase in adsorption of the Cu(II) ion can be attributed to the increase of functional groups such as carboxyl and hydroxyl groups, which are grafted onto the PE film. The leveling off of adsorption amount after a certain graft yield is due to the fact that after a certain graft yields the closely packed grafted chains on PE film hinders diffusion of metal ions into the polymer backbone.

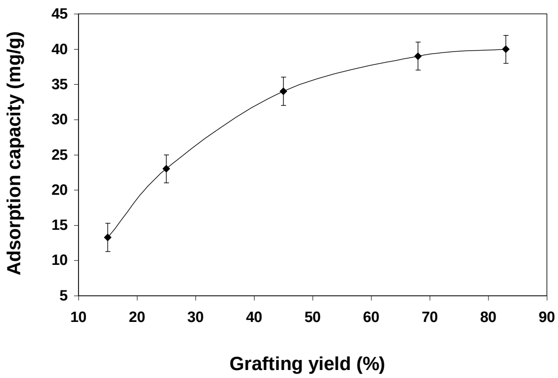

Fig. 6: Effect of grafting percentage on adsorption capacity (Conc of Cu(II) 500 ppm, pH 5, standing time 60 min, monomer ratio 1:1, Conc. of Mohr's salt: 0.4%, solvent: 96% methanol]

The effect of contact time of adsorbent in aqueous medium on Cu(II) adsorption were examined. The grafted PE films were kept into the aqueous solutions of Cu(II) with constant pH (pH 5) and initial metal ion concentration of 500 ppm at room temperature 25 °C. The concentrations of the ions in solution were determined at regular interval of times. The experimental data obtained are shown in Fig. 7. It shows that the adsorption amount increases with increase of standing time and the adsorption equilibrium of the adsorbent for Cu(II) ions was reached after 60 min.

It is well known that the pH of the medium has a great effect on the adsorption capacity of grafted adsorbent, because at different pH values, the protonation and deprotonation behaviors of acidic and basic groups, the surface structure of the adsorbent would be influenced and the metal ions would exist in different forms [34, 36]. The experimental results for the effects of pH on the adsorption of metal ions are shown in figure 8. It can be observed that the adsorption increased significantly with the increase of pH from 3 to 5. At low pH values, the high hydrogen ion concentration at the interface repels the positively charged metal ions and prevents their approach to the adsorbent surface [37]. Again increase of pH beyond 5 caused precipitation of $Cu(OH)_2$, therefore adsorption amount decreases.

Fig. 9 shows the relationship between initial concentration of metal ions and the adsorption capacity. It shows that the adsorption amount of metal ions increased with increasing

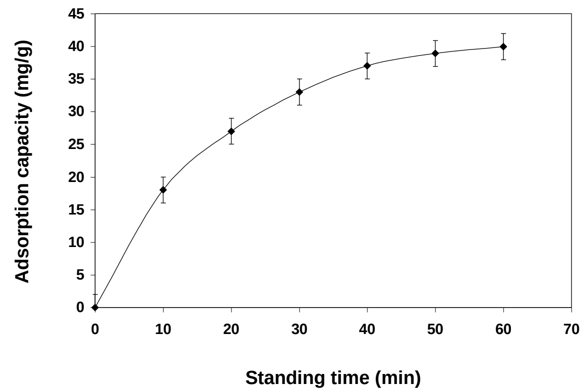

Fig. 7: Effect of standing time on adsorption capacity (Conc of Cu(II) 500 ppm, pH 5, Graft percentage 83)

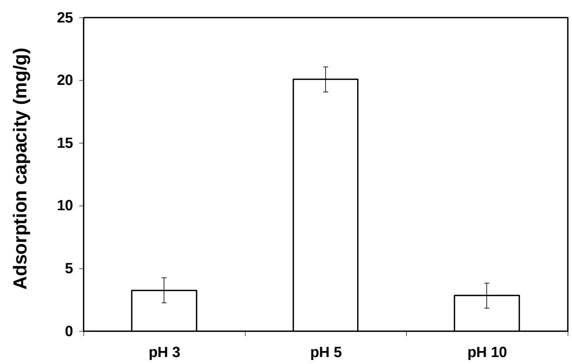

Fig. 8: Effect of pH on adsorption capacity (Conc 500 ppm, time 60, Graft percentage 17)

initial metal ion concentration then reached a plateau value at higher concentration. This is to the fact that the chelating sites of the adsorbent become saturated when the metal ion concentration increases. For interpretation of the Cu(II) adsorption data, the Langmuir isotherm models is used. The linear form of the Langmuir isotherm is presented by

$$C_e/Q_e = C_e/Q_o + 1/(Q_o b) \quad (4)$$

where C_e is the equilibrium concentration (mg L^{-1}), Q_o the monolayer saturation adsorption capacity of adsorbent (mg g^{-1}), Q_e is the equilibrium adsorption capacity and b is Langmuir adsorption constant (Lmg^{-1}). The plot of C_e/Q_e versus C_e shown in Fig. 10 was drawn from the experimental data given in Fig. 9. The relationship between C_e/Q_e and C_e is linear indicating that the adsorption behavior follows the Langmuir adsorption isotherm. From the Langmuir equation the monolayer saturation adsorption capacity of the adsorbent was found as 44.84 mg/L. Cu(II) adsorption capacities of AAc/HEMA grafted PE film compared with some other adsorbents are shown in Table 1.

The desorption of Cu(II) ions from the adsorbent films were carried out by treatment with 2M aqueous solution of HCl. After 30 min the desorption ratio was 98 %.

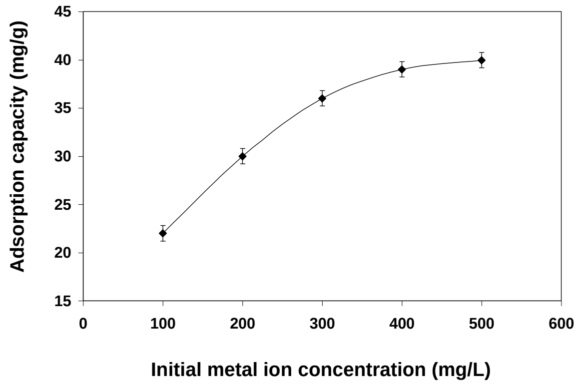

Fig. 9: Effect of initial metal ion concentration on adsorption capacity (pH 5, Graft percentage 83)

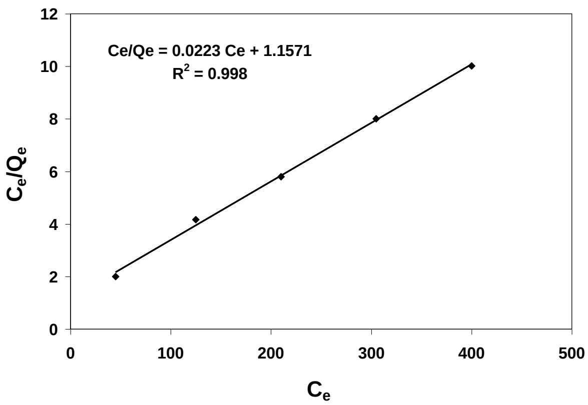

Fig. 10: Langmuir isotherm plot for Cu(II) adsorption

Table 1: Cu(II) adsorption capacity of AAc/HEMA grafted PE compared with some other adsorbents

Adsorbent	Cu^{2+} adsorption capacity (mg/g)
Pristine PE film [present study]	0
Modified AAc/HEMA graft PE film [present study]	44.84
Itaconic acid/acrylamide graft PET fiber [14]	7.73
Methacrylic acid/acrylamide graft PET fiber [13]	31.25
Multi-walled carbon nanotubes [38]	12.34
Sugar beet pulp carbon [39]	14.81

4. Conclusion

A new adsorbent was prepared by gamma radiation induced grafting of acrylic acid (AAc) and 2-hydroxyethyl methacrylate (HEMA) on polyethylene (PE) film. The graft yield was optimized with respect to monomer ratio, monomer concentration and radiation dose. The grafted PE films were studied for adsorption of Cu(II) from aqueous solution. Adsorption capacity was studied under different conditions: contact time, grafting percentage, pH and initial metal ion concentration. It was found that the adsorption isotherm of the ions fitted Langmuir-type isotherms. The highest adsorption capacity calculated is 44.84 mg/g. Present study reveals that the adsorbent prepared by grafting of HEMA and AAc on PE film can be suitable for adsorption of Cu(II).

Acknowledgment

The authors are pleased to acknowledge IAEA for providing technical support for the research. Authors also would like to thank the gamma source division of the Institute of Food and Radiation Biology, Atomic Energy Research Establishment for providing the opportunity to use the irradiation facility.

References

1. F. Fu and Q. Wang, Removal of Heavy Metal Ions from Wastewaters: A Review, J. Environ. Manag., **92(3)**, 407-418 (2011).
2. J. Ui (Ed.), Industrial Pollution in Japan (The Japanese Experience Series), United Nations University Press, Tokyo, (1992). http://www.unu.edu/unupress/unupbooks/uu35ie/uu35ie00.htm.).
3. M. Sciban, M. Klasnja and B. Skrbic, Modified Softwood Sawdust as Adsorbent of Heavy Metal Ions from Water, J. Hazard. Mater., **136(2)**, 266-271 (2006).
4. N. Ünlü and M. Ersöz, Adsorption Characteristics of Heavy Metal Ions onto a Low Cost Biopolymeric Sorbent from Aqueous Solutions, J. Hazard. Mater., **136(2)**, 272-280 (2006).
5. M. Arslan, Z. Temoçin and M. Yiğitoğlu, Removal of Cadmium(II) from Aqueous Solutions using Sporopollenin, Fresenius Environ. Bull., **13(1)**, 1-4 (2004).
6. R. Schmuhl, H. M. Krieg and K. Keizer, Adsorption of Cu(II) and Cr(VI) Ions by Chitosan: Kinetics and Equilibrium Studies, Water SA, **27(1)**, 1-7 (2001).
7. Y. S. Ho, J. C. Y. Ng and G. Mckay, Removal of Lead(II) from Effluents by Sorption on Peat Using Second-Order Kinetics, Separ. Sci. Techno., **36(2)**, 241-261 (2001).
8. S. R. Shukla and V. D. Sakhardande, Column Studies on Metal Ions Removal by Dyed Cellulosic Materials, J. Appl. Polym. Sci., **44(5)**, 903-910 (1992).
9. Y. S. Al-Degs, M. I. El-Barghouthi, A. A. Issa, M. A. Khraisheh and G. M.Walker, Sorption of Zn(II), Pb(II), and Co(II) Using Natural Sorbent: Equilibrium and Kinetic Studies, Water Res., **40(14)**, 2645-2658 (2006).
10. R. Coşkun and C. Soykan, Lead(II) Adsorption from Aqueous Solution by Poly(ethylene terephthalate)-g-Acrylamide Fibers, J. Polym. Res., **13(1)**, 1-8 (2006).
11. H. Bāğ, A. R. Türker, R. Coşkun, M. Saçak and M. Yiğitoğlu, Determination of Zinc, Cadium, Cobalt and Nickel by Flame Atomic Absorption Spectrometry after Preconcentration by Polyethylene terephthalate/ Fibers Grafted with Methacrylic acid, Spectrochimica Acta B, **55(7)**, 1101-1108 (2000).
12. O. Bozkaya, M. Yiğitoğlu and M. Arslan, Investigation on Selective Adsorption of Hg(II) Ions using 4-Vinyl pyridine Grafted Poly(ethylene terephthalate) Fiber, J. Appl. Polym. Sci., **124 (2)**, 1256-1264 (2012).
13. R. Çoşkun, C. Soykan and M. Saçak, Adsorption of Copper(II), Nickel(II) and Cobalt(II) Ions from Aqueous Solution by Methacrylic acid/Acrylamide Monomer Mixture

Grafted Poly(ethylene terephthalate) Fiber, Sep. Purif. Techno., **49 (2)**, 107-114 (2006).

14. R. Coşkun, C. Soykan and M. Saçak, Removal of Some Heavy Metal Ions from Aqueous Solution by Adsorption using Poly(ethylene terephthalate)-g-Itaconic acid Acrylamide Fiber, React. Funct. Polym., **66 (6)**, 599-608 (2006).
15. M. Arslan, Preparation and Use of Amine-Functionalized Glycidyl methacrylate-g-Poly(ethylene terephthalate) Fibers for Removal of Chromium(VI) from Aqueous Solution, Fiber Polym., **11 (3)**, 325-330 (2010).
16. M. Yiğitoğlu and M. Arslan, Adsorption of Hexavalent Chromium from Aqueous Solutions using 4-Vinyl Pyridine Grafted Poly(ethylene terephthalate) Fibers, Polym. Bull., **55 (4)**, 259-268 (2005).
17. M. Yiğitoğlu and M. Arslan, Selective Removal of Cr(VI) Ions from Aqueous Solutions Including Cr(VI), Cu(II) and Cd(II) Ions by 4-Vinly pyridine/2-Hydroxyethylmethacrylate Monomer Mixture Grafted Poly(ethylene terephthalate) Fiber, J. Hazard. Mater., **166 (1)**, 435–444 (2009).
18. M. Karakısla, The Adsorption of Cu(II) Ion from Aqueous Solution upon Acrylic acid Grafted Poly(ethylene terephthalate) Fibers, J. Appl. Polym. Sci., **87 (8)**, 1216-1220 (2003).
19. H. Hamada, A. Razik and E. R. Kenawy, Synthesis, Characterization, and Amidoximation of Diaminomaleodinitrile-Functionalized Polyethylene terephthalate Grafts for Collecting Heavy Metals from Wastewater, J. App. Polym. Sci., **125 (2)**, 1136-1145 (2012).
20. X. Ping, M. Wangn and X. Ge, Radiation Induced Graft Copolymerization of n-Butyl acrylate onto Poly(ethylene terephthalate) (PET) Films and Thermal Properties of the obtained Graft Copolymer, Radia. Phys. Chem., **80 (5)**, 632 - 637 (2011).
21. Y. L. Hsieh, M. Shinawatra and M. D. Castillo, Postirradiation Polymerization of Vinyl Monomers on Poly(ethylene terephthalate), J. App. Polym. Sci., **31 (2)**, 509-519 (1986).
22. E. M. Abdel-Bary, A. A. Sarhan and H. H. Abdel-Razik, Effect of Graft Copolymerization of 2-Hydroxyethyl Methacrylate on the Properties of Polyester Fibers and Fabric, J. Appl. Polym. Sci., **35 (2)**, 439-448 (1986).
23. M. M. Nasef, Gamma Radiation-Induced Graft Copolymerization of Styrene onto Poly(ethylene terephthalate) Films. J. Appl. Polym. Sci., **77 (5)**, 1003-1012 (2000).
24. A. El-Sayed Hegazy, H. Kamal, N. Maziad and A. M. Dessouki, Membranes Prepared by Radiation Grafting of Binary Monomers for Adsorption of Heavy Metals from Industrial Wastes, Nucl. Instru. Meth. B, **151 (1-4)**, 386-392 (1999).
25. A. El-Sayed Hegazy, H. Kamal, N.A. Khalifa and G. H. A. Mahmoud, (2001). Separation and Extraction of Some Heavy and Toxic Metal Ions from Their Wastes by Grafted Membranes, J. Appl. Polym. Sci., **81 (4)**, 849-860 (2001).
26. A. El-Sayed Hegazy, H. A. Abd El-Rehim, A. M. I. Ali, H. G. Nowier and H. F. Aly, Characterization and Application of Radiation Grafted Membranes in Treatment of Intermediate Active Waste, Nucl. Instrum. Meth. B, **151 (1-4)**, 393-398 (1999).
27. H. A. Abd El-Rehim, E. A. Hegazy and A. El-Hag Ali, Selective Removal of Some Heavy Metal Ions from Aqueous Solution using Treated Polyethylene-g-Styrene/Maleic Anhydride Membranes, React. Funct. Polym., **43 (1-2)**, 105-116 (2000).
28. J. V. Gulmine, P. R. Janissek, H. M. Heise and L. Akcelrud, Polyethylene Characterization by FTIR, Polym Testing., **21(5)**, 557-563 (2002).
29. J. Prachayawarakorn and K. Boonsawat, Physical, Chemical, and Dyeing Properties of_Bombyx Mori Silks Grafted by 2-Hydroxyethyl methacrylate and Methyl methacrylate, J. Appl. Polym. Sci., **106 (3)**, 1526-1534 (2007).
30. M. Sadeghi and M. Yarahmadi, Synthesis of Starch- g-Poly (Acrylic acid- co-2-Hydroxy ethyl methacrylate) as Potential pH-Sensitive Hydrogel Based Drug Delivery System, Indian J. Sci. Techno., **4 (9)**, 1090-1095 (2011).
31. K. C. Gupta and S. Sahoo, Grafting of Acrylonitrile and Methyl methacrylate from Their Binary Mixtures on Cellulose Using Ceric Ions, J. Appl. Polym. Sci., **79 (5)**, 767-778 (2001).
32. W. Lin, Y. Lu and H. Zeng, Studies of the Preparation, Structure, and Properties of an Acrylic Chelating Fiber Containing Amidoxime Groups,. J. Appl. Polym. Sci., **47 (1)**, 45-52 (1993).
33. W. Lin and Y. L. Hsieh, Ionic Absorption of Polypropylene Functionalized by Surface Grafting and Reactions, J. Polym. Sci. Polym. Chem., **35 (4)**, 631-642 (1997).
34. H. Lin, M. Kimura, K. Hanabusa, H. Shırai, N. Ueno and Y. Mori, Preparation and Adsorption Properties of Poly(N-vinylformamide/acrylonitrile) Chelating Fiber for Heavy Metal Ions, J. Appl. Polym. Sci., **85 (7)**, 1378-1386 (2002).
35. A. Hebeish and Z. H. El-Hilw, Preparation of DEAE Cotton-*g*-Poly(methacrylic acid) for Use as Ion Exchanger, J. Appl. Polym. Sci., **67 (4)**, 739-745 (1998).
36. R. Liu, B. Zhang and H. Tang, Adsorption Properties of Poly(acrylaminophosphonic-carboxyl-hydrazide)Type Chelating Fiber for Heavy Metal Ions, J. Appl. Polym. Sci., **70 (1)**, 7-14 (1998).
37. M. Yiğitoğlu, M. Ersöz, R. Coşkun, O. Şanli and H. I. Ünal, Adsorption of Copper(II), Cobalt(II), and Iron(III) Ions from Aqueous Solutions on Poly(ethylene terephthalate) Fibers, J. Appl. Polym. Sci., **68 (12)**, 1935-1939 (1998).
38. I. Mobasherpour, E. Salahi and M. Ebrahimi, Thermodynamics and Kinetics of Adsorption of Cu(II) from Aqueous Solutions onto Multi-Walled Carbon Nanotubes, J Saudi Chem. Soc., **18 (6)**, 792-801 (2014).
39. A. Ozer and F. Tumen, Cu(II) Adsorption from Aqueous Solutions on Sugar Beet Pulp Carbon, Eur. J. Miner. Process. Environ. Prot., **5 (1)**, 26-32 (2005).