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Gamma Ray Induced Grafting of Binary Monomers (Acrylic acid/Methyl Methacrylate) onto Polyethylene (PE) Films for Heavy Metal Adsorption

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Abstract

In this research work γ-ray induced grafting of co-monomers acrylic acid (AAc) and methyl methacrylate (MMA) on polyethylene (PE) films was investigated and the grafted films were tested for the removal of heavy metal ions from aqueous solution. Gamma ray induced grafting of AAc and MMA was optimized with respect to monomer ratio, monomer concentration, radiation dose using methanol/H_2O as solvent and mohr's salt as inhibitor. The monomer concentration was varied from 10-40 % (10, 20, 40 %), radiation dose was varied from 5-40 kGy (5, 10, 15, 20, 25, 30, 40 kGy), monomer ratio was varied as (MMA: AAc = 9:1, 8:2, 7:3, 6:4, 1:1, 4:6, 3:7, 2:8, 1:9). Highest graft yield of 450 % was obtained at 40 % monomer concentration, 40 kGy radiation dose and 1:1 monomer ratio. 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 after 30 minutes contact time was determined as 36.6 mg/g at pH 5, initial metal ion concentration 500 ppm and 286 graft percentage. These adsorbents have good future prospects as Cu(II) recovery agent.

Key words: Polyethylene, Acrylic acid, Methyl methacrylate, Radiation grafting, Heavy metal adsorption.

1. Introduction

Heavy metal pollution has been considered as one of the most severe environmental problems today which is sparked by the well-known environmental destruction cases: Minamata disease (organic mercury poisoning), Itai-itai disease (cadmium poisoning) [1]. The treatment of heavy metals is of special concern due to their recalcitrance and persistence in the environment. Toxic heavy metals of particular concern in the treatment of industrial wastewaters include zinc, copper, nickel, mercury, cadmium, lead and chromium. If the metals are ingested beyond the permitted concentration they can cause serious health disorders [2]. Hence it is necessary to treat metal contaminated waste water prior to its discharge to the environment. But the conventional methods for removal of hazardous metal ions from waste water such as precipitation, ion exchange, activated carbon adsorption, electrolytic method etc. have limitations like high cost, low removal rate or difficulty for regeneration and reuse. Therefore many researches have focused concentration on the study of alternative low cost effective adsorbents from sawdust [3], sporopollenin [4,5], chitosan [6], peat [7], cellulose [8, 9], clay mineral [10, 11] etc.

Recently, grafted polymers have received much attention as alternative heavy metal adsorbent [12-22]. 'Grafting' is a method wherein monomers are covalently bonded onto the polymer chain. The advantage of graft polymerization onto a polymer film is that by this method a variety of functions possessed by the grafted polymer can be imparted to the films while maintaining the mechanical properties of the parent films [23-24]. There are several methods for initiating graft copolymerization, including ionizing radiation, ultraviolet light, plasma treatment, decomposition of chemical initiators, and oxidation of polymers. Among these methods the radiation-induced grafting technique is important because of its extensive penetration into the polymer matrix and its rapid and uniform formation of radicals to initiate grafting without using any toxic chemical initiator [25].

Due to the excellent mechanical and thermal property and low cost, polyethylene (PE) has been used as the base polymer to prepare adsorbent. Numbers of researchers have studied single or binary monomer grafted polyethylene (PE) film for adsorption of heavy metal ion. 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 studied [26]. Ion-exchange membranes were prepared by gamma-radiation grafting of acrylonitrile (AN) and vinyl acetate (VAc) in a binary monomer mixture onto polyethylene and the possibility of their practical use in waste-water treatment to remove some heavy and toxic metal ions were investigated [27]. Graft copolymers that possess ionic characters 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 [28]. Radiation graft copolymerization of styrene /maleic anhydride (Sty /MAn) comonomer onto low density polyethylene (LDPE) membrane was investigated and the affinity of the treated grafted films to recover metal ions was studied. [29].

In the present study a new adsorbent was prepared by grafting of binary monomers acrylic acid (AAc) and methyl methacrylate (MMA) on polyethylene (PE) films. 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 MMA grafted PE 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. Experimental

2.1 Materials and reagents

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

2.2 *Instrument and apparatus*

The grafted PE films were characterized by FTIR Spectrophotometer (AIM-8800 of SHIMADZU Japan). The metal-ion concentrations in the solutions were analyzed by absorption spectro-photometer (AA-6800) of SHIMADZU Japan.

2.3. Grafting of AAc and MMA 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 [Molecular Formula: $(NH_4)_2Fe(SO_4)_2.6H_2O$] as inhibitor and acrylic acid (AAc) and methyl methacrylate (MMA) as monomer and methanol:H_2O (96:4) as solvent. The monomer concentration was varied from 10% to 40% (10, 20, 40 %) and monomer ratio was varied as (MMA: AAc = 9:1, 8:2, 7: 3, 6: 4, 1:1, 4:6, 3:7, 2: 8, 1: 9). The contents of the test tubes were then irradiated with different doses (5, 10, 15, 20, 25, 30, 40 kGy) at dose rate 10 kGy/h. Irradiated PE films were washed with methanol for 1 hour to remove the homopolymers. Then the films were dried in 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:

$$\textit{Graft Yield}\,(\%) = (W_{\text{grafted}} - W_{\text{pristine}}) / W_{\text{pristine}} \times 100\ .$$

2.4. Metal ion adsorption by the grafted PE film

The grafted PE films showed very little Cu(II) adsorption capacity. Therefore grafted PE films were treated with 96% H_2SO_4 at 60°C for 20 minutes to improve the Cu(II) adsorption. The grafted PE films after H_2SO_4 treatment 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 spectro-photometer. The metal ion uptake capacity of the film was calculated as follows:

$$Q = V(C_1 - C_2)/W ,$$

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.

3. Results and disscussion

Grafting of methylmethacrylate (MMA) / acrylic acid (AAc) was carried out on PE films using γ radiation. The PE films were characterized by FTIR Spectrophotometer. The characteristic features of the IR spectrum of PE film (Figure 1) are it's C-H stretching and bending vibration. C-H asymmetric and symmetric stretching vibrations are found at 2916 and 2848 cm^{-1} respectively and C-H bending vibration of CH_2 group is found at 1465 cm^{-1}. In the spectrum of grafted PE film (Figure 2), a strong absorption band is found at 1726 cm^{-1} that denotes C=O group. Another strong absorption band of 1145 cm^{-1} is due to C-O stretching. Absorption bands of C=O & C-O groups indicate grafting of functional groups onto PE film.

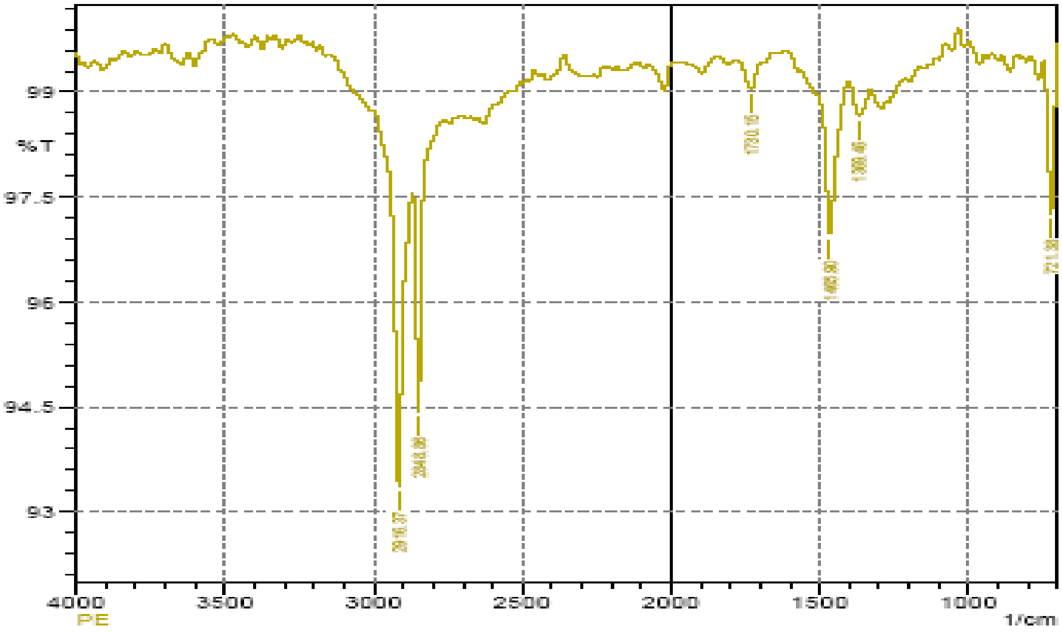

Figure 1: IR spectrum of PE film

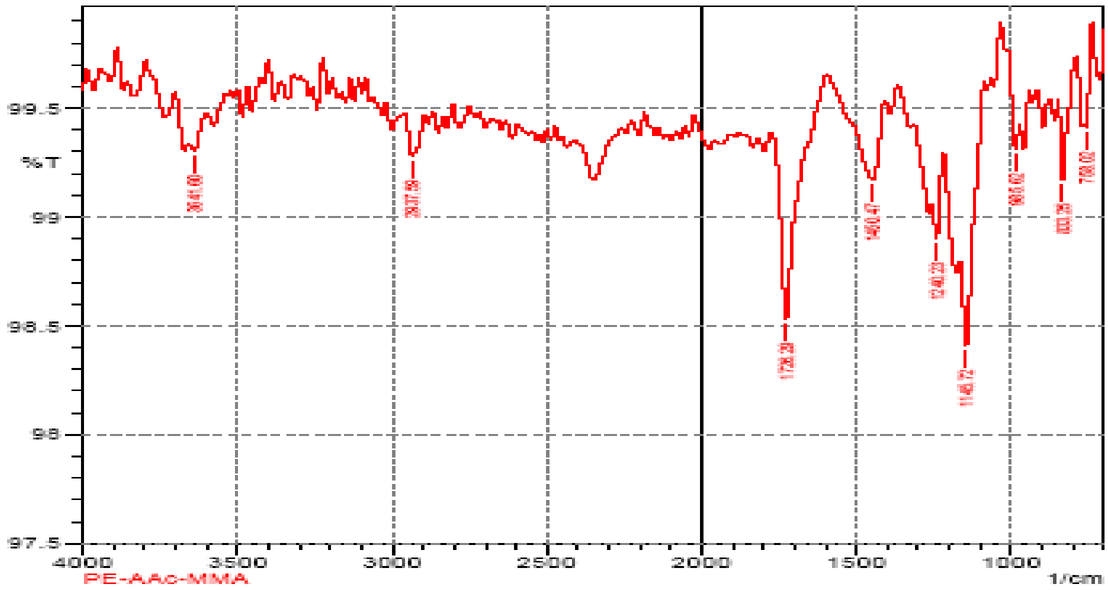

Figure 2: IR spectrum of grafted PE film (Graft yield 250 %)

The graft yield was optimized with respect to monomer concentration, radiation dose and monomer ratio. The effects of monomer concentration and radiation dose on graft yield are shown in figure 3. It can be observed that the graft yield increased with increase in monomer concentration. The graft yield was 186 %, 305 % and 450 % for 10, 20 and 40 wt % of MMA/AAc concentration respectively at 40kGy radiation dose. This might be due the increase of interaction between monomers with the polymer backbone. Increase of monomer concentration beyond 40 % caused noticeable homo-polymerization. It was also observed that the graft yield increased linearly in the lower dose region and showed saturation at higher doses. This saturation feature could be due to the increase of the obstruction of the monomer permeation during the gamma-ray irradiation due to the growing and extending mass of grafted monomers on the PE surface.

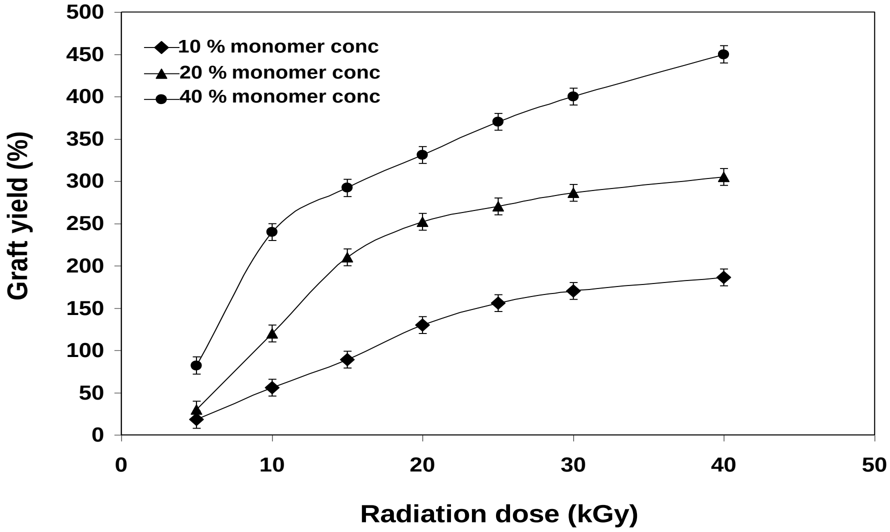

Figure 3: Grafting of MMA / AAc co-monomer on PE films at different monomer concentration as a function of radiation dose [MMA: AAc = 1 : 1, Conc. of Mohr's salt: 0.4%, solvent: 96 % methanol]

Effect of monomer ratio on graft yield is shown in figure 4. It can be seen that the graft yield increased with increase of AAc in the monomer mixture giving higher values around MMA:AAc = 70: 30 to 50:50. It can be explained as when the monomer ratio is near 1: 1, formation of co-polymer is favored, but with the increase of one monomer in the monomer mixture favors formation of homoplymer of that monomer, therefore the overall graft yield decreased.

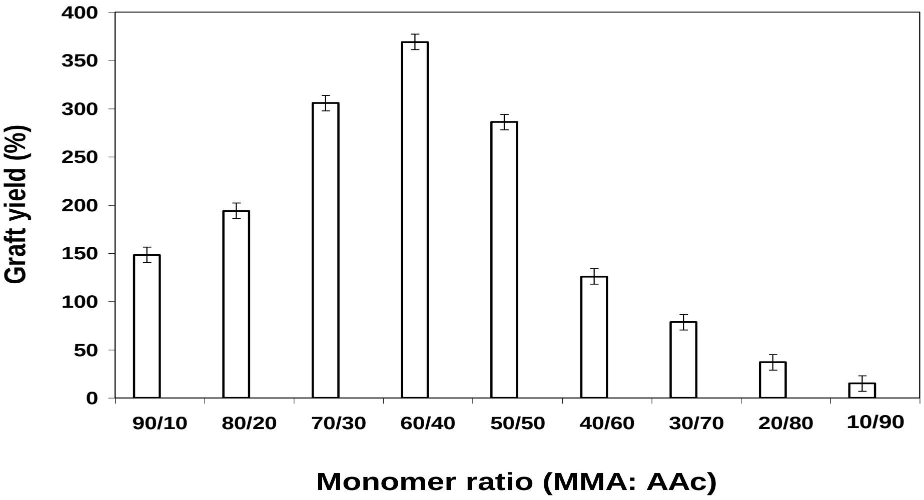

Figure 4: Grafting of MMA/AAc co-monomer on PE films at different monomer ratio [20 % monomer concentration, 30 kGy radiation dose, Conc. of Mohr's salt: 0.4%, solvent: 96 % methanol]

Effect of monomer ratio on graft yield and metal adsorption is shown in figure 5. It was observed that although graft yield is highest for MMA:AAc = 60:40, the adsorption capacity was highest for MMA: AAc = 50/50. The result indicate that MMA was grafted relatively easily on PE film than AAc on the other hand AAc adsorbs Cu(II) relatively easily than MMA. These results indicate the advantage of use of binary monomers than one single monomer. Therefore the rest of the adsorption study was done with MMA/AAc = 50/50 monomer ratio.

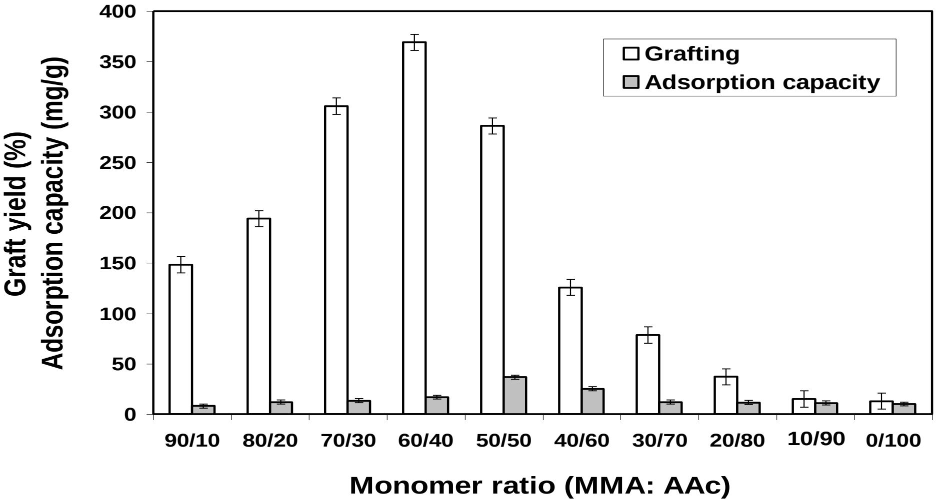

Figure 5: Change of graft yield and adsorption capacity with monomer ratio [at 20 % monomer concentration, 30 kGy radiation dose, Conc. of Mohr's salt: 0.4%, solvent: 96 % methanol]

The effects of the graft yield on the adsorption amount of ions have been studied by performing adsorption experiments in the grafting range 186–400%. The results are shown in Figure. 6. The adsorption amount of Cu(II) ions increased with the increase in graft yield reaching saturation adsorption value of 36.6 mg/g, then graft yield showed slight decrease after 286% graft yield, similar trend is reported in previous studies [30,31–33]. This increase in adsorption of the Cu(II) ion can be attributed to the increase of functional groups such as carboxyl, which are grafted onto the film. Therefore, due to more functional groups more interactions with the ions took place. The decrease of adsorption amount after a certain graft yield is due to the fact that after a certain graft yield the closely packed structure of grafted PE film hinders diffusion of ions into the polymer backbone.

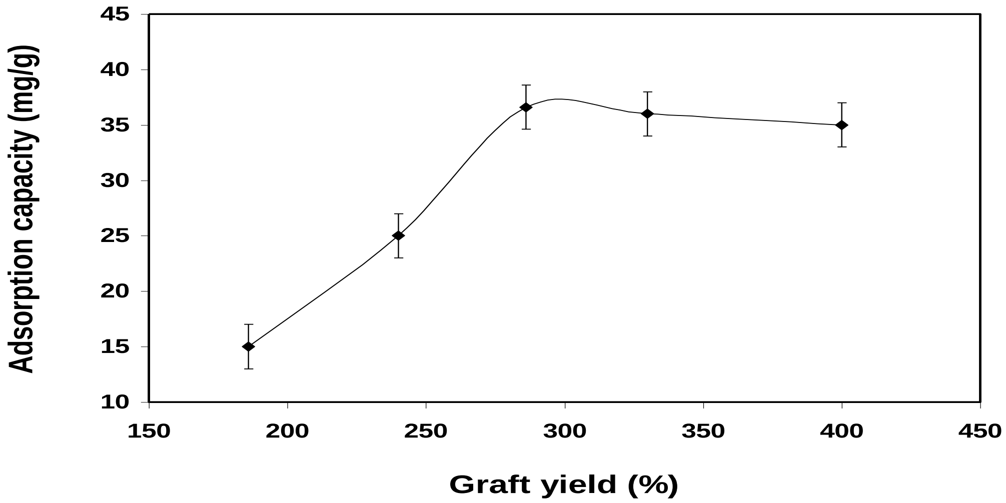

Figure 6: Effect of grafting percentage on adsorption capacity (Conc of Cu(II) 500 ppm, pH 5, standing time 30 min, monomer ratio 1: 1, Conc. of Mohr's salt: 0.4%, solvent: 96 % methanol]

The grafted PE films were kept into the aqueous solutions of Cu(II) at constant pH and initial metal ion concentration at room temperature (25 °C) to study the effect of contact time on adsorption. The concentrations of the ions in solution were determined at regular times. The experimental data obtained are shown in Figure 7. It shows that the adsorption amount increases with increase of time and the adsorption equilibrium reached after 30 min.

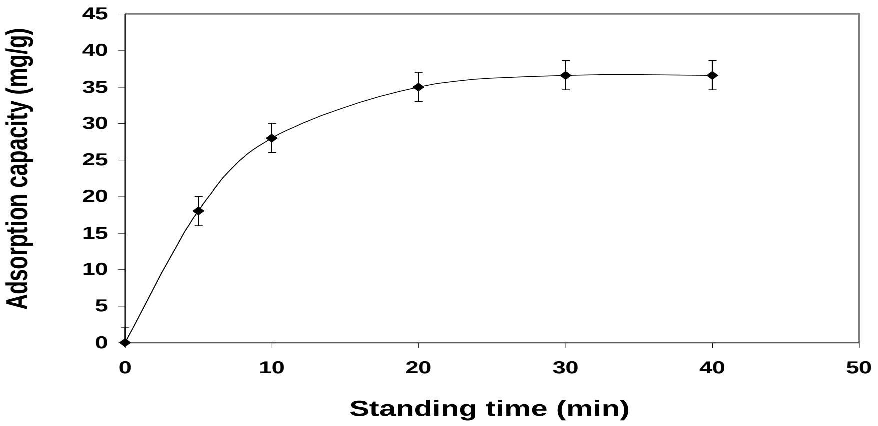

Figure 7: Effect of standing time on adsorption capacity (Conc of Cu(II) 500 ppm, pH 5, Graft percentage 286)

It is well known that the pH of the medium has a great effect on the adsorption amount of grafted adsorbent, because at different pH values, the protonation and deprotonation behaviors of acidic and basic groups could be influenced and the surface structure of the adsorbent and the metal ions could exist in different forms [34, 32]. The experimental results of the effects of pH on the adsorption of the metal ions are shown in Figure 8. It can be seen 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 [35]. Again increase of pH after pH 5 caused precipitation of $Cu(OH)_2$., therefore adsorption amount decreased.

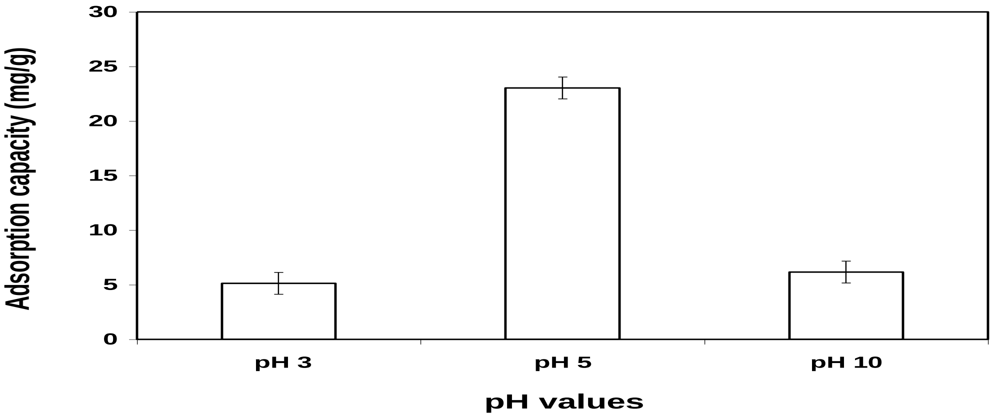

Figure 8: Effect of pH on adsorption capacity (Standing time 3**0** min, Conc of Cu(II) 500 ppm, pH 5, Graft percentage 230)

Figure 9 shows the relationship between initial concentration of metal ions and the adsorption amount. Figure shows that the adsorption amount of metal ions increased with increase of initial ion concentration then reached a plateau value at higher concentration.

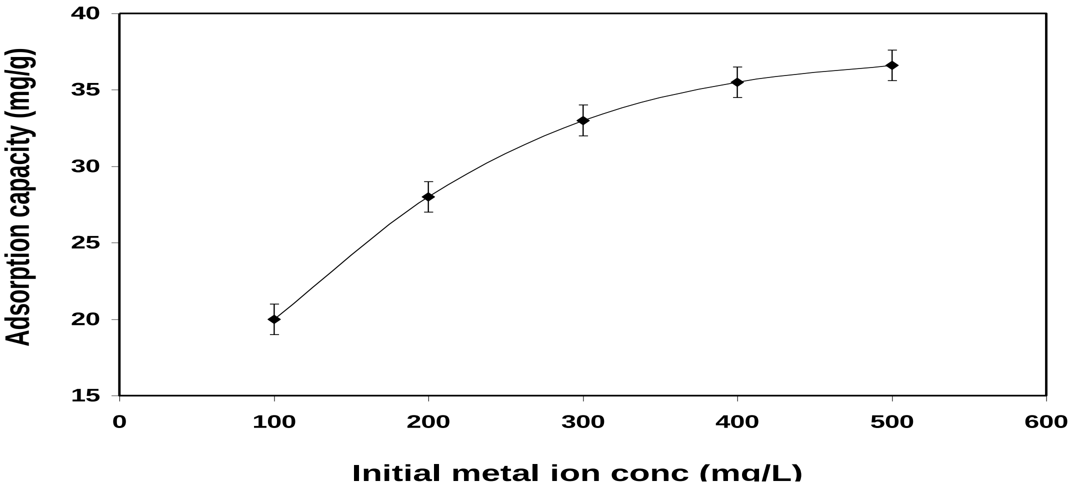

Figure 9: Effect of initial ion conc on adsorption capacity (standing time 30 min, pH 5, Graft percentage 286)

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

$C_e/Q_e = C_e/Q_o + 1/(Q_o b)$ ………………….. (3)

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 Figure 10 was drawn from the experimental data given in Figure 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 40.98 mg/g. Cu(II) adsorption capacity of AAc/MMA grafted PE compared with some other adsorbents is shown in Table 1.

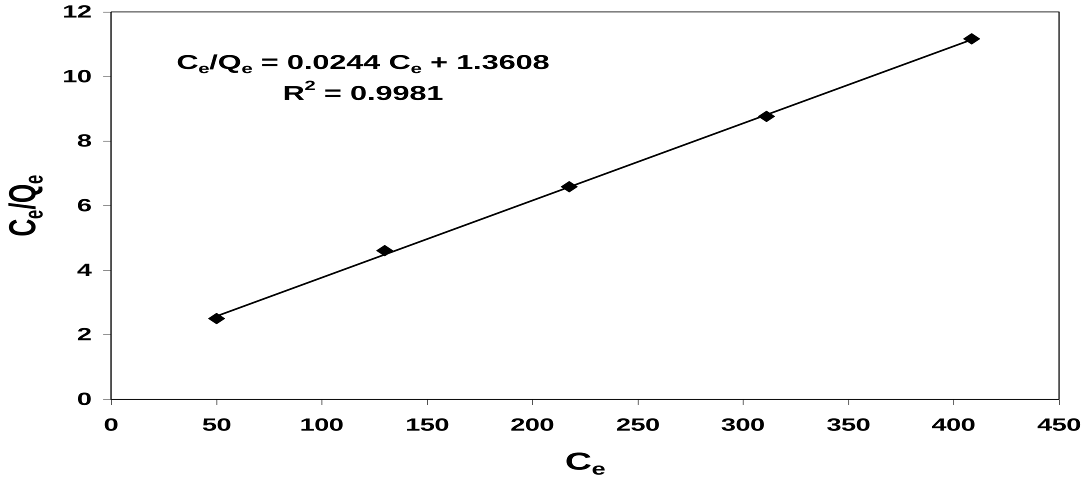

Figure 10: Langmuir isotherm plot for Cu(II) adsorption

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

Adsorbent	Cu^{2+} adsorption capacity (mg/g)
Pristine PE film [present study]	0
Modified AAc/MMA graft PE film [present study]	40.98
Itaconic acid/acrylamide graft PET fiber [14]	7.73
Methacrylic acid/acrylamide graft PET fiber [13]	31.25
Multi-walled carbon nanotubes [36]	12.34
Sugar beet pulp carbon [35]	14.81

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 %.

Conclusions

Gamma radiation induced grafting of acrylic acid (AAc) and methyl methacrylate (MMA) on polyethylene (PE) was investigated. The grafted PE films were characterized by FTIR spectroscopy. 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. The adsorption capacity after 30 minutes contact time was determined as 36.6 mg/g at pH 5, initial metal ion concentration 500 ppm and 286 graft percentage. Present study reveals that the adsorbent prepared by grafting of MMA and AAc on PE film can be suitable for adsorption of Cu(II).

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