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GRAFTING OF POLYETHYLENE FILMS WITH N-VINYL IMIDAZOLE AND ACRYLIC ACID FOR POTENTIAL USE IN WASTEWATER TREATMENT

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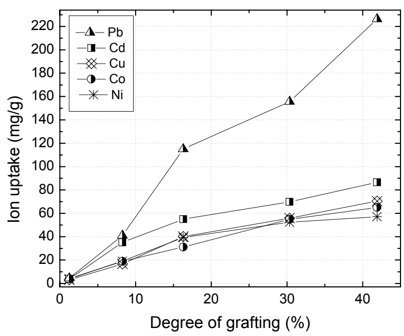
Polyethylene films were successfully grafted with both a basic, N-vinyl imidazole and an acidic, acrylic acid functional groups by gamma irradiation. The influence of different reaction parameters on the grafting process was investigated. These included the type of solvent and composition, comonomer concentration and composition, inhibitor concentration ($FeCl_3$), and the irradiation dose. The results showed that the grafting yield increases with increasing the irradiation dose and the comonomer concentration. The potential use of PE films, grafted with acrylic acid/ vinyl imidazole, to uptake heavy metal ions such as Ni^{2+}, Co^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+} was also evaluated. An increase in the uptake of the metal ions was observed as the grafting yield increases.



INTRODUCTION

Hazardous pollutants became major issues of public interest for last decades due to their toxicity. Therefore, heavy metal ions should be removed from industrial effluents prior to having waste solutions coming in contact with the environment.[1] Certain polymers are capable to form complexes with metal ions, and may be useful in several fields such as hydrometallurgy or biochemistry.[2-3] In recent years more attention has been observed in relation to the applicability of modified polymers for removal or separation of metal ions from contaminated waters and solid wastes.[4-8] The modification of hydrophilic polymers to an adsorbent has been reported to be useful for collecting target ions and molecules.[9-12]

The use of radiation to graft functional groups onto different substrates attracted the attention of many researchers because of the possibility to modify the chemical nature of polymers. The conditions of grafting reactions can be wide-ranging, and graft copolymer with desired properties may be obtained. Widespread work has already been performed on methods for the optimization of the reaction yield.[13-16] The use of a combination of monomers may influence the level of grafting of the individual monomer onto the polymer substrates, in particular when synergism occurs during such reaction.[17] Such grafting reactions can also give more cost-effective grafts under the most favorable reaction conditions.[18]

In order to improve the dye-ability of polypropylene with methylene blue, a study had been performed to graft two monomers 'acrylic acid and N-vinyl imidazole' using gamma irradiation.[19] The present work reports on the grafting of the binary monomer mixtures 'acrylic acid (AAc) and N-vinyl imidazole (Azole)' onto polyethylene, which is more radiation resistive and

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less expensive than polypropylene. Another important contribution of the present study is the use and optimization of wider spectrum of reaction parameters, which influence the grafting reaction. Furthermore, the prepared grafted membranes has been tested for the removal of some toxic heavy metals.

RESULTS AND DISCUSSION

1. Preparation of bi-functional grafted membranes

There are many factors affecting the grafting process of binary monomer mixture such as solvent type and composition, comonomer composition and concentration, inhibitor type and concentration, and irradiation dose.

1.1. Effect of solvent type

Solvents play an important role in enhancing the grafting process of a monomer onto a trunk polymer. The solvent may influence the grafting process by diluting the monomer, and consequently reducing the rate of propagation and kinetic chain length. The solvent may also swell the polymeric substrate to help accessibility and diffusion of the monomer to the active sites and/or may modify the thermodynamic equilibrium of the copolymer in the used monomer solvent mixture.

Fig. 1 represents the grafting yield of vinyl imidazole and acrylic acid onto polyethylene with respect to solvent type and its mixture with water (irradiation dose = 30 kGy; monomer concentration = 20%; inhibitor concentration ($FeCl_3$) = 1%; comonomer composition (Azole/AAc=1:3)). It can be seen that the solvent mixture acetone/ water leads to the maximum grafting yield onto polyethylene.

1.2. Effect of inhibitor concentration

The presence of inhibitors in the reaction medium (monomer/ comonomer solution) is necessary to overcome the trouble of homopolymerization, which affects the grafting reaction and as a result the degree of grafting onto the polymeric membranes. The suppression of the formation of homopolymer is of highest value when reactive monomers such as acrylic acid and methacrylic acid are to be grafted.[20-23]

The influence of inhibitor concentration ($FeCl_3$) on the grafting yield of AAc/ Azole onto PE was investigated, and the results are represented in Fig. 2 (irradiation dose = 30 kGy; monomer concentration = 20%; comonomer composition (Azole:AAc = 3:1); acetone/water composition = (30/70)%). The data show that the grafting yield increases in presence of the inhibitor ($FeCl_3$) up to 4% of inhibitor, and did not show a maximum. The maximum value seems to lay at higher values.

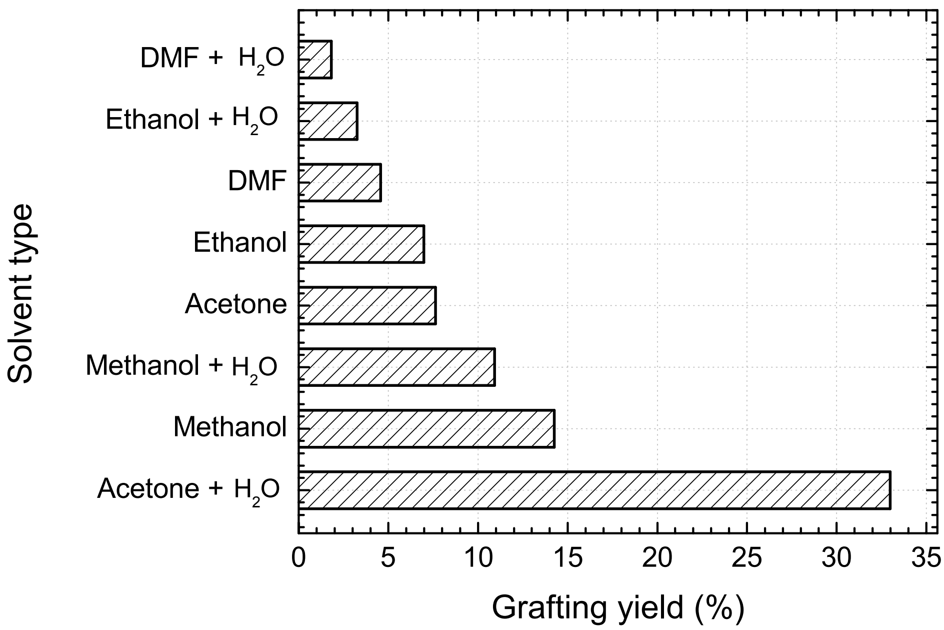


Fig. 1 – Grafting yield for different solvents; the other reaction parameter are constant as follows: irradiation dose = 30 kGy; $FeCl_3$ = 1%; Azole/AAc=1:3; monomer concentration = 20%.

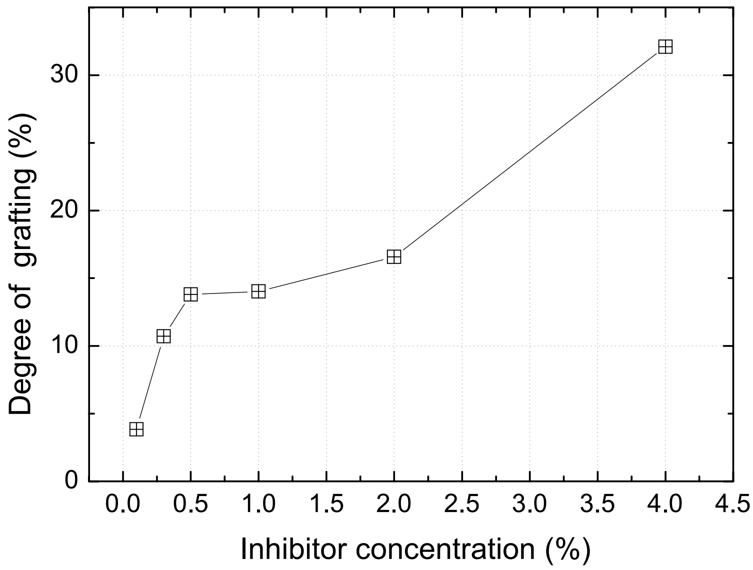


Fig. 2 – Grafting yield onto polyethylene vs. the inhibitor concentration; irradiation dose = 30 kGy; Azole: AAc = 3:1; acetone/water = 30/70; monomer concentration = 20%.

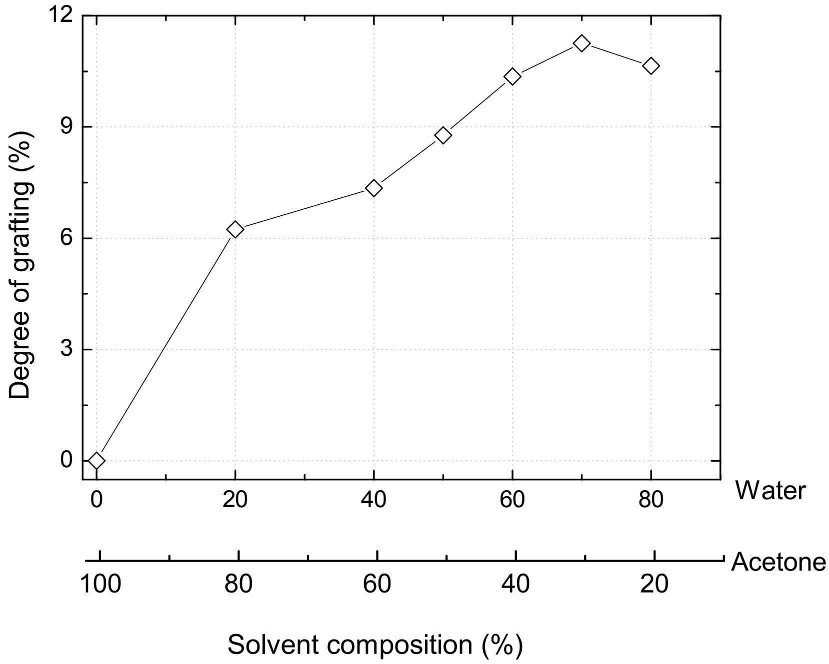


Fig. 3 – Grafting yield onto polyethylene vs. the solvent composition; irradiation dose = 30 kGy; monomer concentration = 20%; inhibitor concentration $FeCl_3$ = 1%; Azole/AAc = 1:3.

1.3. Effect of solvent composition

The influence of the solvent composition on the grafting reaction was investigated, and the grafting yield is represented with regard to the water/ solvent content in the solution (irradiation dose = 30 kGy; monomer concentration = 20%; inhibitor concentration ($FeCl_3$) = 1%; comonomer composition (Azole/AAc=1:3) in Fig. 3. The data show that a high water content of 70% is needed to reach the best grafting yield.

1.4. Effect of comonomer composition

The influence of the comonomer composition on the grafting process has been studied because of the synergistic effect of two monomers, which may lead to more efficient grafting processes.[17] The grafting yield of AAc/Azole binary monomer systems of various relative compositions was determined versus the comonomer composition (irradiation dose = 30 kGy; monomer concentration = 20%; inhibitor concentration ($FeCl_3$) = 4%; solvent composition%

(acetone/water) = (30:70)), and the resulted data are represented in Fig. 4.

1.5. Effect of comonomer concentration

The concentration of the monomer/ comonomer to be grafted plays a major function during the membrane preparation by the radiation-induced graft copolymerization method. The content of the monomer in the solution strongly affects its mobility towards the grafting zone, and accordingly the final degree of grafting varies.[24] The effect of dilution of AAc/Azole monomers mixture on the graft copolymerization onto PE was investigated and the results were presented in Fig. 5. It can be seen that the degree of grafting increases with increasing the comonomer concentration in the reaction medium. The increase in the grafting yield with comonomer concentration may be due to the increase in diffused monomer into the bulk polymer. The high concentration of free radicals at grafting sites favors propagation of growing chains and consequently, the grafting yield increases.

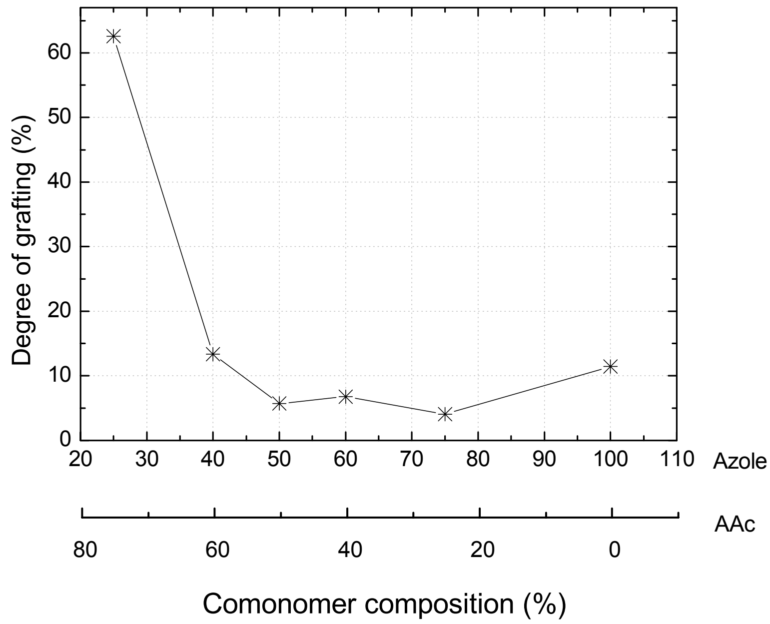


Fig. 4 – Grafting yield onto polyethylene vs. the comonomer composition; reaction parameter: irradiation dose = 30 kGy; monomer concentration = 20%; $FeCl_3$ = 4%; acetone/water = 30:70.

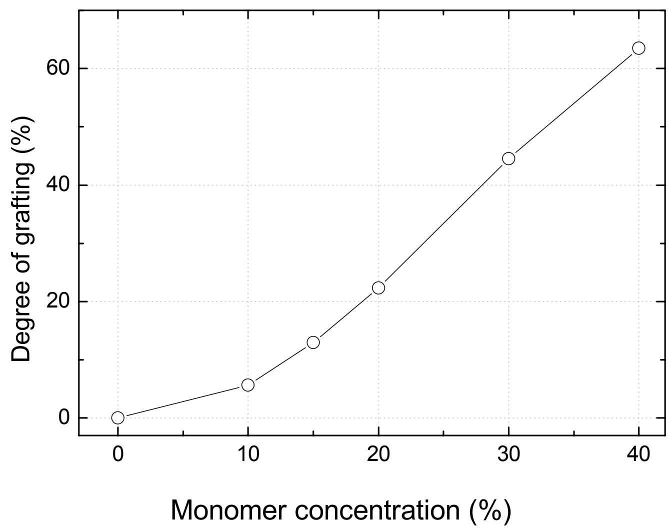


Fig. 5 – Grafting yield onto PE with respect to comonomer concentration; $FeCl_3$ = 1%; Azole/AAc = 1:3; acetone: water = 30: 70; irradiation dose = 30 kGy.

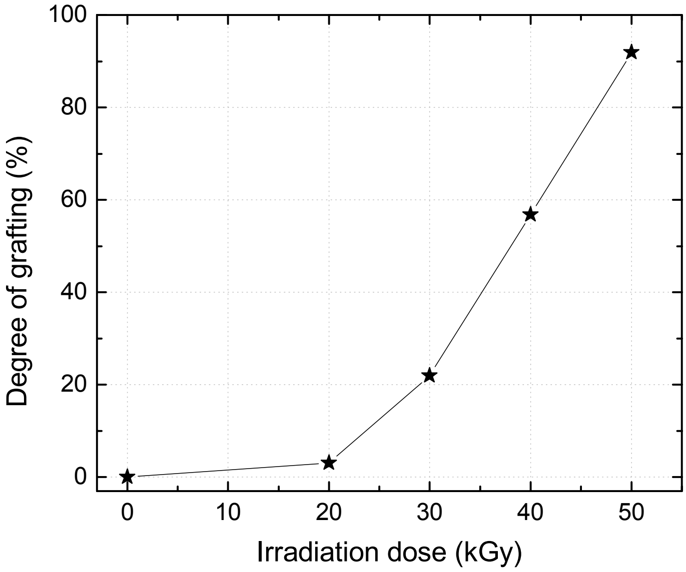


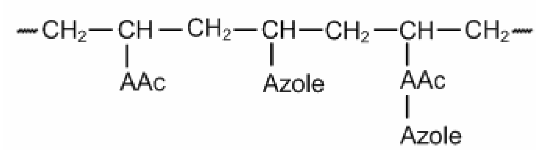
Fig. 6 – Grafting yield onto PE vs. the irradiation dose; $FeCl_3$ = 1%; Azole/AAc = 1:3; acetone: water = 30: 70; comonomer concentration = 40%.

1.6. Effect of irradiation dose

Since gamma irradiation acts as an initiator for the graft copolymerization process, the reaction is mainly of a free radical mechanism.[3] Therefore, the grafting is governed by the concentration of free radicals formed in both the polymer substrate and co-monomer solution. Fig. 6 shows the grafting yield of AAc/Azole binary monomers onto PE films versus the irradiation dose; the other reaction parameter are constant as follows: comonomer concentration = 40%; inhibitor ($FeCl_3$) = 1%; comonomer composition (Azole/AAc=1:3); solvent composition (acetone: water = 30: 70). The grafting yield generally increases with increasing the irradiation dose till a maximum, and then tends to level off or decrease due to degradation. The graph indicated that the maximum seems to lay at higher dose than the used ones. It also be assumed that the increase in the irradiation dose increased the concentration of free radicals in the polymer substrate as well as in the AAc/Azole comonomer solution.

2. IR spectroscopic analysis

FTIR spectra were used to provide evidence that the two monomers were grafted on the PE matrix and to obtain useful information about the grafting mechanism. The IR spectra of grafted and ungrafted films are shown in Fig. 7. The bands at 2700–3000 cm^{-1} are due to the -CH stretching of the -CH group of PE. The appearance of the new bands at 3400 and 1720 cm^{-1} was indicative of the -OH and C=O groups of the acid; the new band in the region around 1260 cm^{-1} was indicative of the N-C-N band of the vinylimidazole, [19] and the band appearing at 3160 cm^{-1} could be assigned to the C–H (ring) stretching mode for poly(vinyl imidazole), which is comparable to the literature. These new bands confirmed the grafting process. The grafted PE films could be represented by the following structure:



3. Ion uptake

Heavy metals are toxic pollutants, and should be removed from wastewaters due to their undesired effects on human physiology and ecological systems.[25]

The ion uptake of PE-g-Azole/AAc membranes versus the degree of grafting is represented in Fig. 8. As the degree of grafting increases, the removal capacity of the grafted membrane to adsorb metal ions, increases. This behavior can be reasonably attributed to the increase in the number of functional groups grafted onto the polymer backbone. The ion uptake capacity of the prepared of PE-g-Azole/AAc membranes is comparable with other grafted systems published in the literature.[26-27]

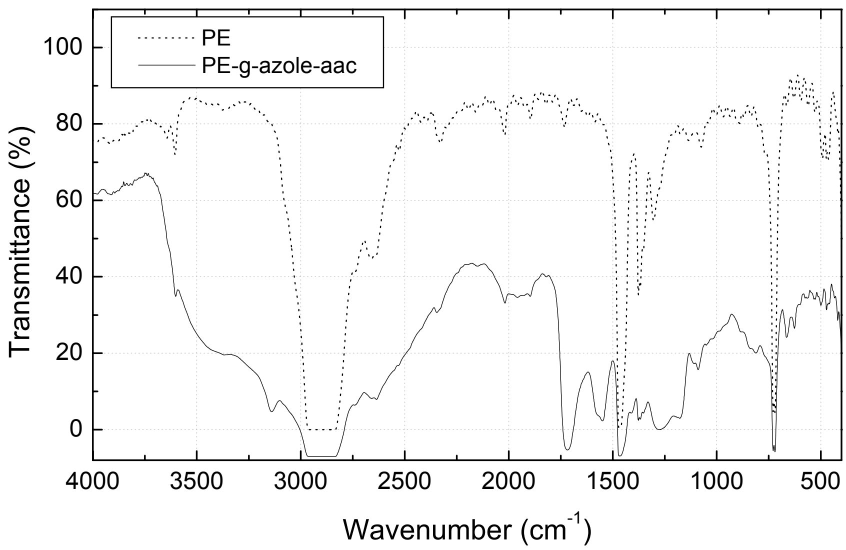


Fig. 7 – FTIR spectra of the original PE and PE-g-AAc/Azole films.

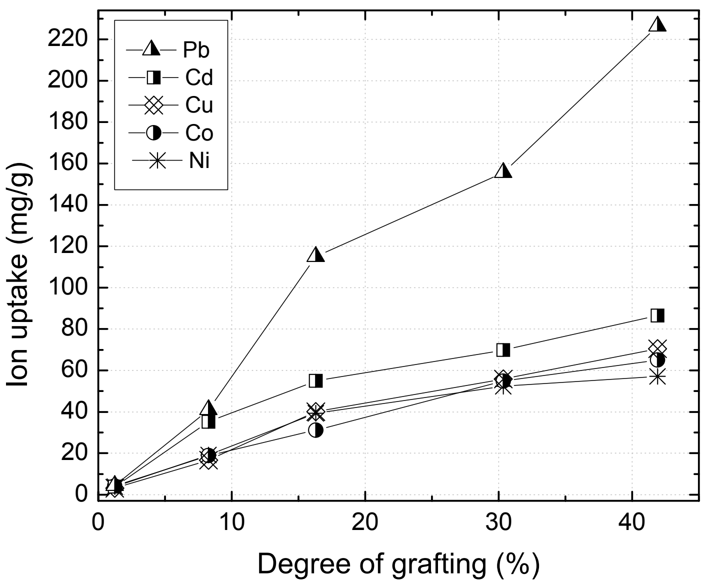


Fig. 8 – Uptake of Co^{2+}, Pb^{2+} , Ni^{2+} and Cd^{2+} ions versus the grafting yield of PE-g-AAc/Azole; initial feed concentration = 2000 ppm; time = several days; ambient temperature = 22 ^{o}C.

EXPERIMENTAL

1. Materials

Polyethylene films (thickness 100 μm) were obtained from the company PKN Orlen S. A., Poland. Methanol (purity > 99.8) and acetone (purity > 99.8) were supplied by Merck, Germany. N-vinyl imidazole (purity > 99%) and acrylic acid (purity > 99%), were purchased from Fluka, Germany. Ethanol (purity 99.8%) was obtained from Riedel de Haën, Germany.

2. Graft copolymerization

The direct radiation-induced grafting of acrylic acid and N-vinyl imidazole monomers onto PE films was used as a preparation technique. PE strips were washed with acetone, dried at 50 ^{o}C, weighed and then vertically immersed in the monomer or binary monomer solution in glass ampoules; N_2 gas was bubbled in the solution for few minutes in order to remove oxygen. The glass ampoules containing all the reactants and polymer substrates were subjected to ^{60}Co gamma rays at a dose rate of about 1.88 kGy/h. The grafted films were removed and washed thoroughly with distilled water, which is a good solvent for AAc and Azole and then immersed in water to extract the residual monomer or homopolymer which may be accumulated in the grafted films. The films were then dried in an oven at 50 ^{o}C. The degree of grafting was determined by the percent increase in weight as follow:

$$\text{Degree of grafting } (\%) = \frac{W_g - W_o}{W_o} \times 100 \qquad (1)$$

Where W_o and W_g are the weights of initial and grafted films, respectively.

3. FTIR spectroscopy

FTIR spectra were recorded using a Jasco spectrometer (FT/IR-4200 type A) operated on ATR mode and MCT detector. Spectra were recorded at 4 cm^{-1} resolution in the region from 400-4000 cm^{-1} and a total of 32 scans. A separate background spectrum was substracted after each collection.

4. Maximum swelling

The clean dried grafted films of known weight (after the washing procedure mentioned above) were immersed in distilled water until a constant weight was reached (equilibrium swelling); the films were then removed, blotted quickly with absorbent paper and weighed. The maximum swelling (S_{max} (%) was then calculated by the following equation:

$$S_{\max}(\%) = \frac{W_S - W_o}{W_o} \times 100 \quad (2)$$

where W_S is the weight of membrane at equilibrium, and W_o is the weight of dried membrane.

5. Ion uptake

The dry membranes were immersed in the metal feed solution of concentration (2000 ppm). An atomic absorption instrument (Avanta; GBC scientific equipment) was utilized to determine the remaining metal ions in their feed solutions: Ni, Co, Cu, Pb, and Cd. The ion uptake was calculated according to the following equation:

$$\text{Metal Ion Uptake} = \frac{\text{adsorbed metal ions (mg)}}{\text{weight of the dry gel (g)}} \quad (3)$$

CONCLUSIONS

Polyethylene films were successfully grafted with acrylic acid/ N-vinyl imidazole binary mixtures by gamma irradiation. The grafting conditions were optimized with regard to their influence on the grafting yield.

The grafted films showed capability to adsorb some metal ions (Ni^{2+}, Co^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+}) from their contaminated solutions. The adsorption capacity increases as the grafting yield increases. The big difference in adsorption of Pb^{2+} ions compared with the other studied metal ions suggests that the grafted membranes may be considered for the separation of Pb^{2+} ions from them.

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