Sorption of Some Heavy Metal Ions from Aqueous Solutions by Polypropylene Fibers Grafted with Acrylic Acid under the Effect of Gamma Irradiation

M. S. Hassan

Radiation Chemistry Dept., National Centre for Radiation Research and Technology (NCRRT), P. O. Box; 29 Nasr City, Egypt.

POLYPROPYLENE FIBERS (PP) grafted with poly acrylic acid (PAAc) were prepared under the effect of gamma irradiation to be used as an adsorbent matrix for Co\(^{2+}\) and Ni\(^{2+}\) ions from aqueous solutions. The different factors which affect the grafting process such as grafting solution, inhibitor concentration, irradiation dose and the monomer concentration were investigated. The grafted PP fibers were characterized by using Fourier-transform infrared (FTIR), X-ray diffraction (XRD), Thermogravimetric analysis (TGA), Differential scanning calorimetry (DSC) and Scanning electron microscopy (SEM). The effect of grafting yield on the mechanical properties of grafted PP fibers was also studied. The different conditions which affect the adsorption capacity of grafted PP fibers towards the metal ions, such as solution pH and contact time were investigated. The adsorption isotherm was studied according to the Langmuir isotherm model. The effect of regeneration cycles on the adsorption capacity of grafted PP fibers was investigated.

Keywords: Polypropylene, γ-rays, Metal ions, adsorption.

Heavy metal pollution can cause serious environmental problems due to its toxic and carcinogenic effects on the natural environment and its accumulation in living organisms (Nriagu et al., 1988 and Liu et al., 2008). The toxicity of heavy metals might be caused by blocking essential functional groups of bio molecules and by disrupting the integrity of bio membranes (Bayramoglu et al., 2002, Jang et al., 2008 and Zhao et al., 2008). In recent years, the removal of hazardous heavy metals from water and soil environments and industrial waste steams has attracted considerable attention. Enhanced metal separation techniques that require less energy with minimal impact on the environment are desirable.
In order to remove dissolved heavy metal ions from various environments, conventional techniques including chemical precipitation, ion exchange, reverse osmosis, membrane separation, electrochemical treatments and solvent extraction processes are widely used (Akkaya et al., 2008). In general, these techniques are often costly or ineffective, especially in removing heavy metal ions at low concentrations (Laus et al., 2011).

Radiation-induced graft polymerization is widely used to produce high performance chemically active polymer materials for adsorption and separation processes on the basis of various commercial polymers available in different forms (films, fibers, resins, textiles, powders) (Bhattacharya et al., 2004 and Nasef et al., 2004). Direct grafting desirable functional groups to polymer is one of approaches to synthesize polymer adsorbents. Adsorbents can be easily synthesized by radiation-induced graft polymerization. This technique creates an active radical in the trunk polymer by means of ionizing radiation and the polymeric graft chains propagate from the active radical in the trunk polymer (Makay, 1996). In general, synthesized polymers, such as polyethylene and polypropylene, have been used as trunk polymers due to their reactivity in the grafting process and high mechanical strength.

In the present work, radiation grafting of PP fibers with PAAc to use as an adsorbent materials for heavy and toxic metals from waste water was investigated. The main aim is to obtain homogeneously distributed graft copolymer chains with high grafting yield. The properties of the prepared graft copolymer were studied by IR, XRD, TGA and DSC. The mechanical properties of the grafted fibers were also determined.

Experimental

Materials

Commercial polypropylene fibers used for this study were manufactured by the Oriental weavers Co., Egypt. and used as a base substrate. AAc monomer, and 1,1',2,2'-tetrachloroethane were purchased from Fluka Chemical Co., Switzerland. Toluene, benzene, methanol and acetone solvents were purchased from El-Nasr Pharmaceutical Chemicals Co., Egypt. Nickel sulphate and Cobalt sulphate were supplied by El-Nasr Pharmaceutical Chemicals Co., Egypt.
Gamma irradiation

Irradiation was carried out in the Cobalt-60 gamma cell source (made in Russia) installed at the NCRRT, Cairo, Egypt. The direct radiation was used for induced grafting process of AAc onto polypropylene fibers.

Characterization of grafted PP fibers with PAAc

The prepared grafted PP fibers were analyzed by FTIR, in a wide range wavelength (400-4000cm⁻¹) and in solid state using Mattson 5000 FTIR spectrometer (Mattson Instruments, Madison, WI). SEM study of the prepared PP fibers was carried out by JSM–640, JEOL at 15 kV. The dried sample was sputter-coated with gold using a microscope sputter coater and viewed through the microscope. XRD studies were performed using Philips (PW 1390), using Nickel- filtered Cu-Kα radiation. The diffractograms were scanned from 2 °C to 40° at room temperature. TGA was determined by using Shmadzu-30 (TGA-30) at a heating rate of 10°C/min in air over a temperature range from room temperature up to 600°C. DSC was performed using a Perkin Elmer DSC-7 calorimetry equipped with data station. A heating rate of 10 °C/min was utilized and the scans were carried out under nitrogen atmosphere. The recorded melting temperatures (Tm) were determined.

Mechanical testing

The mechanical properties including tensile strength (Tb) and elongation (Eb) to break were tested at room temperature. Every data point is the average of 5 tests. A Mecmesin (Model 10-I) equipped with software was used employing a crosshead speed of 50mm/ min. In this system the different mechanical parameters were calculated directly.

Determination of metal ions adsorption capacity by grafted PP fibers

The adsorption capacities (q) of grafted PP fibers towards the different metal ions were determined. A constant weight of dry grafted PP fibers was immersed in a definite volume of metal salt solutions containing a definite concentration of metal ion in flasks under shaking. The remaining metal ions concentrations were determined by using standard solution of EDTA (Skoog et al. 1995). The adsorption capacity q (mg/ g) was calculated according to Equ. 1:

\[ q = \frac{(C_o - C_e) V}{W} \]  

(Equ. 1)

where, $C_o$ & $C_e$ are the initial and equilibrium metal ion solution concentrations (mg/L), respectively, $W$ is the wt of grafted PP fibers (g), $V$ is the volume of metal salt solution (L) (Chiu et al., 2003).

**Results and discussion**

**Grafting of PP fibers with PAAc**

In the grafting of individual monomers by radiation, it is easy to control the grafting process by controlling the factors affecting the graft yield. The different factors which affect the grafting of PAAc onto PP fibers such as solvent composition, inhibitor concentration, monomer concentration and irradiation dose were investigated. It was found that: (a) The best solvent which gives the highest grafting yield was benzene, in which, its solubility parameter is close to the solubility parameter of PAAc, so its leads to that the polymerization proceeds with high efficiency (Bador, 1991). (b) The addition of 0.1% of ammonium ferrous sulphate to the aqueous AAc is enough to enhance radiation grafting and minimize the homopolymer formation (Gupta et al., 1989). (c) The grafting yield increases with increasing of the irradiation dose, as a result the free radicals formation, which leads to the increase in the grafting yield (Kerndorff et al., 1980). In this study the maximum irradiation dose used was 10 (kGy), to protect the mechanical properties of grafted PP fibers from the radiation degradation. (d) The grafting yield increases with increasing of the AAc monomer concentration up to 30%, which give 23% grafting yield at 10 (kGy) radiation dose. By increasing AAc monomer concentration further more 30%, the grafting yield tends to level off as a result of homopolymer formation of PAAc (Langenbach et al., 2003).

**Characterization of grafted PP fibers**

**FTIR**

FTIR spectroscopic analysis was used to confirm the formation of graft copolymerization of PAAc onto PP fibers. Fig. 1. shows the IR spectra of PP and grafted PP fibers with PAAc (23% grafting yield). The characteristic vibration peaks of PP were shown in Fig. 1, as stretching aliphatic -CH (at 3000-2850 cm$^{-1}$), C=C of vinyl group at (1680-1600 cm$^{-1}$) and binding -CH$_3$ (at 1450-1375 cm$^{-1}$). But for grafted PP with PAAc showed the same characteristic vibration bands of PP were found beside new characteristic absorbed bands of –CO of carboxylic acid (at 1320-1210 cm$^{-1}$), –C=O of carboxylic acid (at 1720-1700 cm$^{-1}$), -OH of

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Carboxylic acid (at 3500 cm\(^{-1}\)), -CH out of plane (at 1000-650 cm\(^{-1}\)) and accompanied with increasing of –CH aliphatic and –CH\(_3\) groups intensity due to the introducing of PAAc onto the PP skeleton (Bozzi et al., 1987 and Sekine et al., 2010).

**FTIR**

![FTIR spectra of PP fibers and PP-g-PAAc (23%).](image1)

**XRD**

The XRD spectra of PP fibers, PP fibers grafted with PAAc (23%) are showed in Fig. 2. and the XRD parameters are given in Table 1. The PP fibers show a definite characterized peak at about (2θ) = 16.85. It can be noticed sharp peak intensity represents the crystalline nature of PP fibers.

![XRD scans of polypropylene and PP-g-PAAc fibers.](image2)

The intensity of the characterized peak of PP fibers was decreased after grafting with PAAc. This is due to dilution of the crystalline fraction by the incorporation of the amorphous PAAc chains into the polymer matrix (Hegazy et al., 1999).

Table 1. XRD parameters of PP & PP-g-PAAc fibers.

<table>
<thead>
<tr>
<th>Substrate fibers</th>
<th>20° at Strongest peak</th>
<th>d(Å)</th>
<th>Intensity (kcps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>16.85</td>
<td>5.26</td>
<td>1497</td>
</tr>
<tr>
<td>PP-g-PAAc</td>
<td>16.96</td>
<td>5.22</td>
<td>1255</td>
</tr>
</tbody>
</table>

**Mechanical properties of the grafted PP fibers**

The mechanical properties including $T_b$ and $E_b$ at break of PP fibers and grafted PP fibers with AAc at different grafting yield were studied. It must be noted that in the grafting processes of PP at low doses of irradiation were used to protect the PP fibers from irradiation degradation varying AAc contents to achieve different grafting yields (Grazyna et al., 2007). Fig. 3. illustrates the $T_b$ of PP fibers and grafted PP fibers with AAc. At different grafting yields. It can be seen that $T_b$ were decreased at small percentage of grafting yield due to the degradation effect of irradiation, then it tend to increases with increasing of the grafting yield, due to the formation of cross linked network structure formed via hydrogen bonding of carboxylic acid groups of PAAc graft chain, but it was still less than the $T_b$ of ungrafted PP fibers (Cheng et al., 2006). Fig. 3. illustrates also the $E_b$ at break of PP fibers before and after grafting with AAc. It can be seen that the $E_b$ % was decreased gradually by increasing of the grafting yield due to the formation of PAAc cross linking, which increase the rigidity of PP fibers (Said et al., 2010).

**TGA**

The initial TGA thermograms and the rate of thermal decomposition reaction ($dw/dt$) or the derivative of the thermogravimetric analysis curve were...
plotted against temperature for ungrafted and grafted PP fibers with 23% PAAc as shown in Fig. 4 & 5. The effect of graft copolymerization with PAAc on the thermal decomposition (wt loss %) of PP fibers was summarized in Table 2. From Fig. 4 & 5, and Table 2, it can be seen that the thermal degradation of PP fibers proceeds by one step process with a maximum decomposition temperature ($T_{\text{max}}$) at ~309$^\circ$C. Degradation started at ~250$^\circ$C and ended at ~600$^\circ$C, giving about 1% residue. In the case of grafted PP fibers, two degradation stages were observed for the decomposition in which, major wt loss of the first step started at ~180$^\circ$C and ended at ~311$^\circ$C with a maximum decomposition temperature ($T_{\text{max}}$) at ~272$^\circ$C with an accompanying of ~42% wt loss corresponds to the loss of PAAc part in the grafted PP fibers. The second step of decomposition started at ~311$^\circ$C and ended at ~600$^\circ$C with a maximum decomposition temperature ($T_{\text{max}}$) at ~372$^\circ$C with a measured wt loss of 60%.

![Graph of weight remaining vs temperature](image.png)

Fig. 4. TGA thermograms of PP and PP-g-PAAc (23%) fibers.

It can be concluded that the thermal stability of PP fibers was increased by grafting with PAAc, in which the maximum decomposition temperature was increased by ~13% after grafting by 23% grafting yield of PAAc.

Table 2. Thermal parameters of PP and grafted PP fibers with PAAc.

<table>
<thead>
<tr>
<th>PP substrates</th>
<th>200$^\circ$C</th>
<th>300$^\circ$C</th>
<th>350$^\circ$C</th>
<th>400$^\circ$C</th>
<th>450$^\circ$C</th>
<th>500$^\circ$C</th>
<th>$T_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>0.3</td>
<td>20.8</td>
<td>73.9</td>
<td>95.9</td>
<td>97</td>
<td>97.2</td>
<td>309.1</td>
</tr>
<tr>
<td>PP-g- PAAc (23%)</td>
<td>2.5</td>
<td>9</td>
<td>21.2</td>
<td>40.1</td>
<td>83.3</td>
<td>90.7</td>
<td>272, 371.6</td>
</tr>
</tbody>
</table>

Fig. 5. The rate of thermal decomposition reaction of PP and PP-g-PAAc.

**DSC**

The effect of graft copolymerization of PP fibers with PAAc on the crystalline melting temperature of PP fibers was investigated by DSC thermal analysis. Fig. 6 shows the DSC scans of the crystalline melting transition behaviour for the ungrafted and grafted PP fibers with PAAc at a graft yield 23%. It can be seen that $T_m$ of PP fibers was $\sim 165^\circ$C and its $\Delta H_m$ was 59.2. After graft copolymerization with PAAc, $T_m$ was decreased to $\sim 148^\circ$C and the $\Delta H_m$ decreased also to 15.5. This could be attributed to the introduction of PAAc grafted chain into the PP fiber matrix, causing change in morphological structure (Hegazy, 2012). In which the PAAc have a lower $T_m$ than PP fibers at $\sim 139$ (Elias et al., 1998).

**SEM**

Characterization of the PP fibers by SEM was made to compare the difference in the physical appearance of ungrafted and graft copolymerized PP fibers with PAAc (23% grafting yield). SEM photographs of PP fibers and PP graft copolymerized with PAAc are given in Fig. 7. The smooth crystalline appearance of ungrafted PP fibers was shown in Fig. 7(a). On the other hand, it can be seen that the PP fibers became coarser, groovy and the diameter average was increased by $\sim 20\%$ due to the formation of PAAc upon the surface of PP fibers as shown in Fig. 7(b).

Fig. 6. DSC scan of crystalline melting transition for ungrafted and grafted PP fibers with PAAc (23%).

Fig.7. SEM micrographs of the surface morphology of: (a) ungrafted PP fibers & (b) grafted PP fibers with PAAc (23%).

Metal ions adsorption by the grafted PP fibers

The influence of the different parameters, which affecting the adsorption capacity of grafted PP fibers towards the metal ions such as pH, contact time was investigated as shown in Fig. 8.

Effect of pH on the metal ions adsorption capacity

The pH is known to be an important variable affecting the adsorption affinity of metal ions. It can influence the protonation of the functional groups on the q as well as the solution chemistry of the heavy metal ions. Fig. 8, shows the effect of solution pH on the adsorption capacity of Co^{2+} and Ni^{2+} for grafted PP fibers with PAAc, at initial concentration of metal salts 1000mg/l for 60 min

at the room temperature. The pH ranges under investigation were from 2-7, to avoid the significant formation of precipitation at alkaline medium for the metal ions (Yiming et al., 2012). The adsorption capacity of Co\(^{2+}\) and Ni\(^{2+}\) was found to increase when the pH range was increased from 2 to 3, then it tend to increase gradually with increasing of the pH range. At low pH range (pH 2), more H\(^+\) competed with metal ions for adsorption sites, which made it more difficult for metal ions to bind to activated sites. Also, carboxylic groups existed in the form of –COOH and –COO\(^-\), which can hinder the interaction between grafted PP fibers and metal ions. On the other hand, at higher pH range (pH≥ 3), more ionized carboxylic groups were available, increasing the interaction between the carboxylic groups and metal ions and causing an increasing in Co\(^{2+}\) and Ni\(^{2+}\) adsorption capacity (Yiming et al., 2012). It was found also that at the same conditions, the adsorption capacity of Co\(^{2+}\) ion by PP grafted fibers with PAAc was grater than it for Ni\(^{2+}\) ion, which could be attributed to the complex stability formed between the metal ion and polymer functional groups. The higher stability of complex, the higher the affinity is obtained. In this study, the complex stability of Co\(^{2+}\) was more than it for Ni\(^{2+}\), which gives higher adsorption capacity (Hegazy, 2012).

Effect of contact time on the metal ions adsorption capacity

The effect of contact time on the adsorption capacity of metal ions at various contact times (15, 30, 60, 120, 150 and 200 min) was studied. Fig. 8. shows the effect of contact time on the adsorption capacity of Co\(^{2+}\) and Ni\(^{2+}\) ions by grafted PP fibers with 23% PAAc, at initial concentration of metal salts 1000mg/l. The adsorption capacity for the both of metal ions under investigation (Co\(^{2+}\) and Ni\(^{2+}\)) was increased rapidly at the beginning of the contact time up to 60 min , then tend to level of with increasing of the contact time, in which more than 85% of the total adsorbed metal ions was taken at the first h. This could be attributed to the presence of many adsorbed sites of the grafted PP fibers not complexed with any metal ions at starting time. After 60 min, the adsorbed metal ions remained nearly constant and hardly increased (Yiming et al., 2012). It was found also that at the same conditions, the adsorption capacity of Co\(^{2+}\) ion by PP grafted fibers with PAAc was grater than it for Ni\(^{2+}\) ion, due to its higher complex stability.

Fig. 8. The effect of different pH ranges and contact time on the metal ions adsorption capacity by PP-g-PAAc fibers.

**Adsorption isotherm**

The adsorption isotherms are important for the discussion of the interaction of the adsorbent molecules with the adsorbent surface. As shown in Fig. 9, the adsorption capacity increases with increasing of the initial concentrations of the metal ion concentration, for both of Ni$^{2+}$ and Co$^{2+}$. This could be attributed to that the increasing in the metal ion concentrations can accelerate the metal ion diffusion into the polymeric network. The maximum adsorption capacity of grafted PP fibers towards the metal ions can be determined by using the Langmuir model (Zheng et al., 2011). The Langmuir isotherm assumes that the adsorption process occurs at specific homogeneous sites on the PP grafted fibers and is the most commonly used for monolayer adsorption process, as shown in Equ. 2.

$$q_e = q_m b C_e / 1+b C_e$$ \hspace{1cm} (2)

where, $q_e$ is the equilibrium adsorption capacity of metal ion on grafted PP fibers (mg/g), $C_e$ is the equilibrium metal ion concentration (mg/l), $q_m$ is the monolayer adsorption capacity of the grafted PP fibers (mg/g) and $b$ is the Langmuir adsorption constant (L/mg).

The slopes and intercepts of plots of $C_e/q_e$ versus $C_e$ were used to determine $q_m$ and $b$ as shown in Fig. 10, in which $q_m$, $b$ and correlation coefficient ($r^2$) were found to be 426.1, 1.346 and 0.98926 for Ni$^{2+}$, while they were 325.5, 1.089 and 0.98926 for Co$^{2+}$ metal ion.

Desorption and regeneration of grafted PP fibers

The desorption of the grafted PP fibers after usage for metal ions adsorption was achieved by soaking in 0.1 mol HNO₃ for 60 min, on water bath shaker followed by washing with distilled water. The regeneration process was done by using of 0.1 mol/l NaOH. The regenerated PP fibers were reused for 5 cycles. The q of the grafted PP fibers towards metal ions was determined with repeating the adsorption cycles. From Fig. 11, it can be seen that the q of the grafted PP fibers was decreased by repeating the regeneration cycles, nevertheless, the type of adsorbed metal ions in which, it decreased to 83.16 and 92.65% compared to the initial adsorption capacity for Ni²⁺ and Co²⁺ ions, respectively, after the first cycle of regeneration, up to 13.9 and 20.59% after the fifth cycle of regeneration. Thus, It may conclude that the regenerated grafted PP fibers is suitable up to two cycles, in which it loses about 64 and 78% of its adsorption capacity towards Ni²⁺ and Co²⁺ ions, respectively.

![Fig. 9. Effect of the initial ion concentrations on the q of metal ions by grafted PP fibers with PAAc.](image)

![Fig. 10. The Langmuir plots for the q capacity of the metal ions by grafted PP fibers with PAAc.](image)

Fig. 11. The effect of regeneration times on the adsorption capacity of grafted PP fibers.

**Conclusion**

PP fibers were graft copolymerized by PAAc under the effect of low dose of gamma irradiation. From the results, it can be concluded that:

- The higher graft yield with suitable mechanical properties of PP fibers was obtained at 10 kGy irradiation dose, by using 30% monomer concentration.

- The higher adsorption capacity of grafted PP fibers was at pH ≤ 3 and contact time for 60 min.

- The adsorption isotherm was according to the Langmuir model.

- The grafted PP fibers can be regenerated and reused with acceptable adsorption capacity up to 2 cycles.

**References**


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استخلاص بعض ايوانات العناصر الثقيلة من المحاليل المائية

باستخدام شعيرات البولي بروبيلين المطوعة بحمض الأكريلك

تحت تأثير أشعة جاما

محمود صلاح الدين حسن

قسم الكيمياء الأساسية، المركز القومي لبحث وتطوير الأشعاع، مس. ب: 24

في هذا البحث تم تطعيم شعيرات البولي بروبيلين باستخدام حمض الأكريلك تحت تأثير جرعة منخفضة من أشعة جاما. وقد تم دراسة العوامل المؤثرة على عملية التطعيم مثل نوع المذيب، استخدام مشطب، الجرعة الإشعاعية وكذلك تركيز المونومير. تم توصيف شعيرات البولي بروبيلين المطوعة باستخدام الإشعاع تحت الحمراء،أشعة أكس noticeably، الليثات الحمراء، السح من المورفولوجي باستخدام الميكروسكوب الإلكتروني وكذلك تأثير التبطيع على الخصائص الميكانيكية للشعيرات المطوعة. وقد تم استخدام الشعيرات المطوعة في استخلاص ايوانات عصرية الكوبالت والتبكن من المحاليل المائية، وقد تم دراسة العوامل المؤثرة على كفاءة استخلاص تلك الايوانات من حيث الأداء الهيدروجيني للمحلول وكذلك تأثير زمن عمر الشعيرات المعالجة على كفاءة استخلاص الايوانات. كذلك تم دراسة ضمانية وكفاءة إعادة استخدام الشعيرات المطوعة في استخلاص ايوانات المعادن أكثر من مرة بعد إعادة تنشيطها.