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Separation of copper ions from iron ions using PVA-g-(acrylic acid/N-vinyl imidazole) membranes prepared by radiation-induced grafting

Zaki Ajji[a,*], Ali M. Ali[b]

[a] Polymer Technology Division, Department of Radiation Technology, Atomic Energy Commission of Syria, P.O. Box 6091, Damascus, Syria
[b] Faculty of Technical Sciences, Tishreen University, Tartous, Syria

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ABSTRACT

Acrylic acid (AAc), N-vinyl imidazole (Azol) and their binary mixtures were graft copolymerized onto poly(vinyl alcohol) membranes using gamma irradiation. The ability of the grafted membranes to separate Cu ions from Fe ions was investigated with respect to the grafting yield and the pH of the feed solution. The data showed that the diffusion of copper ions from the feed compartment to the receiver compartment depends on the grafting yield of the membranes and the pH of the feed solution. To the contrary, iron ions did not diffuse through the membranes of all grafting yields. However, a limited amount of iron ions diffused in strong acidic medium. This study shows that the prepared membranes could be considered for the separation of copper ions from iron ions. The temperature of thermal decomposition of pure PVA-g-AAc/Azol membrane, PVA-g-AAc/Azol membrane containing copper ions, and PVA-g-AAc/Azol membrane containing iron ions were determined using TGA analyzer. It was shown that the presence of Cu and Fe ions increases the decomposition temperature, and the membranes bonded with iron ions are more stable than those containing copper ions.

1. Introduction

Heavy metals, even at very low concentrations, are toxic pollutants, and have to be removed from wastewater streams due to their undesired effects on human physiology and ecological systems [1]. Micro-filtration membranes have attracted increased attention for their potential capability in the field of separation, and it has been shown to be an effective technique in removing heavy metals from aquatic media. Membrane separation technologies including reverse osmosis, nano-filtration and ultrafiltration are also promising methods, from the simplicity and energy-saving points of view, for the separation of heavy metal ions.

Graft polymerization of vinyl monomers onto polymer substrates has attracted considerable interest because it imparts some desirable properties, such as chelation, ion exchange, biocompatibility, and protein adsorption. A number of articles have been reported in the literature about modification of PVA membranes by means of radiation-induced graft copolymerization of monomers [2–4]. Also investigations have been carried out with regard to the use of grafted membranes in the field of separation and adsorption processes [3–7].

Poly(N-vinyl imidazole) hydrogels were applied to immobilize glucose oxidase [8,9], and for ion uptake [10–12]. Also, hydrogels consisting of N-vinyl imidazole and acrylonitrile were prepared regarding chelation and separation of metals [13,14].

The ability to transport metal ions through a polymer membrane can be improved by modification of the physical properties and the chemical structure of the membrane. In previous studies, PVA-g-AAc/Azol membranes were prepared by radiation grafting of the AAc/Azol comonomer onto PVA films, and used for the adsorption of copper ions from contaminated water [4]. The grafted membranes were also applied for the adsorption of methyl violet and brilliant blue with regard to the pH of the dye solution and the grafting yield [15].

In the present work, a trial was made to separate Cu ions from Fe ions using PVA-g-AAc/Azol membranes. Factors affecting the transport of Cu and Fe ions through the grafted membranes were also investigated.

2. Experimental

2.1. Materials

Various chemicals were supplied by Merck, Germany as: PVA (MW = 72,000, for synthesis), methanol (purity > 99.8, Merck, Germany), acetone (purity > 99.8), and dioxane (purity > 99.5%). N-vinyl imidazole (purity > 99%), acrylic acid (purity > 99%), were

* Corresponding author. Tel.: +963 11 2132580; fax: +963 11 6112289.
E-mail address: scientific@aec.org.sy (Z. Ajji).

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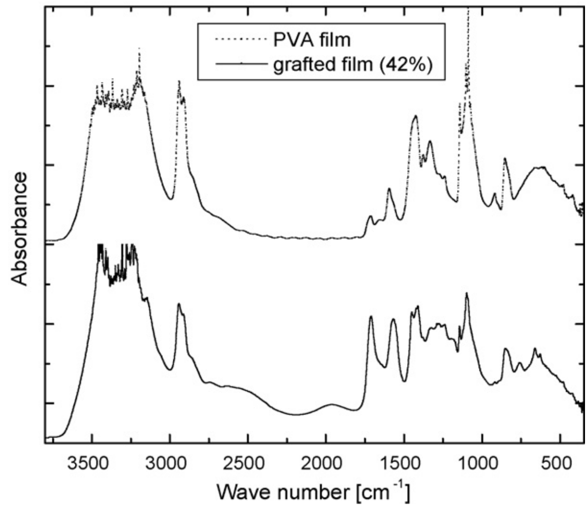

Fig. 1. FTIR spectra of PVA film and PVA-g-AAc/Azol membrane (grafting yield 42%).

purchased from Fluka, Germany. Ethanol was obtained from Riedel de Haën, Germany (purity 99.8%).

2.2. Preparation of the PVA films

The PVA membranes were prepared using the direct radiation-induced grafting of acrylic acid/imidazole monomers onto PVA films. The influence of reaction parameters on the properties of the membranes was reported in a previous work [4]. Fig. 1 shows the FTIR spectra of pure PVA film and a grafted one, which were recorded using a Jasco spectrometer (FT/IR-4200 type A). One band can be observed at a wave number of 667 cm^{-1}, which can be assigned to the imidazole ring in the vinyl imidazole unit [16]. Also a band centered at 750 cm^{-1} assigned to the C–H ring bending vibrations of azole ring [17], can be seen. The band appearing at 1717 cm^{-1} can be assigned to C=O stretching vibration, and the characteristic anti-symmetric vibration of COO^- usually appears in the 1550–1600 cm^{-1} region [18]; in our spectrum this band is centered at 1575 cm^{-1}. The band for the C–H (ring) stretching mode for poly(vinyl imidazole) appears at 3160 cm^{-1}, which is comparable to the literature [18]. There are also two bands at 1285 cm^{-1} and at 1241 cm^{-1}, which could be assigned to C–H (ring) in-plane bending and C–N (ring) stretching modes, respectively [18].

2.3. Ion separation

The membranes were placed between two cell compartments. The transported amounts of Cu or Fe ions were determined with respect to the pH of the feed/receiver solutions, and the grafting yield of the membranes. The concentration of the solutions was measured using a double-beam UV–vis spectrophotometer (Shimadzu, type UV-1601).

2.4. Thermogravimetry (TGA)

The dynamic weight loss tests were conducted using a Mettler instrument (TG50). The tests were carried out in a nitrogen atmosphere, purged (30 mL/min) using sample weights of 10–15 mg at a heating rate of 10 °C/min. The resolution of the balance was given as 1 μg for weights less than 100 mg, and the temperature precision of the instrument was ±2 °C.

3. Results and discussion

3.1. Transport of Cu and Fe ions

Fig. 2 represents the transported Cu ions with time through PVA-g-AAc/Azol membrane of a degree of grafting of 76%, and the pH of feed and receiver solutions was 4.9, 6.8, respectively. An inductive period before the transfer of the Cu ions into the receiver solution was observed (after ~200 min). This induction period may be attributed to the interaction between the Cu ions with the functional groups bonded to the membrane at the beginning of the transportation process. Similar experiments were carried out with Fe ions, but it was found that the Fe ions did not penetrate through the membrane, and the membrane itself became colored. These results suggest that PVA-g-AAc/Azol membrane has an affinity to adsorb iron ions and allow Cu ions to move through it to reach the receiver solution.

A further experiment was therefore carried out using a mixture of Cu and Fe ions placed in the feed solutions in order to investigate the separation of the two ions. The transported amounts to the receiver cell compartment are shown in Fig. 3. In both figures, an inductive period can be seen, and the transfer into the receiver solution occurred after ~200 min. This induction period may be attributed to the interaction between the Cu and Fe ions (at the beginning of the transportation process) with the functional groups bonded to the membrane. After a short time, the less stable Cu ions/membrane compound allowed the transfer of Cu ions, unlike the more stable Fe ions/membrane compound, resulting in the transporting of Cu ions into the receiving solution. The Fe ions seemed to have a higher ability to build a stable complex with the carboxylic, hydroxyl, and imidazole functional groups of grafted membranes than the Cu ions.

3.2. Effect of degree of grafting

There are several factors influencing the transportation of metal ions through membranes such as porosity, amount and type of functional groups (degree of grafting), pH and concentration of metal feed solution, etc. Fig. 4 shows the effect of grafting yield on the transportation process of Cu^{2+} and Fe^{3+} ions through PVA-g-AAc/Azol membranes. It is obvious that the concentration of transported Cu ions increases with time, and it gives a curvature relationship after an induction period. This behavior is observed

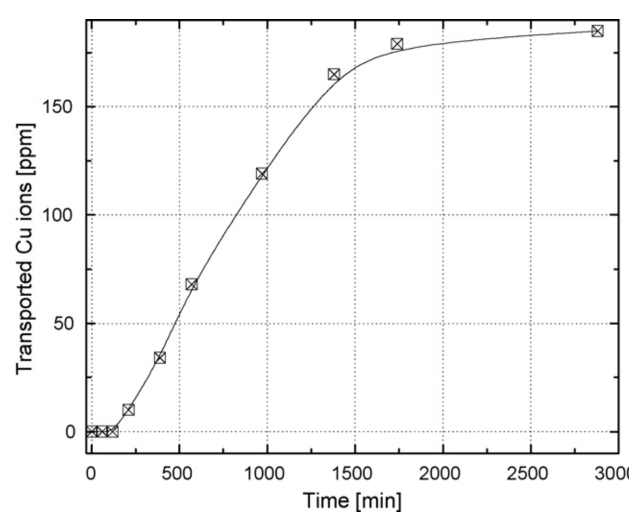

Fig. 2. Transportation of Cu ions through PVA-g-AAc/Azol membrane having degree of grafting 76%; pH of the feed and receiver solutions are 4.9 and 6.8, respectively. The concentration of feed solution is 1 g/L of Cu ions.

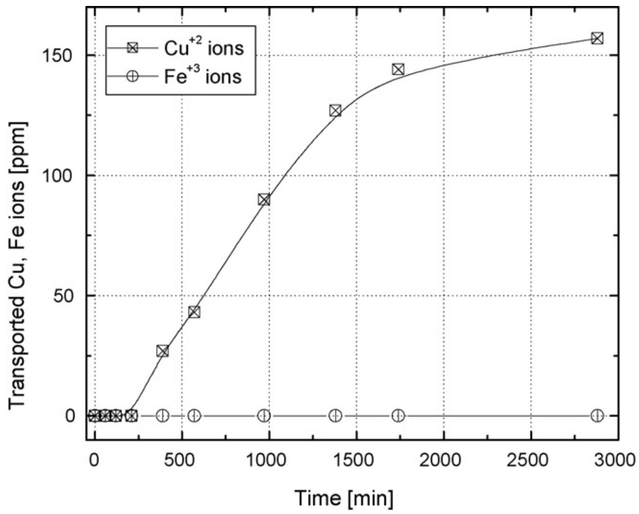

Fig. 3. Transportation of Cu and Fe ions through PVA-g-AAc/Azol membrane having degree of grafting 76%; pH of the feed and the receiver solutions are 3.5 and 6.8, respectively. The feed solution contains 1 g/L of Fe and Cu with the composition of 1:1.

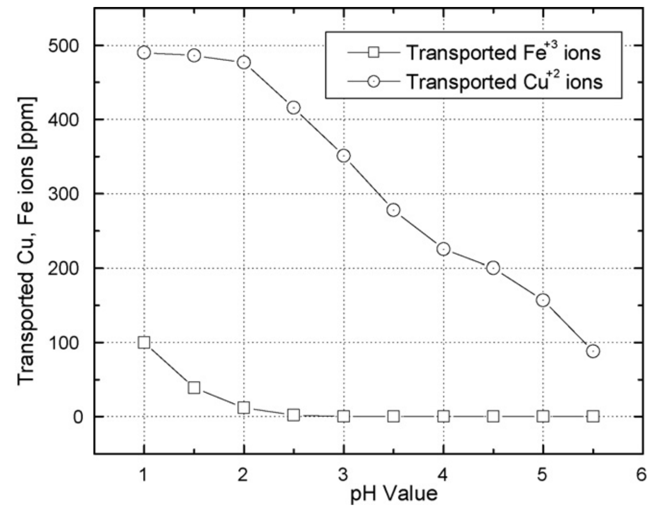

Fig. 5. Transportation of Cu and Fe ions through PVA-g-AAc/Azol membrane having degree of grafting of 76% with respect to pH values; the feed solution contains 1 g/L Cu^{2+} or 1 g/L Fe^{3+}; measurements were taken after 2 days.

for all membranes that have different degrees of grafting. However, the rate and concentration of transported Cu^{2+} ions increases as the degree of grafting decreases. Meanwhile, the Fe^{3+} ions were not transported into receiver solution, but rather they seem to be caught by the membrane.

The decrease in transported copper ions with increasing grafting yield could be explained by higher crosslinked network structure of the membrane, which restricts the diffusion of ions through it. This behavior can be attributed to increased degree of crosslinking of polymer chains in the whole graft copolymer as the degree of grafting increases. As a consequence, the diffusion of water through the membrane decreased resulting in retarding the diffusion of Cu^{2+} ions throughout the membrane. Therefore, at higher grafting yield, the rate and the amount of transported Cu^{2+} ions decreased and a much longer time is needed for its transportation.

3.3. Effect of pH

It is well known that the transportation and chelation of metal ions through/with the membranes depends on the pH of metal feed and receiver solutions. Fig. 5 shows the transported Cu^{2+} and Fe^{3+} ions with respect to the pH of the feed solutions, respectively. It can be seen that the change in the pH value of the feed solution resulted in remarkable change in the amount of transported Cu^{2+} ions. In addition, the concentration of transported Cu^{2+} ions through the grafted membrane increased as the pH value of the feed solution decreased, and tends to level off for a pH value ≤ 2.5 (Fig. 5). The transport of Fe ions to the receiver solutions was limited when the pH of the feed solution became higher than 2.5; then the transportation of Fe ions took place slowly at pH < 2.5 as shown in Fig. 5.

A mixture solution of Cu and Fe ions has been tested for pH values ≥ 2.5 as shown in Fig. 6. It can be seen that the decrease in pH of the feed solution resulted in increasing the rate and concentration of transported Cu ions. This behavior may be explained as the carboxylate ion exists in the acidic form, and the nitrogen atom of the imidazole ring is protonated in the strong acidic medium. Thus both ligands are not available to form a bond with the metal ions. On the other hand Fe ions did not penetrate to the receiver compartment at these pH values. This result can be attributed to the fact that trivalent Fe ion form a more stable and stronger complexes with

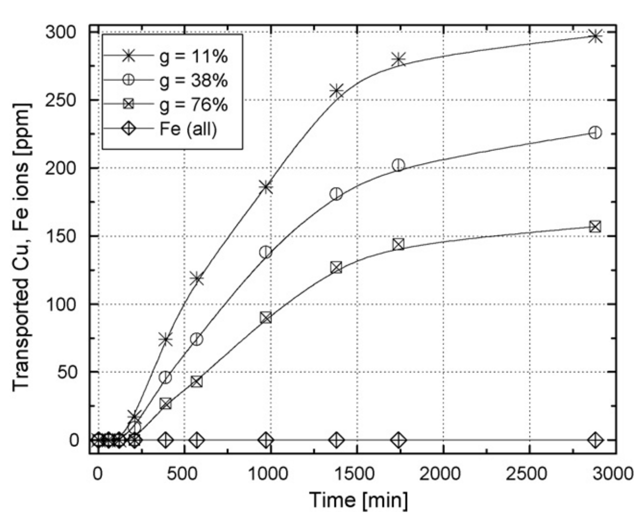

Fig. 4. Effect of grafting yield on separation process of Cu from Fe ions through PVA-g-AAc/Azol membranes; pH of the feed and receiver solutions are 3.5 and 6.8, respectively. The feed solution contains 1 g/L of each of Fe^{3+} and Cu^{2+}.

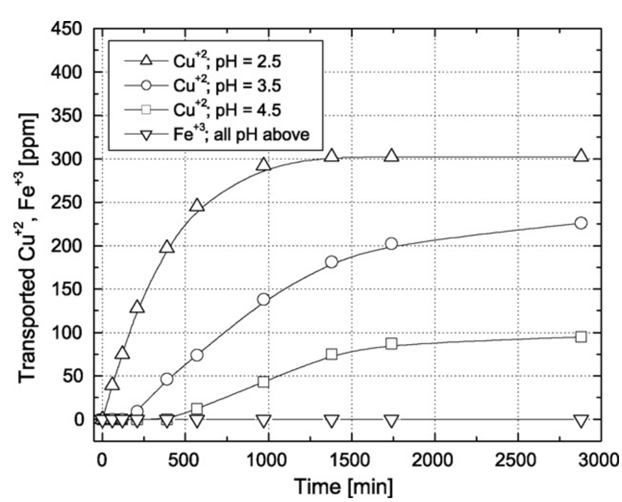

Fig. 6. Effect of pH on transport process of Cu and Fe ions through PVA-g-AAc/Azol membrane having degree of grafting 76% at different pH values; the feed solution contains 1 g/L of Cu and Fe ions with a composition of 1:1.

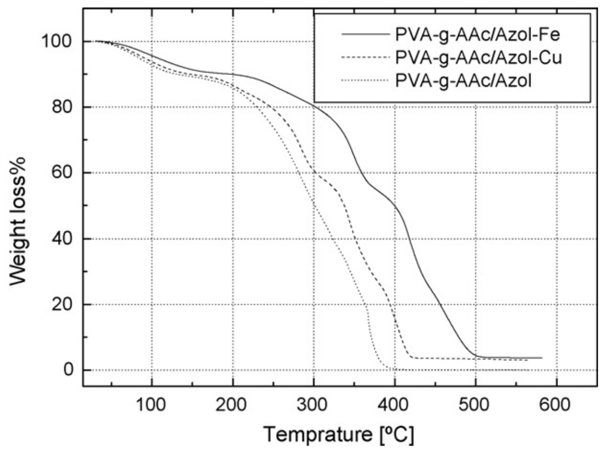

Fig. 7. TGA thermograms of PVA-g-AAc/Azol, and PVA-g-AAc/Azol treated membranes with Fe and Cu ions.

functional groups compared with divalent Cu ion because Fe has a d^5 electronic configurations; metals with d^5 and d^{10} electronic configurations have a high complexation constants [19].

Since the functional groups in strong acidic medium are not available to form bonds ($pH \leq 2.5$), the transportation of Fe and Cu ions may take place by concentration gradient mechanism.

3.4. Thermal gravimetric analysis (TGA)

Fig. 7 shows the percent weight loss during the dynamic thermogravimetric analysis of PVA-g-AAc/Azol membrane, and membranes containing Cu and Fe ions, which are already used in the transportation or separation experiments. It can be seen that thermal decomposition of the polymer membrane containing metal ions occurred at higher temperatures than that for the pure polymer membrane. This result can be explained by the formation of bonds between the membrane–functional groups and the metal ions, which enhanced the thermal stability [19,20].

It can also be seen that the decomposition temperature of grafted membrane containing Fe ion was higher than that of the grafted membrane containing Cu ions. This indicates that the bonds of Fe ions with the membrane are more stable than that of Cu ions with the membrane in a good agreement with the results obtained from separation experiments of Cu from Fe ions.

The TG spectra show also that PVA-g-AAc/Azol grafted membranes possess a good thermal stability at a wide range of temperature, which is of great interest for practical applications.

4. Conclusion

Polymer membranes based on poly(vinyl alcohol) grafted with acrylic acid and N-vinyl imidazole using gamma radiation were prepared. Cu ions diffusion depends on the grafting yield and the pH of the feed solution. It decreases with increasing grafting yield and the pH of the feed solution. In strong acidic medium ($pH \leq 2$) the transported amount of copper was around 490 ppm, and decreases with increasing pH. There is a limited Fe ion diffusion in strong acidic medium (around 100 ppm) and levels off for $pHs \geq 2.5$. This study shows that the prepared membranes could be considered for the separation of copper ions from iron ions.

TGA analysis indicates that PVA-g-AAc/Azol membranes containing Fe ions are more stable than PVA-g-AAc/Azol membranes containing Cu ions, which further supports the separation experiment.

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