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Radiation Copolymerization of Hydrogels Based in Polyacrylic Acid/Polyvinyl Alcohol Applied in Water Treatment Processes

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Abstract: Poly (acrylic, polyvinyl alcohol) copolymer hydrogel having varied PVA (Polyvinyl alcohol) content is prepared by gamma induced radiation polymerization. This hydrogel is used in water purification. The gel fraction and the swelling property are found to be 82% and 273% respectively at absorbed dose 20 kGy. The kinetic swelling and effect of solution pH on the swelling percent are also studied. The functional and bond structure is characterized by FT-IR (Fourier transform infrared spectroscopy). The hydrogel has been applied for the separation of Cu(II), Co(II) and Ni(II) ions from a test water solution. The factors affecting the metal uptake such as pH, time, and initial feed metal concentration are studied. It is found that, at pH 5 and after 24 h the maximum adsorption amount are 193 mg/g, 155 mg/g and 150 mg/g for Cu^{2+}, Co^{2+} and Ni^{2+} respectively in case of PAAc. In case of P (PVA/AAc), there are increase in maximum capacity to be 197 mg/g, 194 mg/g and 160 mg/g towards Cu^{2+} , Co^{2+} and Ni^{2+} ions, respectively. The selectivity of hydrogels towards the different metal ions is studied by EDX (Energy dispersive X- ray) and follows the order Cu(II) > Co(II) > Ni(II). Microstructure of the prepared hydrogel before and after adsorption are investigated by means of SEM (Scanning electron microscope).

Key words: Hydrogels, irradiation, copolymerization, water decontamination, heavy metals.

1. Introduction

Heavy metal contaminants such as Cu, Co, Ni are one of the most important problems threatening our world, because of their high solubility in the environments. These metals may aggregate in the human body cause serious health problems, such as growth and development or cancer, organ damage, nervous system damage, and can lead to death [1].

There are a lot of techniques applied to remove such these metals such as filtration, neutralization, chemical precipitation, chelating, ion- exchange resin [2]. These techniques have a lot of technical, economic, and environmental and health problems. However, adsorption is an attractive method because of its high efficiency, low cost, easy handling and availability of using different types of adsorbents.

Recently, the most important adsorbent material is hydrogels, which are three-dimensional networks, swell not dissolve due to their network structure; they have received much concern for removing heavy metal ions from wastewater due to their ability of including different hydrophilic functional groups such as (COOH, OH, NH_2) in the polymeric structure. The swelling of the hydrogels increases with an increase in the such groups in the network [3]. Also, these hydrogels are highly susceptible to variation in pH of the medium, which enables them to use as ion exchangers [4].

There are many physical or chemical methods for constructing three – dimensional polymeric networks,

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but the most effective methods are using gamma irradiation. Due to negligible by-product formation, fast gelatin and no need of catalysts.

In the present work, the main aim is to develop a good chelation and ion exchanger hydrogels, that can be obtained by radiation induced crosslinking of poly vinyl alcohol and acrylic acid. These hydrogels (PVA/AAc) have been characterized using different methods such as FTIR (Fourier transform infrared spectroscopy) and SEM (Scanning electron microscope) and used for heavy metal uptake of different metals. The competitive adsorption has been studied by EDX (Energy dispersive X- ray).

2. Experimental

2.1 Materials

AAc (Acrylic acid) is purchased from (Merck Germany) and used as received. PVA (Polyvinyl alcohol), in the form of powder having an average molecular weight (MW) of 15,000. Whereas the other chemicals, such as citric acid, sodium di-hydrogen phosphate buffer analytical reagent as well as the metals such as copper sulphate, cobalt sulfate, and nickel sulfate have been purchased from EL-Nasr Company for Chemical Industries, Egypt and used without further purification.

2.2 Preparation

An aqueous solution of 5% PVA is used; and dissolved with magnetic stirrer at 70 °C for 5 h, then cooling at room temperature. Different ratios of PVA solution of 2, 4, 6, 8, 12 ml are added to 2 ml aqueous solution of AAc acid and 10 ml of distilled water is added. The resulting solutions are poured into glass tubes, and then they have been irradiated by γ- rays from ^{60}Co source at radiation dose 20 kGy with dose rate 2.08 kGy/h at the National Center for Radiation Research and Technology, Atomic energy authority, Egypt. After polymerization, the gels are cut into discs of 2 mm and they are soaked and washed repeatedly with distilled water to ensure the removing of any unreacted chemicals then air – dried at room temperature**.**

3. Characterization

3.1 Gel Fraction and Swelling Percent Determination in the Co-Polymerized Hydrogels

The prepared hydrogel after dried is weighted (W_g), and then soaked in distilled water for 24 h at 100 °C for removing the soluble parts from hydrogel. The hydrogel was then dried and reweighted (W_d). The gel fraction of the hydrogel is determined from the following equation:

$$Gel\% = \frac{W_g}{W_d} \times 100 \tag{1}$$

where, W_g and W_d represent the weights of the dry hydrogel and the gelled part after removal and drying, respectively.

The weighted dried gel was soaked in distilled water then the gel was removed and the excess water on the surface was removed with filter paper and then reweighted. The swelling ratio was calculated as follows:

$$Swelling\% = \frac{W_t - W_o}{W_o} \times 100 \tag{2}$$

where, W_t is the weight of swollen gel sample at time t, W_o is the initial weight of dry gel samples.

3.2 FT-IR Spectroscopy

FT-IR spectroscopy is used to determine the chemical bond structures. the dry hydrogels were grounded and pressed with KBr and then measured with FTIR spectroscopy (Mattson 1000, Unicam, England) from 400 to 4,000 cm^{-1}.

3.3 Scanning Electron Microscopy (SEM)

SEM is used to determine the surface morphology of the samples The dry sample, spread on a double sided conducting adhesive tape, pasted on a metallic stub, and then coated with 100 micron of gold in a sputter coating unit 2 min and absorbed in electron microscope at 20 kV.

3.4 Ultraviolet Spectroscopy (UV)

UV-vis Pye Unicam Spectrophotometer Type SP 8-200 is used to determine the metal ion concentration before and after treatment at room temperature.

3.5 Application in Metal Uptake

The fixed weight of the prepared hydrogel is mixed with certain metal ion concentration. The concentration of metal ions remaining in the solution is detected by UV (Ultraviolet spectroscopy) and used for the calibration process. The pH and temperature of the metal feed solutions were adjusted before it is applied for treatment processes. The adsorption amount (E) is calculated as

$$E(mg/g)=\frac{V(C_i-C_t)}{W} \qquad (3)$$

where, V is the volume of solution, W is the weight of the hydrogel (g).

Whereas, C_i, and C_t are the concentrations of metal ions in mg/L before and after the adsorption, respectively. Factors affecting the adsorption capacity are studied [4].

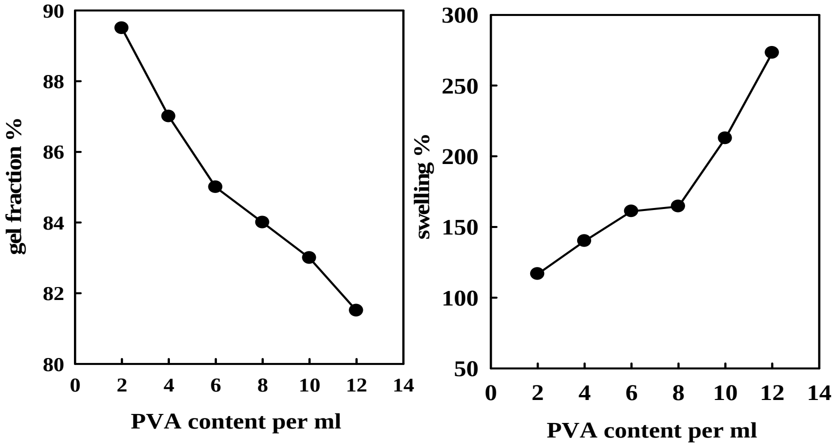
4. Result and Discussion

4.1 Effect of Copolymer Composition on Gel Fraction and Swelling Percent

It is well known that, the gel fraction value is observed, the more effective the crosslinking reaction is. The gel fraction and swelling percent of PVA/AAc copolymer hydrogel against different PVA amounts (2, 4, 6, 8 and 12 ml) is presented in Fig. 1. From Fig. 1a, at 2 ml of PVA the maxiumum gel fraction is estimated. The gel fraction decreases as the PVA amounts increase. The increase in PVA hydrogel causes reduction in crosslinking and in the entanglement reaction and consequently the gelation process is reduced clearly. From Fig. 1b, the swelling degree increases as PVA content increases due to the increasing of the polarity of the hydrogels by increasing the hydrophilic hydroxyl group in PVA chains [5].

It is well known that the absorbed dose is an important factor affecting the degrees of crosslinking. Fig. 2 shows the influence of absorbed dose on the fraction of gelation and swelling percent of copolymer hydrogel. In Fig. 2a, the gel fraction increases with increasing absorbed dose. This can be described by, increase of the absorbed dose, due to increase in free radical formation which leads to an increase in crosslinking as well as gel fraction [6].

Fig. 2b shows that the swelling percent of the hydrogel increases with increasing the absorbed dose from 5 to 20 kGy and then decreases. The increase is attributed to ease of solvent diffusion whereas the decrease is due to the enhancement of the crosslinking at higher doses which restrict the swelling process [7].



(a) (b)

Fig. 1 (a) and (b): Effect of PVA content on gel fraction and swelling property of PVA/AAc hydrogel at 20 kGy.

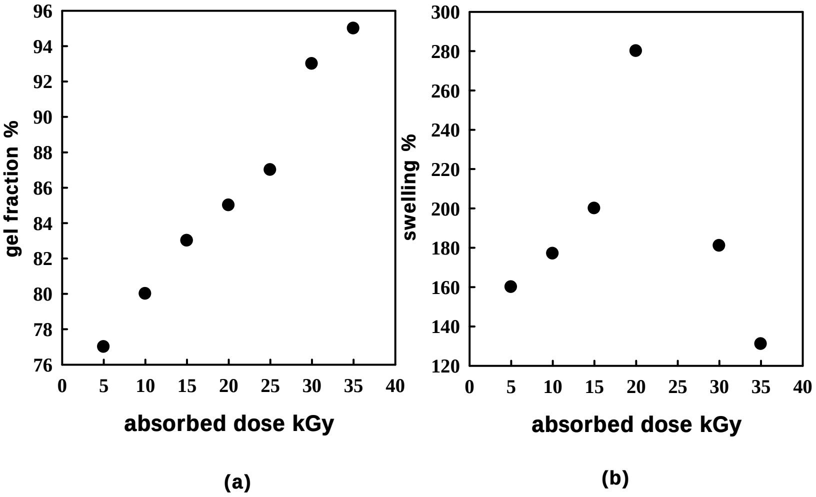


Fig. 2 (a) and (b): Effect of absorbed dose on gel fraction and swelling property for PVA/AAc copolymer hydrogel.

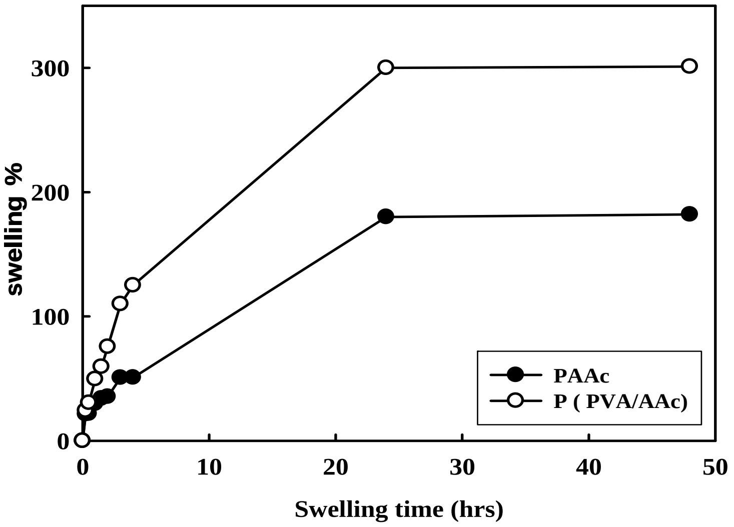


Fig. 3 Effect of contact time on the swelling % of P (PVA/AAc), PAAc at 20 kGy.

4.2 Effect of Time on the Swelling Percent of Hydrogel

The effect of the time on the swelling ratio for PAAc and P (PVA/AAc) at distilled water has been shown in Fig. 3. The figure shows that the swelling percent of the hydrogels increases with increasing time up to 24 h and then leaves off. It can be noted that, the swelling percent P (PVA/AAc) is greater than of PAAc at the same swelling time. This is due to mixing of the function groups of AAc and PVA.

4.3 Effect of PH on the Swelling % of Copolymer Hydrogel

The influence of pH from 2 to 12 on the swelling percent of PAAc and P (PVA/AAc) is plotted in Fig. 4. It is observed that, the swelling % increases with increasing in the pH of the medium. At lower pH, the swelling ratio is low due to the formation of hydrogen bonding between PVA and carboxyl groups which restricted the chain mobility. As the pH increases, the carboxylic groups (COOH) of AAc are ionized and produce carboxylate ions (COO-) and the electrostatic repulsion between these groups, facilate the diffusion of water molecules, thus enhancement the swelling [8].

4.4 FT-IR Spectroscopic Measurements

FTIR spectroscopy is an important technique to confirm

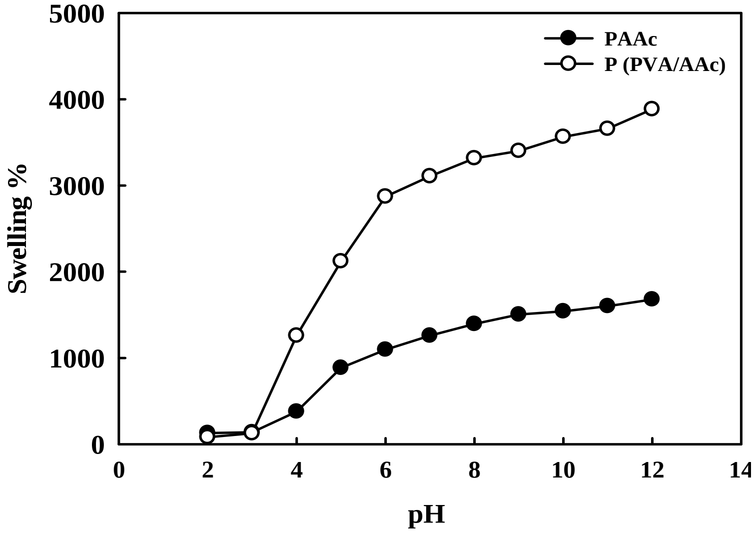


Fig. 4 Effect of pH on the swelling ratio of PAAc and P (PVA/ AAc) at absorbed dose 20 kGy.

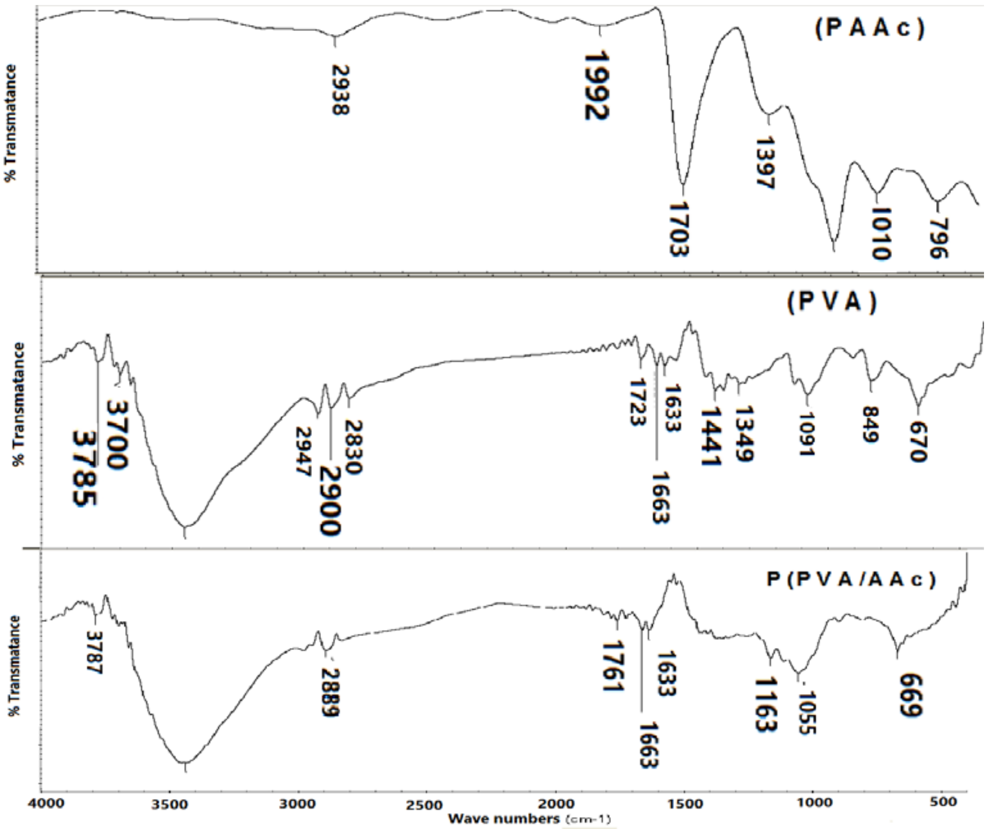


Fig. 5 The FTIR spectra of PVA, PAAc and P (PVA/AAc).

the formation of copolymer hydrogel. The FT-IR spectra of PVA, PAAc and P (PVA/AAc) are shown in Fig. 5. The spectra of PVA show a wide band around 3,455 cm^{-1} for the OH stretching vibrations. The bands of CH-CH_2 asymmetric and symmetric stretching found at 2,947 cm^{-1} and 2,830 cm^{-1} respectively. The C-C and C-O stretching, vibration is observed at 1137 cm^{-1} and 1091 cm^{-1} respectively. The stretching of the acetate group of PVA appear at 1723 cm^{-1} corresponds to the C=O. The spectrum of PAAc shows a characteristic stretching peak of the C=O group at 1,703 cm^{-1}.

In the spectrum of PVA/AAc hydrogel, the broad band at 3434 cm^{-1} due to OH of carboxylic group of AAc is overlapping with the OH of PVA. The band at 1,761 cm^{-1}, confirm that, hydrogen bond interactions of PVA are replaced by hydrogen bond between PAAc and PVA. The C-O stretching, vibration at 1,091 cm^{-1} is slightly strengthened. This may be due to the esterification reaction between carboxylic groups in PAAc and the hydroxyl group in PVA [3].

5. Application of the Prepared Copolymers in Metal – Ion Removal from Aqueous Solutions

5.1 Effect of PH of Metal Ion Solution

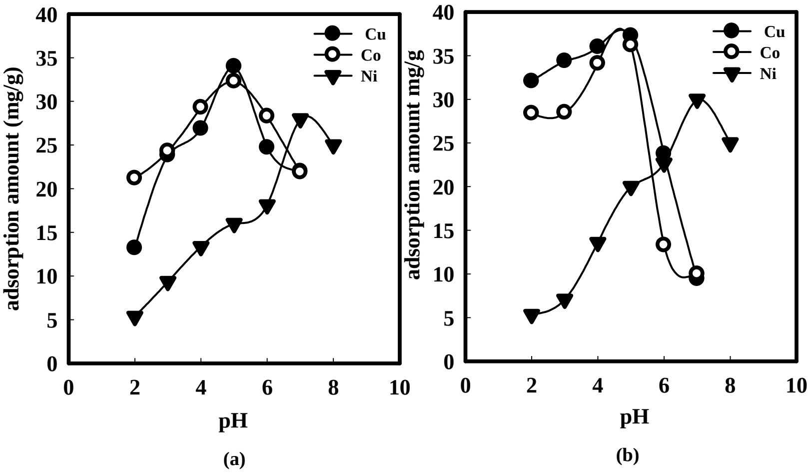
Fig. 6 illustrates the change of adsorption amount of PAAc and P (PVA/AAc) respectively, with changing pH of solution from 2 to 7 with initial 1,000 ppm of metal ions for 24 h. It is found that, the adsorption capacity increases with increase pH of the solution, this may be due to that, at low pH (acidic solution), the carboxylic group of hydrogels form protonation that induces an electrostatic repulsion of cationic metal ions. Therefore, there are competition between these groups and metal ions, which leads to a decrease in adsorption amount by increasing the pH. Electrostatic repulsion decreases by unprotonation of carboxylic groups, leading to increase of adsorption amount. The pH 5 is chosen as the optimum pH for PAAc and PVA/AAc for all metal ions [9-12]. It is noted that, adsorption amount at all pH values is slightly higher in the P (PVA/AAc) compared to the PAAc.

5.2 The Effect of Contact Time on Adsorption Amount

Fig. 7 shows the influence of contact time in the adsorption amount of two hydrogels for the three different metal ions. The adsorption amount increases by increasing contact time and become maximum after 24 h for different metal ions and then leave off [13]. The maximum capacity are found to be of 150 mg/g, 155 mg/g and 193 mg/g for Cu^{2+}, Co^{2+} and Ni^{2+} respectively in case of PAAc. In case of P (PVA/AAc), there are increase in maximum capacity to be 197 mg/g, 194 mg/g and 160 mg/g towards Cu^{2+}, Co^{2+} and Ni^{2+} ions respectively [14].

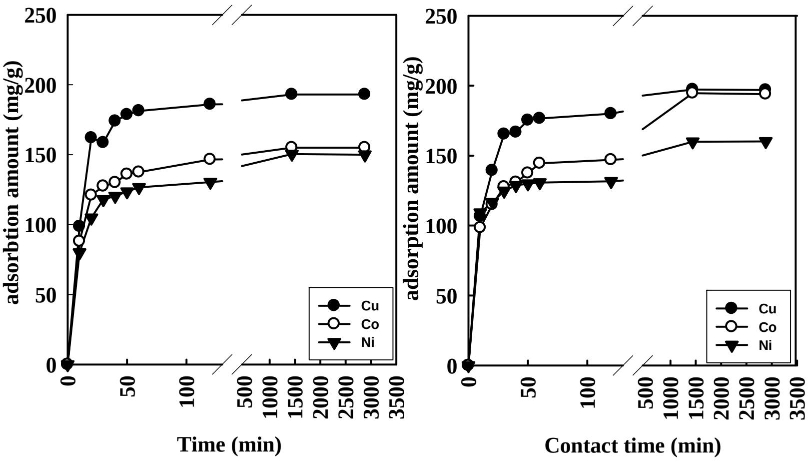
5.3 Effect of Initial Concentration on Metal Uptake

Fig. 8 illustrates the influence of initial metal ion concentration on the adsorption amount of PAAc and P (PVA/AAc) hydrogel respectively. For PAAc the adsorption amount of Cu^{2+}, Co^{2+} and Ni^{2+} increases with increasing the initial concentration from 40 ppm up to 100 ppm for Cu^{2+} and Co^{2+} and up to 250 ppm for Ni^{2+} respectively, and then decreases. However, for P (PVA /AAc), the adsorption capacity of Cu^{2+} and



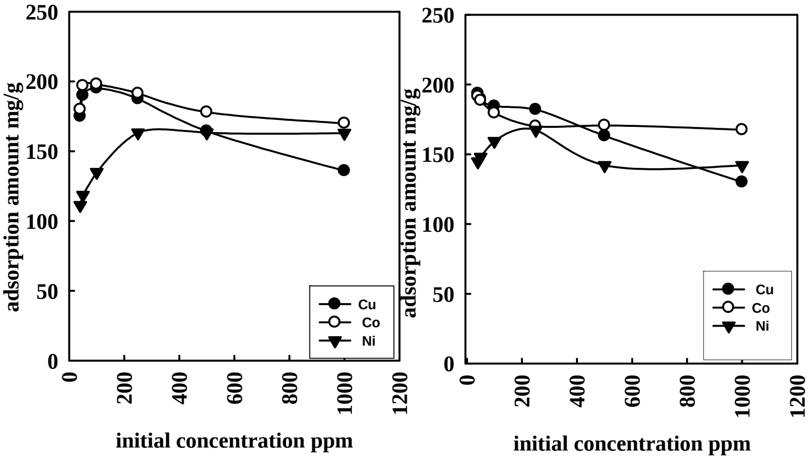
(a) (b)

Fig. 6 Effect of pH on the adsorption amount of different metal ions for (a) PAAc and (b) P (PVA/AAc).



(a) (b)

Fig. 7 Effect of contact time on the adsorption of metal ions (a) by PAAc and (b) by P (PVA/AAc).



(a) (b)

Fig. 8 (a) and (b): Effect of initial metal ion concentration on adsorption amount of (a) PAAc and (b) P (PVA/AAc) hydrogels respectively.

Co^{2+} shows a maximum at 40 ppm and then decreases with increasing concentration (Fig. 8b). For Ni^{2+} metal ion the adsorption capacity increases to 250 ppm, and then decreases. These results can be explained by the fact that, at a low initial solution concentration, the surface area and adsorption sites are high. At higher initial solution concentrations, the total available adsorption sites are limited, thus resulting in a decrease in the adsorbed amount [13].

5.4 Effect of Temperature on Adsorption Capacity

The effect of different temperature ranging from 20 °C to 70 °C on the adsorption amount using 0.5 g of the P (PVA/AAc) immersed in 100 ml of Cu^{2+} ion solution with 100 ppm at pH 5 for 24 h is illustrated in Fig. 9. In addition, at lower temperatures this hydrogel display the high efficiency, which decreases after 20 °C. The decrease in adsorption by increasing the adsorption medium temperature illustrate that the nature of the adsorption process is exothermic. This can be explained by the tendency of the Cu^{2+} ions to have a higher velocity at high temperatures. So it can escape from the adsorption sites to solution, which resulted in a decrease in the adsorption amount [15].

5.5 Scanning Electron Microscopy

The surface morphology of the P (PVA/AAc) copolymer hydrogel before and after loading of Cu^{2+}

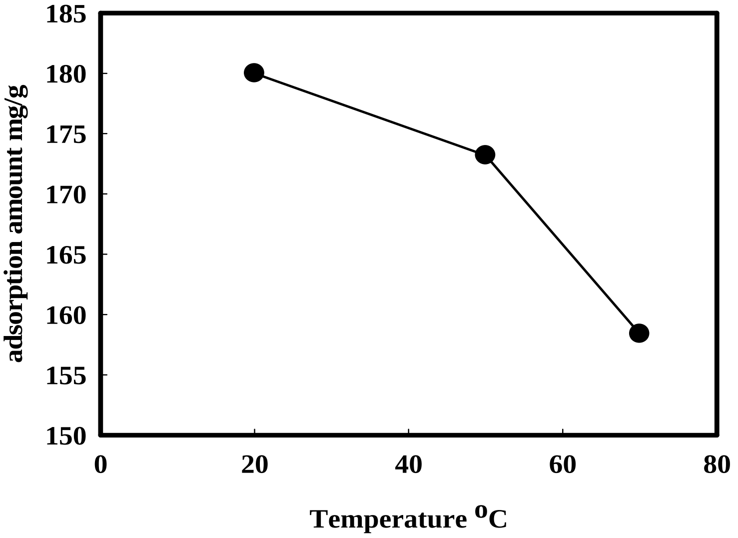


Fig. 9 Effect of temperature on adsorption amount of PVA/AAc towards Cu^{2+}.

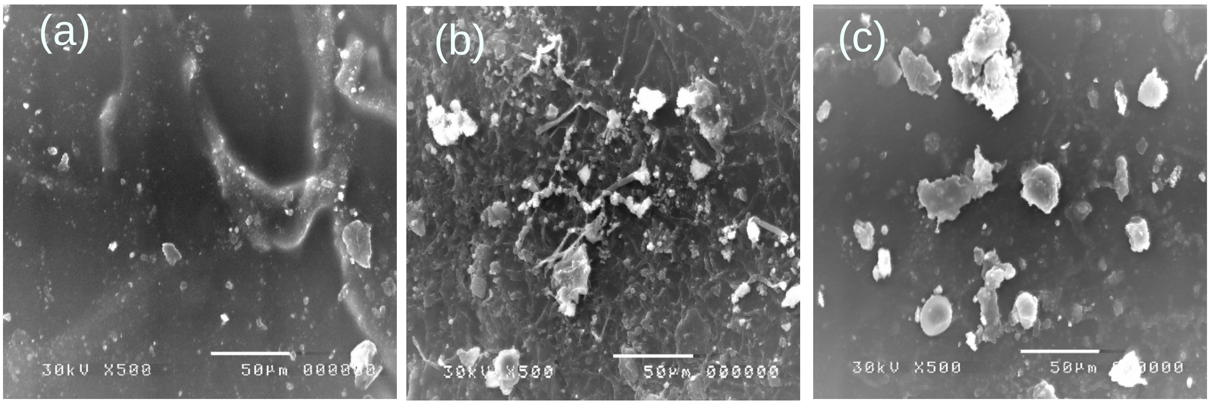
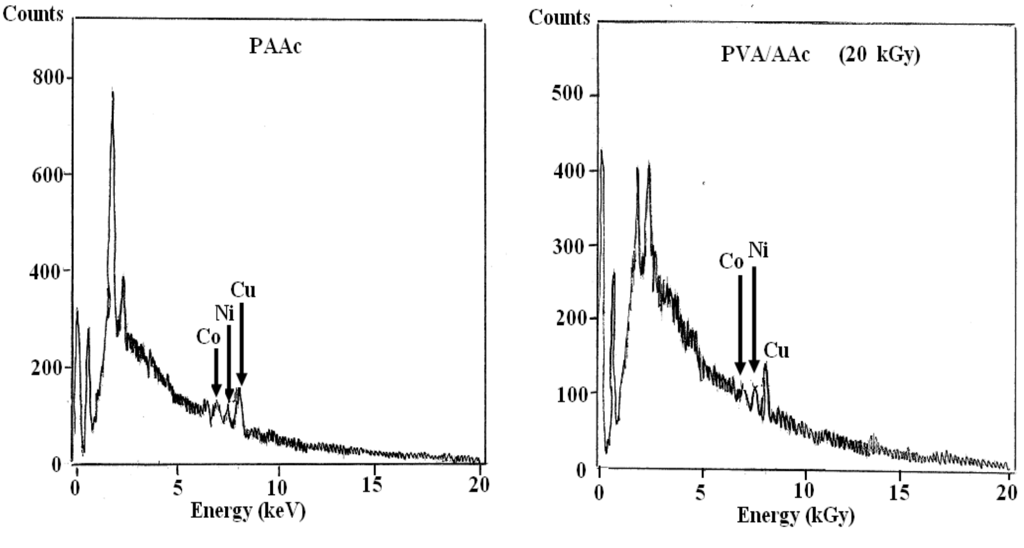


Fig. 10 Surface morphology analysis of (PVA/AAc) hydrogel at irradiation dose 20 kGy (a) before metal uptake, (b) after adsorption of Cu^{2+} and (c) Co^{2+} metal ions.



(a) (b)

Fig. 11 Affinity of (a) PAAc and (b) PVA/AAc toward Cu, Co and Ni at 1,000 ppm.

Table 1 Affinity of hydrogel and nanocomposite hydrogel for adsorption of Cu(II), Co(II) and Ni(II).

Hydrogel		Affinity of metal uptake ratios		
		Cu^{2+}	Co^{2+}	Ni^{2+}
PAAc	$Cu^{2+} > Co^{2+} > Ni^{2+}$	65.7%	17.5%	16.8%
PVA/AAc	$Cu^{2+} > Co^{2+} > Ni^{2+}$	66.2%	20.1%	13.5%

and Co^{2+} metal ions is investigated by the scanning electron microscope and shown in Fig. 10. We can find that the hydrogel surface is smooth before metal uptake. After uptake; it is tough and the adsorbed metal ions appeared on the hydrogel surface.

5.6 Energy Dispersive X- Ray Analysis

The competitive adsorption for the hydrogels is studied and illustrate in Fig. 11.

From Fig. 11 and Table 1, it was found that the PAAc and PVA/AAc adsorb the three metals with the order of Cu(II) > Co(II) > Ni(II) in their competitive adsorption.

6. Conclusions

In this study Co-60 irradiation is used for the synthesis of poly vinyl alcohol co acrylic acid (PVA/AAc) copolymer hydrogel, for the purpose of separation of some heavy and toxic metals from water. The crosslink chemical structure of the copolymer has been confirmed by Fourier transform infrared spectroscopy (FTIR). The optimum preparation conditions such as the effect of copolymer composition and absorbed dose on gel fraction and swelling behaviours are determined. It is found that, with 12 ml PVA a maximum swelling percent is obtained 273% at gel fraction 82% and absorbed dose of 20 kGy. The prepared hydrogels are examined for Cu^{2+}, Co^{2+} and Ni^{2+} removals from aqueous solutions. Study the factor affecting the adsorption amount such as pH, treatment time, initial metal ion concentration and solution temperature illustrate that, the adsorption of metal ions on hydrogel increases with increasing time and reach a maximum after 24 h and at pH 5 for Cu^{2+}, Co^{2+} and Ni^{2+} in P (PVA/AAc) and PAAc. The competitive adsorption for the three metals is also studied by EDX. The Microstructure of the prepared hydrogels before and after adsorption is investigated by means of SEM.

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