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Characterization of Some Hydrogels Used in Water Purification: Correlation of Swelling and Free-Volume Properties

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Abstract

In this study, the main objective is to develop a good chelation and ion exchange hydrogel. This hydrogel is obtained by polymerization of dimethyl amino ethyl methacrylate (DMAEMA) and acrylic acid (AAc) by gamma irradiation, for the purpose of separation of some heavy and toxic metals from water. UV spectroscopy is applied to determine the metal ion concentration before and after treatment. The FTIR spectral analysis has identified the bond structure of PAAc, DMAEMA and P (DMAEMA/AAc) hydrogels. Microstructure and nanostructure are investigated by means of SEM and positron annihilation lifetime spectroscopy (PALS) respectively. A maximum swelling percent is found for 80/20 DMAEMA/AAc at free-volume hole size and fraction of 97 Å^3 and 3.4% respectively. The P (DMAEMA/AAc) and PAAc hydrogels have been applied for Cu^{+2}, Co^{+2} and Ni^{+2} removals from aqueous solutions, and the factors affecting the adsorption capacity are determined. The adsorption capacity of P (DMAEMA/AAc) is found to be higher than the corresponding ones PAAc. Its experimental results showed that, the maximum adsorption of P (DMAEMA/AAc) after 24 h occurs at pH 7 with concentration of 250 ppm for Ni^{+2} ions and at pH 5 with concentration of 40 ppm for Cu^{+2} and Co^{+2} ions. The adsorption affinity of P (DMAEMA/AAc) hydrogel at different treatment contact times is in the following order Ni > Cu > Co. However, the order becomes Co > Ni > Cu by the variation of the pH of the metal ion solution; the variation of its concentration leads to a different order of Cu > Co > Ni.

Keywords

Hydrogels, Irradiation, Copolymerization, FTIR, PAL, Water Decontamination

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1. Introduction

Heavy metals, such as Cd, Cr, Cu, Ni, As, Pb, Co, and Zn, are the most hazardous, because of their high solubility in the aquatic environments. They can be absorbed by living organisms, aggregate in the human body, and cause serious health impacts as cancer, organ damage, nervous system damage, and sometimes death [1]. There are a lot of techniques to remove such heavy metal ions. These techniques include filtration, chemical precipitation, chelating, ion-exchange and adsorption [2]. The disadvantages of these techniques are due to their cost, environmental and health problems related to low efficiency, long-time processing and high-energy consumption. However, adsorption is an attractive method because of its high efficiency, easy operation, low cost and availability of different adsorbents.

Hydrogels are hydrophilic polymer networks that are capable of absorbing large amounts of water. However, they are insoluble because the hydrogel chains are joined covalently in the form of three-dimensional networks. In addition, they have been used for removing heavy metal ions from wastewater due to three-dimensional network structures and their ability of joining different functional groups. These ionisable groups, such as carboxylic when ionized, produce fixed ions that repel one another, and this repulsion leads to greatly enhanced swelling of the network [3].

In the present work, copolymerization of dimethyl amino ethyl methacrylate and acrylic acid P (DMAEMA/AAc) for heavy metal uptake of different metals has been synthesized by gamma irradiation, which is found to be a very effective and clean method for controlling polymerization reactions. In addition, it is an environmentally-friendly way to polymerization initiation without the need of catalysts. On the other hand, this hydrogel contains various functional groups, especially amine (-NH_2) and carboxyl (-COOH), which show high hydrophilicity, and can be used as chelation and ion exchangers [4]. The hydrogel P (DMAEMA/AAc) has been characterized using different methods such as Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and positron annihilation lifetime spectroscopy (PALS).

2. Experimental

Preparation

Different weight ratios of DMAEMA/AAc [(0/100), (20/80), (40/60), (60/40), (80/20), (100/0)] are added to 10 ml of distilled water in small glass tubes. The mixture is then irradiated with a ^{60}Co source at absorbed dose 20 kGy with dose rate 2.08 kGy/h at the National Center for Radiation Research and Technology, Atomic Energy Authority, Egypt. After copolymerization, the formed polymeric cylinder was removed and cut into discs of 2 mm thickness, and then dried at room temperature.

3. Characterization

3.1. Gel and Swelling Measurements

The hydrogel is dried at room temperature for 24 h and weighted (W_g), then immersed in distilled water for 24 h at 100˚C to separate the soluble part from the hydrogel. The hydrogel is then dried again and weighted again (W_d). Its gel fraction is determined from the following equation:

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

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

The clean, weighted dried gel is soaked in distilled water at room temperature for 24 h. The gel is removed and the excess water on the surface was removed with filter paper and weighted. The swelling ratio was calculated as follows

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

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

In order to determine the chemical bond structures, the dry hydrogel is grounded and pressed with KBr and then measured with FTIR spectroscopy (Mattson 1000, Unicam, England) from 400 cm^{-1} to 4000 cm^{-1}.

3.3. Scanning Electron Microscopy (SEM)

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

3.4. Positron Annihilation Lifetime Spectroscopy (PALS)

Positron lifetime measurements are carried out at room temperature using a 1 μCi ^{22}Na source sealed between two Kapton foils (thickness less than 1 mg/cm^2) with a small active diameter of l - 2 mm in sandwich geometry with the pellets and a standard fast-fast coincidence lifetime spectrometer. The time resolution of (full width at half-maximum, FWHM) about 250 ps has been used in the present study. The lifetime spectra were recorded for each sample with about 5 × 10^6 counts accumulated under the peak.

Lifetime analysis using the computer program LT 9.0 [5], decomposes a PAL spectrum into three different states of positron annihilation as follows: the shortest component with lifetimes and intensity (τ_1 & I_1) is related to para-positronium (p-Ps) annihilation. The intermediate (τ_2 & I_2) is the one indicating annihilation of free positron in the polymer matrix as well as in amorphous crystalline interfaces; the longest one (τ_3 & I_3) represents a pick-off annihilation of the ortho-positronium (o-Ps) in free volumes. Assuming that, the free-volume holes are spheres, the average radius (R) of holes and the fractional free-volume holes (F) were calculated as follows [6]-[9].

$$\tau_3 = 0.5\left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R + \Delta R}\right)\right]^{-1} \qquad (3)$$

where ΔR = 1.656 Ǻ is an empirical parameter, which is obtained by fitting the measured lifetime of cavities with known size [9].

By fitting the above equation with the measured τ_3 values, R and $V_h = (4/3)\pi R^3$ can be evaluated. The relative intensity of the longest component, I_3, is generally correlated to the relative fractions of holes, which can be considered as trapping centres for positronium (Ps). A semi-empirical relation may be used to determine the relative fraction of the free-volume (F) in polymers [9] as follows:

$$F = C V_h I_3 \qquad (4)$$

where C is a normalization constant. In common polymers, the value of C ranges from 0.001 to 0.002.

3.5. 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.

4. Application in Metal Uptake

The fixed weight of the prepared hydrogel is submerged in metal solutions of a definite concentration. The concentrations of metal ions remaining in the solution were detected by ultraviolet spectroscopy (UV) and used for the calibration process. The adsorption amount (E) was calculated as

$$E\left(\text{mg/g}\right) = \frac{V\left(C_i - C_t\right)}{W} \qquad (5)$$

where, V is the volume of solution (L), W is the weight of the hydrogel (g), C_i, and C_r are the concentrations of metal ions in mg/L before and after the adsorption, respectively. The factors affecting the metal uptake are studied and discussed [1] [4] [10].

5. Result and Discussion

FTIR spectroscopy is an important technique in studying the copolymer vibrational structure. The width and intensity of the spectrum bands, as well as the position of the peaks confirm the functional groups that take part in the formation of copolymer. **Figure 1** shows the FTIR spectra of PAAc, DMAEMA and P (DMAEMA/AAc).

For DMAEMA bands at 1455 cm^{-1} and 1253 cm^{-1} are due to CH_3 bending vibration, the weak band at 2943 cm^{-1} is due to the CH_2-CH group conjugated with the carbonyl group. Strong peak at 1718 cm^{-1} is assigned to the ester carbonyl stretching, vibration which shows a shift due to conjugation of carbonyl group. A weak stretching vibration band at 2780 cm^{-1} is due to parafines (NCH_3). For PAAc, the band at 2938.37 cm^{-1} is due to the CH_2 group and the band at 1703 cm^{-1} is for the stretching vibration of the carbonyl group, which are shifted due to conjugation of C=C group. For the P (DMAEMA/AAc) spectrum the conjugation disappeared from the ester carbonyl group and the acid carbonyl group is observed due to the formation of the hydrogel of P (DMAEMA/AAc).

5.1. Effect of Copolymer Composition

Figure 2(a) shows the effect of different composition of P (DMAEMA/AAc) hydrogel on gel fraction, which decreases from 98% with increasing DMAEMA percent reaching a minimum at 80/20 composition. This is due to the decrease of -C=C-groups in AAc which reduces the formation of free radicals during irradiation, leading to a decrease in the crosslinking density as well as the gel fraction [3].

In **Figure 2(b)**, the swelling percent, however, increases as the DMAEMA/AAc ratio increases and a maximum occurs at the ratio 80/20 (DMAEMA/AAc). This proves that the presence of amine group in the DMAEMA structure increases the hydrophilicity of the copolymer produced, due to its loosely bound chains. This is in accordance with the increase in free-volume hole size (V_h) from 67 Å^3 to 97 Å^3 and its fraction (*F*%) from 1.8% to 3.4% as shown in **Figure 3(a)** and **Figure 3(b)**.

However the PAL results show that, for initial AAc a small free-volume hole size of 80 Å^3 with a fraction of 1.7% is estimated as compared to the free-volume hole size of 120 Å^3 with a fraction of 5.3% for initial

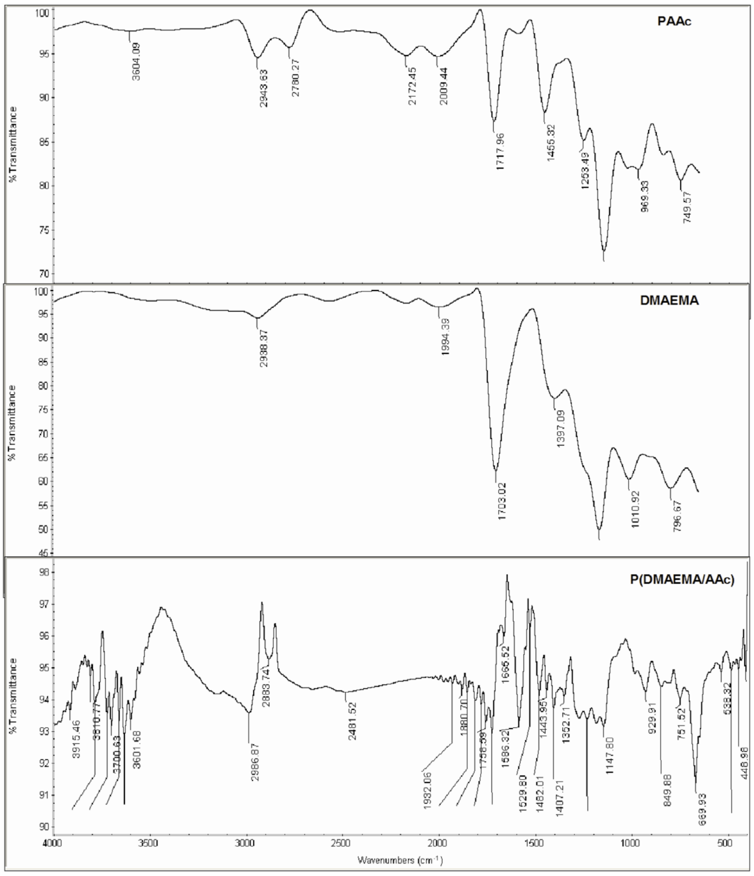
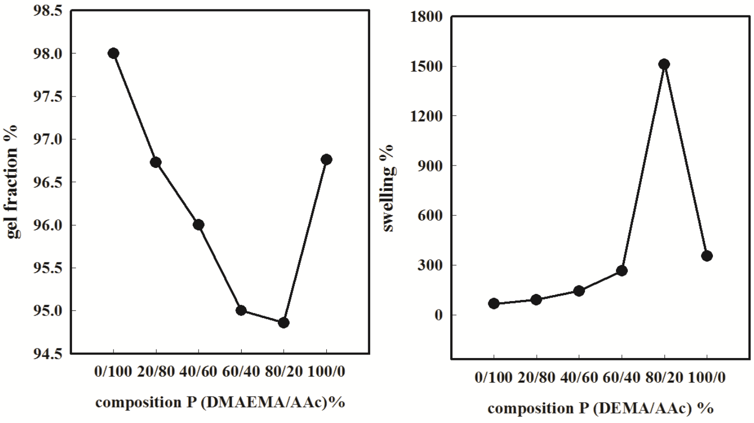
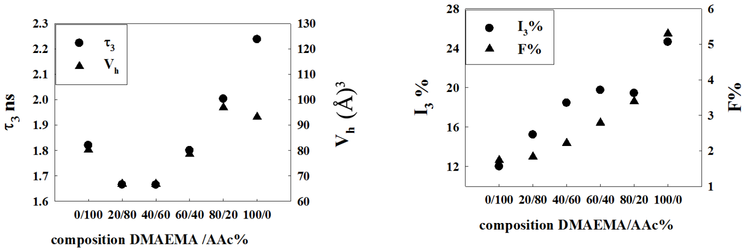


Figure 1. FTIR spectra of PAAc, DMAEMA and P (DMAEMA/AAc) hydrogels.



(a) (b)

Figure 2. Effect of copolymer composition on (a) the gel fraction; and (b) swelling percent (%) of P (DMAEMA/AAc) hydrogel with absorbed dose 20 kGy.



(a) (b)

Figure 3. The effect of different composition of P (DMAEMA/AAc) hydrogel on the o-Ps lifetime components (τ_3 and I_3) and free-volume parameters (V_h and F%).

DMAEMA. This is due to the presence of the high electron negativity of the oxygen atom in the carboxyl group (COOH) of PAAc which is known to be electron-attracting and increasing the secondary bond density between polymer chains leading to a decrease in free-volume hole parameters in the polymer.

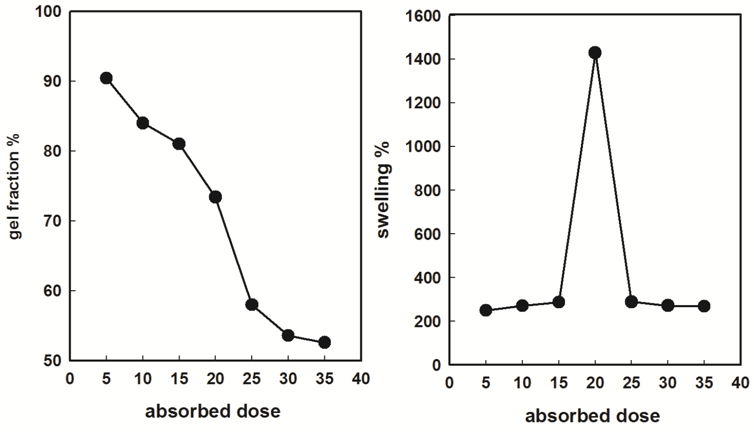
5.2. Effect of Absorbed Dose

Figure 4(a) shows the effect of absorbed dose on the fraction of gelation of (80/20) DMAEMA/AAc hydrogel. It is found that, the gel fraction decreases with the increase in the absorbed dose from 5 kGy to 35 kGy. This is due to the degradation of DMAEMA chains when exposed to radiation leading to break of the main chains, and consequently to a decrease in the gel fraction [11] [12].

On the other hand, the swelling degree of the hydrogel increases by increasing the absorbed dose reaching a maximum at 20 kGy followed by a steep decrease at higher doses as shown in **Figure 4(b)**.

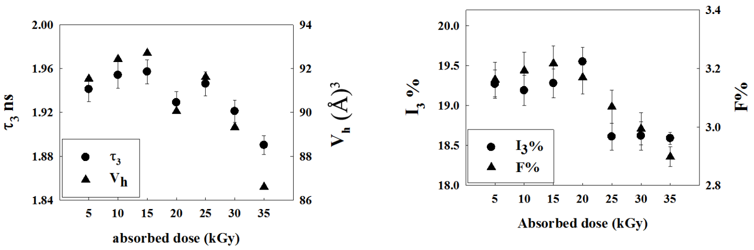
A maximum is also observed in the free-volume hole size (V_h) and its fraction (F%) as shown in **Figure 5(a)** and **Figure 5(b)** followed by a decrease in V_h from 92 Å^3 to 87 Å^3 and from 3.2% to 2.9% in F% at higher doses. This can be explained in terms of increase in crosslinking [12], which leads to a decrease in V_h due to the tightness of the network structure. These results explain the steep decrease in the swelling behaviour.

It is to be noted that the size and fraction of free-volumes play an important role in the swelling mechanism, which is demonstrated in **Figure 6(a)** and **Figure 6(b)** and **Figure 7(a)** and **Figure 7(b)** showing a correlation of swelling percent with V_h & F% as a function of composition and absorbed dose respectively. It can be concluded that, the free-volume properties considerably control the porosity and surface hydrophilic/hydrophobic property of the hydrogel.



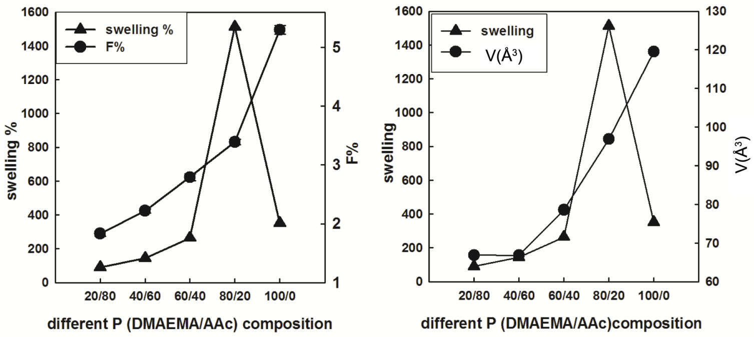
(a) (b)

Figure 4. Effect of absorbed dose on (a) the gel fraction; and (b) swelling percent (%) of (80/20) DMAEMA/AAc hydrogel.



(a) (b)

Figure 5. The effect of absorbed dose on the o-Ps lifetime components (τ_3 and I_3) and free-volume parameters (V_h and F%) of 80/20 DMAEMA/AAc hydrogel.



(a) (b)

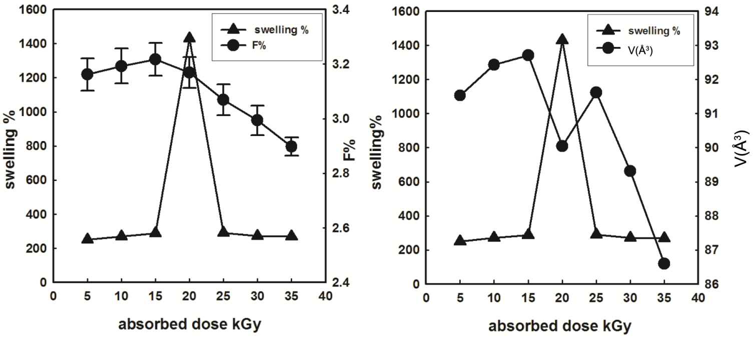
Figure 6. Correlation of swelling percent with free-volume parameters (V_h and F%) as a function of DMAEMA/AAc composition.

5.3. Factors Affecting Adsorption Capacities of Cu, Co, Ni Ion in P (DMAEMA/AAc) and PAAc Hydrogels

5.3.1. Effect of pH of Metal Ion Feed Solution

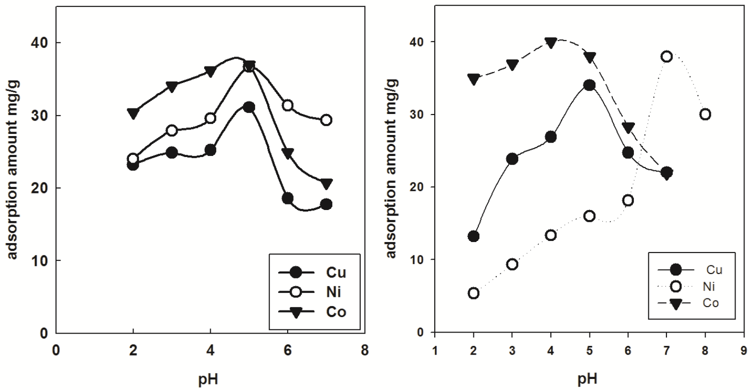
The adsorption amount of these hydrogels towards Cu^{+2}, Co^{+2} and Ni^{+2} ions with pH ranging from 2 to 7 with initial metal concentration of 1000 ppm for 24 h at room temperature is shown in **Figure 8(a)** and **Figure 8(b)**.

It is found that, the adsorption amount of metal ions increases in the two hydrogels as the initial pH value of



(a) (b)

Figure 7. Correlation of swelling with free-volume parameters (V_h and F%) as a function of absorbed dose of 80/20 DMAEMA/AAc hydrogel.



(a) (b)

Figure 8. Effect of pH on the adsorption amount of different metal ions at metal concentration of 1000 ppm, for 24 hrs for (a) PAAc, (b) P (DMAEMA/AAc) hydrogels.

the solution increases. This can be explained by the fact that at low pH (acidic solution), the carboxylic (COOH) and amine (NH_2) groups hydrogels easily form protonation, that induces an electrostatic repulsion of cationic metal ions. Therefore, competition exists between protons and metal ions, which results in the decrease of adsorption amount. By increasing the pH, electrostatic repulsion decreases and the unprotonation of groups occur, which leads to increase of metal ion uptake. The optimum pH is 7 only for Ni ions in P (DMAEMA/AAc) and 5 for the other metals [13]-[15]. It is to be noted, that for all ions the adsorption amount at all pH values is slightly higher in P (DMAEMA/AAc) hydrogel compared to the PAAc. Its adsorption affinity is in the following order $Co^{+2} > Ni^{+2} > Cu^{+2}$.

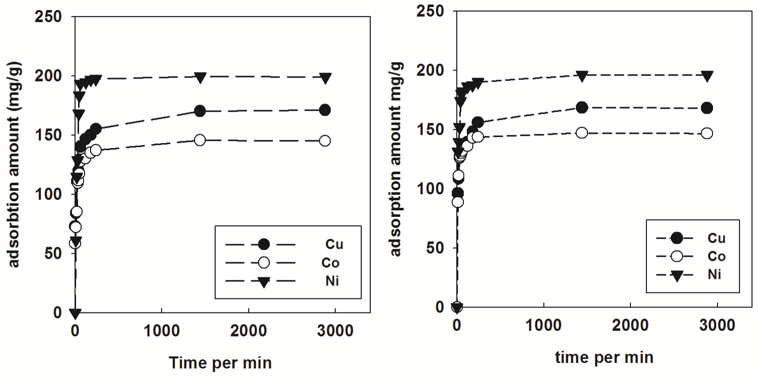
5.3.2. The Effect of Contact Time on Metal Uptake

Figure 9(a) and **Figure 9(b)**, show the adsorption amount of PAAc and P (DMAEMA/AAc) hydrogels as a function of contact time for different metal ions.

The metal uptake increases with time to reach its maximum capacity after 24 h for different studied metal ions and then becomes constant at higher contact times. The variability of contact time showed a maximum uptake of 145 mg/g, 168 mg/g and 196 mg/g for PAAc. In P (DMAEMA/AAc) hydrogel a weak increase in the maximum uptake is observed, which shows the values of 147 mg/g, 171 mg/g and 199 mg/g towards Co^{+2}, Cu^{+2} and Ni^{+2} ions respectively [16]. The maximum adsorption amount of P (DMAEMA/AAc) follows the order $Ni^{+2} > Cu^{+2} > Co^{+2}$.

5.3.3. Effect of Initial Concentration on Metal Uptake

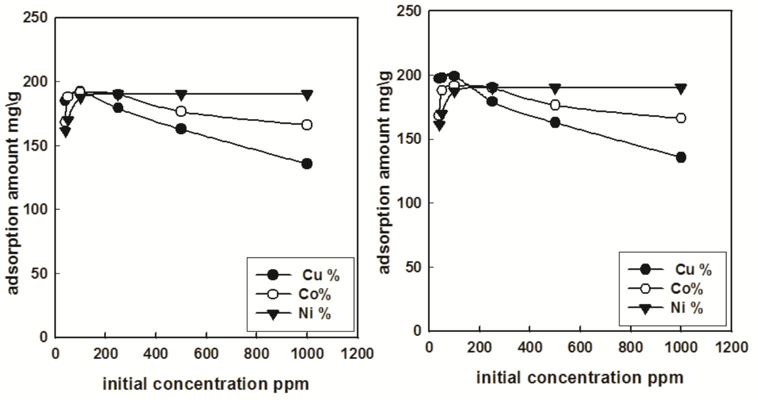
Figure 10(a) and **Figure 10(b)** shows the effect of initial metal ion concentration from 40 to 1000 ppm on the



(a)

(b)

Figure 9. Effect of treatment time on the adsorption amount of metal ions (a) for PAAc and (b) for P (DMAEMA/AAc).



(a)

(b)

Figure 10. Effect of initial metal ion concentration on adsorption amount of PAAc and P (DMAEMA/AAc) hydrogels.

adsorption amount of PAAc and P (DMAEMA/AAc). For PAAc the adsorption amount increases with increasing initial concentration up to 100 ppm for Cu^{2+} and Co^{+2} and up to 250 ppm for Ni^{+2} and then decreases. However, in case of P (DMAEMA/AAc) hydrogel, the adsorption amount of Cu^{+2} and Co^{+2} shows a maximum at 40 ppm and then decreases with increasing concentration. For Ni^{+2} metal ions the adsorption amount 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 the availability of adsorption sites are relatively high. At higher initial solution concentrations, the total available adsorption sites are limited, thus resulting in a decrease in the percentage of removal [17]. The adsorption amount of P (DMAEMA/AAc) follows the order $Cu^{+2} > Co^{+2} > Ni^{+2}$.

The surface morphology of the P (DMAEMA/AAc) hydrogel before and after adsorbing metal ions is shown in **Figures 3(a)-(c)**.

Before adsorption, the hydrogel image displays regular structure. Furthermore, the hydrogel shows very small pores on the surface (**Figure 11(a)**). These pores facilitate the diffusion of metal ions. The smoothness of the surface leads to increase in the surface area which also increases adsorption capacity. After adsorption, the adsorbed metal ions appear on the hydrogel surface as small splatter as shown in **Figure 11(b)** and **Figure 11(c)** in agreement with Duran, *et al.* [2].

6. Conclusions

- In this work Co-60 radiation is used for the synthesis of poly dimethyl amino ethyl methacrylate Co acrylic acid (DMAEMA/AAc) copolymer hydrogel, for the purpose of separation of some heavy and toxic metals

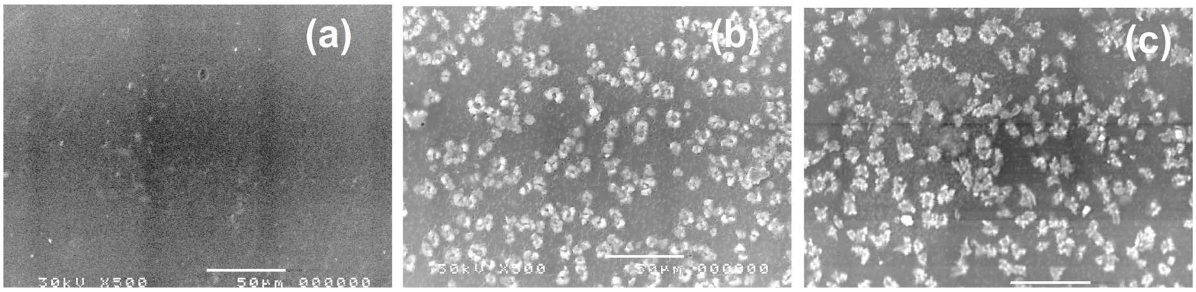


Figure 11. Surface morphology analysis of (80/20) DMAEMA/AAc hydrogel. (a) Before metal uptake; (b) After adsorption of Cu^{+2}; and (c) Co^{+2} metal ions with solution concentration 1000 ppm and pH 5 after 24 hrs.

from water.

- The crosslink chemical structure of PAAc, DMAEMA and P (DMAEMA/AAc) hydrogels has been confirmed by FTIR.
- The optimum preparation conditions such as the effect of copolymer composition and absorbed dose on gel fraction and swelling behaviours showed that the maximum swelling ratio for P (DMAEMA/AAc) is obtained at composition with 80/20 which corresponds to an optimum free-volume hole size and fraction of 97 $Å^3$ and 3.4%, respectively.
- A positive correlation is observed between these free-volume parameters and swelling percentage with the variation of composition and absorbed dose. It can conclude that, the free-volume properties considerably control the porosity and surface hydrophilic/hydrophobic property of the hydrogel.
- The adsorption capacity of PAAc and P (DMAEMA/AAc) has been compared for the separation of Co^{+2}, Cu^{+2} and Ni^{+2} ions from a test water solution. The factors affecting the metal uptake, such as pH, time, and initial feed metal concentration are determined.
- After 24 h, the results of maximum adsorption of P (DMAEMA/AAc) are found to be 199 mg/g at pH 7 for Ni^{+2}. For Cu^{+2} and Co^{+2} they are 171 and 147 mg/g, respectively at pH 5, which is higher than the maximum adsorption of PAAc of 196, 168, 145 mg/g for Ni^{+2}, Cu^{+2} and Co^{+2} respectively.
- The surface morphology of the hydrogels before and after metal adsorption has been determined by SEM, showing a pore structure before metal uptake as well as small splatter after metal adsorption.

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