



Gamma Radiation Preparation of Poly (Acrylamide/Maleic Acid/Gelatin) Hydrogels for Adsorption of Chromium Ions from Wastewater

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Abstract: Poly (acrylamide/maleic acid/gelatin) P(AAm/MA/G) hydrogels have been prepared by gamma radiation and their adsorption for chromium ion from aqueous solutions have been investigated. The structural of the hydrogels was monitored by FTIR. The swelling behavior of the hydrogels has been investigated in distilled water and different pH's values at ambient temperature. The P(AAm) hydrogel showed fair pH-dependent swelling whereas P(AAm/MA) and P(AAm/MA/G) hydrogels exhibit a higher swelling by increasing the pH. The chromium ion solutions have been exposed to gamma radiation for precipitation. The results showed that the precipitation (%) decrease by increasing the initial chromium ions concentration. The possibility of using different hydrogels for the uptake of irradiated chromium ion solutions was investigated. The P(AAm/MA) hydrogel showed higher chromium ion uptake compared to that by P(AAm) and P(AAm/MA/G). The adsorption studies show that, the chromium uptake is pH dependent. Lowering of the chromium ion concentration has been achieved after the treatment of chromium ion solution by gamma radiation followed by adsorption onto hydrogels.

Keywords: Chromium Ion, Gamma Radiation, Adsorption, Hydrogels

1. Introduction

Many industries such as electroplating, tanning, anodizing and chrome mining release inorganic pollutants as chromium ions one of the well-known toxicity, this can lead to the contamination of fresh water and marine environment. Chromium ions are not biodegradable and accumulated in living organisms. Extensive exposure to chromium ions may cause cancer in the digestive tract and lungs. It also may cause epigastric pain, nausea, severe diarrhea, and hemorrhage. The removal of chromium ions from industrial effluents is essential before it is mixed with drinking water sources.

It is well known that some metals are harmful to life and some of them are significantly toxic to human being and ecological environments (1). Numerous techniques are available for wastewaters purification and metal recovery operations. These techniques employed for heavy metal removal include precipitation, ion exchange, adsorption, filtration, electrode position and reverse osmosis (2).

Chromium ions can exist as chromium (II), chromium (III), or chromium (VI). Chromium (VI) is toxic to man when ingested and produces lung tumors when inhaled. The exact level of chromium that can be continuously consumed by

humans without adverse effects is not known; however, a limit of 0.05 mg/l, which appears to be very conservative. Ionizing radiation is capable of reducing heavy metal ions to lower oxidation states leading to its precipitation from solution (3-5).

Low radiation doses are sufficient for disinfection of wastewater and it can also effectively reduce water soluble toxic metal ions, therefore rendering the metals less available for uptake by plant and living organisms. Adsorption via polymeric hydrogels has also showed their ability to remove toxic metal ions from the aqueous solutions. Adsorption and binding capacity of poly (acrylamide) P(AAm), poly (acrylamide/maleic acid) P(AAm/MA) and poly (acrylamide/maleic acid/gelatin) P(AAm/MA/G) hydrogels were used in the removal of irradiated chromium ions from electroplating wastewater (6-8).

The aim of this study is to investigate the swelling properties and adsorption characteristics of acrylamide hydrogels which contain an anionic monomer typically maleic acid and super swelling gelatin. Dynamic swelling study is important for the swelling characterization of hydrogel system. The present study deals with the purification of wastewater of chromic plating path containing chromium (VI) by different gamma irradiation doses followed by adsorption onto super

swelling hydrophilic P(AAm/MA/G) hydrogels. The optimum conditions for the preparation of the hydrogel were determined and characterized by FTIR. The parameters that influence the adsorption such as initial chromium (VI) concentration, time, pH and weight of hydrogel samples were investigated at room temperature.

2. Materials and Methods

2.1. Materials

Acrylamide (AAm) of purity of 99.9% (Merck, Germany) maleic acid (MA) of purity 99.9% (Aldrich, Germany) and Gelatin from EL-Nasr Co. for medical supplies, Cairo, Egypt. Citric acid, sodium citrate, sodium dihydrogen phosphate, and disodium hydrogen phosphate were purchased from EL-Nasr Co. for Chemical Industry, Egypt, and used without further purification.

2.2. Hydrogel Sample Preparation

Aqueous solution of (1 g AAm), (1 g AAm, 50 mg MA) and (1 g AAm, 50 mg MA and 5 mg G) in 3 ml distilled water were prepared for P (AAm), P (AAm/MA) and P (AAm/MA/G) hydrogels respectively. The prepared solutions were placed in fine glass test tubes and gamma irradiated to 30 kGy at ambient temperature using a ^{60}Co gamma source Chamber 4000 A with a dose rate 3.84 kGy/h. The cylindrical shape hydrogels were cut into disks of 2 mm thickness, dried to a constant weight. The samples were extracted by hot distilled water at 80 °C for 6 h and dried at 40 °C until a constant weight for later evaluation. The gelation percent (G%) was calculated gravimetrically by using the following equation:

$$G (\%) = (W_g/W_o) / 100$$

Where W_g and W_o was the weight of dried sample after and before extractions, respectively.

2.3. The Swelling Studies

The cylindrical shaped hydrogels were soaked in distilled water and phosphate buffer solution of pH's from 3.45 to 7 at room temperature. Swollen hydrogel samples removed from water or buffer solution at regular intervals and dried superficially with filter paper, weighed then placed in the same bath. The measurements were continued until equilibrium swelling was obtained for each sample. The weight swelling ratios (%) Q was calculated using the following equation:

$$\text{Swelling } (\%) = (W_t - W_d / W_d) \times 100$$

where W_d the mass of dried hydrogel and W_t the mass of the swelling gel after time t .

2.4. Fourier-Transform Infrared (FTIR) Measurements

The prepared hydrogels were dried and ground to a fine powder, then mixed with dried KBr and pressed to a disk for I. R. analysis. FTIR spectra of hydrogels measured by FTIR spectrometer (Mattson 1000, Pye- Unicam, England) in the

range from 400–4000 cm^{-1} .

2.5. Ultra Violet - Visible Spectrophotometer

The radiation process was carried out by exposing the chromic acid solutions to gamma cell facility at National Center for Radiation Research and Technology, Nasr City, Cairo, Egypt with a dose rate 1.21 kGy/h and gamma radiation dose ranged between 1 and 5 kGy. The remaining chromium ions in the solution after gamma radiation were analyzed at λ_{max} 350 nm by using a double-beam UV visible Sp200, Pye-Unicam, England.

2.6. Radiation Adsorption Purification

The chromium ion solutions were gamma irradiated with 1-5 kGy irradiation doses. The concentration of the irradiated solution was considered as the initial concentration of the adsorption study. A fixed weight of the dry hydrogel was immersed in different chromium ion solutions after irradiation. The concentration of the remaining chromium ions were detected by double-beam UV visible spectrophotometer. The adsorption amount A in (mg/g) was calculated by the following equation:

$$A = [(C_o - C_i) \times V] / W$$

where V is the volume of solution (l), W is the weight of the hydrogel (g), C_o , and C_i are the concentrations of chromium ions (mg/l) before and after the adsorption, respectively.

3. Results and Discussion

3.1. Gel Content Percent

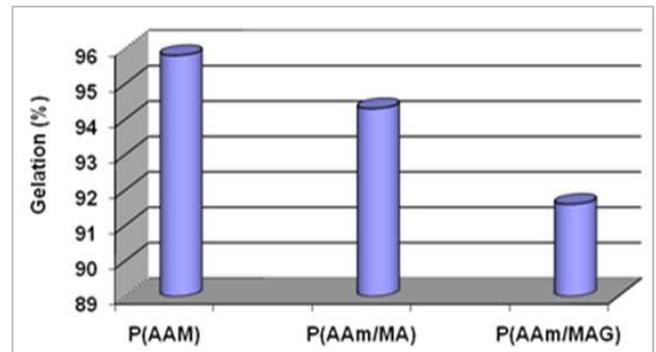


Fig. 1. Gelation percent of different hydrogels at 30 kGy.

In this study ionizing radiation was used for preparation of P(AAm/MA/G) copolymeric networks. Maleic acid does not homopolymerize due to its 1, 2-disubstituted structure, when it is irradiated in aqueous solution. In the presence of monomer with a high polymerization tendency such as acrylamide it is randomly incorporated into the main chain (9). When aqueous solution of AAm/MA/G is irradiated with gamma rays, polymerization and cross-linking reaction takes place simultaneously (10, 11). The radiolysis products of water especially hydroxyl free radicals are very effective in attacking the monomer and formed P(AAm/MA/G) hydrogels (9, 12). A typical dependence of gel content on the

compositions of the hydrogel was given in figure 1. From the figure it can be seen that, the gelation (%) decreased with the addition of both maleic acid and gelatin. These results indicate that maleic acid and gelatin being grafted on the acrylamide backbone (13).

Swelling studies

3.2. Effect of Hydrogel Composition

When a hydrogel is brought into contact with water or a buffer solution, the solution diffuses into the network and a volume phase transition occurs, resulting in the expansion of the hydrogel. Diffusion involves the migration of fluid into the hydrogel or dynamically formed spaces between the hydrogel chains. Swelling of the hydrogel involves large segmental motion resulting, ultimately, in the increased separation of the hydrogel chains. The swelling equilibrium occurs when the values of the osmotic force driving the fluid into the network and of the elastic force of the stretched sub-chains become equal. Figure 2 show the time dependence of swelling (%) of P(AAm), P(AAm/MA) and P(AAm/MA/G) hydrogels. From the figure it can be seen that the swelling behavior of the hydrogels is greatly influenced by its composition. As expected, the swelling of these hydrogels increase at a short time (4–6 h) and level off to maximum swelling at a longer time (120 h). From figure 2 it can be also seen that the swelling % increases by introducing the maleic acid and the gelatin. The introduction of carboxylic acid unit in the hydrogel creates repulsion not only between the negatively charged COO^- together but also between COO^- and the lone pair of electrons on the N atom of acrylamide and gelatin molecules which may increase the rate of translation of water molecules into the hydrogels (14, 15).

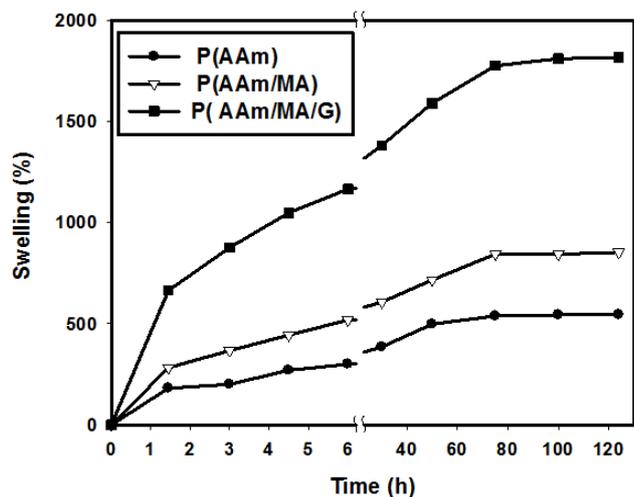


Fig. 2. Swelling (%) of P(AAm), P(AAm/MA) and P(AAm/MA/G) hydrogels at different immersion time.

3.3. Effect of PH on Swelling (%)

The presence of carboxylic groups in the hydrogel is supposed to undergo significant change in their swelling percent by changing the pH of the external media. Carboxylic acid-containing networks exhibited pH-responsive swelling behavior where the carboxylic acid groups became ionized at

higher pH values than pKa of the carboxylic groups. As the pH of the swelling medium was above pKa value which was about 5, the ionization of the carboxylic acid groups of the gel occurred. This resulted to higher water absorption as the pH increased. Figure 3 represents the equilibrium swelling of P(AAm), P(AAm/MA) and P(AAm/MA/G) hydrogels at room temperature in phosphate buffer solution of pH range from 3.5 to 6.8. Consistent with poly-anionic behavior, swelling of the hydrogels was found to increase with pH. For P(AAm), the swelling (%) was found to be independent on the pH value. This may be attributed to the fact that P(AAm) is a non-ionic hydrogel and it doesn't have any anionic group that could be ionized in aqueous solution and it may also due to the high crosslinking and high gelation (%) (16).

For P(AAm/MA) and P(AAm/MA/G) hydrogels, the pH of the solution becomes an even more important factor in determining the swelling kinetics and the equilibrium swelling value due to the presence of the carboxylic group of MA in the main chain of the hydrogel. The maximum extent of swelling was reached at pH 6.8, this being due to the complete dissociation of acidic groups of MA at this pH value (17). Figure 3 shows a sudden increase in the swelling at pH 's from 4.8 to 6.8. These results indicate that under acidic conditions, anionic carboxylate groups are protonated, and the copolymeric network collapsed. At a higher pH than the pKa value where the maximum percentage swelling occurred at pH 6.8 which may be due to the complete neutralization of carboxylate acid groups.

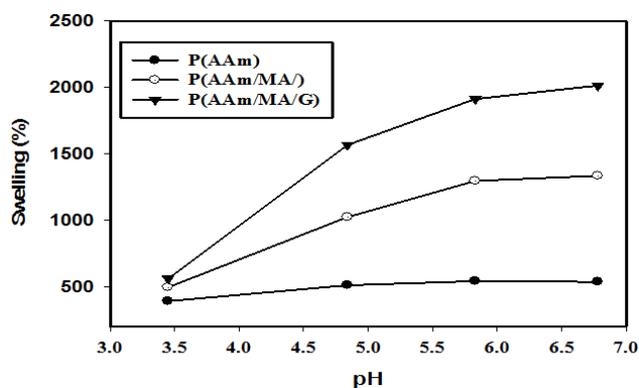
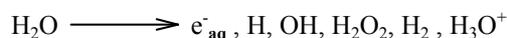


Fig. 3. Effect of pH values on the equilibrium swelling (%) of different hydrogels.

3.4. Radiation Precipitation of Chromium Ion

Applying gamma radiation technique to purification of wastewater has been carried out and the results are shown in figure 4 and 5. It was found that the chromium ions concentration decrease by increasing the irradiation dose this decrease in the chromium ions concentration was observed in all solution samples after being exposed to gamma radiation dose from 1 to 5 kGy. Aqueous solutions exposed to gamma radiation generate free radicals and stable products (18).



The hydrated electrons react with H_3O^+ to produce H (19)





The radiolytically produced Cr(V) is unstable and is further reduced to the stable Cr³⁺ ion via a tetravalent chromium intermediate (20, 21). It was observed that maximum decrease in the chromium ions concentration occurred at irradiation dose 5kGy. Figure 5 represents the effect of irradiation dose on the precipitation (%) of chromium ions at different initial concentration. From the figure it can be notice that the precipitation (%) increases by increasing the irradiation dose from 1 to 5 kGy for all different chromium ion concentrations. Figure 5 also showed that, maximum precipitation (%) occurred in dilute solution (45mg/l) where, a dose of 5kGy achieved precipitation of 98.9, 86.1 and 45.9% for concentration 45, 90 and 135 mg/l, respectively. The high efficiency of precipitation on dilute solution may be attributed to the fact that, the energy of gamma radiation absorbed by chromium solution reacts effectively with a very dilute solution than the concentrated one.

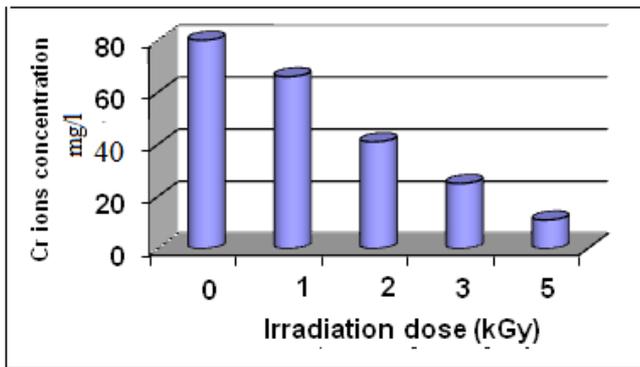


Fig. 4. Effect of irradiation dose on Cr ions concentration at initial concentration 80mg/l.

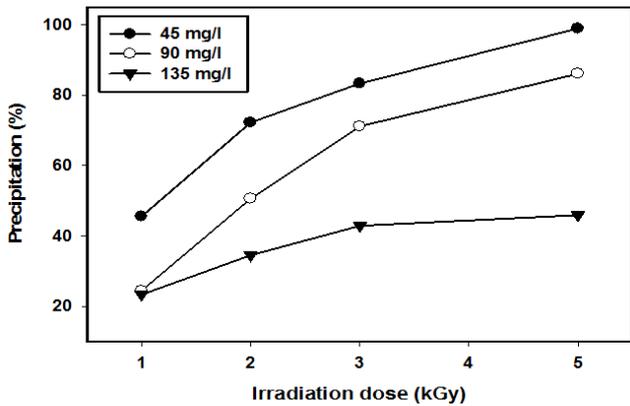


Fig. 5. Effect of irradiation dose on the precipitation (%) of chromium ions at different initial concentrations.

3.5. FTIR Characterization of Hydrogel

To probe the possibility of chemical interaction between AAm, MA and G molecules, FT-IR spectra of P(AAm/MA/G) hydrogels were shown in figure 6. The spectrum of P(AAm/MA/G) hydrogels shows the broad peak at 3600-3000 cm⁻¹ due to both the presence of carboxylic groups of maleic acid as well as -NH stretching of amide groups present in

acrylamid and gelatin molecules. A peak corresponding to the carbonyl group (C=O) of the (CONH₂) of the acrylamid unit is observed at 1665 cm⁻¹, while a characteristic peak at 1600 cm⁻¹ arises from the carbonyl group C=O of the maleic acid. The spectra also shows the absorbance peaks of C=C at 1650, NH stretch at 1600, CH and OH bands at 1450 - 1500 and 1300 - 1450 and C-O stretch at 1100 -1150. The formation of an interpenetrating network (IPN) of P (AAM / MA / G) hydrogel through NH₂ groups of gelatin, CH₂=CH- of acrylamide and conjugated C=C of maleic acid can be suggested due to the disappearance of =C-H sp² at 3100 and C=C conjugated at 1660.

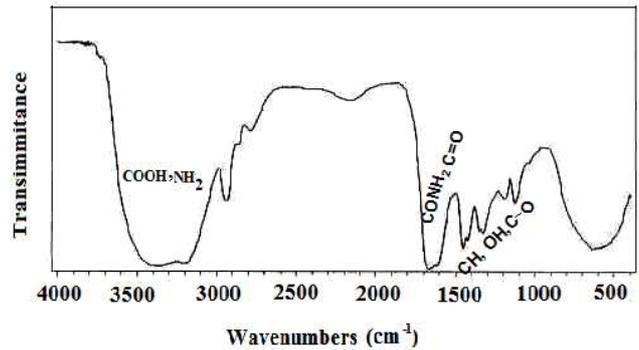


Fig. 6. FTIR spectrum of P(AAM/MA/G) hydrogel prepared by gamma irradiation dose 30 kGy.

3.6. Adsorption Recovery of Chromium Ion

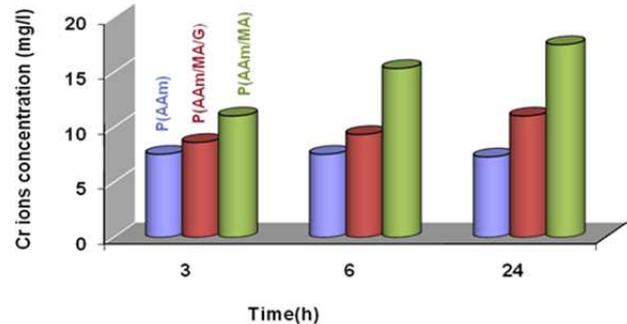


Fig. 7. Effect of hydrogel composition on the chromium ions uptake (mg/g) at different time intervals.

The irradiated chromium solutions still contain chromium ions, thus further experiments will be carried out by adsorbing these solutions onto P(AAm), P(AAm/MA) and P(AAm/MA/G) hydrogel. A fixed weight of the dry hydrogel was immersed in chromium solution after irradiation by a dose of 3 kGy. The concentration of the irradiated solution was found to be 98.91 mg/l which was considered as the initial concentration of the adsorption treatment. Figure 7 shows the chromium ion uptake by the different hydrogels at various time intervals. From the figure it can be seen that the chromium ion uptake increases by increasing the time of treatment. P(AAm / MA) hydrogel showed to has the highest chromiumion uptake, while P (AAm) hydrogel shows the lowest adsorption towards the chromium ion. The difference in the efficiency of different hydrogels towards chromium ion

uptake may be attributed to the hydrogel structure. The presence of a diprotic acid like maleic acid in the hydrogel network structure increases the adsorption of chromium ion onto the carboxylate group $-\text{COO}^-$ (22, 23).

3.7. Effect of PH Values on Adsorption

The pH value of the medium has a great effect on the adsorption process of the chromium ion by the hydrogel which influences its swelling and the interaction between hydrogel and metal ion. The adsorption of chromium ion on P(AAm), P(AAm/MA) and P(AAm/MA/G) hydrogels at various pH values was investigated by batch technique and represented in figure 8 (a, b and c). The adsorption increases with increasing the pH value of the medium and the maximum recovery of Cr(VI) was obtained in the acidic range (24). The higher recovery at higher pH than the pka value may be due to the increase in the degree of swelling which increase the diffusion of the metal ions into the hydrogel this may be also enable to chelation of a great number of chromium ions with the carboxylic groups of maleic acid.

For this reason, it can conclude that the recovery of Cr (VI) is more suitable at pH 4.84 than at alkaline due to at pH 4. 84 HCrO_4^- is the predominant Cr(VI) species in the queous phase (24). The mechanism of the interaction of hydrogel and metal ions has many possible mechanisms. One of them is the

oxygen of the carbonyl groups of maleic acid is responsible for the interaction of the metal ions with hydrogel, since the mobile π - electrons are pulled strongly towards oxygen. Carbonyl oxygen is electron rich, the metal ion acts as electron acceptor and taken up by coordination to the donor oxygen of the carbonyl group. From the results it is clear that, there is dependence of metal ion uptake on the hydrogel composition. P(AAm) possess low metal uptake that possess low degree of swelling at low pH values of the metal ion solutions. These results may be due to the fact that, the amide group of the acrylamide is protonated in acidic medium as a result of the presence of lone pair of electrons on nitrogen atom which is capable of attracting the hydrogen proton from the medium and forming co-ordination bond, therefore the P(AAm) hydrogel prevents the diffusion of the metal ions inside the hydrogel to reach the functional groups of the hydrogel. As a result, the adsorption of the metal ions was reduced. In neutral medium the amide group is not protonated, so it is capable of coordinating the metal ions and the ability of metal uptake by the hydrogel increases. By introduction of maleic acid to the network structure of the hydrogel, the swelling ability of the hydrogel increases, so the possibility of the metal ions to reach the chelation functional groups increases and the ability of adsorption of chromium ions by the hydrogel increases (25).

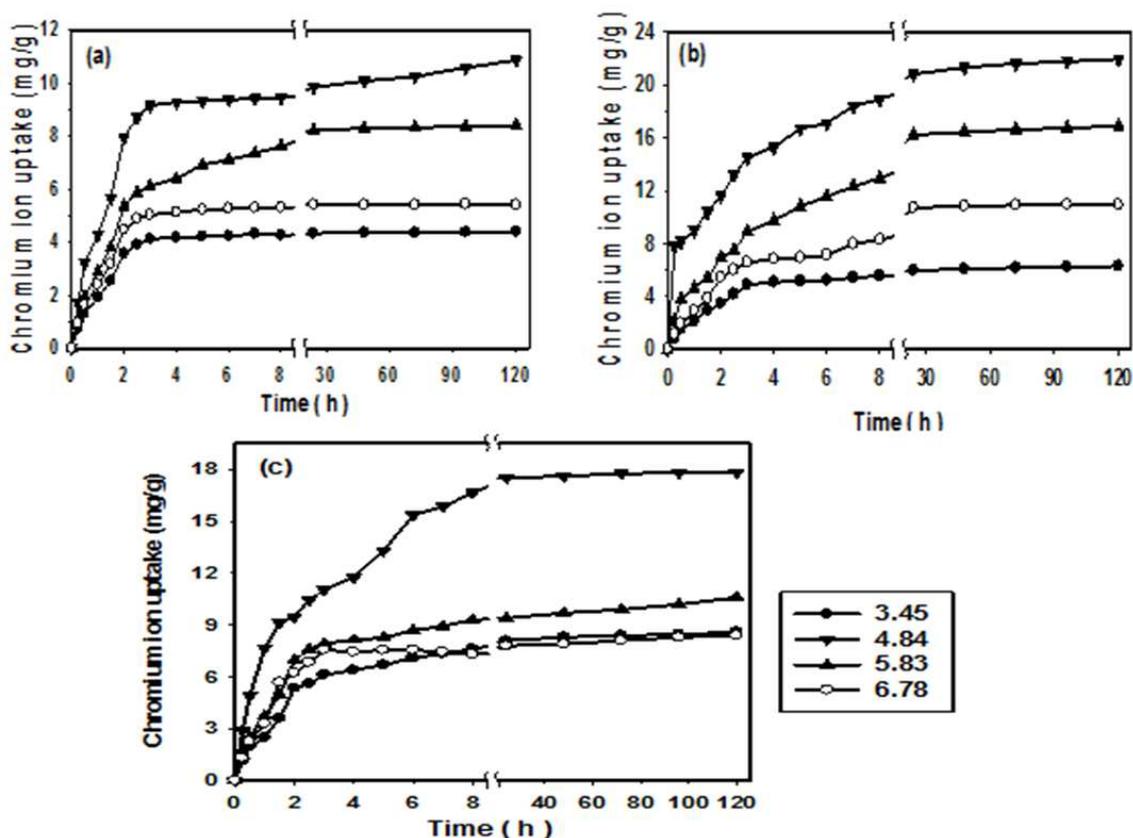


Fig. 8. Chromium ions uptake (mg/g) at different pH values onto different hydrogels (a) P(AAm), (b) P(AAm/MA) and P(AAm/MA/G).

4. Conclusions

This study demonstrate the preparation of different

polymeric materials have the affinity to recovery of chromium ions after exposed to different irradiation dose. The high efficiency of precipitation of chromium ions by the effect of

gamma radiation has been achieved especially in dilute solution. The recovery of chromium ion has been enhanced by gamma irradiation at different doses. The swelling properties of the prepared hydrogels are evaluated and the results demonstrate that the swelling (%) is highly dependent on the hydrogel composition and also affected by the change of the medium pH. The investigation herein points in the use of hydrogel materials for environmental applications where, hydrogels can be employed in various aqueous environments as they swell and develop charges to interact with chromium ions. In addition, the adsorption capacity of chromium ions for hydrogels composite is possible as hydrogels prone to chromium ions adsorption on their surfaces.

From the data it can be concluded that, the recovery of chromium ion has been enhanced by gamma irradiation at different doses was followed adsorption of the irradiated samples onto different hydrogels. It can also be seen that, the adsorption of chromium ion is not only pH dependent but it also shows the influence of the hydrogel composition on the adsorption rate and adsorption. As a result, the recovered water contains chromium ion concentration to no detectable levels can be obtain in the water treatment plant. It was also possible to design a batch treatment system to remove chromium ion at pH within the acidic range after treatment by gamma irradiation followed by adsorption onto hydrogels to obtain recovery water can be reused in different purposes. Through the combined treatment of gamma irradiation followed by adsorption, the complete removal of all the studied pollutants was achieved.

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