

Synthesis, Characterization and Application of Poly (Acrylamide-Maleic Acid-Acrylonitrile) by Gamma Irradiation Induced Grafting Polymerization

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Abstract

The present work was focused on the progress in preparation of functional acrylamide polymeric resin prepared by γ -irradiation initiated grafting polymerization of Poly (acrylamide-maleic acid-Acrylonitrile) P(AM-MA-AN) in the presence of N,N'-methylenediacylamide(DAM) as a cross linker. The influences of synthesis conditions particularly such as co-monomer concentration, concentration of the polymer and radiation dose were examined. The capacity of the resin was evaluated at these different experimental conditions. The physico chemical properties were investigated as a function of the swelling degree and percent conversion of the copolymer. The structure of the prepared polymeric resin was confirmed by FTIR, TGA, SEM and surface area. Results showed that the monomers were successfully grafted into the polymer matrixes. Batch adsorption technique has been studied for the adsorption of U(IV) and La(III) which represents the rare earth elements from aqueous solution. The results demonstrated that, at pH 5, the maximum adsorption capacity for U(IV) was higher than that of lanthanum(III) and reached to 84 and 71 mg/g, respectively.

Key words: Grafting copolymers, Irradiation, Lanthanum, Uranium, Sorption.

1. Introduction

One of the commonly used methods for modifying the surface and bulk properties of polymeric materials is to graft monomers onto them by using an irradiation technique known as radiation-induced grafting. Radiation-induced grafting method has the advantages such as simplicity, low cost, control over process and adjustment of the materials composition and structure. In addition, this method assures the grafting of monomers that are difficult to polymerize by conventional methods without residues of initiators and catalyst. Polyacrylamide P(AM) is one of the most widely used materials as flocculant. It finds wide applications in many fields, e.g. municipal water treatment [1,2], sewage treatment [3], reverse osmosis membranes [4], mineral processing [5] drag reducing [6], oil recovery [7,8]. This allows the recycling of water in industrial processes.

Sorption of rare earth elements and radionuclide materials allows the result of several applications [9], Provides the extraction of elements which have great value and high price, Protection of the environment from the risks of radionuclides by absorbing materials which have a high capacity and low swelling, the recycling of water in industrial processes and so saves greatly the consumption of water in industry. These reasons all together show that the production and use of the resin is a national objective, proposal.

2. Materials and methods

2.1 Chemicals and reagents

All chemicals and reagents were of analar grade and were used without further purification. Salts of lanthanum, was obtained from Merck, Hydrochloric acid was purchased from Porlabo, pH of solutions was adjusted by the addition of NH₄OH which

obtained from Fluka. For all experiments bi-distilled water was used for solvation, preparation, dilution and analytical purposes. De-oxygenated water was prepared by boiling bi-distilled water for about 15 minutes followed by cooling under a stream of pure dry nitrogen gas at room temperature [10,11].

2.2 Equipments and instruments

A cobalt-60 gamma cell of type MC-20 (Russia), was used as an irradiation source for polymerization at the Cyclotron Project, Inshas, Egypt. It has two chambers of 5 liters for sample irradiation. The samples were irradiated in glass bottles at room temperature in the presence of air compressor. A digital analytical balance of model WH 205-4, Wiggan Hauser manufacturing (Germany), with a sensitivity of 1×10^{-4} g, was used for weighting the samples and the standards. The balance was calibrated periodically for quality control of the analysis. A laboratory oven, OF-02G, JEIO TECH manufacturing (Korea), was used for drying the polymeric samples. A programmable shaker thermostat, BS-21, Lab. Companion, JEIO TECH manufacturing (Korea), was used for shaking samples during the preparation and experimental processes. Bi-distilled water system GFL Bi-Dest 2104, KARL KOLB manufacturing (Germany), was used for obtaining the double distilled water. pH meter of model 420A+, thermo Orion manufacturing (USA), was used for adjusting the pH of solutions. The pH meter was calibrated by using three buffer solutions, pH 4.01, 7.0 and 10.01 at 25°C, prepared by dissolving buffer tablets in 100 ml H₂O.

The prepared resins were dried and grinded to a fine powder, then mixed with KBr and pressed to a disk for IR analysis. The Fourier transformed infrared spectra were performed on a computerized

Acomputerized UV/Vis double beam spectrophotometer of model T80, PG Instruments Ltd. (England), was used for spectrophotometric determination of metal ions [12].

Thermal analysis was undertaken using a Shimadzu thermogravimetric analyzer model TGA-50 (Tokyo, Japan). The prepared polymeric materials were washed several times with bi-distilled water, Dried under vacuum. In order to remove water completely, the samples were dried for 30 min before being characterized by TGA. The thermal stability was investigated at a heating rate of 10°C/min, under nitrogen atmosphere (20 ml/min) from room temperature up to 600°C. The TGA thermograms were used to determine the activation energy and the rate of thermal decomposition reaction.

The morphology of the prepared resins was Determined JEOL-JSM 6510 LA (Japan). Scanning electron microscope, at accelerating voltage of 15 kV. Was used for investigating the pore structure of different prepared resins at high magnification and resolution by means of an electron beam.

2.3 Preparation of Polymeric Resin

2.3.1 Preparation of poly (polyacrylamide - maleic acid – acrylonitrile) p (am-ma-an) resin

Poly(Acrylamide –Maleic acid- Acrylonitrile) P(AM-MA-AN) by grafting polymerization technique of monomers and polymer in de-oxygenated water using γ -rays . About 48 g of MA was dissolved in 100 ml bi-distilled water, mixed with 32ml of AN and 3gm ammonium ferrous sulphate as inhibitors and complete the mixture to 200 ml bi-distilled water , the solution was mixed with 4.5 gm DAM as crosslinker dissolved in 50 ml bi-distilled water, the total solution mixed with 12 g of PAM which dissolved in 50 ml bi-distilled water.

The mixture was transferred into glass ampoules and nitrogen gas was purged into the ampoules to remove air from the solutions. The glass ampoules were sealed and then subjected to gamma-rays a irradiation dose 15 kGy in air at ambient temperature. The obtained resins were cut into small pieces with a stainless steel scissors, soaked in acetone for removal of unreacted monomers, washed with bi-distilled water, dried and stored.

2.4 Adsorption studies

Adsorption experiments were carried out at 25°C in magnetically stirred (180 rpm) cylindrical glass vessels with batch conditions. The samples (50 mg) of resin were mixed with La³⁺ and U⁴⁺ metal ions in acetate buffer solution (10 mL) with a concentration of 100 mg/L. The amount of residual metal ions in the solution were determined by u.v spectrophotometer after 2 h. In these experiments, samples were stirred with metal ion solutions under the experimental

conditions described previously, and the residual metal ions concentrations were determined at regular time intervals. All of experiments studying the effect of Shaking time , various pH values, initial metal ion concentration and its effect on the metal uptake, were done in triplicate, and the q value (mg of metal ions /g of resin) of the polymers was calculated with eq (1):

Metal ions concentrations were measured by computerized UV/Vis double beam spectrophotometer using 4-(Pyridyl-2-azo) resorcinol (PAR) as sensitive coloring reagent. Based on the initial and final metal concentrations, the percent uptake and the capacity of the resin were determined as following equations (1 and 2):-

$$q(\text{mg} / \text{g}) = \frac{(C_i - C_e)V}{m} \quad (1)$$

$$\% \text{ uptake} = \frac{(C_i - C_e)}{C_i} 100 \quad (2)$$

Where (q) is the maximum capacity (mg/g), C_i and C_e are the initial and equilibrium concentrations (mg/L) of metal ions respectively. V is the volume of solution in liter and, m is the weight of the resin in gm.

Batch experimental were performed at pH = 4 and metal ion concentration 100 mg/l and at various shaking time ranged from 5min to 24 hrs. For these investigations 0.05g of the studied exchangers were immersed into 10 ml of solutions. The mixture was centrifugated and filtrated using 0.45 μ m Whatman membrane filter. Finally, the concentration of metal ions was measured.

pH has a significant impact on the adsorption of La³⁺ and U⁴⁺ metal ions. To determine the pH at which the maximum uptake of all metal ions would be take place, series of 50 ml test tubes each containing 0.05 g of resin was mixed with 10 ml of the desired metal ion concentration (100 mg/L). The pH was adjusted at different values ranging from 1.0 to 5.0. The tubes were then shaken for 3 hrs to attain equilibrium, centrifugated and filtrated using 0.45 μ m Whatman membrane filter.

The effect of initial metal concentration on the adsorption process onto resin and composite was studied at various initial metal concentration ranged from 100 to 2000 mg/L for all studied metal ion. For these investigations, 0.05 g of each resin or composite was contacted with 10 ml of aqueous solution containing different metal concentration. The mixture was shaken at room temperature for 3hrs. The mixture was centrifugated and then filtrated. Finally, the concentration of metal ions was measured.

2.5 Calculations used for physico-chemical properties of resin

During the study of the optimum condition for the preparation of polymeric resin studying the effect of physic chemical properties through following experiments and equations is very important. The

clean, dried, resin of known weights were immersed in distilled water at room temperature for 24 hrs, then removed from water and the excess water on the surface was discarded, an increase in resin weight was measured and the swelling degree (P_s) was calculated according to Eq (3) as following:-

$$P_s = \frac{(W_f - W_i)}{W_i} 100 \quad (3)$$

Where W_f is the weight of the swollen polymer and W_i is the weight of dry polymer.

The capacity of the resin was evaluated by mixing 10 ml of Cu^{2+} solution with 0.01 gm of studied resin that was already prepared in sodium form. The mixture was centrifugated, filtrated. The concentration of Cu^{2+} metal ions was measured and the capacity was calculated according to Eq (1).

Percent conversion of the reactants into polymeric resin was calculated at different reaction parameters such as Co-monomer, polymer concentrations and irradiation dose. This percentage was used as indicator to get the maximum conversion yield and it was calculated as shown in Eq(4):-

$$\% \text{conversion} = \frac{(W)}{W_s} 100 \quad (4)$$

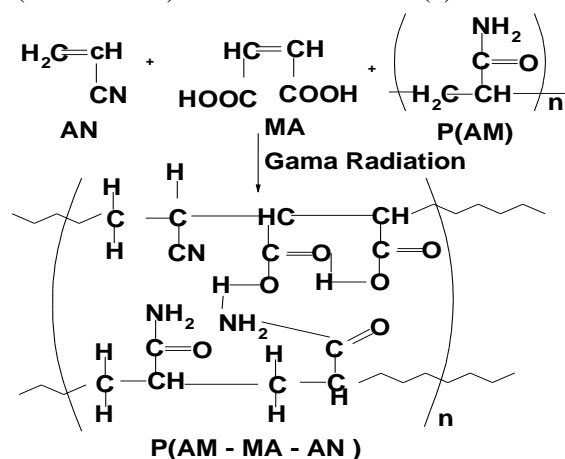
Where W is the weight of polymer and W_s is the weight of add reactants.

3. Results and discussion

3.1.1 Preparation of poly(acrylamide-maleic acid-acrylonitrile) p (am-ma-an) resin

A number of articles have been published describing the synthesis of modifying polymeric resin containing several function groups, for their use in the adsorption of metal ions from aqueous system.

P(AM-MA-AN) resin was prepared by grafting copolymerization of MA and AN monomers onto P(AM) hydrogel as a grafting polymer in the presence of DAM as a crosslinker and ammonium ferrous sulphate as inhibitor, using gamma-radiation technique. The reaction mechanism for synthesis of P(AM-MA-AN) resin is shown on Sch (1).



Sch (1) Synthesis of P(AM-MA-AN) resin.



3.1.2 Influence of the components on polymerization process

The capacity of the resin depends on the experimental conditions of the polymerization process, such as irradiation dose, the concentration of the added polymer, the polymer/monomer molar ratio and the concentration of crosslinker. These factors are discussed as shown in the following sub-section.

3.1.2.1 Influence of Co-monomer concentration on the polymerization process

The influence of the monomer concentration on the capacity of the obtained resin towards Cu^{2+} metal ion was studied at irradiation dose of 10.0 kGy, The results are shown in Table (1). The maximum Cu^{2+} capacity was achieved at 3:2 Wt% of co-monomers concentration, i.e. at maximum swelling degree and conversion %.

The amide and carboxylic groups of P(AM) and MA in the resin structure are primarily responsible for the specific binding of metal ion due to the coordination between Cu^{2+} metal ions and ($-\text{NH}_2$, COOH) groups. The capacity increases with increasing of co-monomer concentration till 3:2 Wt% of MA and AN and then decrease. With the increasing of co-monomers concentration, the probability of association between the co-monomer and the added polymer increases which, increases the degree of crosslinking between the polymer chains of the resin. In addition, the number of carboxylic groups increases upon increasing the co-monomer concentration hence, the capacity of the obtained resin increases.

3.1.2.2 Influence of P (AM) concentration on the polymerization process.

The Influence of the composition of the added polymer on the capacity of the obtained resin toward (Cu^{2+}) metal ion was studied at irradiation dose of 10.0 kGy, the concentration of MA in to AN (3:2 Wt%) means 2.4 to 1.2 Wt%, 0.2 Wt% of DAM as crosslinker, the concentration of ammonium ferrous sulphate 0.1 wt% and various concentration of P(AM) ranged from 0.1 to 1.0 wt %, the results shown in Fig (1A,1B,1C)

Fig (1A) demonstrated that the maximum Cu^{2+} ion capacity was achieved at 0.6 Wt% of PAM, i.e. at maximum capacity and the highest conversion yield increases till 0.6 Wt % and then decreases. On increasing the amount of added polymer, the association between the Co-monomers and the added polymer increases, which leads to increase in the extent of crosslinking between the polymer chains of the resin. After 0.6 Wt%, further increase of the crosslinking decreases the capacity of the obtained resin.

Table (1) Influence of the co-monomers concentration on capacity, Swelling degree and Conversion yield of P(AM-MA-AN) resin.

(MA : AN)gm	Capacity (mg/g)	Swelling degree	% Conversion
3 : 1	89	2.70	90
2.8 : 1.2	98	2.90	92
2.6 : 1.4	109	3.30	97
2.4 : 1.6	112	3.40	100
2.2 : 1.8	98	2.87	100
2 : 2	74	2.12	100

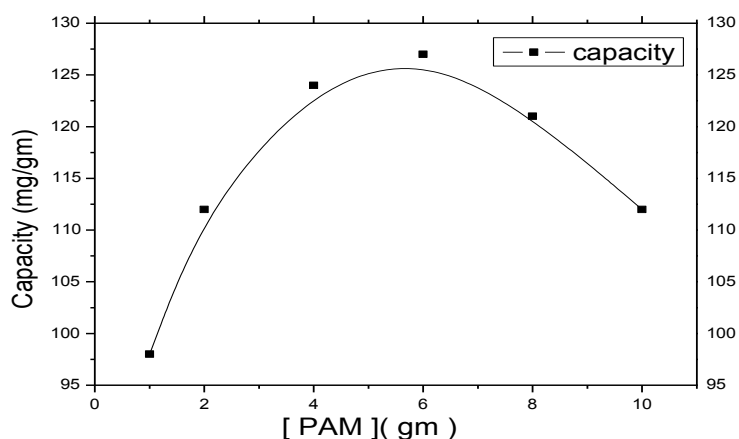


Fig (1) Influence of (PAM) concentration on the capacity of P(AM-MA-AN) resin.

3.1.2.3 Influence of irradiation dose on the polymerization of P(AM-MA-AN) resin

The Influence of irradiation dose on the capacity of the obtained resin towards (Cu²⁺) was studied at polymer concentration 0.6 wt%, co-monomers concentration of MA to AN 3:2 wt%, 0.2 wt % DAM the concentration of ammonium ferrous sulphate, 0.1 wt% and various irradiation doses from 5.0 to 30.0 kGy. The results are shown in Fig. 2(a,b, c).

Fig (2A) showed that the capacity increases till 20.0 kGy and then decrease with further increasing

of the irradiation dose. The maximum metal ion uptake was achieved at irradiation dose 20.0 kGy, The increase in the capacity of the resin upon increasing the irradiation dose can be attributed to the increase in the degree of crosslinking between the polymeric chains of the resin which, leads to formation of suitable attachments. With further irradiation dose, the decrease in the capacity may be due to the higher increase in the extent of crosslinking may be deteriorate a large number of available function groups.

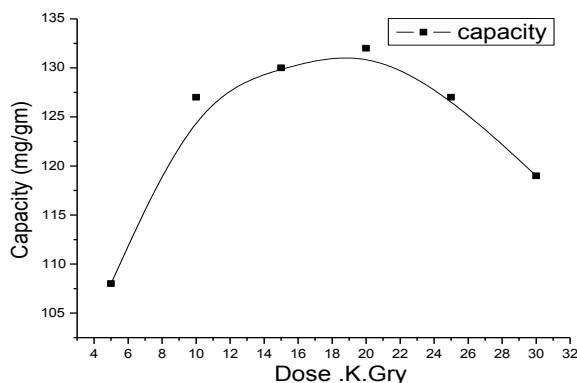


Fig (2) Influence of irradiation dose on capacity of P(AM-MA-AN) resin.

Based on the previously obtained results, it could be stated that the optimum preparation conditions of P(AM-MA-AN) resin. was achieved at 0.6 Wt% polymer, co-monomers concentration of MA to AN 3:2 wt%, the concentration of

ammonium ferrous sulphate 1.0 Wt%, irradiation dose (20.0) kGy and 0.2 wt % of DAM. At these optimum conditions, the percent conversion was found to be 100 % with a relatively low swelling

degree reached to 1.7 and the maximum capacity toward Cu^{2+} metal ions found to be 132.2 mg/g.

3.1.3 Characterization of the prepared polymeric resins.

3.1.3.1 FTIR analysis of P (AM-MA-AN) resin

FTIR spectrum of P (AM-MA-AN) is shown on Fig (3) and summarized in Table (2) . The absorption peaks appeared at 3439, 2168 and 1705 cm^{-1} are attributed to contributions of amide ($-\text{CONH}_2$), cyano ($-\text{C}\equiv\text{N}$) and carboxylic ($-\text{COOH}$) groups of AM, AN and MA, respectively. Free $>\text{NH}$ stretching was observed by the absorption peak at 3439 cm^{-1} that are belong to amide ($-\text{CONH}_2$) group of PAM. The presence of these peaks verifies the polymerization of AM, MA and AN by gamma-radiation technique[13-15].

CONH₂) group of PAM. The presence of these peaks verifies the polymerization of AM, MA and AN by gamma-radiation technique[13-15].

3.1.3.2 Scanning electron microscope

The morphology of P (AM -MA-AN), resin is observed by SEM in Fig (3) . from Fig (3) we can clearly observe in thin-layer P (AM -MA-AN) that the spontaneous stacking curls form petal-shaped aggregates. This flocculent aggregate in the absence of external forces will remain stable, and it is difficult to separate from each other. SEM image shows that there are limited porous structures on the surface of the resin.

Table (2) Assignment of FTIR bands of P (AM-MA-AN) and P(AM-MA-AO) resins.

Absorption bands of original groups (cm^{-1})		P (AM-MA-AN)
Amide:		
Free $>\text{NH}$ stretching	3500,3400	3439
Bonded $>\text{NH}$ stretching	3350,3180	--
$>\text{C}=\text{O}$ stretching (Amide I mode)	1650	--
$>\text{NH}$ bending	1650,1590	1589
Aliphatic:		
$>\text{CH}_2$ stretching	2926-2853	2925
$>\text{CH}_2$ bending	1485-1445	--
$-\text{CH}_3$ bending	1470-1430 and 1380	--
Ester:		
$>\text{C}=\text{O}$ stretching	1750-1735	--
$>\text{C}-\text{O}$ stretching	1300-1100	1261

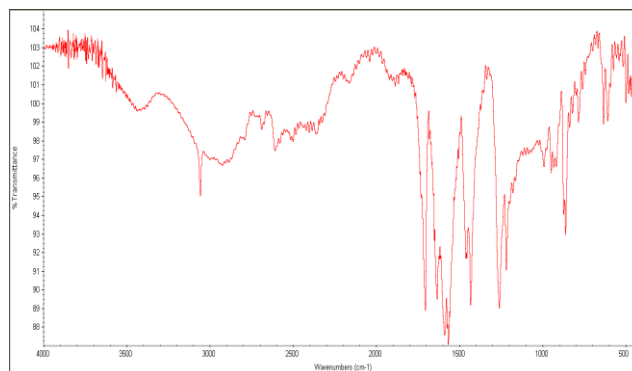


Fig (3) FTIR spectrum of of P(AM-MA-AN)

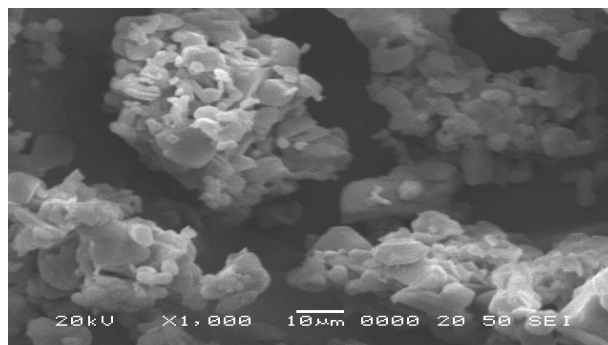


Fig (4) The scanning electron micrograph of P(AM-MA-AN) resin.

3.1.3.3 Thermogravimetric analysis (TGA)

The TGA and DTA curves of dried samples of P (AM -MA-AN) resin heated at the rate 10°C/min occur in three stages as shown on Fig (5). The first stage from 74 to 241°C with a maximum at 161.41°C, the weight loss in this region is 51.7% may be attributed to removal of all surface and matrix-bound moisture from the polymer (absorbed or coordinated water molecules). The second stage occurs from 241 to 495°C, with maximum rate of weight loss at 311.95, 412.64 and 471.96°C. The weight loss in this region is 24% This

decomposition may be corresponding to the loss of ammonia by imidation of adjacent amide groups on a chain, or amide groups on neighbouring chains Sch (2) also due to water and CO₂ release as result of dehydration of maleic acid Sch (3) and decarboxylation of maleic acid anhydride Sch (4). Beyond 495°C there is a third stage of very slow weight loss extending to 1000 °C with a maximum at 907 °C. The weight loss in this region is 26% and may be related to chain scission and carbonization processes.

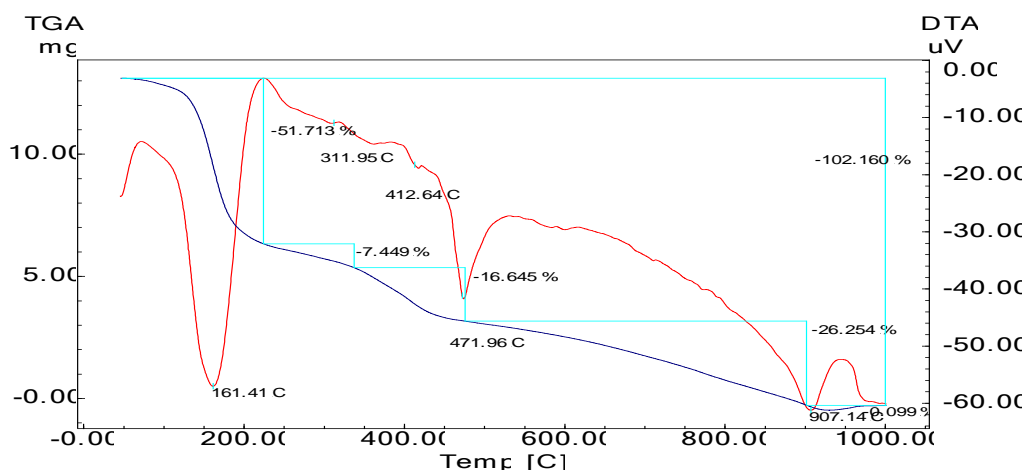
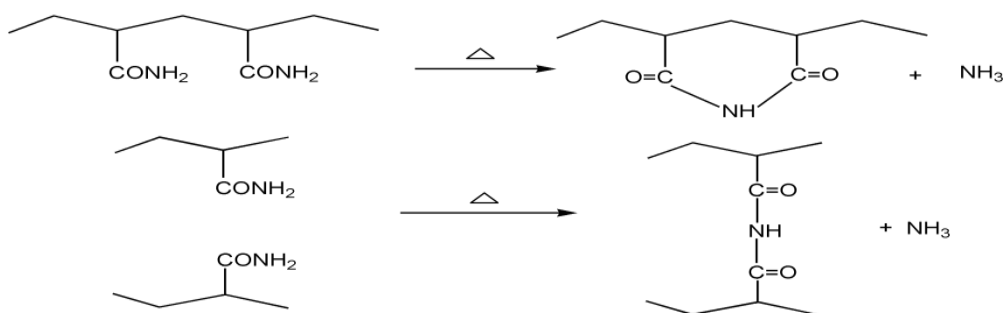
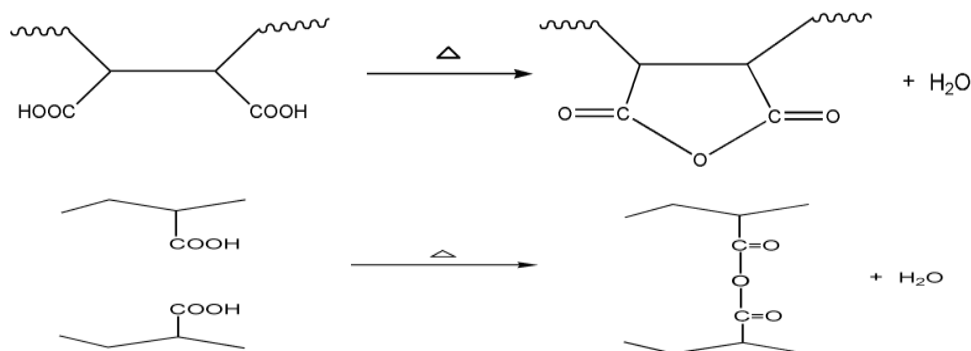


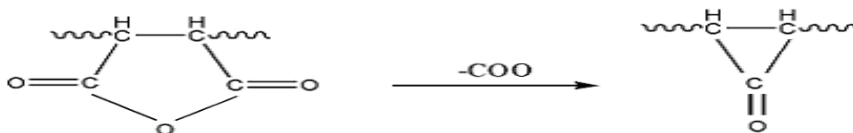
Fig (5) The TGA and DTA curves of of P(AM-MA-AN) resin.



Sch (2) Effect of heat on amide groups (imidation).



Sch (3) Effect of heat on MA (dehydration).



Sch (4) Decarboxylation of MA anhydride.

3.1.4 Use of P (AM-MA-AN) resin for the adsorption of La^{3+} and U^{4+} metal ions from aqueous solution .

3.1.4.1 Effect of contact time

The influence of contact time on the rate of the adsorption of U^{4+} and La^{3+} metal ions uptake is shown on Fig (6). The adsorption results of P(AM-MA-AN) resin show an initial rapid adsorption rate, it continued to increase at a relatively slow speed with contact time and reached an equilibrium

point after (3h's), with maximum uptake (70.5, 33.6). It can be attributed to the fact that, at the initial stage, the active function groups are more and the metal ions can interact easily, so a high adsorption rate is obtained. Besides, the driving force for adsorption is the concentration gradient between the bulk solution and the solid-liquid interface, and the concentration gradient is high in the initial period, which results in a high adsorption rate.

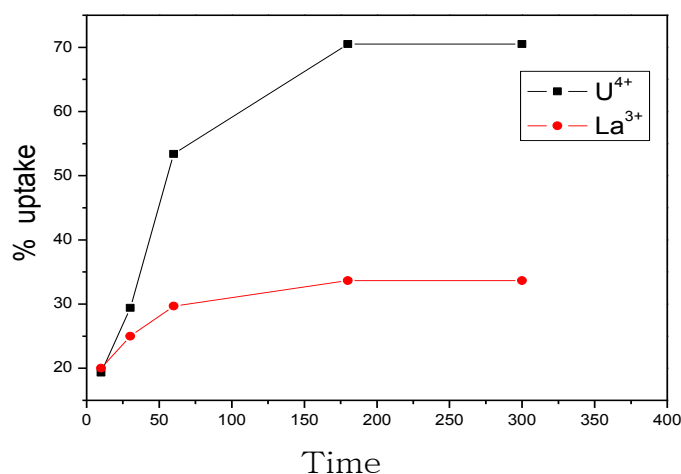


Fig (6) Effect of contact time the adsorption of La^{3+} and U^{4+} metal ions onto, P(AM-MA-AN) resin.

3.1.4.2 Effect of pH

The role of pH is very important for the adsorption of La^{3+} and U^{4+} metal ions on the prepared resin . The amount of metal ions uptake on to polymer strongly depends the pH of the system. was studied from aqueous solutions of different pH within range 1 to 5, for an initial metal ions concentration of 100 mg/L, and 0.05 gm of the prepared resin. The results as shown in Fig (7) clarify that the adsorption of U^{4+} and La^{3+} metal ions increases with the increasing of pH of the solution and reaches the maximum value at pH 5.0. While, the increase in pH of the solution (over pH 5.0) may be causing the precipitation of metal ions according to the precipitation curve was studied previous, It is also found that, the adsorption of U^{4+} metal ions is higher than the adsorption of La^{3+} metal ion, illustrated by percent uptake reach to 48.3 for La and 87 for U^{4+} . It is clear that, P(AM-MA-AN) is effective for the quantitative removal of U^{4+} metal ions at that range of the pH . This can be explained in terms, the dissociation of amide and carboxylic groups increase with the increase of pH

providing additional binding of function groups for the adsorption of metal ions. at higher acidic conditions, i.e., low pH value of about 1.0-3.0, low adsorption of metal ions was occurred. This is attributed to the competition between H^+ ions and metal ions for the active function groups.

Through the previous Batch experiments which performed on the P(AM-MA-AN) resin, by studying the effect of time and pH was found that the maximum metal uptake of P(AM-MA-AN) resin toward metal ions arranged as follows U^{4+} and La^{3+} metal ions. From this trend, U^{4+} characterized by high adsorption capacity toward the resin, so the effect of initial metal ion concentration toward U^{4+} will be concerned by detailed study.

3.1.5 Effect of initial metals ions concentration on the adsorption process of P (AM-MA-AN) resin

Batch experiments were performed to study the effect of the initial metal ion concentration for U^{4+} metal ion from 25 to 2000 mg.L^{-1} , was tested with a

fixed amount of the sorbent 0.05 gm L^{-1} , and shaking time 3 hr's at pH 5. was carried out onto P(AM-MA-AN) resin.

The functional groups of P(AM-MA-AN) resin as weak acid are dissociated at higher pH values and consequently, the adsorption of metal ions from the solution takes place. The present of functional groups on the surface of the adsorbent is expected

to be negatively charged, which facilitate the adsorption of the positively charged metal ions, consequently, the adsorption capacity of U^{4+} metal ion increases and reach plateau at (84 mg/ gm) as shown in Fig (8).

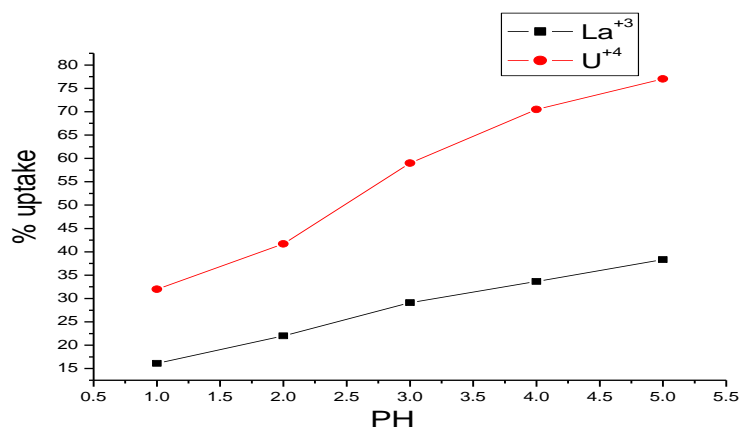


Fig (7) Effect of pH on the adsorption of La^{3+} and U^{4+} metal ions onto, P(AM-MA-AN) resin.

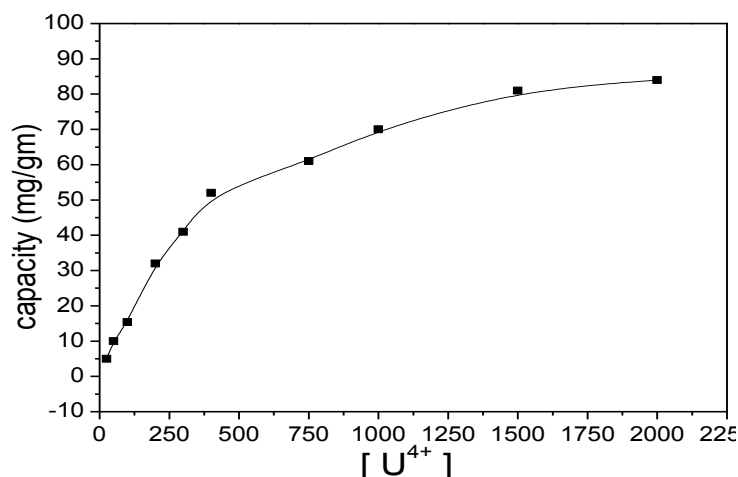


Fig (8) Effect of initial metal ion concentration on the adsorption of U^{4+} metal ions onto P(AM-MA-AN) resin.

4. Conclusion

In this study, P(AM-MA-AN) resin has been successfully prepared by gamma irradiation through systematic study and its application in metal binding was investigated. It was found that the adsorption capacity of the prepared polymeric resin increases by increasing the Co-monomer content. It was found that the maximum adsorption values of metal ions of concern were obtained at pH 4 the maximum adsorption value toward Cu^{2+} metal ion found to be 132.2 mg/g .

The structure of the prepared polymeric resins was confirmed using infrared spectroscopy (IR). Thermal properties were simultaneously studied by thermogravimetric analysis (TGA).

Batch adsorption was performed for the removal of La^{3+} and U^{4+} from aqueous solution summarized

in the study of effect the contact time, pH, and initial metal ion concentration and the The highest equilibrium degree of capacity for U^{4+} metal ion 84 mg/g at pH 5, at 0.6 Wt% polymer, co-monomers concentration of MA to AN 3:2 wt%, the concentration of ammonium ferrous sulphate 1.0 Wt%, irradiation dose (20.0) kGy and 0.2 wt % of DAM..

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