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Synthesis, Characterization and Application of Modified Acrylamide-Styrene Sulfonate Resin and Composite for Sorption of Some Rare Earth Elements.

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Abstract:

The present work was attempt to prepare three new sorbents including Poly(Acrylamide–sodium styrene sulphonate) P(AM–SSS) hydrogel, Poly(Hydroxamic acid-Sodium styrene sulphonate) P(HA–SSS) modified polymeric resin and Poly(Acrylamide–sodium styrene sulphonate–silicon oxide) P(AM–SSS–SiO$_2$) composite by irradiation template polymerization. The effective reaction parameters such as absorbed dose (kGy), crosslinker and monomer concentration and the polymer/monomer ratio on the degree of template polymerization were optimized to get the maximum conversion percentage and high capacity. The physico-chemical swelling behavior for hydrogel was higher than resin and composite. Modification of the hydrogel into modified polymeric resin was achieved by using hydroxylamine hydrochloride. The modification process is indicated by FTIR characteristic absorption bands of–O–H and >N–O– groups of the hydroxamic groups. Furthermore, organic–inorganic composite has been prepared by introducing Silica into the polymer which, indicated by FTIR characteristic adsorption bands of the silica network at 1209 cm^{-1} and 960 cm^{-1}. The application of the prepared sorbents for removal of La^{3+}, Ce^{3+}, Nd^{3+}, Eu^{3+} and Pb^{2+} from aqueous solution was investigated by batch technique. Various factors influencing the sorption behaviors were tested such as shaking time, pH and initial metal ion concentration. The obtained results showed that the prepared composite has better uptake percentage and higher capacity than resin and hydrogel and the sorption efficiency of metal ions towards the three adsorbent materials obey the order La^{3+}> Ce^{3+} > Nd^{3+}> Eu^{3+}> Pb^{2+} .

1. Introduction

Nowadays, irradiation technique is used for polymer processing and modification. The irradiation of polymeric materials with ionizing radiation (e.g. gamma rays, X-rays, accelerated electrons and ion beams) leads to the formation of very reactive intermediates, free radicals, ions and excited states. These intermediates can follow several reaction paths that result in disproportion, arrangements and/or the formation of new bonds. The main interaction of ionizing radiation with polymers concerns its molecular weight is its ability to induce crosslinking or scission which may results in the formation of a wide range of materials without introducing any chemical initiators and without dissolving the sample. Generally, cross-linking and chain scission occur simultaneously but one of them may dominant over the other [1]. So using of gamma radiation facility gives a good result for preparation study [2]. Radiation processing of polymer materials involves subjecting the polymers to the irradiation, usually in a continuous mode for modifications of the polymers to improve properties[3-4]. Modified polymeric resins [5-8] may offer several properties and different applications. Several attempts have been made to modify the properties of superabsorbent polymeric materials [9-10]. Much more attention has been focused on the improvement of the swelling ability, metal uptake, and thermal stability of superabsorbents.

Polymer/inorganic composites have been regarded as promising materials for many applications, because they are known as good adsorbents for removing metal ions, collect the advantages of organic and inorganic materials, and their unique properties, such as catalysis[11], adsorption, packaging [12,13] electronic or photonic devices[14] and there are known to display enhanced mechanical, thermal and fire retardation properties [15] in comparison with their corresponding virgin polymers. Many investigators have introduced composite resins consisting of inorganic sorbents and organic binding matrices [16,17]. Inorganic adsorbents (metal oxides, metal hydrates, metal phosphate, clay minerals, etc.) were added to polymers for preparation of polymer composite resins. Bao and Wang [18] have successfully synthesized composite to improve the swelling and capacities as well as to reduce the production cost. However, low swelling properties in saline solutions still limit their applications. Carbon nanotubes [19] also dispersed into the polymer networks to reinforce the hydrogels. Unfortunately, there are also some defects, such as complex synthesis process and high production cost.

The present work was aimed to study the optimum condition for preparation of novel polymers and composite containing sulphonic function groups, amide groups and silica. In this respects, trials have been done to modify the properties of absorbent polymeric materials. These trials will be focused on the improvement of the swelling ability, metal uptake, and removal capacity of absorbents. The effects of the reaction parameters, such as the total absorbed dose, mass ratio of AM to SSS,

concentration of crosslinker and monomer on the template parameters were systematically investigated in order to improve the sorption of some valuable light rare earth elements (REEs) [20].

2. Experimental.

2.1. Chemicals and Reagents.

All the experiments were performed using de-oxygenated bi-distilled water, under a stream of pure dry nitrogen gas at room temperature [8]. The main chemicals and reagents used with analytical grade**.**

2.2. Equipments and Instruments.

A digital analytical balance of model WH 205–4, Wiggen Hauser manufacturing (Germany), with a sensitivity of 1×10^{-4} g, was used for weighting the samples and the standards. 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 the samples during experimental processes. Thermo Orion manufacturing (USA) was used for adjusting the pH of solutions.

The prepared resins were dried and grinned to a fine powder then mixed with KBr and pressed to a disk for IR analysis. The FTIR (Fourier transformed infrared) spectra were performed on a computerized spectrophotometer in the range of 4000-400 cm^{-1}, Bomem, Hartmann & Braun, Michelson, MB–Series 157 (Canada).

Computerized UV/Vis double beam spectrophotometer of model T80, pG Instruments Ltd. (England), was used for spectrophotometric determination of metal ions.

The surface areas of the samples were calculated from the adsorption isotherms by the BET method. 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 and composite was determined using JEOL-JSM 6510 LA (Japan) scanning electron microscope at accelerating voltage of 15 kV. 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.

2.3. Preparation of Hydrogel, Resin and Composite.

2.3.1. Preparation of Poly (Acrylamide– Sodium styrene sulphonate) Hydrogel.

P(AM-SSS) hydrogel was prepared by radiation-induced template polymerization of polyacrylamide polymer with sodium styrene sulphonate monomers in de-oxygenated water in the presence of N,N'-methylenediacrylamide (DAM) as a crosslinker .

About 2 g of PAM were dissolved in 50 ml bi-distilled water, 0.4 g of DAM and 10 g of SSS were dissolved into another 50 ml bi-distilled water. The solutions were mixed then transferred into glass ampoule and nitrogen gas was purged inside the ampoules to remove the air from the solution. The glass ampoule was sealed and then subjected to gamma-rays at irradiation dose (15.0 kGy). After irradiation, the obtained hydrogel was cut into small pieces with a stainless steel scissors, soaked in acetone for removal of unreacted monomers, washed with water, dried and stored. The prepared resin was treated with 0.1 N NaOH to neutralize the carboxylic groups, then left to dry at room temperature.

2.3.2. Preparation of Poly (Hydroxamic acid-Sodium styrene sulphonate) resin.

P(HA-SSS) resin in hydrogen form was prepared by modification of P(AM) present in P(AM-SSS) hydrogel using hydroxylamine solution through the following steps:- The solutions of calculated amounts of hydroxylamine hydrochloride and sodium hydroxide were added to a solution containing (5%) of P(AM- SSS) hydrogel. The resulting mixture was stirred for 5 min at room temperature. The reaction was continued for 6 h at 70°C. Ammonia vapor was liberated during the reaction. After completion of the reaction, the resin was separated from solution by filtration and washed several times with water. The resin was treated with 3 N HCl solution for at least 5 min. Finally, the resin was filtered and washed several times with water till it becomes chlorine free and dried at 50°C to a constant weight [21,8].

2.3.3. Preparation of Poly (Acrylamide–Sodium styrene sulphonate–silicon oxide) composite.

P (AM-SSS-SiO$_2$) composite was prepared by radiation induced polymerization of polyacrylamide polymer with SSS monomer and silicon oxide in de-oxygenated water in the presence of DAM as a crosslinker .

About 2 g of PAM were dissolved in 50 ml bi-distilled water and 0.4 g of DAM, 10 g of SSS and 0.3 g silica were dissolved in another 50 ml bi-distilled water. The total mixture (100 ml) was transferred into glass ampoule and nitrogen gas was purged into the ampoule to remove air from the solution. The glass ampoule was sealed and then subjected to gamma-rays at irradiation dose (15 kGy). After irradiation, the obtained product was cut into small pieces with a stainless steel scissors, soaked in acetone for removal of unreacted monomers, washed with water, dried and stored.

2.4. Adsorption Studies.

The interaction of the prepared polymeric resins and composite with La^{3+}, Ce^{3+}, Nd^{3+}, Eu^{3+} and Pb^{2+} metal ions aqueous solution was carried out by contacting 0.05 g of the prepared resin or composite with 10 ml of aqueous solution containing 100 mg/l of each element individually under mechanical stirring for 3 hrs at room temperature. The polymeric resin was separated from the aqueous solution by centrifugation and then filtration using 0.45μm whatman membrane filter to ensure the removal of suspended material in solution.

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:-

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

$$\% \ uptake = \frac{(C_i - C_e)}{C_i}100 \qquad \ldots\ldots\ldots\ldots (2)$$

Where (q) is the maximum capacity (mg/g), C_i and Ce 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 gram.

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

pH has a significant impact on the adsorption of La^{3+}, Ce^{3+}, Nd^{3+}, Eu^{3+}, and Pb^{2+} 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 shaked for 3 hrs to attain steady state, centrifuged and filtrated using 0.45μm 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 from100 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 shaked at room temperature for 3hrs. The mixture was centrifuged and then filtrated. Finally, the concentration of metal ions was measured.

2.5. Mathematical calculation of the degree of polymerization.

Series of experiments were carried out to test the effect of monomer, polymer, crosslinker concentrations and the irradiation dose on the swelling degree, percent conversion and resin capacity. The resin capacity was evaluated by mixing 10 ml of Cu^{2+} solution with 0.01 g of studied resin that was already prepared in sodium form. The mixture was centrifuged, filtrated. The concentration of Cu^{2+} metal ions was measured and the capacity was calculated as shown in Eq. 1.

Swelling degree of the resin was evaluated to explain the physico-chemical behavior of polymer in water. In this respects, 50 mg of resin was kept in 10 ml of metal ion solution for 24 hours at room temperature. After filtration, the surface water on the swollen resin sample was removed by softly pressing between the folds of filter paper. An increase in resin weight was measured and the swelling degree (P_S) was calculated as shown in Eq. 3 as following:-

$$Ps = \frac{(Wf - Wi)}{Wi}100 \ldots\ldots\ldots\ldots(3)$$

Where Wf is the weight of the swollen polymer and Wi is the weight of dry polymer.

Percent conversion of the reactants into polymeric resin was calculated at different reaction parameters such as monomer, polymer, crosslinker 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 :-

$$\%conversion = \frac{(W)}{Ws}100 \text{ ....(4)}$$

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

3. Results and discussion

3.1. Intermolecular polymerization process of Poly (Acrylamide–sodium styrene sulphonate) hydrogel.

When an aqueous solution of P (AM) template polymer and SSS monomer is exposed to gamma-radiation, free radicals are formed on the chains of both P(AM) template polymer and SSS monomer. The radiolysis products of water especially hydroxyl free radicals are very effective in forming free radicals on both P(AM) template polymer and SSS monomer. Therefore SSS monomer is polymerized in the form of P(SSS) chains. The formation of free radicals along the P(AM) chains leads to the formation of networks of the copolymers P(AM) and P(SSS) and then crosslinking takes place simultaneously.

The bond formed between P (SSS) and P(AM) is expected to be more stable than that formed by the hydrogen bonding complexes. This stabilization is attributed to the strong intermolecular affinity between the polymer chains and the hydrogen bonding between the sulphonic groups of P(SSS) and carbonyl groups of P(AM) as well as between the sulphonic groups of P(SSS) and the amide groups of P(AM). These interactions are mainly responsible for the interpolymer association as described in Scheme 1.
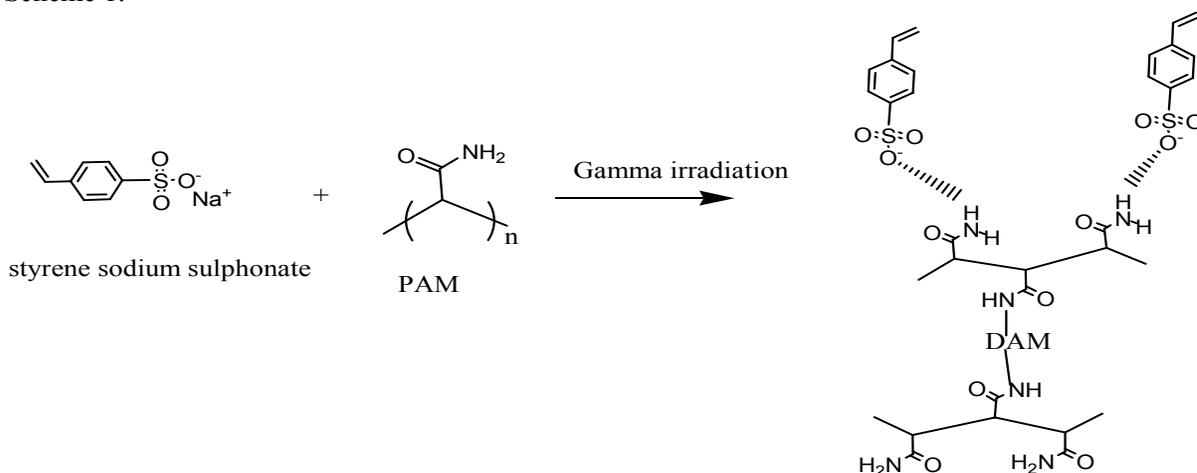
Sch. 1 Structure of the prepared P (AM-SSS) hydrogel, DAM= (- CH$_2$- CH$_2$-CONH) $_2$NH.

3.1.1. Factors affecting on the polymerization process.

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

The results for the influence of monomer concentration on the capacity of the obtained hydrogel towards Cu^{2+} metal ions are shown in Fig. 1(a, b and c). The maximum Cu^{2+} capacity was achieved at 10% SSS, i.e. at maximum swelling degree and conversion %. The -NH$_2$ and -SO$_3$H groups of P(AM) and SSS in the hydrogel structure are primarily responsible for the specific binding of metal ion due to the coordination between Cu^{2+}metal ions and (–NH$_2$, –SO$_3$H) groups. Fig. 1-a shows that the capacity increases with increasing of monomer concentration. On increasing the SSS concentration, the probability of association between the monomer and the added polymer increases which, increases the degree of crosslinking (permanent trapped entanglements) between the polymer chains of the resin. In addition, the number of sulphonic groups increases upon increasing the monomer concentration hence, the capacity of the obtained resin increases.

Fig 1-b shows that no significant change in swelling degree until 5.0 Wt %. This may be due to the low concentration of monomer that is not enough to give high gel %. Further increase of the swelling degree was obtained with increasing of monomer concentration to 10 Wt %. This can be attributed to the higher association probability between the monomer and the added polymer which increases the degree of crosslinking to an equilibrium limit wherein the polymer becomes completely saturated by the solvent.

Fig. 1-c shows that percent conversion increases with increasing of monomer concentration and steady state occurs in the range from 7.5 to 10 Wt %. On increasing the monomer concentration, the probability of association between the monomer and the added polymer increases which, increases the degree of crosslinking between the polymer chains of the resin.
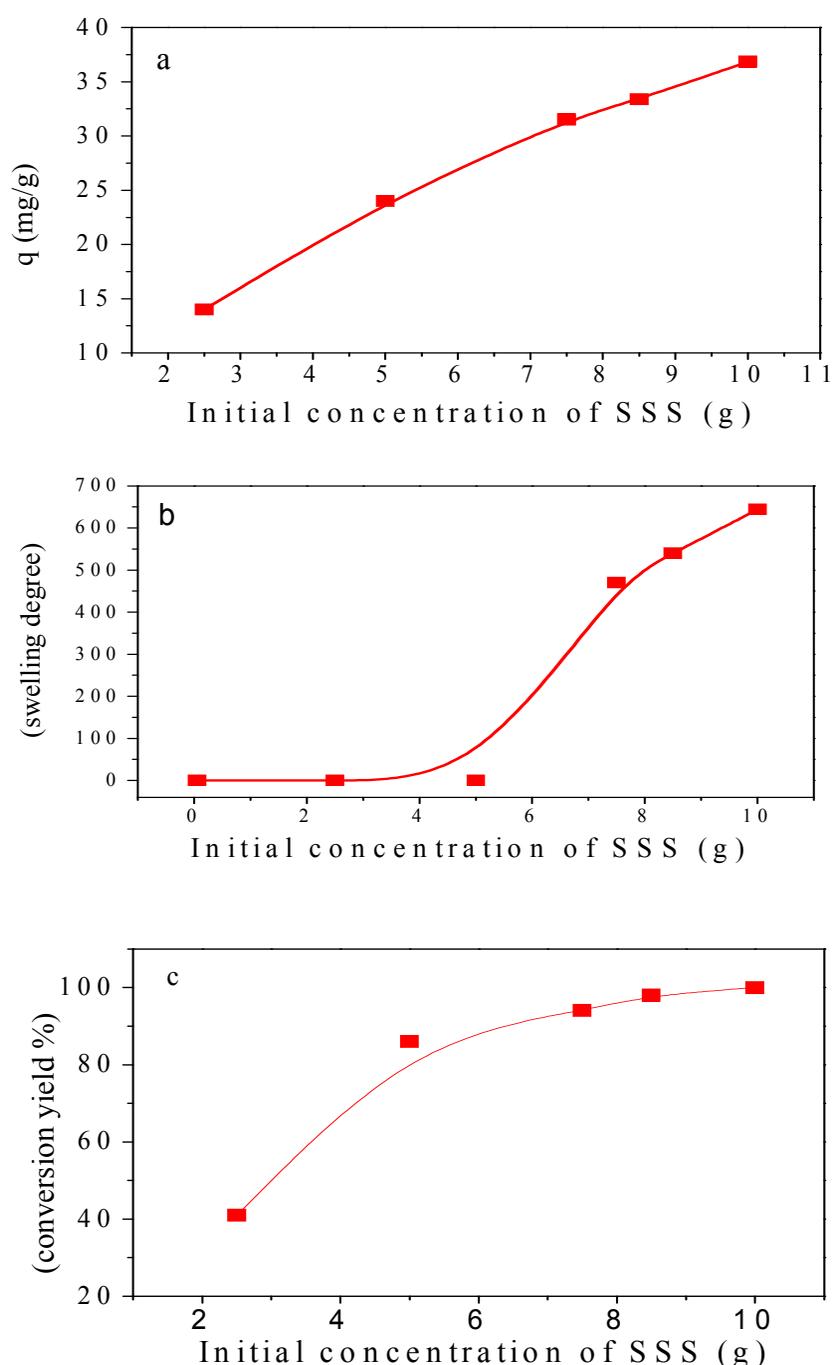
Fig. 1 Influence of the monomer concentration on (a) capacity, (b) swelling degree and (c) conversion yield of P(AM-SSS) hydrogel.

The other effective parameter such as polymer concentration, irradiation dose and crosslinker concentration were studied in details and the results were presented in the supplementary document for brevity. Based on the previously obtained results, it could be stated that the optimum preparation conditions of P(AM–SSS) resin was achieved at 0.2Wt% polymer concentration, 10 Wt % SSS concentration, irradiation dose (15.0) kGy and 0.4 wt % of DAM. At these optimum conditions, the percent conversion was found to be 100 % with a relatively high swelling degree reached to 327 and the maximum capacity toward Cu^{+2} metal ions found to be 93.23 mg/g.

3.1.2. Intermolecular polymerization of the modified Poly(Hydroxamic acid- Sodium styrene sulphonate) resin.

P(PHA-SSS) resin was prepared from the reaction of P(AM-SSS) hydrogel with hydroxylamine hydrochloride . Schematic presentation of estimated reaction between water-soluble P(AM) and hydroxylamine hydrochloride to form P(HA-SSS) resin in the hydrogen form is shown on Scheme 2.
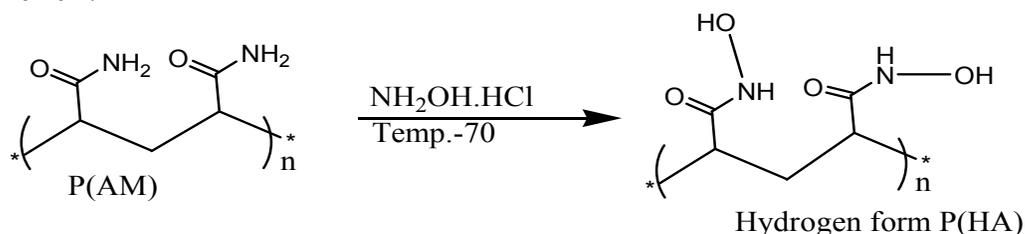
Sch. 2 Modification process of P (AM-SSS) to P (HA-SSS).

3.1.3 Intermolecular polymerization of Poly (Acrylamide–Sodium styrene sulphonate–silicon oxide) Composite.

P(AM-SSS-SiO$_2$) was prepared by gamma-radiation induced template polymerization of (SSS) on P(AM) as a template polymer in the presence of silicone oxide extracted from rice husk ash, in the presence of DAM as a cross-linker as shown in Scheme 3.
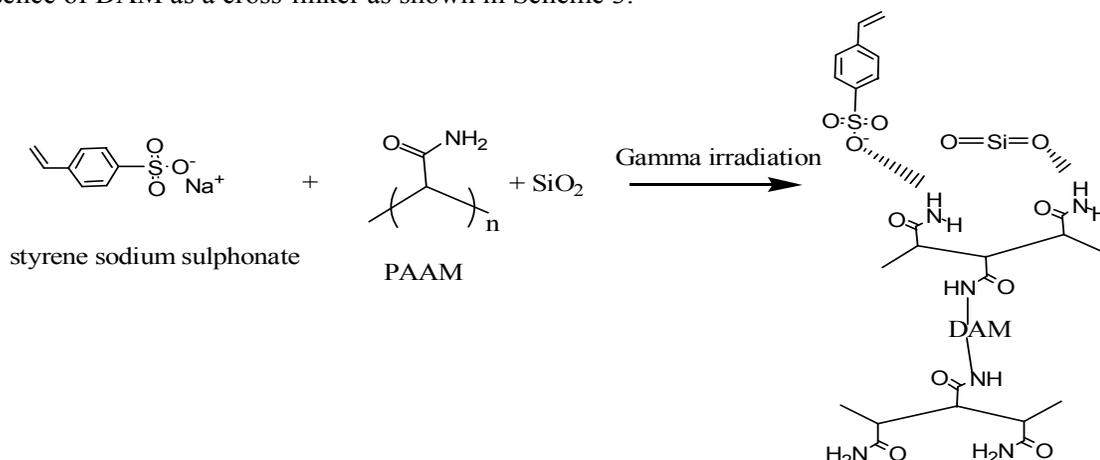

Sch. 3 Synthesis and the expected structure of P (AM- SSS-SiO$_2$) composite.

The Influence of silicon oxide concentration on the capacity of the obtained composite towards (Cu^{2+}) was studied at various silicon oxide concentrations ranged from 0.1 to 0.7 Wt %. The results are shown in Fig. 2 (a, b, c). Fig. 2-a showed that the capacity increase at silicon oxide concentration 0.3Wt % and then decreases with increasing of silica concentration. This is due to increase of extent of crosslinking between the polymeric chains. The interaction between the functional groups and the metal ions decreases by further increase of silicon oxide concentration.

Fig. 2-b demonstrated that swelling degree decrease linearly with increasing of silica concentration. This can be attributed to the increase in the extent of crosslinking between the polymeric chains consequently, the interaction of the polymeric matrix with the solvent decrease.

Fig. 2-c showed that the conversion percentage increases with the increasing of silica concentration up to 0.08 Wt %. Insignificant changes in the percent conversion was observed at 0.1 Wt % due to the increase of the crosslinking inside the composite matrix as mentioned above.
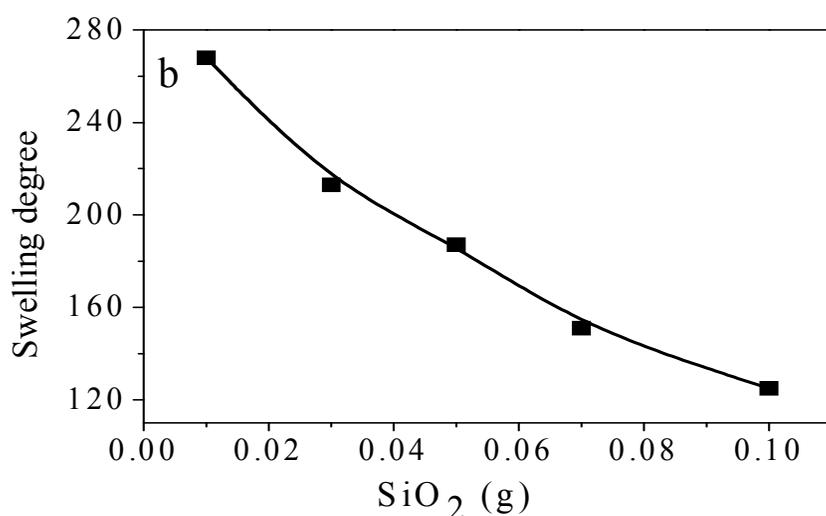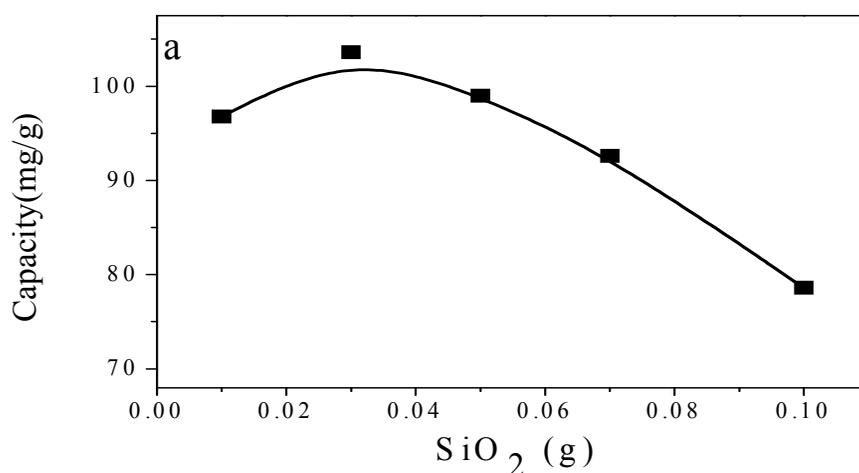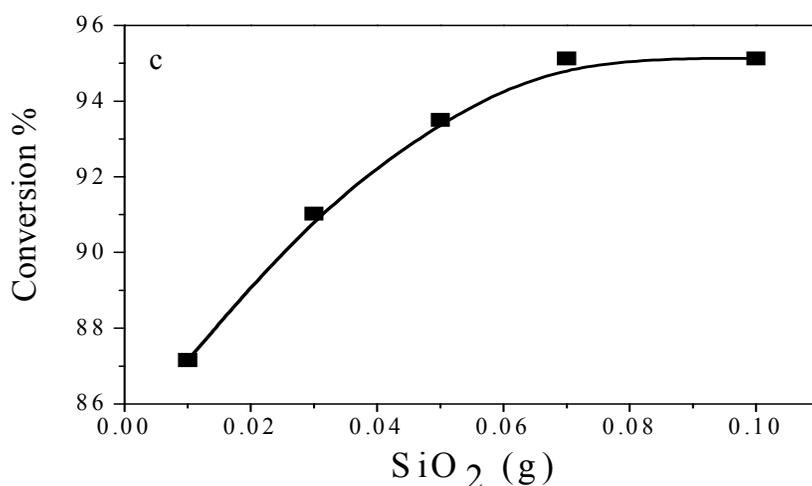
Fig. 2 Influence of SiO$_2$ concentration on (a) capacity (b) swelling degree and (c) conversion yield of P (AM–SSS-SiO$_2$) composite.

The optimum condition for preparation of P(AM –SSS-SiO$_2$) composite was found to be at polymer concentration 0.2 Wt %, SSS concentration 10 Wt %, irradiation dose (15.0) kGy and DAM concentration 0.4 wt % and silicon oxide concentration 0.3 Wt %.

3. 2.Characterization of the prepared adsorbents.

3. 2.1. FTIR Analysis

FTIR spectrum of the prepared P (AM-SSS) hydrogel is presented in Fig 3-a, FTIR spectroscopy indicates that hydrogen bonding is forming between P(SSS) network and linear P(AM). The stretching frequency of >C=O for P(AM) was observed by the absorption peak at 1650 cm^{-1} [8], free >NH stretching was observed by the absorption peak at 3445 cm^{-1} that are belong to amide (–CONH$_2$) group of PAM. The stretching frequency of (>C–C aromatic) for SSS appear at absorption peak at 1415 cm^{-1}, the peak appear at 833.37 cm^{-1} indicate the presence of aromatic SP^2 C–H bending which belong to para disubistituted aromatic. The broad band at 2360 cm^{-1} implies inter- molecular hydrogen bonding between sulfonic acid and amind group. The absorption peaks at 1038 cm^{-1} and 1201.6 cm^{-1} represent symmetric and asymmetric stretching in O=S=O[21]. The peak at 622.5 cm^{-1} confirms the presence of –S–O stretching bond [22]. The presence of these peaks verifies that the polymerization process of PAM and SSS by gamma-radiation technique has been successfully occurred.

FTIR spectrum of the prepared P (HA-SSS) resin is presented in Fig. 3-b. FTIR spectroscopy indicates that, hydrogen bonding is forming between P (SSS) network and linear P (HA). The stretching frequency of >C=O for P(HA) give absorption peak at 1650 cm^{-1} [8] and free >NH stretching give absorption peak at 3448 cm^{-1} that is belong to (–CONHOH) group of P(HA). The stretching frequency of (>C–C aromatic) for SSS give absorption peak at 1415 cm^{-1}, the peak appear at 833.37 cm^{-1} indicate the presence of aromatic SP^2 C–H bending which belong to para disubistituted aromatic, in which the aromatic compounds have characteristic weak overtone bands that show up between 1650–2000 cm^{-1}. Characteristic absorption bands of hydroxamic –O–H and >N–O– groups are observed at 3220 and 980 Cm^{-1} respectively. The presence of these peaks indicate that the conversion of PAM into P(HA) was takes place and verifies the polymerization of PHA, SSS by gamma-radiation technique.

FTIR spectrum of the prepared P(AM-SSS-SiO$_2$) composite is presented in Fig. 3-c. FTIR spectroscopy indicates that, hydrogen bonding is forming between P(SSS) network and linear P(AM). The stretching frequency of >C=O for P(AM) shifts from 1674 to 1651 cm^{-1}, SSS give absorption peak at 1415 cm^{-1}. The peak appears at 833.37 cm^{-1} indicates the presence of aromatic SP^2 C–H bending which belong to para disubistituted aromatic. The broad band at 2360 cm^{-1} implies inter- molecular hydrogen bonding between sulfonic acid and amind group. The absorption peak at 1038 cm^{-1} (symmetric O=S=O) is also observed [23]. The FTIR spectrum of the composite shows bands at 1209 cm^{-1} and 960 cm^{-1} characteristic of the silica network [21].
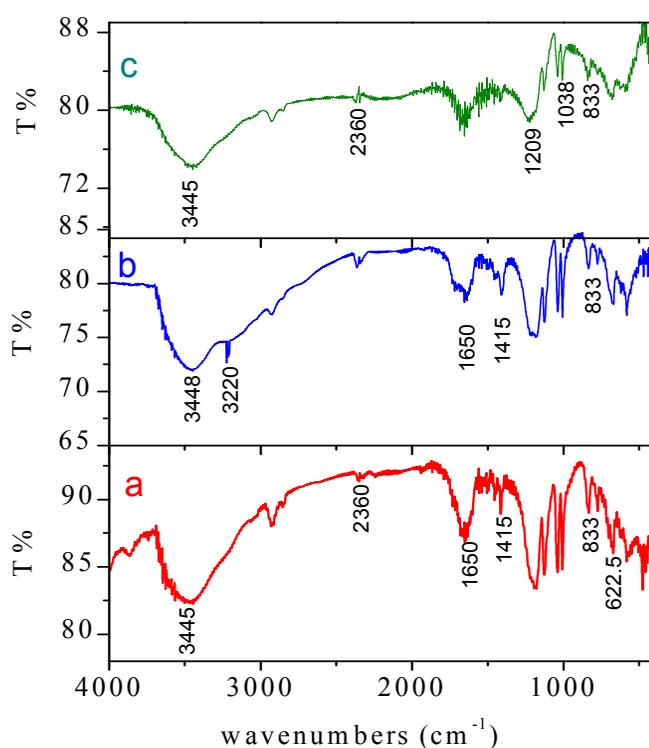
Fig. 3 FTIR spectra of (a) P(AM–SSS) hydrogel, (b) P(HA–SSS) resin, and (c) P(AM–SSS–SiO₂) composite .

3. 2. 2. Scanning electron microscope

SEM (Fig.4-a) image of P(AM– SSS) hydrogel revealed its morphological structure and the surface appearance. SEM image clearly suggest the uniformly distribution of SSS monomer into P(SSS) on to PAM resin. SEM image shows that there are limited porous structures on the surface of the hydrogel while, the composite has more defined porous structures.

The synthesized modified polymeric resin was investigated by scanning electron microscopy (SEM) technique to observe the surface appearance. As shown in Fig. 4-b, the SSS monomer was uniformly distributed into P(SSS) increasing the surface area of the modified polymeric resin. It can be observed that the surface is uniform. This may be related to the conversion of the amide groups to hydroxamic group.

As shown in SEM image of composite (Fig. 4-c), the composite have a local unidirectional porous structure which, indicated that silicon oxide was successfully intercorporated inside the polymeric structure and on the surface of the composite matrix. In contrast, in the case of the resin without silica, more defined porous structures are observed.
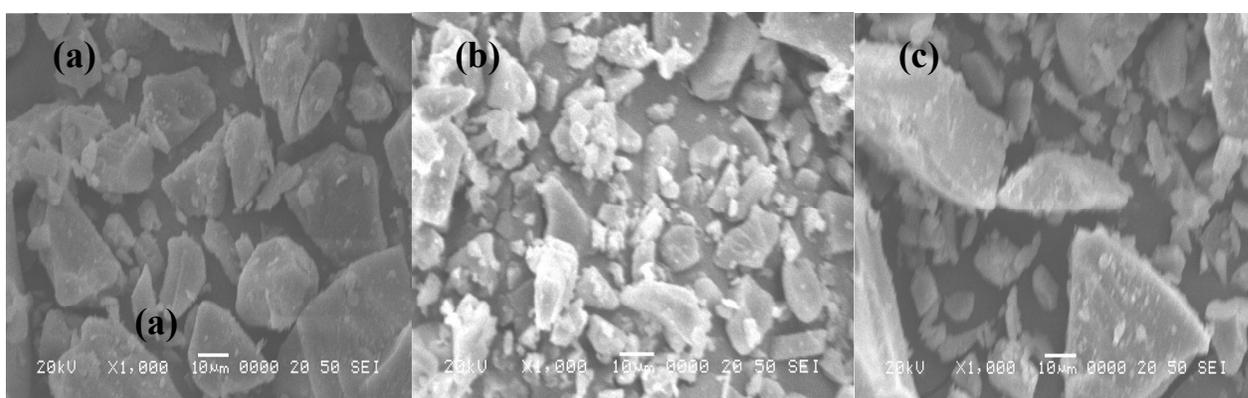

Fig. 4 Scanning electron micrograph of (a) P(AM–SSS) hydrogel, (b) P(HA–SSS) resin and (c) P(AM–SSS–SiO₂) composite.

### 3.2.3. Thermogravimetric analysis (TGA).

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were used to provide an alternative model of the kinetics of the prepared polymer degradation [24]. For P(AM–SSS) hydrogel, the curves of TGA and DTA are shown on Fig. 5-a. The prepared polymeric hydogel was heated at the rate of 10°C/min. The degradation proceeds in three stages. The first stage from (50 to 196)°C with a maximum endothermic peak at 103°C exhibits a weight loss of 20.088 % which, is due to the removal of absorbed or coordinated water molecules. The second stage from (380 to 821)°C which, show endothermic peaks at (452–549–674)°C exhibits a weight loss of 45.12% due to release of SO_2 and cyclization process due to the removal of ammonia or water molecules from two amide

groups. The third stage from (822 to1000°C), the weight loss in this region is 13.281 % may be due to removal of volatile hydrocarbons and complete degradation to the oxide form.

The TGA and DTA curves for the modified polymeric resin P(HA–SSS) are shown in Fig. 5-b. The degradation thermogram proceeds in three stages. The first stage from (59 to 182)°C with a maximum endothermic peak at 92.36°C exhibits a weight loss of 20.07% due to removal of physically absorbed or coordinated water molecules. The second stage from (185 to 415)°C with a maximum at 372°C exhibits a weight loss of 19% due to the decomposition of uncoordinated amide group[25]. This decomposition was carried out through a cyclization process with the removal of ammonia or water molecules from two amide group. The reaction is similar to the intramolecular or intermolecular de-amination in the pyrolysis of other amides. The splitting of these molecules occurs either by intermolecular or intramolecular according to Eq. 5 or 6 [26-27]. The third stage from (416 to 800)°C with a maximum at (512–619–737)°C exhibits the removal of SO_2, NH_3 due to degradation of the acrylamide portion and the decomposition of P(HA) resin. This third stage is characterized by a weight loss of 44.2% due to a short chain fragments created by chain scission. This decomposition of P(HA) resin was carried out through a cyclization process with the removal of water molecules from two adjacent hydroxamic groups. The weight loss in this stage is greater than that occurring in the other two stages.

As shown in Fig. 5-c, TGA and DTA charts of dried sample of P(AM-SSS-SiO$_2$) composite occurs via four stage process. The first stage multi-step decomposition from (57 to 200°C), with the weight loss in this region is 21.34%, may be attributed to removal of all surface and matrix-bound moisture from the polymeric composite [28]. The second stage from (200 to 620°C), with the weight loss 22.195%, may be attributed to the degradation of the acrylamide portion and removal of NH_3 gas by imidation of either adjacent amide groups on a chain or amide groups on neighboring chains and desulphonation of sulphonic acid. The third stage from 620 to 850°C, with the weight loss 26.4%, may be due to removal of silica, SO_2 and desulphonation of sulphonic acid. The fourth stage from (850 to 1000°C) may be due to process accompanying by main chain scission, removal of volatile hydrocarbons and complete degradation to the oxide form[28].

DTA as shown in Fig. 5-c shows that the endothermic peak at (99.24°C) may be due to removal of external water molecules and the two enothermic peaks at (471–609°C) may be due to desulphonation (Removal of the sulfonate group from an organic molecule). The two endothermic peaks at (664 and 884°C) may be attributed to release of ammonia gas. Endothermic peak at 920°C may be corresponding to chain scission and finally the possibility of the oxides formation.
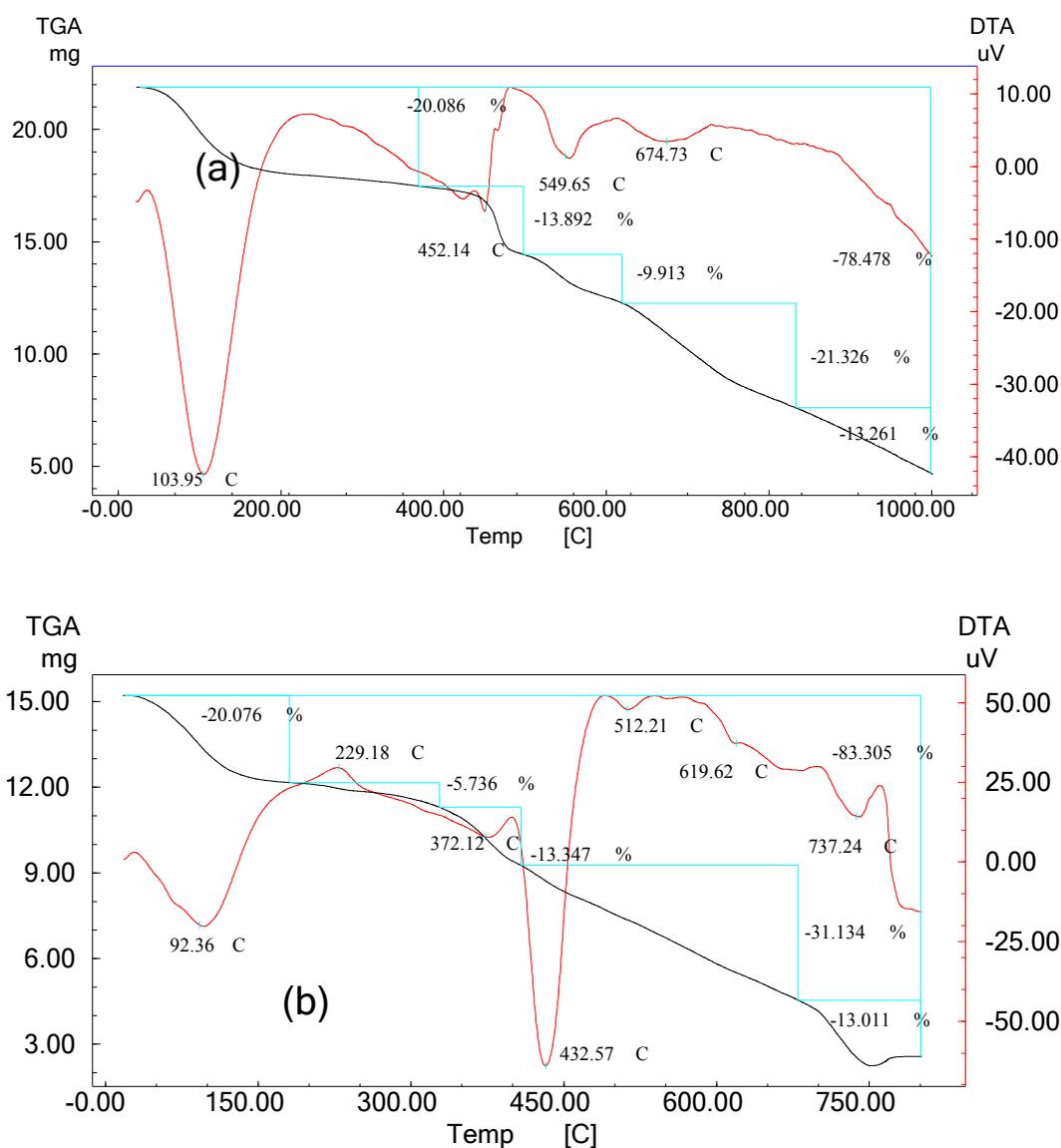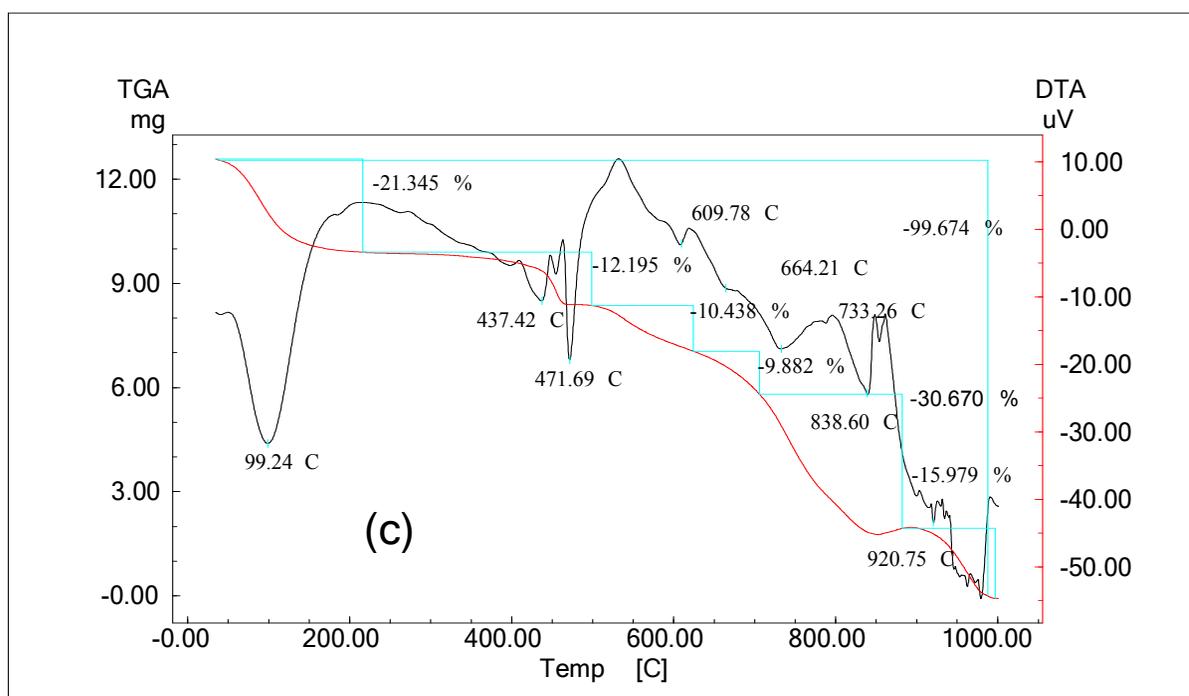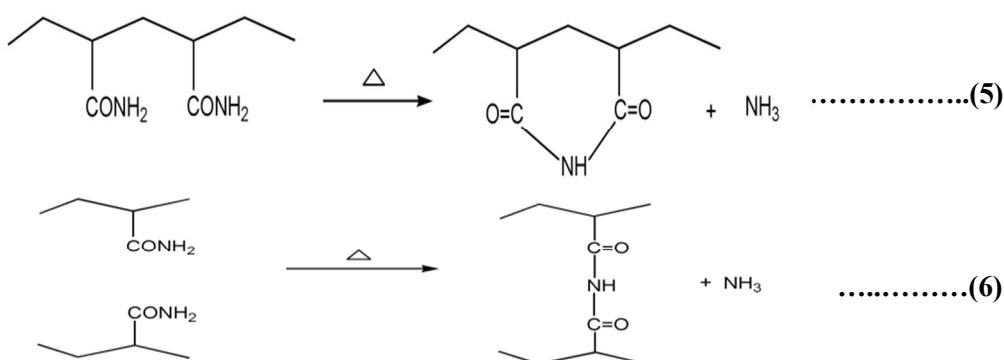
Fig. 5. DTA and TGA curves for (a) P(AM-SSS) hydrogel, (b)P(HA-SSS) resin and (c) P(AM-SSS- SiO₂) composite.

$$\ldots\ldots\ldots\ldots(5)$$

$$\ldots\ldots\ldots\ldots(6)$$

3.2.4. Surface Morphology of the Prepared Polymeric Resins.

The specific BET- surface area and pore volume of P(AM -SSS) hydrogel, P(HA-SSS) resin and P(AM-SSS-SiO₂) composite are summarized in table 1. For P(AM-SSS) hydrogel and the modified resin, the surface area and pore volume are relatively low which, indicated that the porosity is very low. The prepared polymeric composite containing silica has a relatively high surface area and pore volume compared with the previous two materials. The high surface area of the composite depends mainly on particle size distribution, particle shape and number of pores on the composite[29,30]. All of these parameters are mainly responsible for the metal ions adsorption capacity.

Table 1 Surface area and pore volume of the prepared hydrogel, resin and composite.

Sorbent	Pore volume (cm³/g)	Surface area (m²/g)
P(AM -SSS) hydrogel	0.078	17.8
P(HA - SSS) resin	0.092	28.9
P(AM -SSS- SiO₂) composite	0.31	64.5
Amidoxime resin [30]	0.96	45.1

3.3. Sorption behavior of Rare Earth Elements (REEs) .
3.3.1. Metal Hydrolysis.

The main sorption processes of La^{3+}, Ce^{3+}, Nd^{3+}, Eu^{3+} and Pb^{2+} metal ions are mainly affected by the side reaction that may be occurred due to the precipitation at different pHs. In this respects, series of experiments have been tested separately to evaluate the degree of contribution of each of the two reaction mechanisms (sorption and precipitation).

Firstly, the results of the precipitation process of 100 mg/l of each metal ions in acetate buffer solution at different pH values are shown in Table 2. Based on the obtained data, it could be observed

that all the investigated ions are partially precipitated at pH 6. Therefore, the sorption experiments for all the metal ions were tested in the pH range from 1 to 5 to avoid the metal hydrolysis.

**Table 2 Precipitation of La^{3+}, Ce^{3+}, Nd^{3+}, Eu^{3+}and Pb^{2+} at different pH values.**

X	pH						
	1	**2**	**3**	**4**	**5**	**6**	**7**
La(III)	Zero	Zero	Zero	Zero	zero	11 % ± 0.7	23% ± 1
Ce(III)	Zero	Zero	Zero	Zero	zero	12 % ± 0.4	27% ± 0.9
Nd(III)	Zero	Zero	Zero	Zero	zero	15 % ± 0.6	34% ± 1
Eu(III)	Zero	Zero	Zero	Zero	zero	14 % ± 0.8	32 % ± 1.2
Pb(II)	Zero	Zero	Zero	Zero	zero	10 % ± 0.5	21% ± 1.1

3.3.2. Adsorption of REE on P(AM- SSS) hydrogel, P(HA-SSS) resin and P(AM -SSS-SiO$_2$) composite.

3.3.2.1. Effect of Contact Time.

The effect of contact time on the adsorption of La^{3+}, Ce^{3+}, Nd^{3+}, Eu^{3+} and Pb^{2+} metal ions onto P(AM- SSS) hydrogel in each H and Na form, P(HA-SSS) resin and P(AM-SSS-SiO$_2$) composite are illustrated in Fig. 6 (a,b,c,d and e) for the adsorption of metal ions respectively.

The adsorption results show an initial rapid adsorption rate with time then reached to steady state. The corresponding maximum uptake were found to be (59, 72, 81, 93) for La^{3+}, (57, 69,79, 91) for Ce^{3+}, (58, 69,76 , 89) for Nd^{3+}, (50, 52, 58, 64) for Eu^{3+},(36, 42 ,48, 54) for Pb^{2+}. Based on the obtained results, it was found that firstly, P(AM-SSS-SiO$_2$) composite have the higher uptake more than P(HA- SSS) resin and P(AM- SSS) in Na form then P(AM- SSS) in H form. Secondly, the maximum uptake for composite toward metal ions are arranged with the following order La^{3+}>Ce^{3+}> Nd^{3+}> Eu^{3+}> Pb^{2+}. This may be due to the descending order of the basicity of metal ions. The basicity determines the extent to which cations hydrolyze in aqueous solution. The obtained results are in good agreement with the following order of decreasing basicity: La^{3+}>Ce^{3+}>Nd^{3+}>Eu^{3+}. The sorption affinity of the P(AM-SSS-SiO$_2$) composite obey the order of decreasing ionic radius La^{3+}>Ce^{3+}>Nd^{3+}>Eu^{3+}.
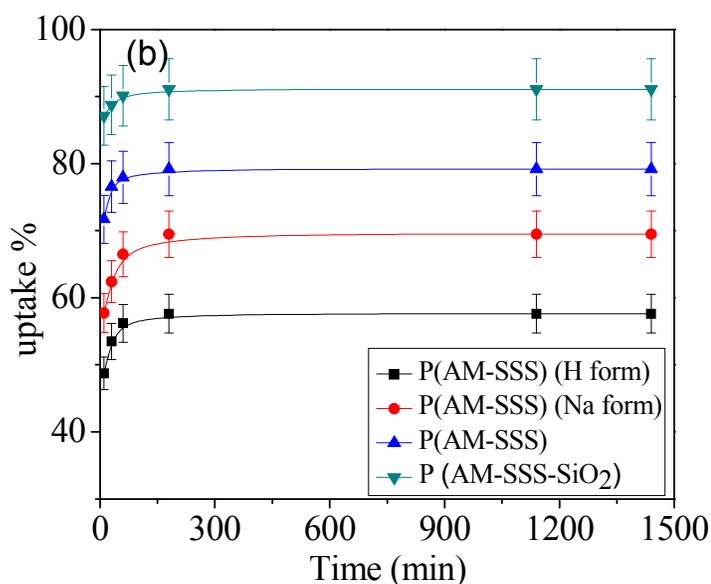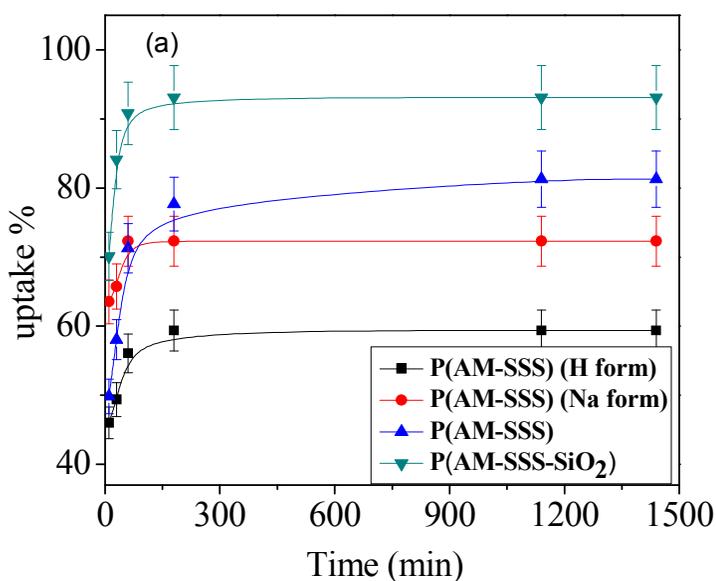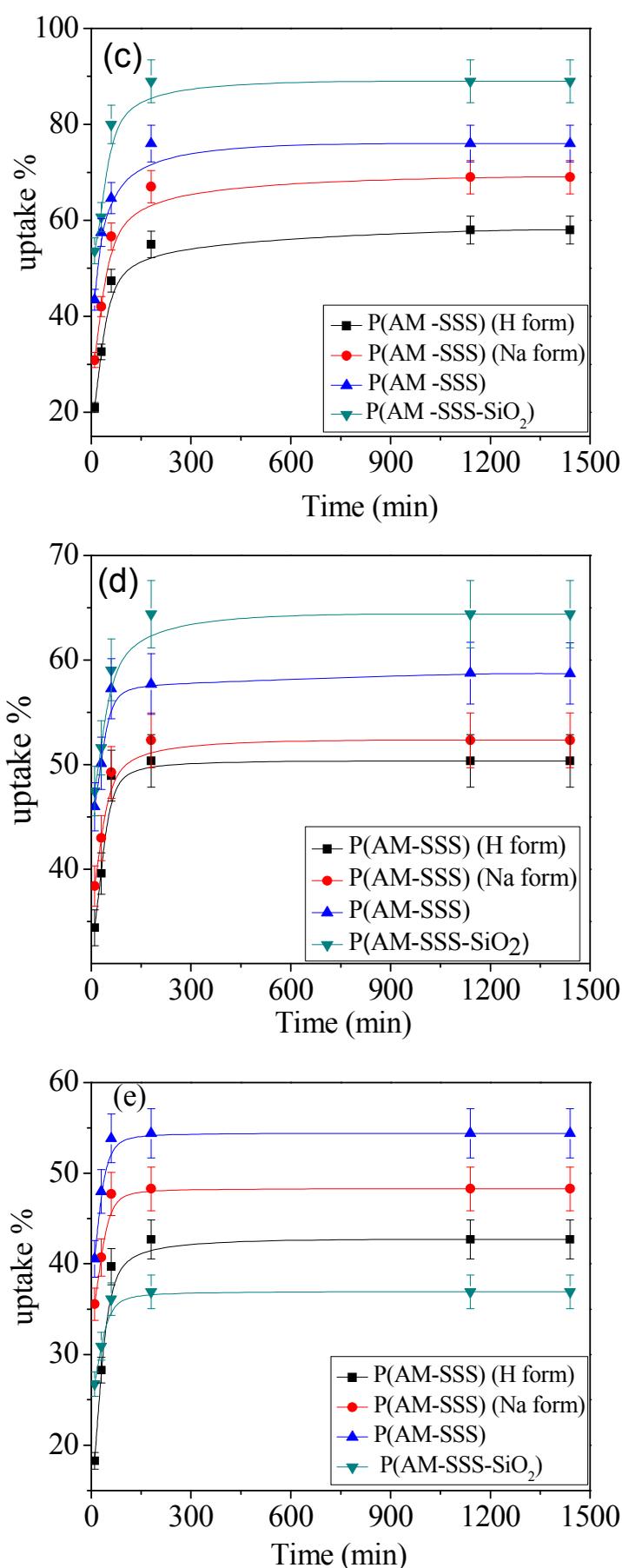
Fig. 6 Effect of contact time on the adsorption of (a) La^{3+} (b) Ce^{3+}(c) Nd^{3+} (d) Eu^{3+}and (e) Pb^{2+} metal ions onto P(AM–SSS) hydrogel, P(HA–SSS) resin and P(AM-SSS-SiO$_2$) composite.
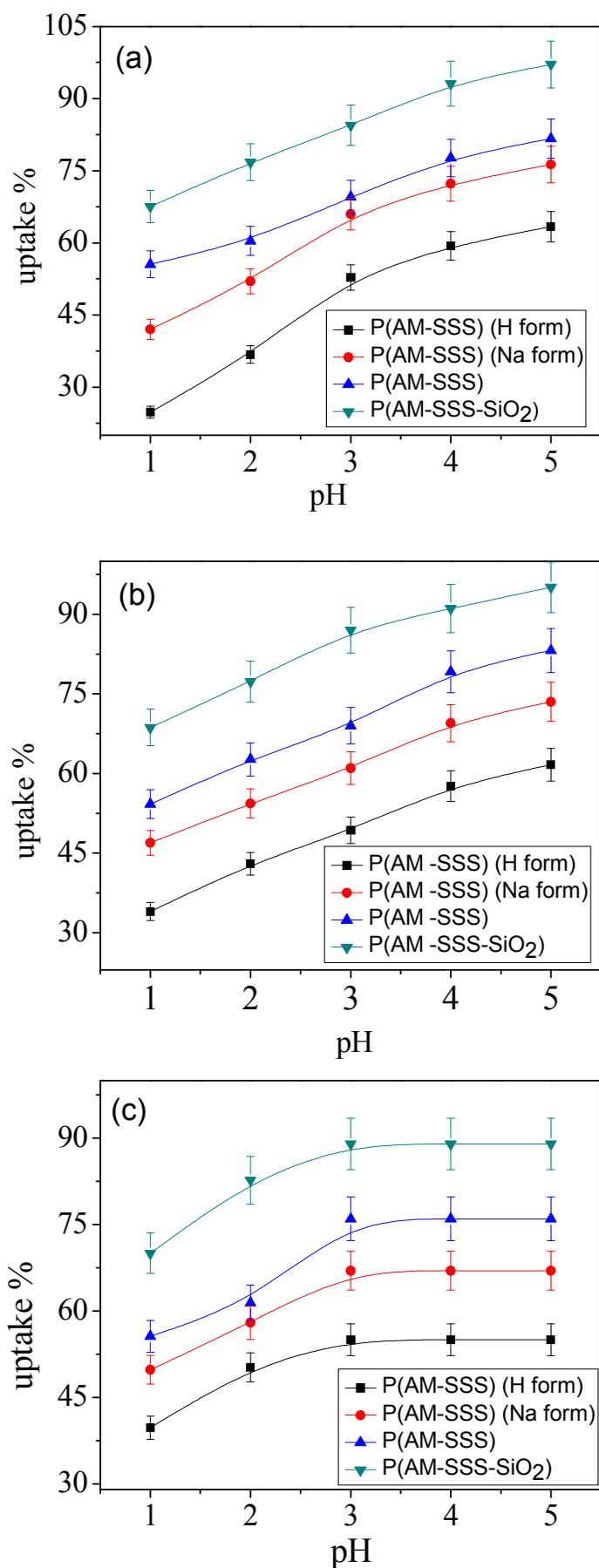
3.3.2.2. Effect of pH.

Series of experiments were carried out to evaluate the effect of pH on the metal uptake of P(AM–SSS) hydrogel, P(HA–SSS) resin and P(AM–SSS-SiO$_2$) composite at   different pH values, as shown in Fig.7(a,b,c,d and e). The increase in pH of the solution over pH 5.0 will leads to precipitation of metal ions according to the studied precipitation results in Table 1. The adsorbed amount of metal ions increases with the increasing the pH value of the aqueous solution and the maximum uptake for P(AM–SSS) in hydrogen and sodium forms, Modified polymeric resin P(HA- SSS) and P (AM– SSS–SiO$_2$) composite were reached to (63.3, 76.3 , 81, 97 %) for La^{+3}, (61.6, 73.4, 83 , 95%) for Ce^{+3}, (55, 67, 76 , 89%)   for Nd^{+3}, (50.7, 55, 61 , 67%) for Eu^{+3} and (36.9, 42.6, 48.2, 54.4 %) for Pb^{2+} respectively. The maximum adsorption onto the studied resin and composite were obtained at pH 5.0. It is clear that P(AM- SSS- SiO$_2$) composite is more effective for the quantitative removal of La^{3+} ,

Ce^{3+}, Nd^{3+}, Eu^{3+} and Pb^{2+} metal ions than the other modified polymeric resin P(HA-SSS) and the P(AM-SSS) hydrogel in H and Na form respectively .

The reaction mechanism could be explained based on the dissociation of amide, sulphonic groups that increase with the increase of pH providing additional binding sites for the adsorption of metal ions. At higher acidic conditions, i.e. low pH value of about 1.0–2.0, low adsorption of metal ions was obtained due to the competition between H^+ ions and REEs metal ions on the effective amide and sulphonic function groups. With the increase of the pH of the solution, the amount of adsorbed metal ions increases and maximum adsorption was obtained at pH of 5.0.

In some cases hydrogen bonds may be formed between the active sites of the adsorbent surface causing the surface layer to shrink, this surface layer acts as a barrier slowing down the adsorption of metal ions. This behavior was observed during the sorption of Nd at pH = 3–5 as shown in Fig. 7-c.
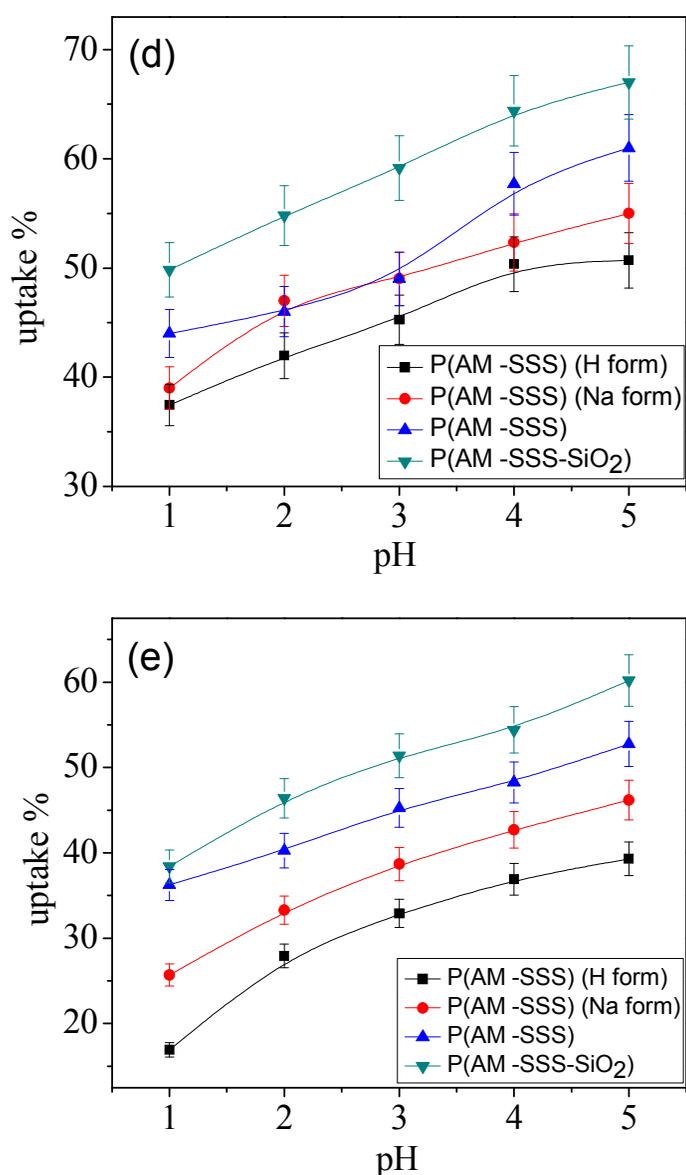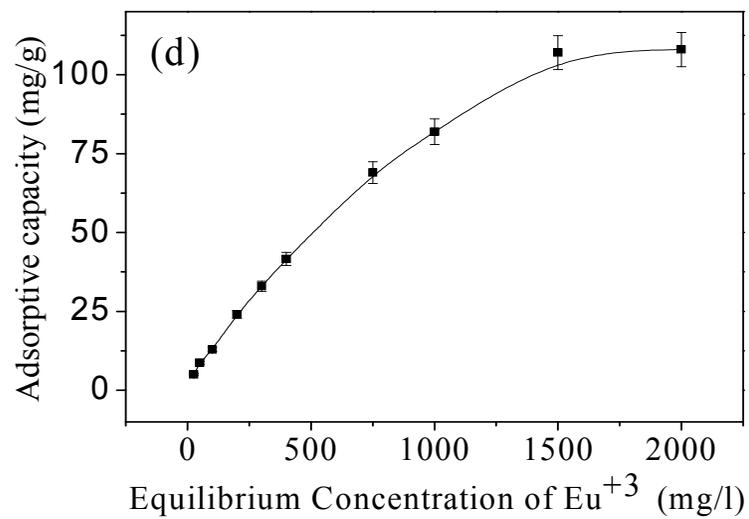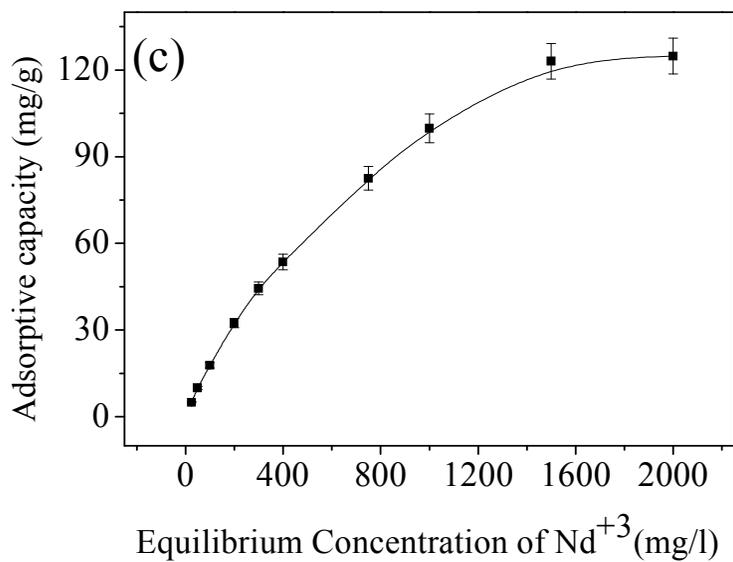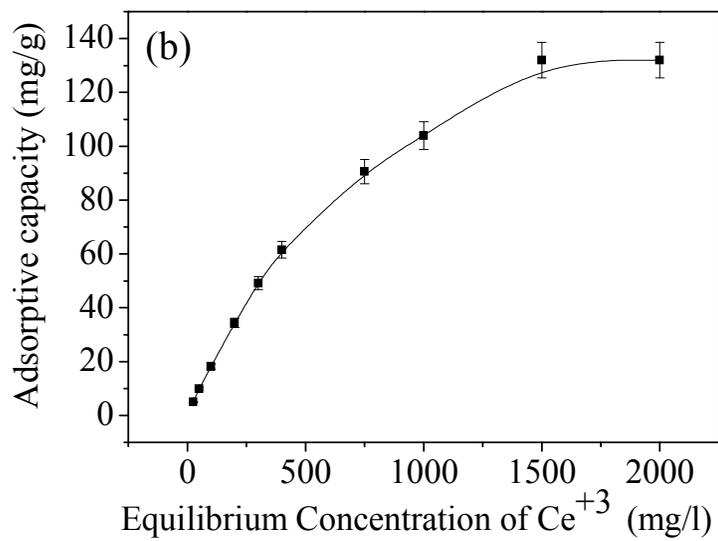
Fig. 7 Effect of pH on the adsorption of (a) La^{3+} (b) Ce^{3+}(c) Nd^{3+} (d) Eu^{3+}and (e) Pb^{2+} metal ions onto P(AM-SSS) hydrogel (H and Na form), P(HA-SSS) resin and P(AM-SSS-SiO$_2$) composite.

3.3.2.3. Effect of initial metal ions concentration on the adsorption process of P(AM-SSS-SiO$_2$) Composite.

The initial metal ion concentration provides an important driving force to overcome all mass transfer resistance of metal ions between the aqueous and solid phases. Batch experiments were performed to study the effect of the initial metal ion concentration of La^{3+}, Ce^{3+}, Nd^{3+}, Eu$^{3+,}$ and Pb^{2+} on their adsorption uptake onto P(AM -SSS-SiO$_2$) composite. The obtained results of initial metal ion concentration illustrated in Fig 8 (a, b, c, d and e), the maximum capacities were found to be 136, 132, 124, 108 and 98 mg/g for La^{3+}, Ce^{3+}, Nd^{3+}, Eu^{3+} and Pb^{2+} onto P(AM-SSS-SiO$_2$) composite respectively. The maximum capacities of the P(AM- SSS- SiO$_2$) composite toward the investigated metal ions are arranged with the following order La^{3+}>Ce^{3+}> Nd^{3+}> Eu^{3+}> Pb^{2+}. The high capacity of the composite may be due to presence of silica which introduces inside the matrix and increase the active sites. The polymeric composite characterized by high surface area compared by the two prepared resins. The sorption efficiency increases at low initial metal ion concentrations due to the presence of large number of the sorption sites and function groups that were easily occupied by the metal ions. As the initial metal ion concentration increases, most of sorption sites become occupied and the sorption efficiency begins to become constant. The capacity of the composite is mainly correlated to the basicity and the ionic radius of metal ion. The capacity of the composite towards the rare earth ions was arranged in the order of decreasing basicity and ionic radius as follows:- La^{3+}>Ce^{3+}> Nd^{3+}> Eu^{3+}.
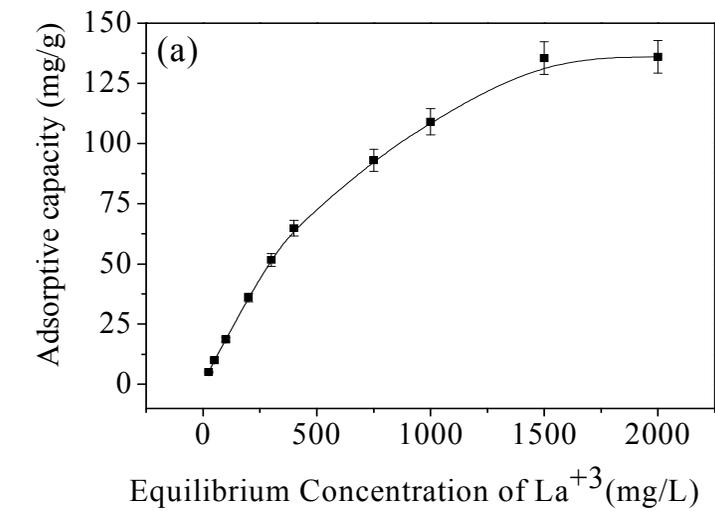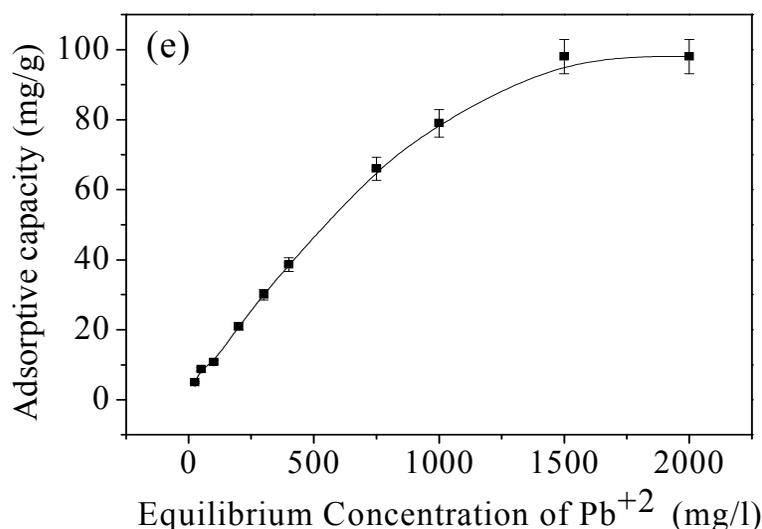
Fig. 8 Effect of initial metal ion concentration on the adsorption of (a) La^{3+} (b) Ce^{3+} (c) Nd^{3+} (d) Eu^{3+} and (e) Pb^{2+} onto P(AM-SSS) hydrogel (H and Na form), P(HA-SSS) resin and P(AM- SSS-SiO$_2$) composite.

4. Conclusion.

The results show that Poly(Acrylamide–sodium styrene sulphonate) hydrogel, Poly(Hydroxamic acid-sodium styrene sulphonate) resin and Poly(Acrylamide–sodium styrene sulphonate–Silicon oxide) composite have been successfully synthesized by template polymerization using gamma induced radiation as initiating system in the presence of N,N'-methylenediacrylamide as a cross-linker. The optimum conditions for preparation of hydrogel are given at sodium styrene sulphonate concentration 10 Wt %, polymer concentration 0.2 Wt %, Cross-linker concentration 0.4 wt% and irradiated at (15.0 kilo Gray). High capacity towards the Cu(II), high conversion percent and low swelling degree of the prepared composite are found at silica concentration 0.3Wt %. The prepared composite have low solubility and low swelling due to the formation of crosslinked structure which, reflect the higher stability towards temperature and radiation. The maximum sorption capacity of the prepared composite was higher than that of the resin and hydrogel in both H and Na forms. The capacity of the composite towards the rare earth ions was arranged in the order of decreasing basicity and ionic radius as follows:- La^{3+}>Ce^{3+}> Nd^{3+}> Eu^{3+}.

Acknowledgments

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New composite was successfully prepared by irradiation polymerization. The composite has higher uptake and capacity for lanthanides than polymer.