

A Simple and Rapid Method for Removal Fe (II) ions from Aqueous Solutions by Using Synthesized Copolymer Derivative of Poly (Styrene – Alternative- Maleic Anhydride) (SMA)

Naser Samadi, Reza Ansari, Bakhtiar Khodavirdilo

Abstract- This study is considered simple and cheap method for removal heavy ions from aqueous solutions. Chelating resins have been introduced to be appropriate materials for the recovery of heavy metals in water remedies. A chelating resin based upon modified poly(styrene-alt-maleic anhydride)(SMA) with Melamine was synthesized. This modified resin was further reacted with 1,2-diaminoethan in the attendance of ultrasonic irradiation for the provision of a tridimensional chelating resin on the nanoscale for the recovery of heavy metals from aqueous solutions. The adsorption behavior Iron (II) ions was explored by the synthesis of chelating resins at various pH's. The gotten resins shown a good inclination for the elimination the Iron (II) ions from aqueous solution, even at acidic pH. The resin was characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, X-ray diffraction analysis. The adsorption process of Iron (II) on SMA, SMA-M and SMA-M-P were tested with Langmuir isotherm model and the isotherm constants were deduced from this.

Keywords: SMA, Iron (II) ions, adsorption, chemical remedies, isotherm

I. INTRODUCTION

Environmental pollution with heavy metal ions exhibits a potential overhang to human, animals and plants. The heavy metal ions do not comport biodegradation and many of them are soluble in aqueous solutions, thus benefit more accessible for vital systems and assemble in the environment [1]. Nowadays, the extraction and elimination of trace metal ions from various matrices have become of very significance and have more consideration. Among heavy metals, iron in slight values is a fundamental element for most life on Earth, containing humans and animals. It is well known that an iron leakage is the most general cause of anemia. On the other side, great amount of iron can cause several health problems. High levels of iron are related with an increased risk for cancer, heart, and liver illnesses [2]. So iron measuring is of very desire and is critical to improve simple, rapid, and effective methods for showing iron in the environment.

Advance finding out of the role of iron in the human body is very obvious beginning with how much of iron is required for the normal function of the human body and what is its duty in the metabolism, up to the results of iron's leakage. Iron leakage is a energetic health problem, both in human and animal. The value of iron in the organism exhibits a balance between the incorporated and resorbed value on one hand and the removed value on the other hand. A daily iron suck, its absorption and administration in different organs and tissues reimbursed its loss and enables the conservation of the constant iron concentration in the human bodies [3]. Etiological factors that conduct to disorders of iron balance in the body are: the scrumpy suck of iron, a tribulation of iron's absorption, the increased loss of iron in acute (harms) and ancient cases (sightless hemorrhage from different tissues and organs) and the increased need for iron, particularly in the cycle of pickup, expectancy, lactation, menopause, old age and convalescence [4-5]. All these terms need the avoidor remedy by giving oral or parenteral iron-based remedies, affiliation the type of anemia and its etiology. Oral therapy, as more proper in medical practice, is used only in terms of good iron absorption from the gastrointestinal term and, if no side effects such as nausea, ailment or puking general for oral performance of iron provision are existent [5-8]. Iron(II) compounds have better absorption and they are originally applied in oral therapy [9]. Some regions in global suffer from the pollution of water with high concentration of iron, which threat human health and conducting to chronic illnesses. Groundwater contamination can happen in different ways, in addition to natural or geochemical pollution, by leakage in canalization, from landfill leachates, etc. It can be cleaved into three main pollution classes, by organic compounds, by microorganisms, and inorganic pollutants. The contamination of groundwater with metals of inorganic pollution comprises a danger environmental problem due to the fact that metals are not biodegradable and can cause carvediscordant effects on human health [10]. The attendance of iron compounds in groundwater, and upshot in drinking water, is a rigid environmental problem. When iron compounds are attendance in both surface and groundwater, even at slight concentrations, they can be linked to different water quality problems and their elimination is fundamental. The Safe Drinking Water Act (SDWA) secondary standards for iron in drinking water is 0.3 parts per million (ppm) . Iron is known to pollute the water reservoir.

Manuscript published on 30 June 2015.

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They can make water appear red or yellow, create brown or black smuts, and give off an easily recognizable metallic savor. Several years ago, it was credit that perforce soil layers, acting as natural filters and conserved earth. Though, nigh without exception, all oral provisions, more or less, cause side effects. The pharmaceutical industry cares to various formulations of the final product to reduce side effects, but the currently gained outcomes have not been satisfactory. New tool methods containing ICP-MS, ICP-AES, and AAS [11–15] have been applied for the measuring of traces of metal ions in different media. In later years, different modified technologies have been used to increase water quality by removing inorganic and organic contaminants. Both photo and electro-chemical oxidation technologies recently have become more popular for water remedy. Doan and Saidi [16] applied combined electrochemical and photochemical oxidation for the elimination of inorganic pollutions like Zn and Ni, and organic pollutions like alkylbenzenesulfonate. They found that the outcomes of blended system are at comparable levels to those gotten in the sole electrochemical system. Peralta-Hernandez et al [17] designed an annular tube reactor of blended photo- electrochemical system for the production of H₂O₂ and Fenton reagent in position, the rate of oxidation was increases fundamentally when the semiconductor anode was explained as compared to the same processes performed in the dark. These processes are introduced as attractive options in dissolving the issues about iron elimination from water specially, if other blend such as ammonia, total dissolved solids or natural organic matter (NOM) are found [18]. To solve this problem, Fe⁺² can be exhibit into the system, making an electro-Fenton's reagent as one of a particular class of oxidation techniques defined as advanced oxidation processes (AOPs) [19]. These processes are characterized by the ability of performing the high reactivity of free hydroxyl radicals. Free hydroxyl radical (OH•) is a nonselective and very strong oxidant agent able to oxidize organic and inorganic pollutants in water and is produced from chemical, electro and photochemical (by using light irradiation) processes. Electro-Fenton process can be increased in attendance of UV radiation [20]. Stephen and Charlotte were used electrolytic cell including aluminum and iron electrodes of high surface area relative to the volume of electrolyte for the production of fine bulks of Al(OH)₃ acting as turbid and adsorption centers for pollution extension in waste water [21]. In the this study an procedure was investigated and evaluated for the elimination of heavy metals like, iron to prevent their hurt to human health. Blended photo electrochemical oxidation technique was explored for the elimination of iron from water, since a little data is accessible on this procedure. The elimination of iron from synthetic solution utilization bench-scale CPE oxidation system was evaluated using various concentrations levels of iron at various conditions. According to develop the adsorption capacity of copolymers for Iron, simple chemical remediation's were applied. An increasing of adsorption capacity for Iron (II) with less 20 % and a decreasing of contact time necessary for to attain the equilibrium until 60 min was gotten, when the SMA was treated with Melamine solution. The main advantage of this melamine is that the increasing of adsorption capacity of polymer is done without to be used additional expensive additives. In this study, the test was leaded according to explore the adsorption of Iron (II) ions from aqueous solutions on treated polymer. The

influence of initial solution pH, polymer dose, initiative Iron (II) concentration and contact time, was investigated according to constitute the optimum experimental qualifications for adsorption process. The Langmuir isotherm model was used for the mathematical description of Iron (II) adsorption on treated polymer with Melamine, and the isotherm constants were concluded from this. In this study first SMA copolymer was synthesized and produced polymer was modified with melamine as a grafting and 1,3 di amino propane as a cross linking [22-25].

II. EXPERIMENTAL

2.1 Material

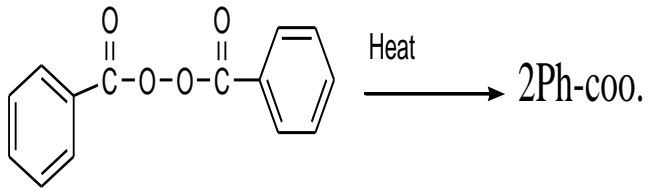
Analytical-reagent grade FeSO₄ .7H₂O and other inorganic chemicals, containing HNO₃ and NaOH, were purchased from Merck (Germany) and were used without further purification. Melamine and the organic solvents, such as tetrahydrofuran (THF) and normal hexane, Maleic Anhydride, Styrene, Triethyl Amine, 1,3-Diaminopropane, Didenzoyl peroxide were also purchased from Merck and were used without further purification. The aqueous solutions were prepared by the dissolution of metal salts in deionized water.

2.2 Equipment

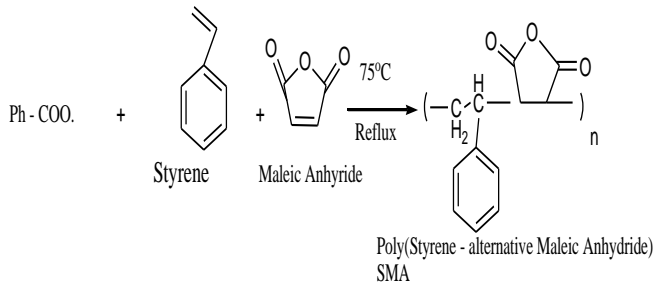
IR spectra were measured with a Fourier transform infrared spectrophotometer (Nexus-670, Thermo Nicolet, USA). The IR (200–4000 cm⁻¹) spectra. The X-ray diffraction (XRD) spectra were scored on an X'pert Philips X-ray photoelectron spectrometer (The Netherlands) with nonmonochromated Mg K α radiation as the excitation source. AAS was used to determine the Fe(II)-ion concentrations in aqueous solutions. The congenital viscosity of the resulting SMA and derivative of SMA copolymers were gotten with an Ostwald viscometer at 25°C in a thermostatic water bath. The elemental analysis of one of the resins was implemented by a CHN analyzer (2400 series II, PerkinElmer Co., USA). The morphology of the particles was tested via scanning electron microscopy (SEM; XL30 Philips, Netherland).

2.3 Synthesis of poly(Styrene – alternative-Maleic Anhydride)(SMA)

*The SMA copolymer was prepared by the free-radical polymerization of maleic anhydride and styrene at 75°C in the presence of benzoyl peroxide as an initiator experience was described as following: 2g (0.0192 mol) of pure styrene and 1.88g (0.0192 mol) of Maleic Anhydride at a molar ratio of 1:1 in were dissolved 50 mL THF. Then 0.018g (0.000768 mol) of Di benzoyl peroxide was added to mixture as an initiator. The reaction mixture was refluxed for 6 h at 75°C under inert gas in presence of ultrasonic irradiation along with vigorous stirring bar in THF. The precipitations were completed by the addition of n-hexane as a nonsolvent and were separated by filtration and washed by n-hexane several times. The product was dried in a vacuum oven for 24 h at 60°C (yield = 98%).



Dibenzoyl peroxide(DBP)



Scheme 1 . Reactions for the formation of poly (Styrene – alternative – Maleic Anhydride) (SMA).

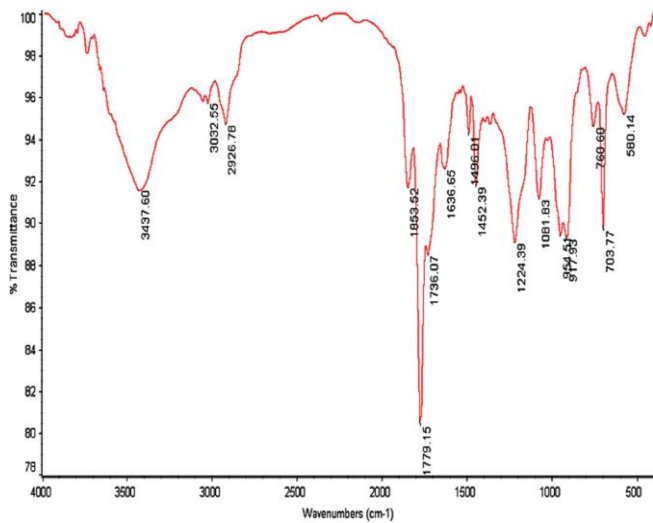
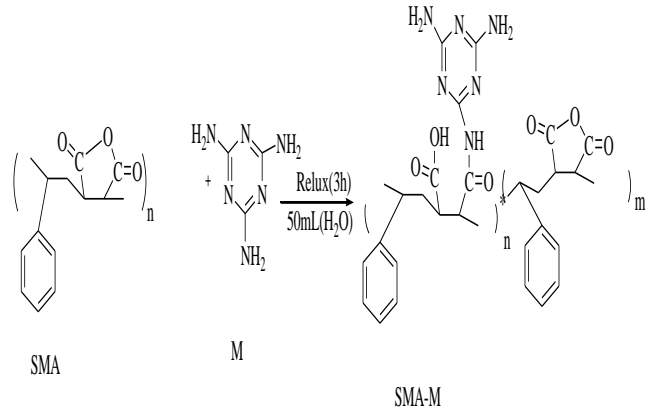


Fig. 1. FTIR spectrum of the SMA copolymer

2.4 Preparation of SMA-M

For synthesis of the grafted SMA copolymer, 1 g (0.005 mol) of SMA copolymer and 0.63 g (0.005mol) of Melamine at a ratio of 1 : 1 were poured into a flask. Then, 0.5 mL (0.004 mol) of triethylamine (TEA) as a catalyst and 50 mL of water as a solvent were charged in a threenecked, round-bottom flask equipped with a condenser, magnetic stirring bar, inlet and outlet for inert gas, and ultrasonic irradiation probe. The reaction mixture was refluxed under these conditions for 3 h. The precipitations were completed by the addition of n-hexane as a nonsolvent and were separated by filtration and washed by n-hexane several times. The product was dried in a vacuum oven for 24 h at 60°C (yield = 98%).The synthesis process of the first chelating resin is shown in Scheme (2)



Scheme 2. Reaction for the formation of modified SMA with Melamine (M)

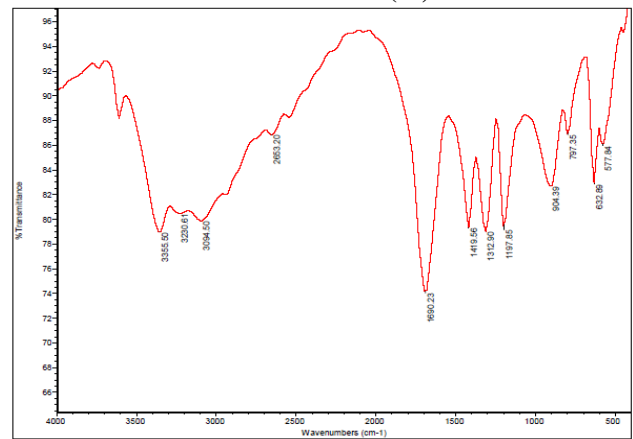


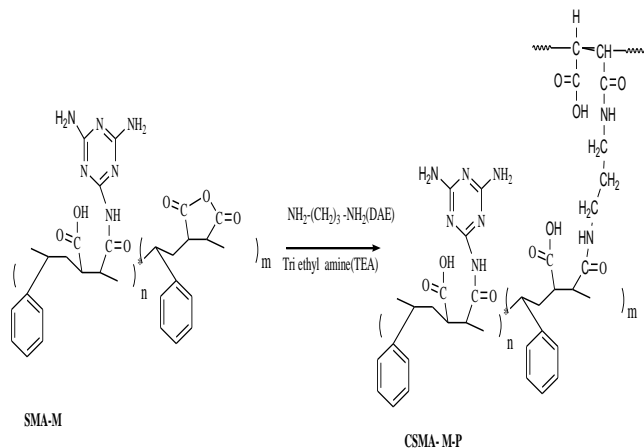
Fig. 2. FTIR spectrum of the SMA -M copolymer (modified of SMA with melamine)

2.5 Synthesis of the 1,2Diaminoethane (CSMA-M-E)

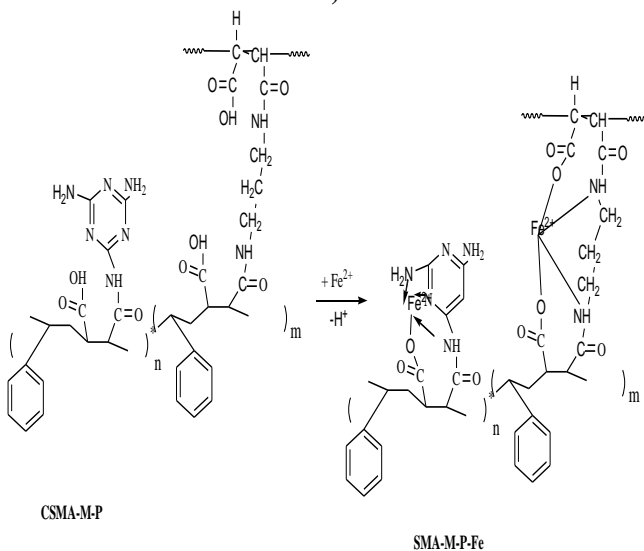
The grafted Melamine (M) functionalized SMA copolymer (CSMA-M) was prepared by simultaneous reaction of the SMA copolymer with Melamine and 0.09 g of 1,2-diaminoethane as crosslinking agent. Then, 0.5 mL (0.004 mol) of triethylamine (TEA) as a catalyst. The reaction mixture was refluxed for 3 h under inert gas in presence of ultrasonic irradiation along with vigorous stirring bar in water. It can be said that the preparation of crosslinked resin in presence of ultrasonic irradiations along with vigorous magnetic stirring give rise polymeric particles in nanoscale. The obtained product was filtered, washed thoroughly with THF, and dried by vacuum oven at 60°C for 24 h. The CSMA-M-E chelating copolymer was prepared by the step-bystep reaction of the SMA copolymer with Melamine as a grafting agent and 1,3-diaminopropane as a crosslinking agent at a molar ratio of 1 : 1 : 0.5 in 50mL of water. The reaction mixture was refluxed for 3 h under inert gas in the presence of ultrasonic irradiation along with vigorous stirring. TEA was used as a catalyst in the reactions. The obtained product was filtered, washed thoroughly with THF, and dried in a vacuum oven at 60°C for 24 h. The yield of the reaction was 96%. The elemental analysis of the CSMA-M-E resin was carried out and showed 65.16% C, 7.64% H, and 8.73% N. The synthesis process of the chelating resins are shown in Scheme (3)



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Scheme 3. Synthesis of the 1,3Diaminoethane (CSMA-M-P)



Scheme 4. The removal of Fe (II) ions with CSM-M-P

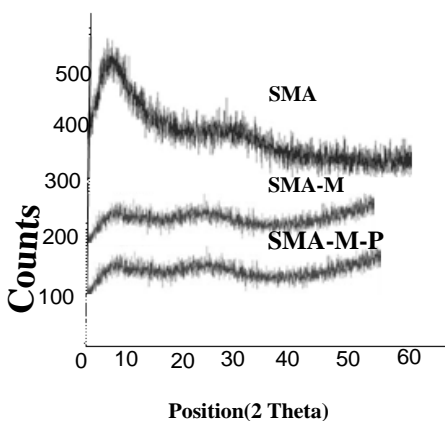


Fig. 3. XRD patterns of the synthesized copolymers

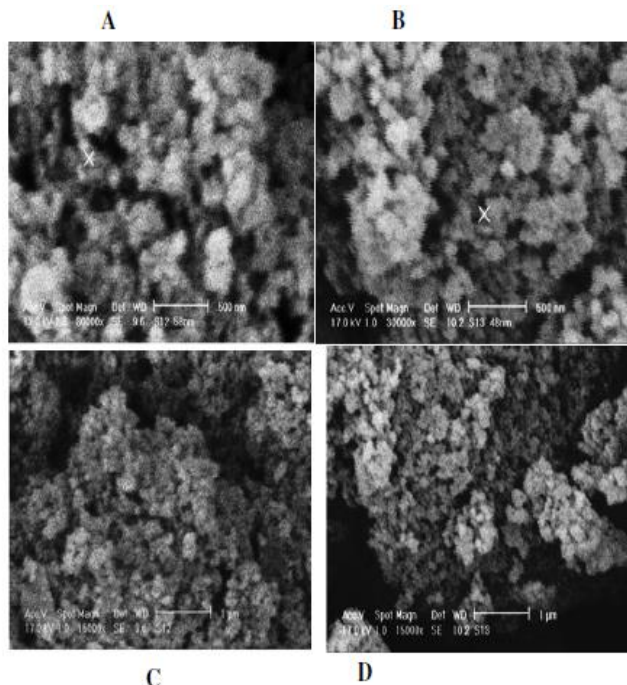


Fig. 4. SEM images of the chelating resins (A) SMA–M scale = 500 nm), (B) SMA–M–P (scale =500nm), and (C) SMA–M (scale =1μm) and SMA–M–P (scale =1 μm).

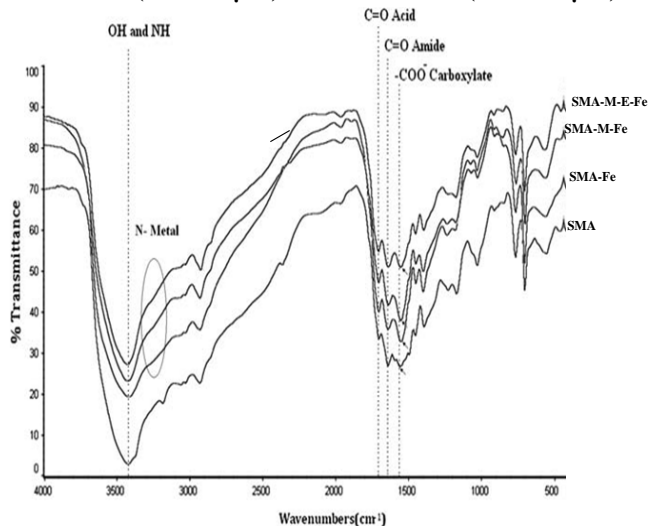


Fig. 5. FTIR spectra of SMA resin before and after complexation of SMA, SMA- M and CSMA-M-E with Fe (II) ions

2.6 Recommended procedure

Dynamic adsorption experiments were performed by the mixture of 50 mg of chelating resin with 50 mL of the Iron-ion solution (50 ppm) in a flask with a magnetic stirrer at 25°C for 4 h. The pH values of the solutions were adjusted to 2, 4, 6 and 8 by the addition of aqueous hydrochloric acid or sodium hydroxide solution. When the adsorption experiment was complete, the mixture was filtered, and the residual metal-ion concentration was determined by AAS. To the test solution, an approximate volume (4mL) of buffer of pH 6 was added and finally the solution was made up to the mark with distilled water.

The solution mixtures were allowed to stand at room temperature for 15min before measuring the absorbance at 25°C. After a determined time with intermittent stirring, the phases were separated by filtration and the Iron (II) concentration in filtrate was analyzed by AAS.

2.7 Adsorption Studies

Fe²⁺ solution was prepared from its soleplate salt, FeSO₄ .7H₂O (Merck) with deionized water. The effect of pH on the Iron adsorption was investigated using 100 ppm Fe²⁺ containing solution over the pH range 2.0–8.0. The pH of silver solutions was adjusted by appropriate using HNO₃ or NaOH. Adsorption tests were conducted in polypropylene beakers. In each adsorption study, 50 mg polymer (dry weight) was added to 25 ml of the Fe²⁺ solution at 25°C and magnetically stirred continuously. After 75min, the aqueous phase was separated from the polymer by centrifugation and the concentration of Fe²⁺ in that phase was determined by using AAS. Each adsorption experiment was performed in triplicate and the mean of 6 AAS measurements was recorded. The effect of the initial Fe²⁺ ion concentration on the adsorption capacity of the polymer at the optimum pH was determined using solutions with concentrations ranging from 10 to 150 ppm. Again, 50 mg polymer (dry weight) was added to 25 mL of the Fe²⁺ solution at 25 °C and magnetically stirred continuously. After 75min, the aqueous phase was separated from the polymer by leach paper and the concentration of Fe²⁺ in that phase was determined by using AAs. The amount of adsorbed Fe²⁺ ions (mg Fe²⁺/g polymer) was calculated from the decrease in the concentration of Fe²⁺ ions in the medium by considering the adsorption volume and used amount of the polymer:

$$q_e = \frac{V(C_i - C_e)}{m} \quad (1)$$

Here, q_e is the amount of metal ions adsorbed onto unit mass of the polymer (mg Fe²⁺/g polymer) at equilibrium; C_i and C_e are the concentrations of the metal ions in the initial solution and in the aqueous phase after treatment for certain adsorption time, respectively (ppm Fe²⁺); m is the amount of polymer used (g – gram) and V is the volume of silver solution (L– Liter). To determine the adsorption rate of Fe²⁺ ions from aqueous solution, same batch adsorption and analysis procedure given above was used and optimum adsorption time was determined. To determine the re-usability of the polymer sample, adsorption/desorption cycles were repeated seven times using the same polymer sample. HNO₃ (0.2 M) was used as desorption agent. Polymer samples carrying 48 mg Fe²⁺/g were placed in this desorption medium (50mL) and stirred magnetically for 75min at 25 °C. After 75min, the aqueous phase was separated from the polymer and the concentration of Fe²⁺ in that phase was determined. Also, the polymer sample loaded with the maximum amount of Fe²⁺ ions was treated with HNO₃ to determine the effect of acidic treatment on the adsorption capacity. In this part, 50 mg (dry weight) portion of polymer containing 45 mg Fe²⁺/g was treated with 50mL of 0.2 M HNO₃ solution at 25 °C for 75min [22–26]. After stirring, the aqueous phase was separated from the polymer and the concentration of Fe²⁺ in that phase was determined. This adsorption/ desorption cycle was repeated by using the same polymer sample to monitor the effect of treatment with acid on the adsorption capacity.

III. RESULTS AND DISCUSSION

3.1 Synthesis and Characterization of the SMA–Melamine Copolymers

The SMA copolymer was obtained by the method considered in ref [27] Figure 1 shows the FTIR spectrum of the SMA copolymer. In this spectrum, the characteristic of anhydride bonds at 1740, 1779, and 1851 cm⁻¹ are exhibited. The innate viscosity of the incoming SMA copolymer was computed with an Ostwald viscometer at 25°C in THF solvent, and it was measured to be 0.42 dL/g. The SMA–M was obtained with the amidation of anhydride moieties of the SMA copolymer. The amine group of Melamine reacted with maleic anhydride repeating groups in the SMA copolymer backbone to form an alkylamide linkage and a carboxylic acid group. Amide bonds are importantly resistant to hydrolysis, so the incoming copolymer was resister in acidic and basic media. To obtain the tridimensional CSMA–M–P copolymer, the reaction was performed with a step-by-step reaction of the SMA copolymer with Melamine (M) as a grafting agent and 1,2-diaminoethane as a crosslinking agent. Figure 5 displays the FTIR spectra of the SMA–M, SMA–M–P, copolymers. The comparison of the SMA–M and derivative's SMA–M spectrum with the SMA spectrum shown that the intensity of anhydride peaks decreased, and the formation of amide groups took place at about 1664 cm⁻¹. In the case of the SMA–M and SMA–M–P copolymers, the FTIR spectra revealed that the grafting reaction was efficient and the anhydride peaks disappeared, and instead, the spectrum shown the characteristics of the absorption peaks of the carbonyl of amide at a lower frequency of about 1618 cm⁻¹ and the carbonyl of carboxylate anion at about 1559 cm⁻¹. All of the pendant carboxylic acids of the resins were converted to free carboxylate ions because of the existence of amine groups in the neighborhoods. It is known that metal complexation to a certain polymeric ligand causes changes in the absorption spectra of the starting polymer. FTIR spectroscopy has been used for the characterization of polymer–metal complexes because the frequency at which a characteristic group of the polymer absorbs is modified by metal-ion complexation, the shift or absence of a certain band present in the starting ligand, and the presence of new bands. Therefore, the first information about the structural changes caused by the complexation of the obtained chelated resin with Fe(II) ions was provided by the FTIR spectra. The shift of infrared absorption bands for the free carbonyl bond (C=O) of the carboxylate groups illustrated whether the bonding between the ligand and each metal ion in the solid phase was covalent or ionic. The more covalent it was, the higher the frequency shift was for the free carbonyl bond absorption. Figure 5 represents the FTIR spectra of the four kinds of metal ions adsorbed in the resins. In this study, the absorption band for C=O in the chelating group shifted to higher frequencies with increasing covalent nature of the carbonyl band in the results of complexation with ionic metals and appeared about 1679–1712 cm⁻¹. It was interesting that the absorption peaks at about 1712 cm⁻¹ decreased with the diameter of metal ions adsorbed.

The larger the diameter of the metal ion was, the smaller the electron attraction was, and the bond of metal ions with carboxylate tend toward ionic properties. The bands at 1623, 1559, 1450, and 1236 cm^{-1} shifted to a lower frequency; this indicated that the metal coordination through the chelating ligands was done in the copolymer network. Also, the absorption bands characteristic of the aromatic parts of the matrix (1024, 912, 764, and 702 cm^{-1}) were not influenced by the metal complexation [35-36]. The XRD patterns of the synthesized copolymers are depicted in Figure 3. The diffraction patterns showed that the copolymers were amorphous. Indeed, there was only a broad diffraction hump at about $2\theta=20^\circ$; this indicated the amorphous nature of the copolymers. So, the presence of the grafting and crosslinking agent in the copolymer backbone did not effect the amorphous structure of the copolymer. Figure 4 shows the SEM micrographs of typical SMA-M and SMA-M-P, in which the particles possessed an almost uniform distribution of size with spherical shapes [37-38]. The diameter of the observed particles in the SEM images was estimated to be under 100 nm.

3.2 Adsorption of Cobalt (II) ion on Polymers

The metal uptake is introduced to various mechanisms of ion-exchange and adsorption processes. During the ion-exchange process, metal ions exchange with protons of surface hydroxyl groups Polymers which we used them were contained hydroxyl groups so, they are reacted with Fe(II) ions and also Iron (II) ions could form polymer – Fe complex because Fe(II) ions were contained unoccupied orbital's so, Iron(II) ions can play acceptor coordination bond role from N,O atoms on copolymers . Any Fe(II) ion can accept two dative bonds from N,O atoms on polymers When the exchange site is a hydroxyl group, exchange reaction occurs and in this case, silver ions Fe(II) exchange with the H^+ ions. The ion-exchange processes in polymers are affected by several factors such as concentration and nature of cat ions, pH, and crystal structure of the polymer. The effect of these parameters has been investigated in several studies due to the importance of polymer's natural stability and its structural changes under in various environments (such as acidic media) in the applications of polymer as an ion exchanger as following reactions (scheme 4) :Under these conditions is expected that the amount of Iron ion retained on polymer to depend on the type of chemical treatment, as well as other experimental parameters, such as initial solution pH, adsorbent dose, initial metal ion concentration and contact time[29-32].

3.3 Effect of initial solution pH

The initial solution pH is an important parameter in the adsorption process of metal ions from aqueous solutions, which affect both the dissociation degree of functional groups from adsorbent surface and the speciation and solubility of metal ions .In this study, the initial solution pH was adjusted with 2N HNO_3 (for $\text{pH}=2.0,4.0,6.0,$ and 8.0) and with acetate buffer (for $\text{pH} = 6.0$). The adsorption efficiency of Iron(II) on polymer as a function of initial solution pH is exhibited in Figure 6.As can be seen from Figure 1, the adsorption efficiency gradually increased with the increase of initial solution pH, and $\text{pH}=6$ is optimized pH for this method. Because the maximum efficiency of Iron (II)

removal is obtained at initial solution $\text{pH} = 6.0$ (acetate buffer), this was considered as optimum value, and was used in all further experiments.

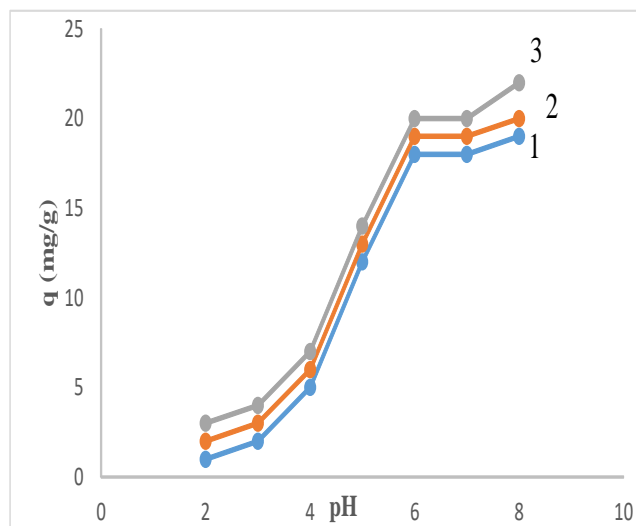


Fig. 6. Effect of initial solution pH on Iron (II) removal on (1) SMA (2) SMA-M (3) SMA-M-P with (50 mg Fe(II)/L, polymer dose = 0.05 g/L; time = 75min ; t = 25 °C)

3.4 Effect of adsorbent dose

Figure 7 presents the effect of adsorbent dose for Iron (II) adsorption on copolymers. It can be observed that varying the adsorbent dose from 3 to 30 g/L, the q values decrease from 9.36 to 4.23 mg/g . Therefore 0.05 g polymer/L was considered sufficient for quantitative removal of Iron (II) from aqueous solutions, and was selected as the optimum value for the adsorption experiments.

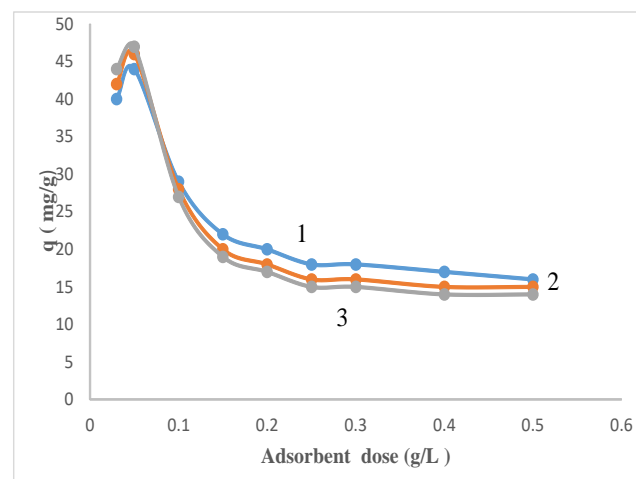


Fig. 7. Effect of adsorbent dose for Iron (II) removal on (1) SMA, (2) SMA-M, (3) SMA-M-P (50 mg Fe(II)/L, pH = 6.0 (acetate buffer), time = 75min,t = 25 °C)

3.5 Effect of initial cobalt (II) concentration

The cobalt (II) removal on polymer was studied as a function of its initial concentration under optimized conditions, initial solution pH and amount of adsorbent.

The amount of cobalt (II) retained on weight unit of adsorbent (q , mg/g) (Fig. 8) increase with the increasing of initial metal ion concentration from aqueous solution. At the same time, the percent of Iron (II) removal (R , %) (Fig. 9) sharply decrease with the increasing of the initial concentration. This opposite trend is determined by the fact that at higher concentrations, the most superficial groups are already occupied and in consequence, the diffusion of Iron(II) ions to the SMA functional groups is inhibited. On the other hand, the efficiency of Iron (II) removal follows the order: SMA-M-E ($q = 45$ mg/g) > SMA-M ($q = 38$ mg/g) > SMA ($q = 36$ mg/g) for an initial Iron (II) concentration of 240 mg/L. The experimental results indicate that in case of polymer SMA-M-P the adsorption capacity for Iron(II) increase with 4.5 %, in comparison with SMA. A good retention of Iron (II) take place at initial metal ion concentration lower than 95 mg/L in case of SMA -M, 65 mg/L in case of SMA, and 120 mg/L in case of SMA-M-P, when the residual concentration is lower than the permissible limit for cobalt discharge. The increasing of initial Iron (II) concentration over these values, determined a decrease of adsorption efficiency, and in consequence for its removal are necessary two or more adsorption steps. These experimental results suggest that the removal of Iron (II) from aqueous solutions, by adsorption SMA, SMA-M and SMA- M-P occurs predominantly by ionexchange interactions, and the efficiency of adsorption process depends on the ionic state of superficial functional groups of adsorbent[33-35]. Thus, in case of SMA of functional groups are un-dissociated and the number of electrostatic interactions between these and the metal ion is low. When, the SMA-M and SMA-M-P the dissociation degree of functional groups increase drastically, and the ion-exchange interactions are facilitated.

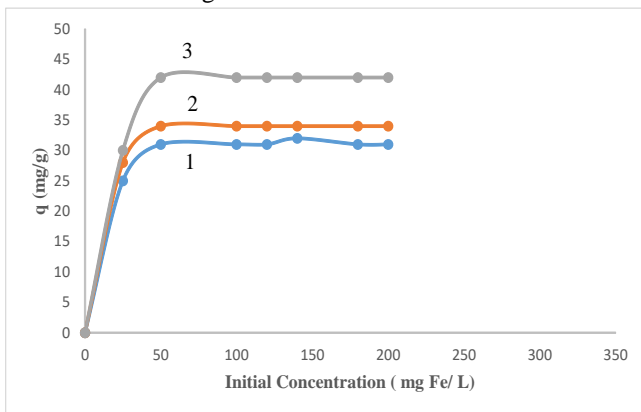


Fig. 8. Effect of initial Iron (II) concentration on the adsorption on (1) SMA, (2) SMA-M, (3) SMA-M-P (50 mg Fe (II)/L, pH = 6.0 (acetate buffer), time = 75 min , t = 25 °C)

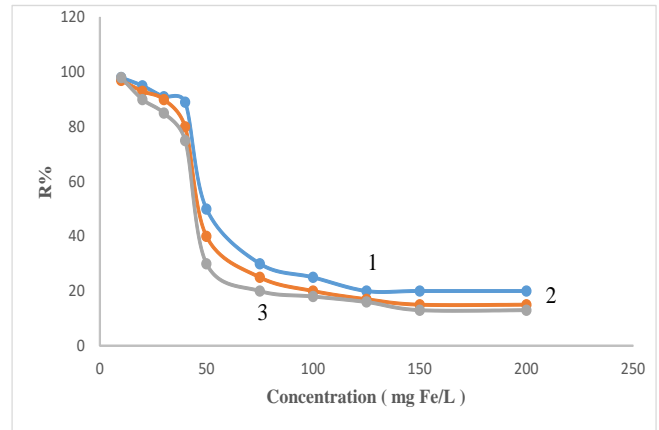


Fig. 9. Effect of initial Iron (II) concentration on the adsorption on (1) SMA, (2) SMA-M, (3) SMA-M-P (50 mg Fe(II)/L, pH = 6.0 (acetate buffer), time =75 min , t = 25 °C)

3.7 Effect of contact time

The effect of contact time between adsorbent and Iron (II) aqueous solutions with an initial concentration of 50 mg/L and pH = 6.0 (acetate buffer) is illustrated in Fig. 4. It can be seen that the Iron (II) removal percent increase rapidly with the contact time up to 240 min for SMA, SMA-M and SMA-M-P. After this fast initial step, the rate of adsorption process becomes slower and the maximum removal is attained

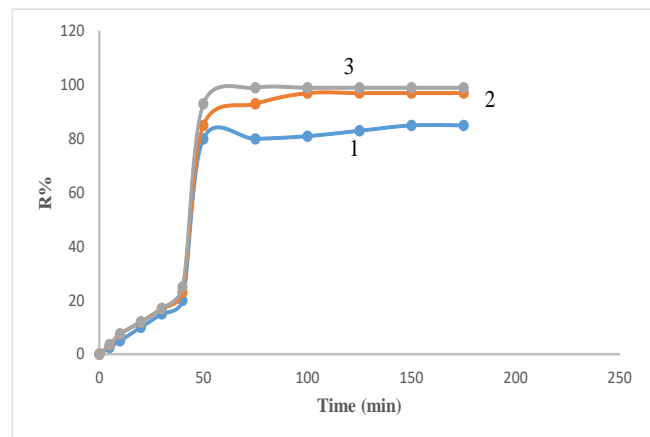


Fig. 10. The effect of contact time on Fe (II) removal on (1) SMA, (2) SMA-M, (3) SMA-M-P (0.05 g polymer/L, t = 25 °C)

Adsorption isotherms

The different values of cobalt removal percents obtained for its adsorption on SMA and derivation of SMA are in agreement with the values of quantitative parameters obtained from Langmuir isotherm model. This model gives the best fit of experimental results. The Langmuir isotherm model can be used when the adsorbed coverage is limited to one molecular layer, and describes chemisorption as the formation of an ionic or covalent bond between adsorbent and metal ion [21]. The linear expression of Langmuir isotherm model is:

$$\frac{C}{q} = \frac{C}{q_{max}} + \frac{1}{q_{max} \times K_L} \quad (2)$$

where: q_{max} is the maximum adsorption capacity (mg/g), q is the equilibrium adsorption capacity (mg/g), c is the equilibrium solution concentration (mg/L) and K_L is the adsorption. The graphical representation of the linear form of Langmuir adsorption isotherm model for the Iron (II) adsorption on un-treated and treated peat moss is illustrated in Fig. 5, and the isotherm model parameters are summarized in Table 1. The change in the free energy (ΔG) was calculated from the Langmuir constant using eq (2):

$$\Delta G = - RT \ln K_L$$

where: R is universal gas constant (8.314 J/mol K) and T is the absolute temperature. The negative values of ΔG (Table 1) indicate that the removal process of Iron (II) by adsorption on SMA and derivation of SMA are feasible and spontaneous. In addition, the lower and negative value of ΔG obtained in case of Iron (II) adsorption on SMA-M-E suggest that after the treatment, the availability of functional groups from adsorbent surface, increase [36-38].

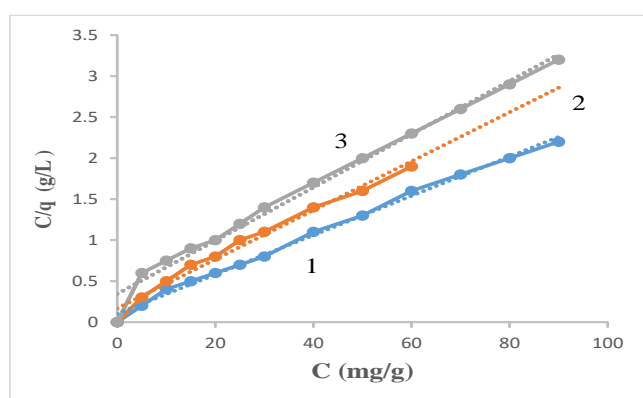


Fig. 11 Application of Langmuir model for Fe (II) adsorption on (1) SAM –M-P, (2) SMA-M

(3)SMA (pH = 6.0 (acetate buffer), 0.05 g adsorbent/L, time =75min)

Table.1 Isotherm constants for cobalt adsorption on studied Polymers

| Parameter | SMA | SMA-M | SMA-M-E |
|---------------------|------------------------|------------------------|------------------------|
| R^2 | 0.9859 | 0.9825 | 0.9957 |
| Regression Equation | $y = 0.0283x + 0.3464$ | $y = 0.0268x + 0.1796$ | $y = 0.0224x + 0.1122$ |
| Q_{max} (mg/g) | 35.34 | 37.31 | 44.64 |
| K_L (L/mg) | 0.0817 | 0.149 | 0.20 |
| ΔG (KJ/mol) | -24.12 | -25.28 | -24.33 |

IV. CONCLUSIONS

In this study was investigated the adsorption behaviour of Iron (II) from aqueous solutions on SMA Copolymer and derivatives of SMA. The adsorption experiments were carried out in batch systems, in order to evaluate the adsorption capacity of SMA polymer before and after treatments. The efficiency of Iron (II) adsorption on un-treated and treated SMA was studied as a function of initial solution pH, adsorbent dose, initial Iron (II) concentration and contact time. The adsorption of the metal ions in acidic media was moderate, and it was favored at pH values of 4-6. The optimum results were obtained at pH = 6.0 (acetate buffer) and adsorbent dose of 0.05 g/L and an initial concentration of

50mgFe(II)/L, when the efficiency of Iron (II) adsorption as a function of polymer type follows the order: SMA-M-P ($q = 44.64$ mg/g) > SMA-M ($q = 37.31$ mg/g) > SMA ($q = 35.34$ mg/g). The experimental results, also indicate that the removal percent of Iron (II) increases with the initial solution and decrease with initial Iron (II) concentration. The Langmuir isotherm model was used for the mathematical description of Iron (II) adsorption on SMA-M-P, SMA-M and SMA. The maximum adsorption capacity (q_{max}) is higher in case of Iron (II) adsorption on SMA-M-P, than in case of Iron (II) adsorption on SMA-M, and both are higher than the value obtained in case of Iron (II) adsorption on SMA. In addition, the change in free energy (ΔG) calculated from Langmuir constant confirm the feasible and spontaneous adsorption of Iron (II) on SMA, SMA-M and SMA-M-P. The FTIR spectra revealed the carboxylate anions and secondary amine in the prepared chelating resin donated electron pairs to the metal ions [39-40].

ACKNOWLEDGEMENTS

The authors would like to thank Prof. Dr. Peyman Najafi Moghadam & Dr. Reza Hasanzadeh (Urmia university) for their help in providing reagents for the synthesis of polymers and thank prof. Dr. Reza Emamali Sabzi who lead us in researching about polymers

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