

## **Synthesized some copolymer derivative of poly (Styrene –alternative- Maleic Anhydride) (SMA) for removal Cobalt (II) ions from aqueous solutions and determination residual cobalt (II) ions by using spectrophotometric method**

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### **ABSTRACT**

Chelating resins have been considered to be suitable materials for the recovery of heavy metals in water treatments. A chelating resin based on modified poly(styrene-alt-maleic anhydride) with Melamine was synthesized. This modified resin was further reacted with 1,2-diaminoethan in the presence of ultrasonic irradiation for the preparation of a tridimensional chelating resin on the nanoscale for the recovery of heavy metals from aqueous solutions. The adsorption behavior cobalt (II) ions was investigated by the synthesis of chelating resins at various pH's. The prepared resins showed a good tendency for removing the cobalt (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 cobalt (II) on SMA, SMA-M and SMA-M-E were tested with Langmuir isotherm model and the isotherm constants were deduced from this.

**Keywords:** SMA, Cobalt (II) ions, Adsorption, Chemical remedies, Isotherm

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### **1. 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]. Cobalt (II) compounds are fundamental in many industries. Their applications in nuclear power plants, metallurgy, mining, pigments, paints and electronic are only few examples where the

attendance of cobalt in waste waters introduces a main environmental problem [2,3]. Prevalent methods for elimination solved heavy metal ions from aqueous media contain chemical dispatch, chemical oxidation and reduction, ion exchange and activated carbon adsorption [3-5]. Thus, these processes have important wastefulness, such as incomplete elimination of heavy metal ions, high quantities of toxic slush, needed additional reagents and have high performance cost. In later years, remarkable notice has been

recovered the use of adsorption technique, in which the adsorbents are natural material or industrial and agricultural wastes, to passively eliminate of heavy metal ions from aqueous effluents. Therefore, the use of polymers [6-8], living and death biomass [9-11] or clay and dependent minerals [12-14] proffers an impressive and cost-operative alternative compared to traditional chemical and physical treatment and depollution techniques. A great number of studies from literature dependent the operations of various such adsorbents for the removal of various heavy metal ions under various experimental qualifications. In most of these is exhibited that such natural or waste products can be good adsorbents for metal ions and some of them have very good ion-exchange properties. The adsorbent applied in this study are copolymer that we synthesized necessary copolymers in polymer laboratory (Urmia university). Due to these makers, the derivative polymers form poly(Styrene – alternative – Maleic Anhydride) (SMA) has in its structure various polar groups (such as carboxylic, amine, amide, etc.) which can chemical bind metal ions from aqueous solutions. In our prior studies [16,17], it has that cobalt (II) can be successfully eliminated from aqueous solutions (> 98 %) when its initial concentration is lower than 10 mg/L. For a higher initial heavy metal ion concentration the cobalt elimination percent's intensively decrease, and the adsorption process is not effective any more. According to develop the adsorption capacity of copolymers for cobalt, simple chemical remediation's were applied. An increasing of adsorption capacity for cobalt (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 cobalt (II) ions from aqueous solutions on treated polymer. The influence of initial solution pH, polymer dose, initiative cobalt (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 cobalt (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 1,2 di amino ethane as a cross linking.

## 2. EXPERIMENTAL

### 2.1. Material

Analytical-reagent grade  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and other inorganic chemicals, including  $\text{HCl}$  and  $\text{NaOH}$ , 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, 1,2 Diamino-ethane, 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.

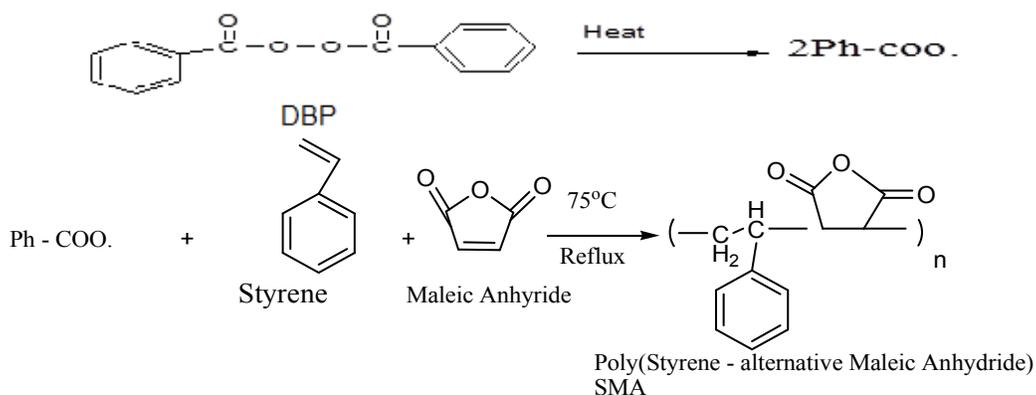
### 2.2. Equipment

IR spectra were measured with a Fourier transform infrared spectrophotometer (Nexus-670, Thermo Nicolet, USA). The UV-Vis (200–800 nm) and IR (200–4000  $\text{cm}^{-1}$ ) spectra. The Xray diffraction (XRD) spectra

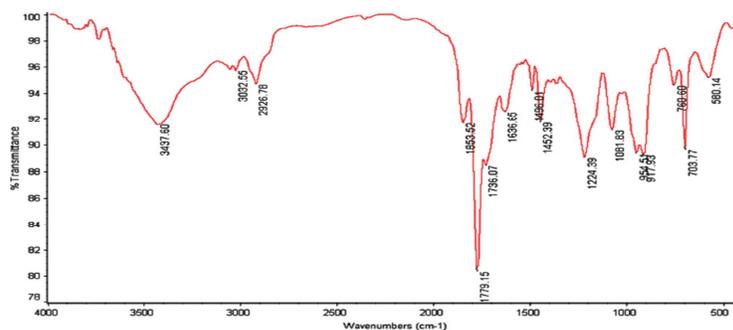
were recorded on an X'pert Philips X-ray photoelectron spectrometer (The Netherlands) with nonmonochromated Mg Ka radiation as the excitation source. UV-visible was used to determine the metal-ion concentrations in aqueous solutions. The inherent viscosity of the resulting SMA copolymer was obtained with an Ostwal viscometer at 25°C in a thermostatic water bath. The elemental analysis of one of the resins was performed by a CHN analyzer (2400 series II, Perkin Elmer Co., USA). The morphology of the particles was examined 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 (0.0192mol) of pure styrene and 1.88g (0.0192 mol) of Maleic Anhydride at a molar ratio of 1:1 were dissolved in 50 mL THF. Then 0.018g (0.000768mol ) 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 non solvent 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%).



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

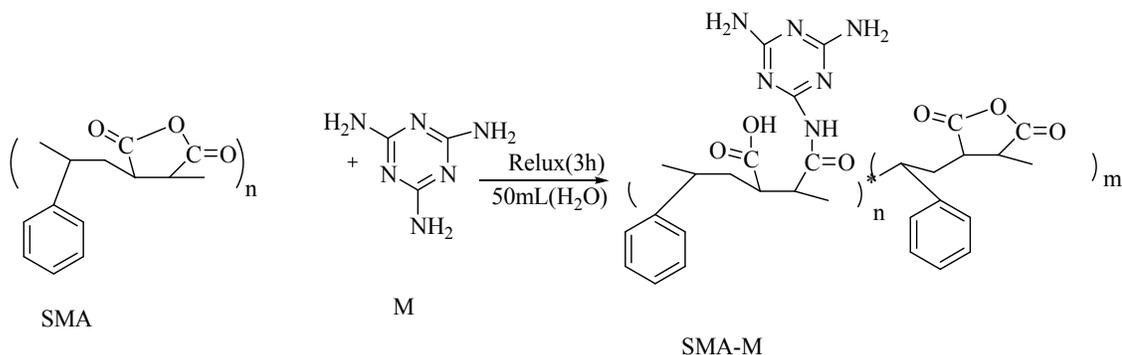


**Fig.1.** FT-IR spectrum of the SMA copolymer

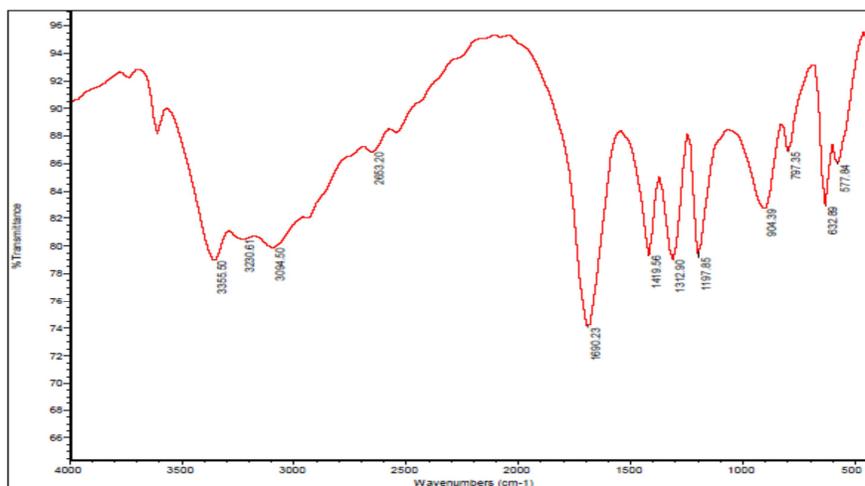
### 2.4 Preparation of SMA-M

For synthesis of the grafted SMA copolymer, 1g (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 three necked, 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.** FT-IR spectrum of the SMA -M copolymer ( modified of SMA with melamine)

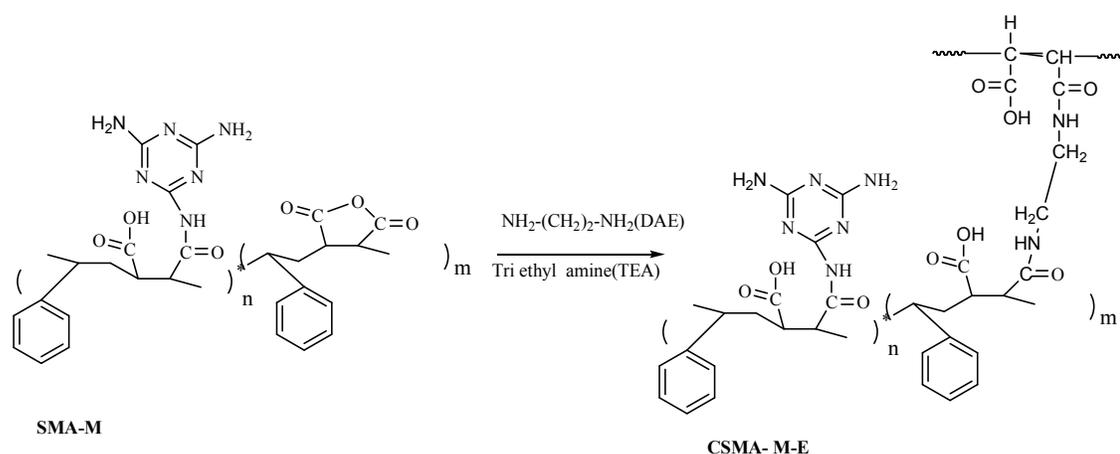
### 2.5 Synthesis of the 1,2-Diaminoethane (CSMA-M-E)

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 nano scale. 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-by-step reaction of the SMA copolymer with Melamine as a grafting agent and 1,2-diaminoethane 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)



**Scheme 3.** Synthesis of the 1,2-Diaminoethane (CSMA-M-E)

### 2.6 Recommended procedure

Dynamic adsorption experiments were performed by the mixture of 50 mg of chelating resin with 50 mL of the cobalt-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 UV as described above. In a series of volumetric flasks (10 mL), an appropriate concentration ( $0.01\text{--}50\mu\text{g mL}^{-1}$ ) of Cobalt (II) solution was added to the reagent solution 1mL of  $\text{NH}_3$  30 w/w%. 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 480nm. After a determined time with intermittent stirring, the phases were separated by filtration and the cobalt (II) concentration in filtrate was analyzed spectrophotometrically with rubeanic acid (Digital Spectrophotometer S 104 D,  $\lambda = 480\text{ nm}$ , 1 cm glass cell, against a blank solution), using a prepared calibration graph [18-21].

### 2.7 Adsorption Studies

$\text{Co}^{2+}$  solution was prepared from its chloride salt,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (Merck)

with deionized water. The effect of pH on the cobalt adsorption was investigated using 100 ppm  $\text{Co}^{2+}$  containing solution over the pH range 2.0–8.0. The pH of cobalt solutions was adjusted by appropriate using  $\text{HNO}_3$  or  $\text{NaOH}$ . Adsorption tests were conducted in polypropylene beakers. In each adsorption study, 50 mg polymer (dry weight) was added to 25 ml of the  $\text{Co}^{2+}$  solution at 25°C and magnetically stirred continuously. After 4 h, the aqueous phase was separated from the polymer by centrifugation and the concentration of  $\text{Co}^{2+}$  in that phase was determined by using UV-visible. Each adsorption experiment was performed in triplicate and the mean of 6 UV-visible measurements was recorded. The effect of the initial  $\text{Co}^{2+}$  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  $\text{Co}^{2+}$  solution at 25 °C and magnetically stirred continuously. After 4 h, the aqueous phase was separated from the polymer by centrifugation and the concentration of  $\text{Co}^{2+}$  in that phase was determined by using UV-visible. The amount of adsorbed  $\text{Co}^{2+}$  ions (mg  $\text{Co}^{2+}$ /g polymer) was calculated from the decrease in the concentration of  $\text{Co}^{2+}$  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  $\text{Co}^{2+}$ /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  $\text{Co}^{2+}$ );  $m$  is the amount of polymer used (g – gram) and  $V$  is the volume of silver solution (L– Liter). To

determine the adsorption rate of  $\text{Co}^{2+}$  ions from aqueous solution, same batch adsorption and analysis procedure given above was used and optimum adsorption time was determined. To determine the reusability of the polymer sample, adsorption/desorption cycles were repeated seven times using the same polymer sample.  $\text{HNO}_3$  (0.2 M) was used as desorption agent. Polymer samples carrying 48 mg  $\text{Co}^{2+}$ /g were placed in this desorption medium (50mL) and stirred magnetically for 4 h at 25 °C. After 4 h, the aqueous phase was separated from the polymer and the concentration of  $\text{Co}^{2+}$  in that phase was determined. Also, the polymer sample loaded with the maximum amount of  $\text{Co}^{2+}$  ions was treated with  $\text{HNO}_3$  to determine the effect of acidic treatment on the adsorption capacity. In this part, 50 mg (dry weight) portion of polymer containing 48 mg  $\text{Co}^{2+}$ /g was treated with 50mL of 0.2 M  $\text{HNO}_3$  solution at 25 °C for 4 h [22-26]. After stirring, the aqueous phase was separated from the polymer and the concentration of  $\text{Co}^{2+}$  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.

### 3. RESULTS AND DISCUSSION

#### 3.1. Synthesis and Characterization of the SMA–Melamine Copolymers

The SMA copolymer was obtained by the method considered in ref [23] Figure 1 shows the FT-IR spectrum of the SMA copolymer. In this spectrum, the characteristic of anhydride bonds at 1740, 1779, and 1851  $\text{cm}^{-1}$  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 0.42dL/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 resistant in acidic and basic media. To obtain the tridimensional CSMA-M-E 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-E, 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  $1664\text{ cm}^{-1}$ . In the case of the SMA-M and SMA-M-E 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  $1618\text{ cm}^{-1}$  and the carbonyl of carboxylate anion at about  $1559\text{ cm}^{-1}$ . 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 Co(II) ions was provided by the FTIR spectra. The shift of infrared absorption bands for the free carbonyl bond ( $\text{C}=\text{O}$ ) 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  $\text{C}=\text{O}$  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  $1679\text{--}1712\text{ cm}^{-1}$ . It was interesting that the absorption peaks at about  $1712\text{ cm}^{-1}$  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  $1623, 1559, 1450, \text{ and } 1236\text{ cm}^{-1}$  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 ( $1024, 912, 764, \text{ and } 702\text{ cm}^{-1}$ ) were not influenced by the metal complexation [25-26]. 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-E, in which the particles possessed an almost uniform distribution of size with spherical

shapes [27-28]. The diameter of the observed particles in the SEM images was estimated to be under 100 nm.

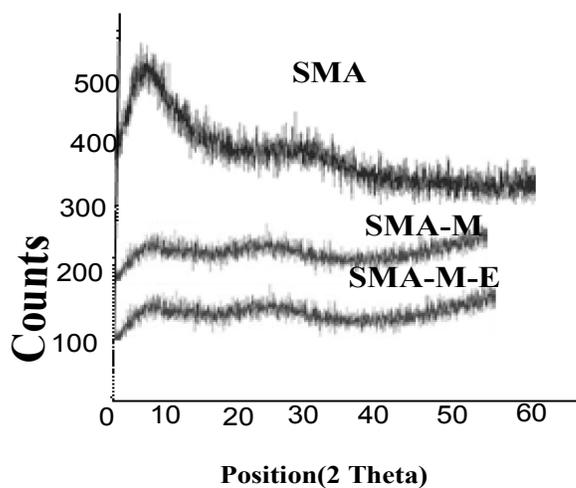


Fig. 3. XRD patterns of the synthesized copolymers

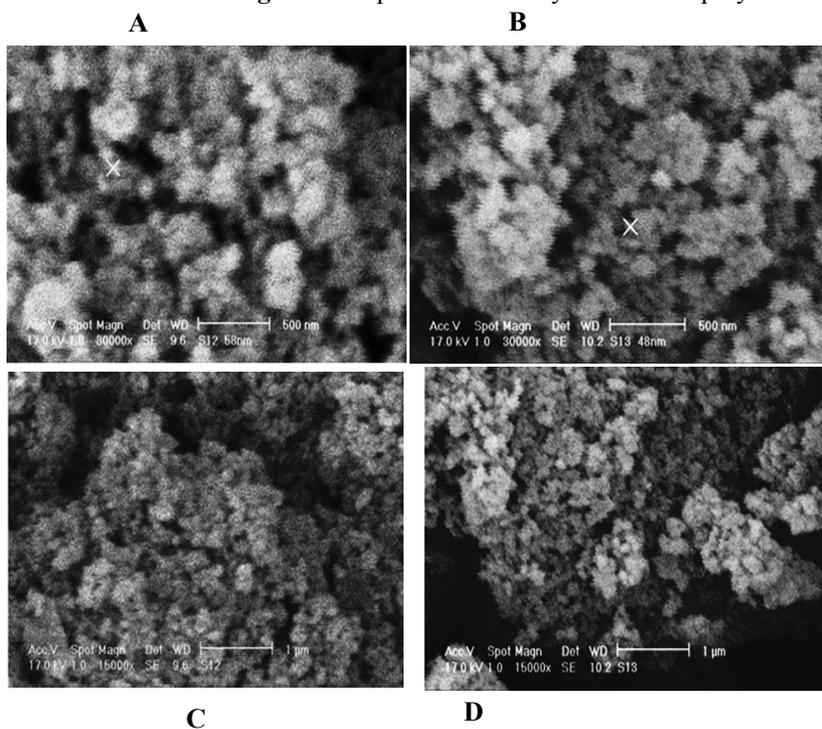


Fig. 4. SEM images of the chelating resins (A) SMA-M scale = 500 nm), (B) SMA-M-E (scale =500nm), and (C) SMA-M (scale =1 μm) and SMA-M-E (scale =1 μm).

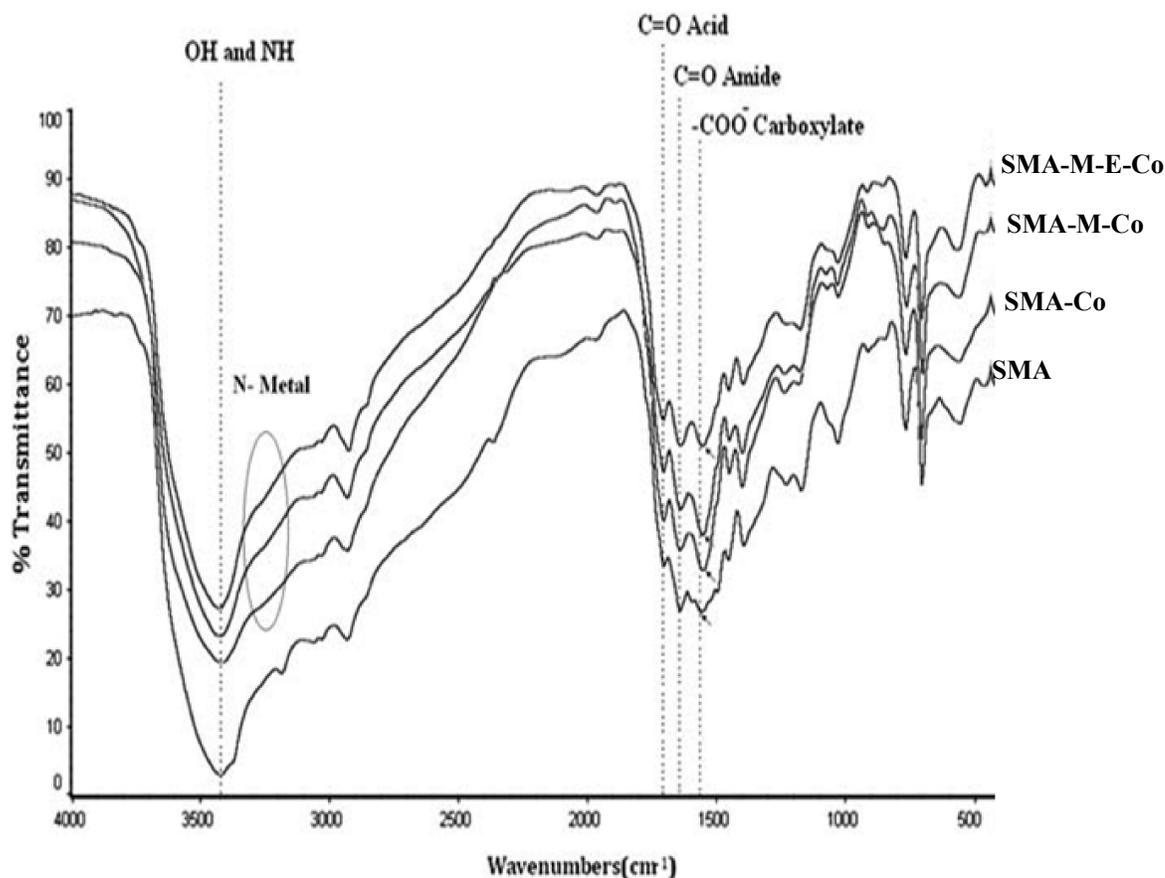
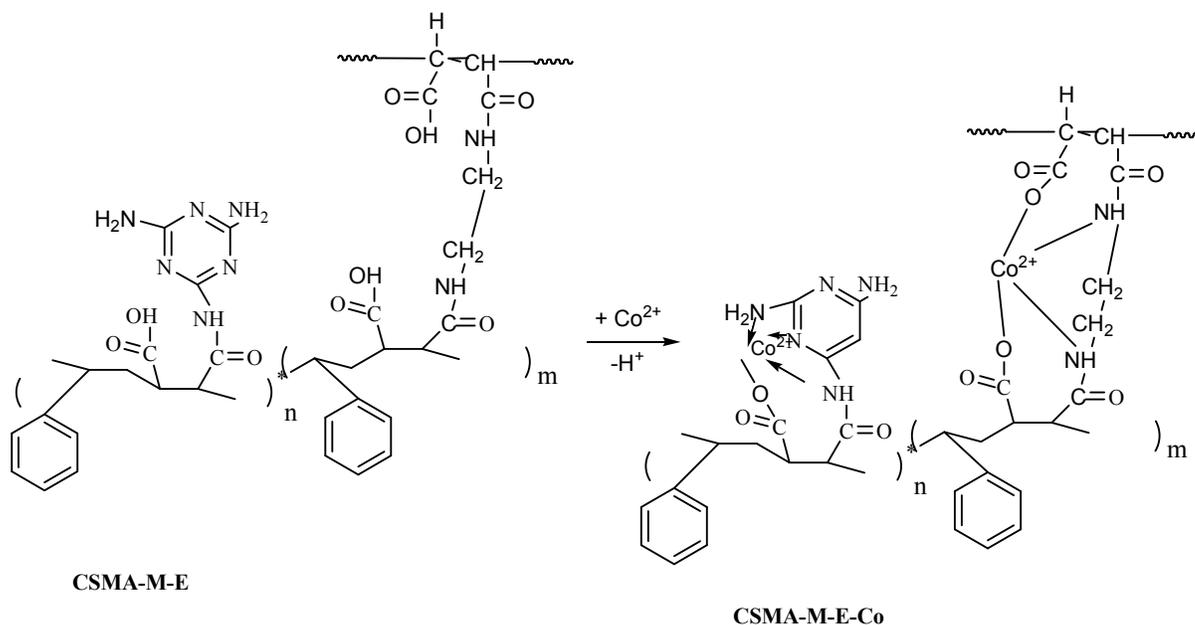


Fig .5. FT-IR spectra of SMA resin before and after complexation of SMA, SMA- M and CSMA-M-E with Co(II) ions

### 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 Co(II) ions and also cobalt (II) ions could form polymer – Co complex because Co(II) ions were contained unoccupied orbital's so, Cobalt(II) ions can play acceptor coordination bond role from N,O atoms on copolymers . Any Co(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 Co(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 cobalt 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].

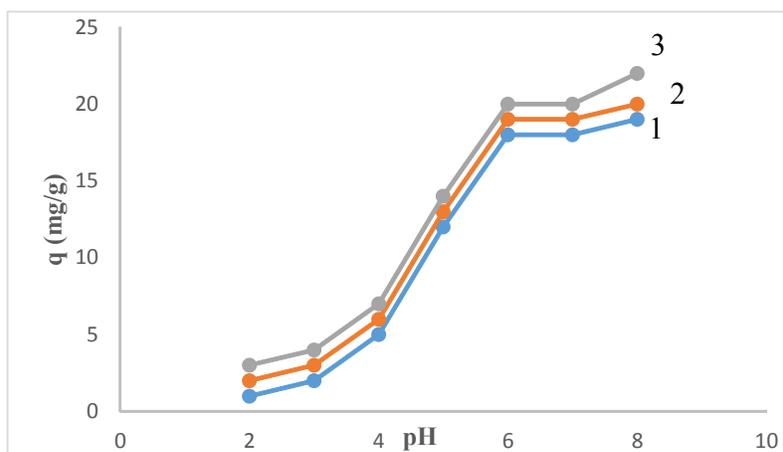


**Scheme 4.** The removal of Co(II) ions with CSM-M-E

### 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<sub>3</sub> (for pH=2.0, 4.0, 6.0, and 8.0) and with acetate buffer (for pH = 6.0). The adsorption efficiency of cobalt (II) on polymer as a

function of initial solution pH is exhibited in Figure 6. As can be seen from Figure 6, the adsorption efficiency gradually increased with the increase of initial solution pH, and pH=6 is optimized pH for this method. Because the maximum efficiency of cobalt (II) removal is obtained at initial solution pH = 6.0 (acetate buffer), this was considered as optimum value, and was used in all further experiments.

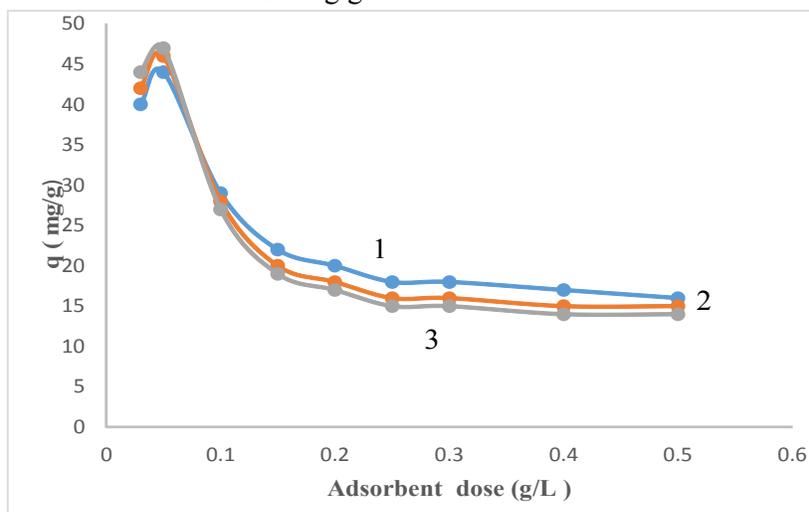


**Fig 6.** Effect of initial solution pH on cobalt (II) removal on (1) SMA (2) SMA-M (3) SMA-M-E with (50 mg Co(II)/L, polymer dose = 0.05 g/L; time = 4 h; t = 25 °C)

### 3.4 Effect of adsorbent dose

Figure 7 presents the effect of adsorbent dose for cobalt (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 cobalt (II) from aqueous solutions, and was selected as the optimum value for the adsorption experiments.



**Fig.7.** Effect of adsorbent dose for cobalt (II) removal on (1) SMA, (2) SMA-M, (3) SMA-M-E (50 mg Co(II)/L, pH = 6.0 (acetate buffer), time = 4h,  $t = 25^{\circ}\text{C}$ )

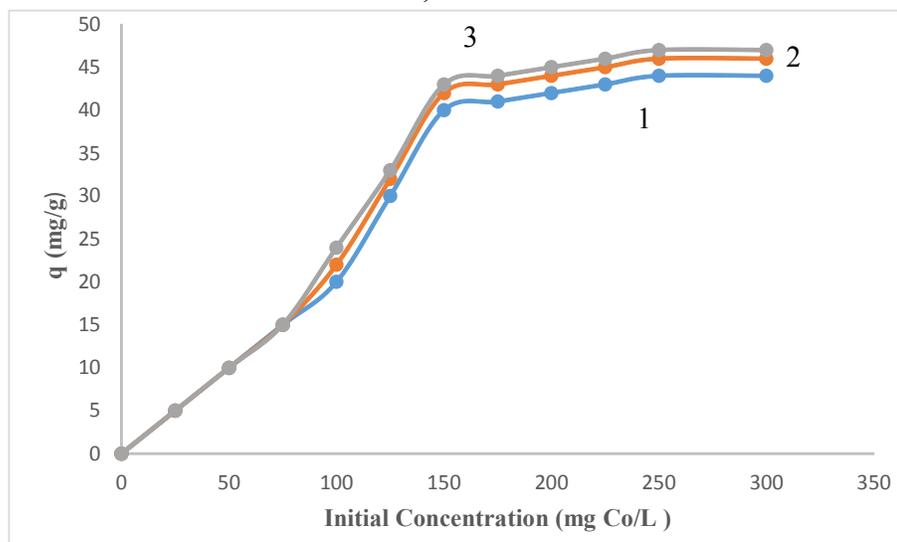
### 3.5 Effect of initial cobalt (II) concentration

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 cobalt (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 cobalt (II) ions to the SMA functional groups is inhibited. On the other hand, the efficiency of cobalt (II) removal follows the order: SMA-M-E ( $q = 48$  mg/g) > SMA-M ( $q = 46$  mg/g) > SMA ( $q = 44$  mg/g) for an initial cobalt (II) concentration of 240 mg/L. The

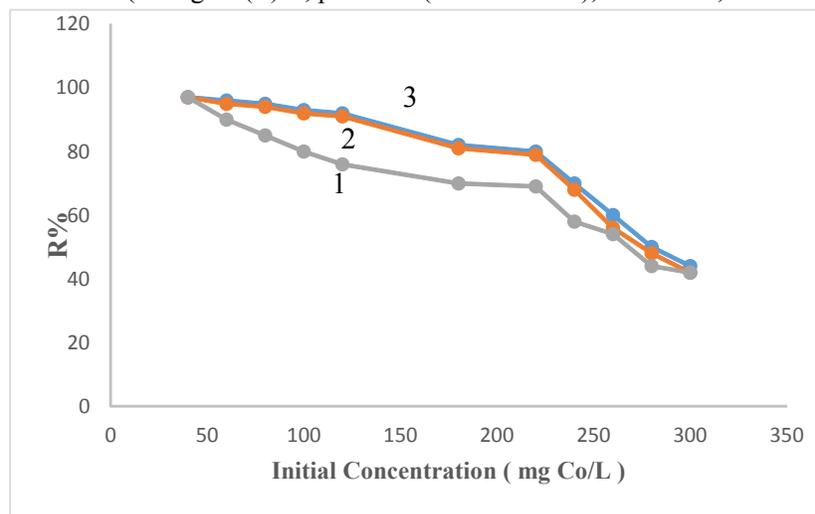
experimental results indicate that in case of polymer SMA-M-E the adsorption capacity for cobalt (II) increase with 4.5 %, in comparison with SMA. A good retention of cobalt (II) take place at initial metal ion concentration lower than 95 mg/L in case of SMA-M, 65 mg/L in case of SMA, and 120 mg/L in case of SMA-M-E, when the residual concentration is lower than the permissible limit for cobalt discharge. The increasing of initial cobalt (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 cobalt (II) from aqueous solutions, by adsorption SMA, SMA-M and SMA-M-E 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 undissociated and the number of electrostatic interactions between these and the metal ion is low. When, the

SMA-M and SMA-M-E the dissociation degree of functional groups increase drastically, and the ion-exchange interactions are facilitated.



**Fig 8.** Effect of initial cobalt (II) concentration on the adsorption on (1) SMA, (2) SMA-M, (3) SMA-M-E (50 mg Co(II)/L, pH = 6.0 (acetate buffer), time = 4 h, t = 25 °C)

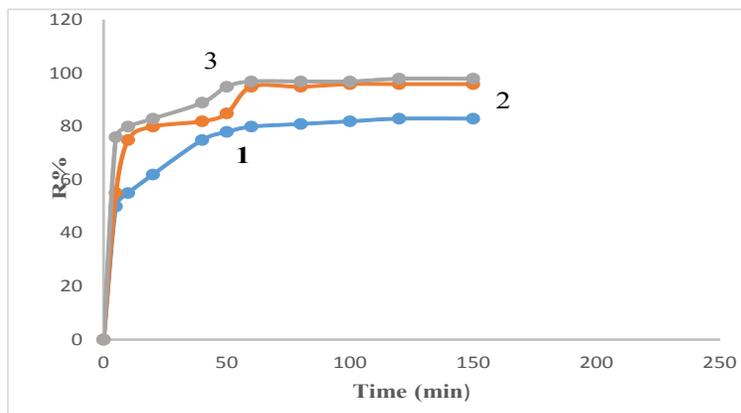


**Fig 9.** Effect of initial cobalt (II) concentration on the adsorption on (1) SMA, (2) SMA-M, (3) SMA-M-E (50 mg Co(II)/L, pH = 6.0 (acetate buffer), time = 4 h, t = 25 °C)

### 3.6 Effect of contact time

The effect of contact time between adsorbent and cobalt (II) aqueous solutions with an initial concentration of 50 mg/L and pH = 6.0 (acetate buffer) is illustrated in Fig. 10. It can be seen that the cobalt (II) removal

percent increase rapidly with the contact time up to 240 min for SMA, SMA-M and SMA-M-E. 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 cobalt (II) removal on (1) SMA, (2) SMA-M, (3) SMA-M-E (0.05 gpolymer/L,  $t = 25\text{ }^{\circ}\text{C}$ )

### 3.7 Adsorption isotherms

The different values of cobalt removal percentages 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 cobalt (II) adsorption on untreated and treated peat moss is illustrated in Fig. 11, and the isotherm

model parameters are summarized in Table 1.

Distribution coefficient ( $K_d$ ) was calculated from eq (3):

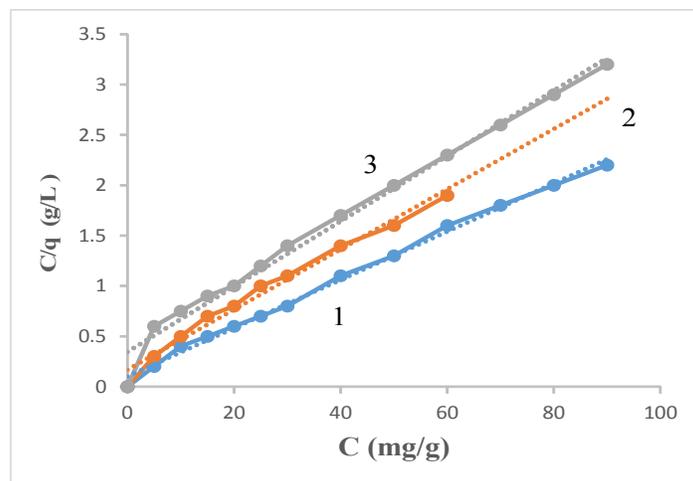
$$K_d = \frac{C_s}{C_e} \quad (3)$$

Where  $K_d$  is distribution coefficient and  $C_s$  and  $C_e$  is concentration of cobalt (II) ions (mg  $\text{Co}^{2+}$ /L) on resin and in solution.

The change in the free energy ( $\Delta G$ ) was calculated from the Langmuir constant using eq (4):

$$\Delta G = -RT \ln K_d \quad (4)$$

where:  $R$  is universal gas constant (8.314 J/mol K) and  $T$  is the absolute temperature. The negative values of  $\Delta G$  (Table 1) indicate that the removal process of cobalt (II) by adsorption on SMA and derivation of SMA are feasible and spontaneous. In addition, the lower and negative value of  $\Delta G$  obtained in case of cobalt (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 cobalt (II) adsorption on (1) SAM –M-E, (2) SMA-M (3) SMA (pH = 6.0 (acetate buffer), 0.05 g adsorbent/L, time =4 h

**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	$y= 0.0324X+0.3455$	$y=0.0299X +0.1676$	$y= 0.024X +0.1025$
$q_{max}(mg/g)$	30.86	33.44	41.67
$K_L (L/mg)$	0.0938	0.179	0.234
$\Delta G(Kj/mol)$	-25.06	- 26.22	-24.52

#### 4. CONCLUSION

In this study the adsorption behavior of cobalt (II) was investigated 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 cobalt (II) adsorption on un-treated and treated SMA was studied as a function of initial solution pH, adsorbent dose, initial cobalt (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 50mg Co(II)/L, when the efficiency of cobalt

(II) adsorption as a function of polymer type follows the order: SMA-M-E ( $q = 41.67 \text{ mg/g}$ ) > SMA-M ( $q = 33.44 \text{ mg/g}$ ) > SMA ( $q = 30.86 \text{ mg/g}$ ). The experimental results, also indicate that the removal percent of cobalt (II) increases with the initial solution and decrease with initial cobalt (II) concentration. The Langmuir isotherm model was used for the mathematical description of cobalt (II) adsorption on SMA-M-E, SMA-M and SMA. The maximum adsorption capacity ( $q_{max}$ ) is higher in case of cobalt (II) adsorption on SMA-M-E, than in case of cobalt (II) adsorption on SMA-M, and both are higher than the value obtained in case of cobalt (II) adsorption on SMA. In addition, the change in free energy ( $\Delta G$ ) calculated from Langmuir constant confirm the feasible and spontaneous adsorption of

cobalt (II) on SMA, SMA-M and SMA-M-E. The FTIR spectra revealed the carboxylate anions and secondary amine in the prepared chelating resin donated electron pairs to the metal ions [39-40].

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