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سنتزنانوذراتی ازپلیمرپلی استایرن آلترناتیو مالییک انیدرید برای حذف یون‌های نقره ازمحلول‌های آبی

رضا انصاری[۱و*]، ناصر صمدی[۲]، بختیار خداوردیلو[۱]
۱. بخش شیمی، دانشکده علوم، پردیس دانشگاهی دانشگاه گیلان، رشت، ایران
۲. بخش شیمی تجزیه، دانشکده علوم، دانشگاه ارومیه، ارومیه، ایران

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Synthesized Nano Particle Derivation of Poly (Styrene -Alternative-Maleic Anhydride) for the Removal of the Silver(I) Ions From Aqueous Solutions

Reza Ansari[1,*],Naser Samadi[2], Bakhtiar Khodavirdilo[1]
1. Department of Chemistry, Faculty of Science, University of Guilan, University Campus 2, Rasht, Iran
2. Department of Analytical Chemistry, Faculty of Chemistry, Urmia University, Urmia, Iran

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چکیده

در این تحقیق پلی استایرن–آلترناتیو–مالئیک انیدرید و مشتقاتی از آن باملامین و ملامین و۱،۲دی آمینواتان و۱،۳ دی آمینوپروپان به ترتیب سنتز شده‌اند. این روش یک روش بسیار ساده، ارزان، دقیق و پلیمرهای بکار رفته توانایی هفت بار بازگردانی را دارند. در این پژوهش قدرت جذب پلی استایرن–آلترناتیو–مالئیک انیدرید–ملامین ومشتقات آن برای حذف یون‌های نقره از محلول‌های آبی مورد بررسی قرار گرفته و این جاذب‌ها برای این کار پیشنهاد شده‌اند. دراین تحقیق اثر هر یک از پارامترهای مختلف مؤثر بر جاذب در فرآیند حذف یون‌های نقره مورد مطالعه و بررسی قرار گرفته و اثر هر یک از آنها بهینه شده است (نظیر زمان جذب، زمان تماس، مقدار جاذب، سرعت چرخش شیکر). بیشترین حذف یون نقره در pH =۶ اتفاق افتاده است و زمان تماس بهینه برای یون‌های نقره ۶۰ دقیقه است. بیشترین ظرفیت جذب CSMA-MP, CSMA-ME, CSMA-M به ترتیب برابر ۶۷,۵۷، ۷۶,۹۰ و ۹۵,۲۴ $\frac{mgAg^{+}}{g_{polymer}}$ بوده است. چنانچه مشخص شده است این جاذب‌ها برای حذف یون‌های نقره از محلول‌های آبی مناسب می‌باشند. این رزین‌ها بوسیله آنالیز FT-IR, SEM, XRD, DSC, TGA مشخص شده اند.

واژه‌های کلیدی

پراش اشعه ایکس، جذب، میکروسکوپ الکترون روبشی، حذف.

Abstract

In this research poly (Styrene–Alternative-Maleic Anhydride) (SMA) and derivations of SMA with Melamine, (Melamine + 1,2 Diamino Ethane) and (Melamine + 1,3 Diamino Propane) CSMA-M, CSMA-ME and CSMA-MP were synthesized, respectively. This method is very simple, cheap, precise and used polymers recyclable to seven terms. The purpose of the present work was exploring the adsorption power of CSMA-M and its derived polymer to removed silver(I) ions from aqueous solution. In this research, batch adsorption tests were exhibited and the effect of different parameters on this removal process has been studied. The effects of pH, adsorption time, metal ion concentration and the acidic remedy on the adsorption process were optimized. The optimum pH for adsorption was found to be 6.0. In adsorption explores, remained Ag^+ concentration arrives equilibrium in a short duration of 60 min. Maximum adsorption capacity, 67.57, 76.90 and 95.24 mg Ag^+/g polymer CSMA-M, SMA–ME and SMA–MP respectively.showed that this adsorbents were appropriate for removing silver(I) from aqueous solution. The resins were characterized by Fourier transform Infra Red(FT-IR) spectroscopy, Scanning Electron Microscopy (SEM), X-ray diffraction(XRD) and Differential Scanning Calorimetry (DSC), (Thermo Gravimetric Analysis) TGA analysis.

Keywords

X-Ray Diffraction; Adsorption; Scanning Electron Microscopy; Removal.

1. INTRODUCTION

Water is one of the most important needs for living in the world. All plants and animals must have water to live. It is also necessary for the human activities. Water pollution is increasing worldwide because jumping improvement of

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*Corresponding Author: ransari272@guilan.ac.ir

industry, increase human population, domestic and agricultural activities. The elimination of metal ions from industrial wastewaters using various adsorbents has been ever of extensive penchant [1-2]. So, industrial wastewaters often include remarkable contents of metal ions that would hazard common health and the environment if discharged without enough remedy. High concentrations of the metals in solution effect humans, animals and plant life. The contaminant of water and soil with metal ions increases relative with the extension of industrial activities [3-4]. In order that lessen processing expenses for these industrial wastewaters, most of the last studies have focused on the use of low expense adsorbents [5-6]. In the last years, application of polymers to control the pollution due to the effluents polluted with heavy metal ions has increased. Polymers have ion-exchange ability to eliminate undesirable metal ions and this property makes polymers desirable for wastewater remedy. The physical structure is porous, enclosing interconnected cavities in which the metal ions and water molecules are contained [7]. Silver is a very useful raw material in various industries due to its excellent malleability, ductility, electrical and thermal conductivity, photosensitivity and antimicrobial properties. Significant amounts of silver are lost in the effluents discharged from such industries and due to the toxicity of silver to living organisms, the removal of this metal from wastewaters is an important concern [8-12]. The presently available technologies for the removal of silver include precipitation, electrolysis, solvent extraction, the use of ion-exchange resins, chelating agents, etc. [13-17]. These processes can be profitably used on a large scale when the metal concentrations in effluents are sufficiently high, i.e. above 100 ppm [18–21]. Taking into account all the above, we have considered it of great interest to assess the ability of locally available polymers, for the removal of Ag^+ from aqueous solution and optimization of conditions for its maximum adsorption. To increase the efficiency of metal removal and to maximize the amount of metal recoverable from solution the effects of various parameters (especially that of pH of the medium and the acidic treatment of the polymers) on the Ag^+ removal process have been investigated. Also, the thermodynamics of the Ag^+ adsorption have been investigated. In recent years, the development of high-performance adsorbents (chelating polymers) on the Nano scale for the removal of heavy-metal ions from aqueous solutions has been considered a research priority in the environmental field. Among synthetic polymers, poly (styrene-alternative-maleic anhydride) (SMA) is a commercial, industrial, copolymer that is cheaper than any other polymer possessing a reactive group in the main chain or side chain for further functionalization .In this study, a novel chelating resin was synthesized by the chemical modification of the SMA polymer by Melamine (M) as a grafting agent under various conditions by the amidation reaction of maleic anhydride repeating groups in the polymer backbone. Also, the prepared resins were further reacted by 1,2-ethylenediamin or 1,3-propylenediamin as a crosslinking agent to form a tree-dimensional resins. The preparation of the cross linked resins with the presence of ultrasonic irradiation along with vigorous magnetic stirring gave rise to polymeric particles on the Nano scale [22]. The adsorption behavior of Ag^+ ions was investigated by synthesizing chelating resins at various pHs. In this work we were synthesized poly (Styrene – alternative- Maleic Anhydride) (SMA) and derivatives of SMA such as CSMA-M E and CSMA-MP. These modified polymers were appropriated for removal Ag (I) ions in aqueous solutions.

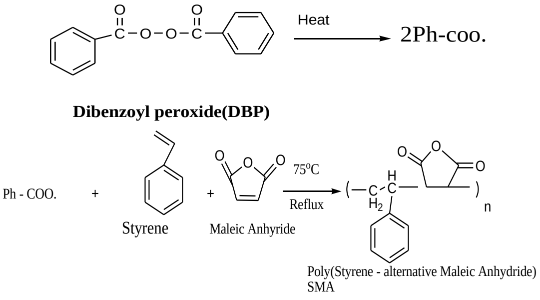
2. EXPERIMENTAL

2.1. Materials and Methods

Analytical-reagent grade $AgNO_3$ and other inorganic chemicals, including HNO_3 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, 1,2 Diaminoethane, 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. IR spectra were measured with a Fourier transform infrared spectrophotometer (Nexus-670, Thermo Nicolet, USA). The X-ray diffraction (XRD) spectra were recorded on an X’pert Philips X-ray photoelectron spectrometer (The Netherlands) with non mono chromate Mg Ka radiation as the excitation source. Atomic absorption spectrophotometry (AAS; Analytik jena nov AA -400, Germany) was used to determine the metal-ion concentrations\in aqueous solutions. The inherent viscosity of the resulting SMA polymer was obtained with an Ostwald Viscometer at 25ºC in a thermostated water bath. The elemental analysis of one of the resin was performed by a CHN analyzer (2400 series II, PerkinElmer Co., USA). The morphology of the particles was examined via scanning electron microscopy (SEM; XL30 Philips, Netherland).

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

The SMA polymer was prepared by the free-radical polymerization of maleic anhydride and styrene at 75ºC in the presence of benzoyl peroxide as an initiator. The experience was described as follows: 2g (0.0192mol) 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 (0.000768mol) of Dibenzoyl peroxide was added to mixture as an initiator. The reaction mixture was refluxed for 6 h at 75ºC under inert gas in the 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 60ºC (yield = 97%).



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

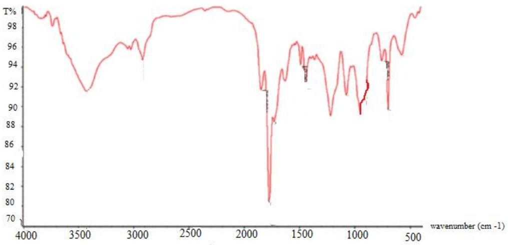
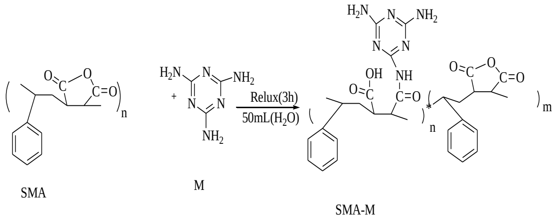


Fig. 1. FTIR spectrum of the SMA copolymer.

2.3. Preparation of SMA-M

For a synthesis of the grafted SMA polymer,1 g (0.005 mol) of SMA polymer 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 Tri ethylamine (TEA) as a catalyst and 50 mL of water as a solvent was 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 normal hexane as a non- solvent and were separated by filtration and washed with normal hexane several times. The product was dried in a vacuum oven for 24 h at 60ºC (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).

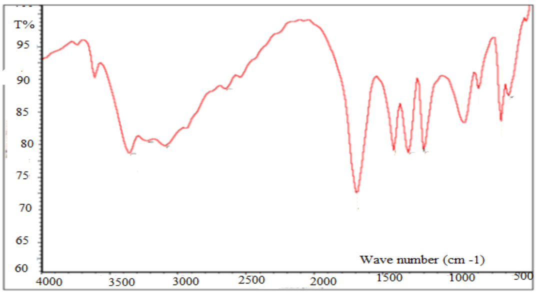


Fig. 2. The FTIR spectrum of the SMA -M polymer (modified of SMA with melamine).

2.4. Synthesis of the SMA with 1,2 Diamino ethane (CSMA-ME) and 1,3 Diamino propane (CSMA–MP)

The grafted Melamine (M) functioned SMA polymer (CSMA-M) was prepared by the simultaneous reaction of the SMA polymer with Melamine and 0.09 g of 1, 2-domination and 1,3 Diamino propane as the cross-linking agent.Then, 0.5 mL (0.004 mol) of tri-ethylamine (TEA) as a catalyst. The reaction mixture was refluxed for 3 h under inert gas in the presence of ultrasonic irradiation along with vigorous stirring bar in the water. It can be said that the preparation of cross linked 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 60ºC for 24 h. The CSMA–M-E chelating polymer was prepared by the step-by-step reaction of the SMA polymer with Melamine as a grafting agent and 1,2-diaminoethane as a cross-linking 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 60ºC for 24 h. The yield of the reaction was 96%. The same procedure was repeated with 1,3-diaminopropane instead of 1,2-diaminoethane as the crosslinking agent for the preparation of CSMA–M-P. The yield of the reaction was 97%. The elemental analysis of the CSMA–M-P resin was carried out and showed 65.16% C, 7.64% H, and 8.73% N. The synthesis process of the chelating resins is shown in Scheme 3.

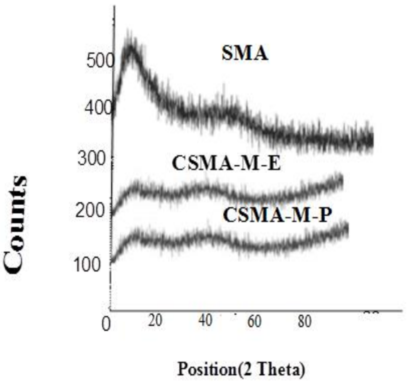


Fig. 3. XRD patterns of the synthesized polymers.

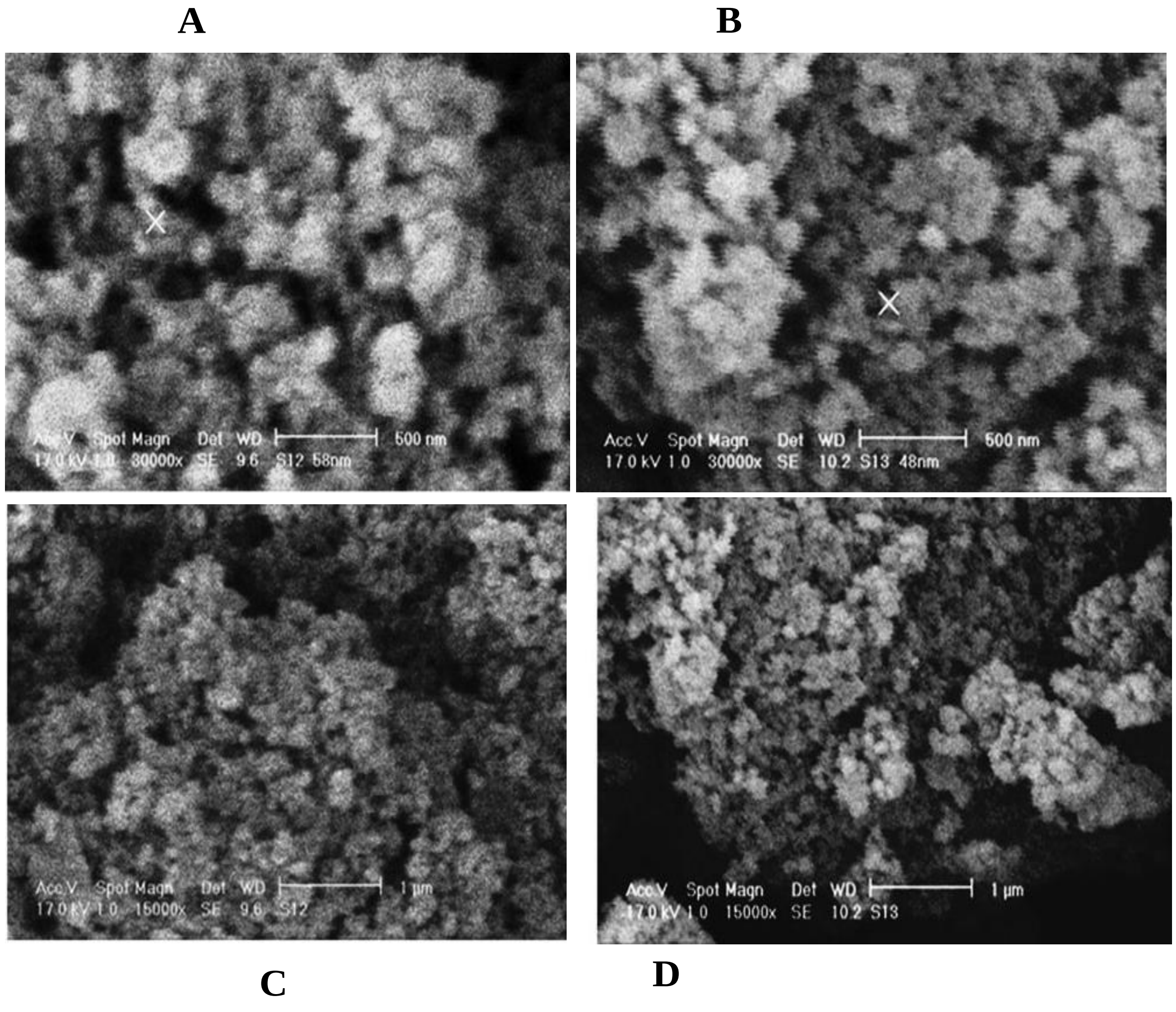
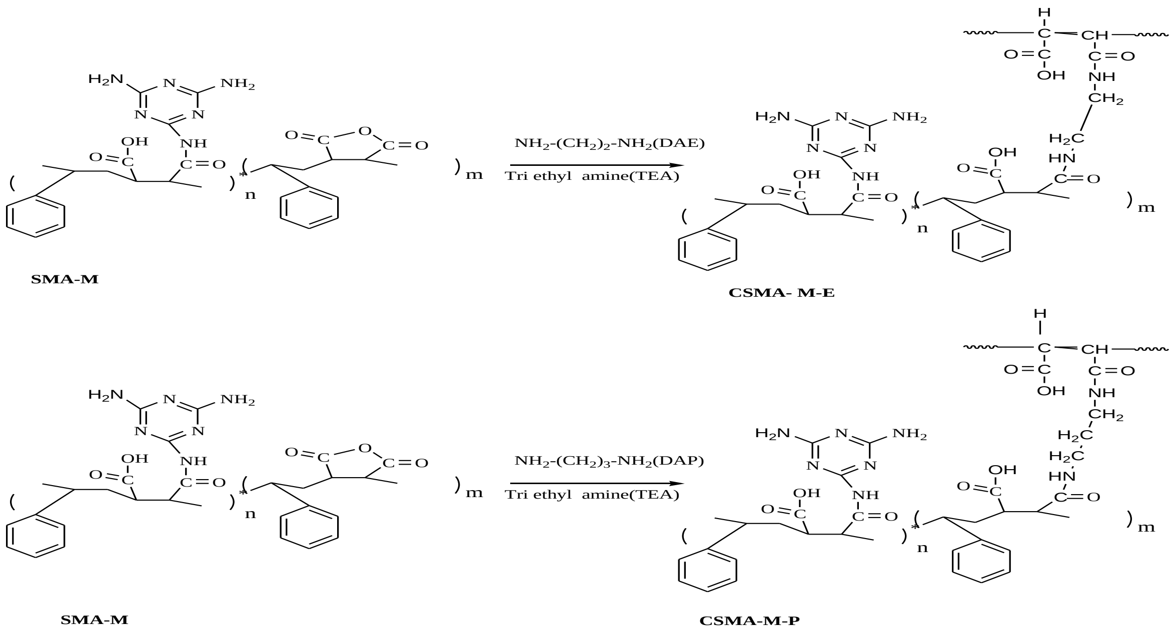


Fig. 4. SEM images of the chelating resins (A) SMA–M-E scale = 500 nm), (B) SMA–M-P (scale =500nm), and (C) SMA–M-E (scale =1µm) and SMA–M-P (scale =1 µm).



Scheme 3. Synthesis of the 1,2 Diamino ethane (CSMA-M-E) and 1,3 Diamino propane(CSMA–M-P).

2.5. Adsorption Studies

Ag^+ solution was obtained from its nitrate salt, $AgNO_3$ (Merck (Germany), >99% sincerity) with deionized water with a conductivity amount of 18.2 MX (stored from Barnstead Nano net Diamond). The effect of pH on the silver adsorption was studied using 100 ppm Ag^+ including solution over the pH ranges 2.0–8.0. The pH of silver solutions was regulated by suitable using HNO_3 or NaOH. Adsorption experiments were poured in polypropylene beakers. In each adsorption study, 50 mg polymer (dry weight) was added to 50 ml of the Ag^+ solution at 25ºC and magnetically stirred continuously. After 1 h, the aqueous phase was separated from the polymer with filtered by leach paper and the concentration of Ag^+ in that phase was measured infiltrate by using Atomic Absorption Spectrophotometer (AAS). Each adsorption test was administrated in triplicate and the mean of 6 AAS determinations was recorded. The effect of the initiative Ag^+ ion concentration on the adsorption capacity of the polymer at the favorite pH was measured using solutions with concentrations ranging from 10 to 150 ppm. Again, 50 mg polymer (dry weight) was added to 50 mL of the Ag^+ solution at 25 ºC and magnetically stirred count continuously only. After 1 h, the aqueous phase was separated from the polymer filtered by leach paper and the concentration of Ag^+ in that phase was measured infiltrate by using AAS. The value of adsorbed Ag^+ ions (mg Ag^+/g polymer) was computed from the decrease in the concentration of Ag^+ ions in the medium by considering the adsorption volume and used value of the polymer:

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad (1)$$

Here, q_e is the value of metal ions adsorbed onto unit mass of the polymer (mg Ag^+/g polymer) at equilibrium; C_i and C_e are the concentrations of the metal ions in the initiative solution and in the aqueous phase after remedy for confidence adsorption time, respectively (ppm Ag^+); m is the value of polymer used (g – gram) and V is the volume of silver solution (L –Liter).To measure the adsorption rate of Ag^+ ions from aqueous solution, same batch adsorption and analysis procedure given above were 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. HNO_3 (0.1M) was used as desorption agent. Polymer samples carrying 62 , 68 and 72 mg Ag^+/g (CSMA-M, SMA–M-E and SMA–M-P respectively) were placed in this desorption medium (50 mL) and stirred magnetically for 30 min at 25 ºC. After 30 min, the aqueous phase was separated from the polymer and the concentration of Ag^+ in that phase was measured. Also, the polymer sample primed with the maximum value of Ag^+ ions was treated with HNO_3 to measure the effect of acidic remedy on the adsorption capacity. In this part, 50 mg (dry weight) portion of a polymer containing 49 mg Ag^+/g was treated with 50 mL of 0.1 M HNO_3 solution at 25 ºC for 3. After stirring, the aqueous phase was separated from the polymer and the concentration of Ag^+ in that phase was measured [40]. This adsorption/ desorption cycle was repeated by using the same polymer sample to monitor the effect of the remedy with acid on the adsorption capacity

3. RESULT AND DISCUSSION

3.1. Synthesis and Characterization of the SMA–Melamine Copolymers

The SMA polymer was obtained by the method considered in ref [23] Fig. 1 shows the FTIR spectrum of the SMA polymer. In this spectrum, the characteristic of anhydride bonds at 1735, 1784, and 1856 cm^{-1} are exhibited. The innate viscosity of the incoming SMA polymer was computed with an Ostwald Viscometer at 25ºC 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 polymer. The amine group of Melamine reacted with maleic anhydride repeating groups in the SMA polymer backbone to form an alkyl amide linkage and a carboxylic acid group. Amide bonds are importantly resistant to hydrolysis, so the incoming polymer was resisting in acidic and basic media. To obtain the tridimensional CSMA–ME and SMA–MP polymers, the reaction was performed with a step-by-step reaction of the SMA polymer with Melamine (M) as a grafting agent and 1,2-diaminoethane or 1,3-diaminopropane as a crosslinking agent. Fig. 5 displays the FTIR spectra of the SMA–M, SMA–ME, and SMA–MP polymers. The comparison of the SMA–M and derivatives 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 1662 cm^{-1}. In the case of the SMA– ME and SMA–MP polymers, 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 1622 cm^{-1} and the Carbonyl of Carboxylate anion at about 1555 cm^{-1}. All of the pendant carboxylic acids of the resins were converted to free carboxylate ions because of the existence of aminopyridine 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 Ag (I) 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. Fig. 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 the increasing covalent nature of the carbonyl band in the results of complexation with ionic metals and appeared about 1687–1702 cm^{-1}. It was interesting that the absorption peaks at about 1700 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 tends toward ionic properties. The bands at 1622, 1555, 1449, and 1238 cm^{-1}shifted to a lower frequency; this indicated that the metal coordination through the chelating ligands was done on the polymer network. Also, the absorption bands characteristic of the aromatic parts of the matrix (1022, 910, 761, and 700 cm^{-1}) were not influenced by the metal Complexation. The XRD patterns of the synthesized polymers are depicted in Fig. 3. The diffraction patterns showed that the polymers were amorphous. Indeed, there was only a broad diffraction hump at about $2\theta= 20^o$; this indicated the amorphous nature of the polymers. So, the presence of the grafting and crosslinking agent in the polymer backbone did not affect the amorphous structure of the polymer [24]. Fig. 4 shows the SEM micrographs of typical SMA–ME and SMA–MP, in which the particles possessed an almost uniform distribution of size with spherical shapes. The diameter of the observed particles in the SMA–ME and SMA–MP images was estimated to be below 100 nm.

3.2. Adsorption of silver (I) ion on Polymers

The silver ion uptake is introduced to various mechanisms of ion-exchange and adsorption processes. During the ion-exchange process, silver ion exchange with protons of surface hydroxyl groups Polymers which we used them were contained hydroxyl groups so, they react with Ag (I) ions and also silver (I) ions could form polymer – Ag complex because Ag (I) ions were contained unoccupied orbital's so, silver(I) ions can play accepter coordination bond role from N, O atoms on polymers. Any Ag (I) ion can accept two dative bonds from N, O atoms on polymers. When the exchange site is a hydroxyl group, the exchange reaction occurs and in this case, silver ions (Ag^+) exchange with the H^+ ions. The ion-exchange processes in polymers are affected by several factors such as concentration and nature of cations, 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 various environments (such as acidic media) in the applications of polymers as an ion exchange as follows reactions (Scheme 4):

$$\text{Polymer-OH} + Ag^+ \longrightarrow \text{Polymer-}O^- Ag^+ + H^+ \qquad (2)$$

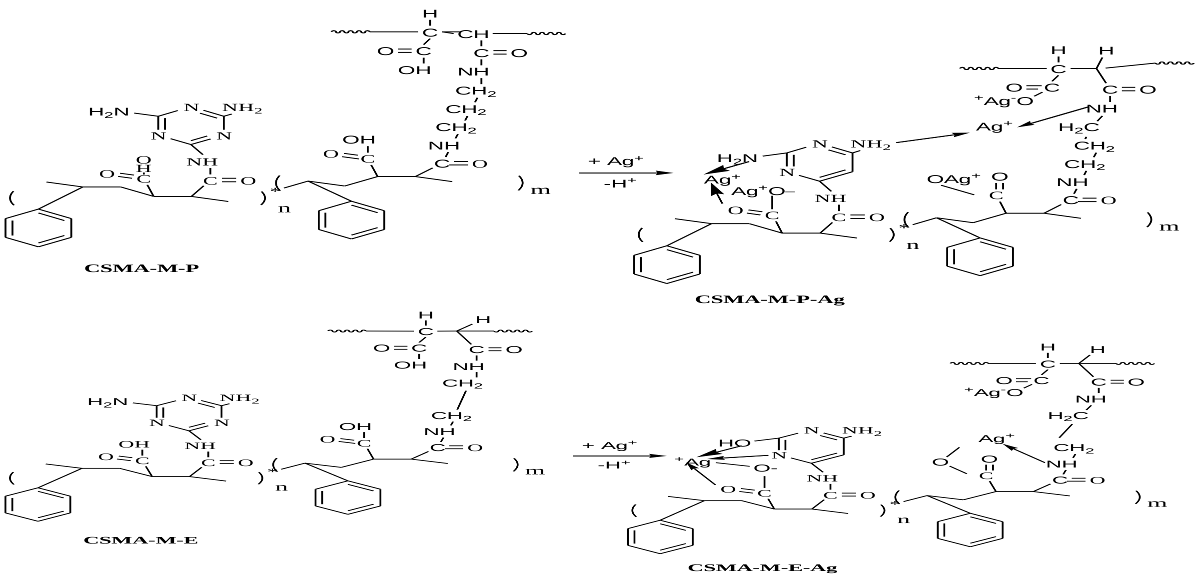
3.3. Influence of variables on Ag^+ adsorption

Effect of time

Table 1 Explains the adsorption of Ag^+ ions by polymer (CSMA-M, SMA–M-E and SMA–M-P) as an accessory of time. The values of Ag^+ ions adsorbed were computed using Eq. (1). The adsorption conditions are given in the figure explanations. The slopes of the lines joining the data points in the figure resound the adsorption estimates. As it is seen, high adsorption rates were appearing at the beginning and then plateau values were reached within 60 min. In a prior study, several adsorbents were used for silver (I) removal and 5 hours are reported as an equilibrium adsorption time [23-25]. The adsorption rate prepared with the polymer seemed to be very satisfactory. Due to the preference of short adsorption times for the minimum energy consumption, CSMA-M can be accepted as an efficient adsorbent for Ag^+ removal when its short adsorption time is considered.

Table 1. Variation of the adsorbed amount of Ag^+ as a function of adsorption time (Ag^+ concentration = 100 ppm, pH = 6.0).

Time (min)	5	10	15	20	25	30	35	40	45	50	55	60	65	70	90
CSMA-Mq_t (mg.g^{-1})	5	8	10	12	13	18	20	25	30	32	35	65	55	54	55
CSMA-ME	9	12	15	18	20	22	24	30	32	35	38	68	64	63	62
CSMA-MP	8	14	15	18	21	23	24	30	33	34	38	70	64	63	61



Scheme 4. The removal of Ag (I) ions with CSM-M-E and CSMA-M-P resins from aqueous solutions.

3.4. Effect of pH

The pH relationship of Ag^+ adsorption onto polymers is exhibited in Table 2. Tests were performed using silver ion solutions at various pH amounts. As it is seen in Table 2, q_e is low at low pH amounts. The value of q_e is increased by increasing the pH value and arrives a plateau at a pH value of 6.0. It is obvious that using solutions at pH amounts between 4.0 and 8.0 gives the highest q_e values. So, we can perform this Ag^+ adsorption process, not only as a confidence pH value, but also in a wide range of pH amounts. These results are in agreement with several prior studies on the silver removal by versatility of materials which evinced that the adsorption capacity is low at pH values below 6.0 because of the contest between the protons and Ag^+ ions for the exchange sites on the polymer particle [26-27]. So, increased external H^+ concentration (due to lower pH) may have affected silver ion removal by ion exchange by direct contest effects between the protons and silver ions for the exchange sites on the polymer. This result can be considered as an evidence for the silver (I) ion removal by an ion-exchange mechanism in this explore.

3.5. The effect of initial Ag^+ concentration

Tests guidance with various initiative Ag^+ concentrations illustrate that the value of Ag^+ ions adsorbed per unit mass of polymer (i.e., the adsorption capacity) increases with the initiative concentration of Ag^+ ions (Table 3). This increase continues up to 100 ppm Ag^+ and ulterior this amount, there is not an important change in the value of adsorbed Ag^+ ions. This plateau exhibits saturation of the active sites accessible on the polymer samples for interplay with metal ions, the maximum adsorption capacity. It can be induced that percentage adsorption for Ag^+ decreases with increasing metal concentration in aqueous solutions. These results exhibited that energetically less suitable sites become circumvented with increasing metal concentrations in the aqueous solution. The metal uptake can be scored to various mechanisms of ion-exchange and adsorption processes as it is dependence in many prior works. The maximum adsorption capacity was computed as 49 mg $Ag^{+/}g$ polymer. Various adsorbents have been reported for the adsorption of Ag^+. SMA was used and an adsorption capacity of 41 mg Ag^+/g polymer was found. In another study, a series of modernity samples were used and an adsorption capacity range was found to be 4–23 mg Ag^+/g polymer.

In a later work, different types of Chitosan were used for Ag^+ adsorption and the maximum adsorption capacity achieved in this case was 43 mg Ag^+/g adsorbent. In another one, coal used for the removal of silver and maximum adsorption capacity was found at 1.87 mg Ag^+/g col.If it is introduced that we have used SMA-M, SMA–ME and SMA–MP for removing silver (I) ion from aqueous solutions and maximum adsorption capacity is 67.57, 76.90 and 95.24 mg Ag^+/g polymer respectively.

3.6. Effect of acidic treatment

When the Ag^+ carrying polymer samples were treated with 0.1 M HNO_3, it was watched that remedy of polymer with an acid solution decreases the adsorption capacity of the polymer sample with developing cycles, as can be seen from Table 4. Nonetheless the fact that, about 90–100% of the initially adsorbed value of Ag^+ has extricated into the acidified water, confidence loss of metal elimination efficiency during developing adsorption/desorption cycles was reported. In an earlier study, this behavior was affiliated to the structural changes formed as an outcome of the interaction of polymer with the acid solution.

3.7. Analysis of Silver in dental-unit (DU) waste water

Dental unit wastewater samples were assembled from The dental chair, Farhangian Hospital,

Table 2.. Variation of the adsorbed amount of Ag^+ as a function of pH
(Ag^+ concentration = 100 ppm; temperature = 25 ºC).

pH		2	3	4	5	6	7	8	9	10
q_t (mg.g^{-1})	CSMA-M	10	25	30	35	63	56	54	55	52
	CSMA-ME	11	26	32	37	69	58	54	56	56
	CSMA-MP	12	27	33	38	72	57	52	53	56

Urmia city, at the end of the working day. An accurate volume of the sample was digested by AAS digested in the presence of suitable volumes of both concentrated HNO_3 and H_2O_2 (30%) for 1 h. The obtained solution was neutralized with NaOH (5 M) and 10mL of this solution was treated under the conditions of the recommended procedure.

3.8. Langmuir isotherm

Adsorption isotherms are significant for the explanation of how Sorbate will interact with a Sorbent and climacteric in modifying the use of adsorbent. These adsorption model parameter amounts of these two equilibrium adsorption models are measured. The Langmuir model introduces one of the first theoretical remedies of non-linear Sorption and offers that uptake happens on a homogenous external by mono layer Sorption without effect between adsorbed molecules. The Langmuir isotherm describes mono layer adsorption, linearized model of the Langmuir isotherm can be exhibited by the following equation (3).

$$\frac{C_e}{q_e} = \frac{1}{q_e\, K_L} + \frac{C_e}{q_{max}} \qquad (3)$$

Where, the equilibrium concentration is C_e (mg/L), the value of Silver (I) ion adsorbed per unit weight of adsorbent at equilibrium is q_e (mg/g), q_{max} is the theoretical maximum adsorption capacity (mg/g), K_L is the Langmuir isotherm constant (L/mg). The amount of R^2, K_L and q_{max} were measured from the slopes and amputates of the linear plots of C_e/q_e versus C_e (Table 5 and Fig. 5).

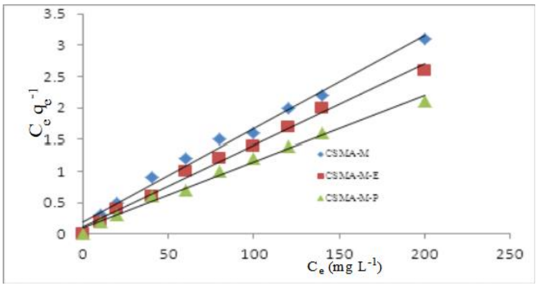


Fig. 5. Langmuir isotherm for Silver (I) ion adsorption on CSMA-M, CSMA-M-E and CSMA-M-P.

The Langmuir parameters can also be used to predict affinity between the adsorbate and the adsorbent using the dimension separation factor (R_L), which has been defined as below:

$$R_L = \frac{1}{1 + K_L\ C_o} \qquad (4)$$

Where K_L is the Langmuir constant (L/mg) and C_o is the concentration of toxic heavy metal ions, in mg/L. The amount of R_L illustrated the type of the isotherm to be either undesirable ($R_L > 1$), linear ($R_L = 1$), desirable ($0 < R_L < 1$), or irreversible ($R_L = 0$). Because R_L is less than 1 ($0 < R_L < 1$) for all of three adsorbents so Langmuir isotherm is desirable (Table 5).

Table 3. Variation of the adsorbed amount of Ag^+ ions as a function of Ag^+ concentration (pH = 6.0; temperature = 25ºC).

Initial concentration of Ag^+ (ppm)		10	20	30	40	50	60	70	100	120	150	200	250
q_t (mg.g^{-1})	CSMA-M	10	25	30	35	55	55	54	62	64	62	63	62
	CSMA-ME	11	27	33	36	58	60	62	70	65	63	60	61
	CSMA-MP	12	28	33	37	62	65	66	75	64	64	59	60

Table 4. The adsorption capacity of the polymer towards Ag^+ions during the acidic treatment cycles. Experimental conditions for Ag^+ adsorption: initial concentration of Ag^+ ions = 100 ppm, pH = 6.0, temperature =25ºC.

Cycle number		1	2	3	4	5	6	7	8
q_t (mg.g^{-1})	CSMA-M	68	60	40	32	30	25	20	19
	CSMA-ME	70	62	42	30	32	27	22	21
	CSMA-MP	75	61	41	29	28	26	21	20

Table 5. Characters of Langmuir isotherm.

Resin	Equation regression	K_L (L.mg^{-1})	R_L	q_m (mg.g^{-1})	R^2
CSMA-M	Y= 0.0148X + 0.192	0.08	0.111	67.57	0.9884
CSMA-ME	Y= 0.0130X + 0.1074	0.121	0.076	76.90	0.9924
CSMA-MP	Y= 0.0105X + 0.104	0.100	0.090	95.24	0.9912

3.9. Desorption studies

In metal ion removal process, it is significant to easily desorb the adsorbed metal ions under appropriate conditions. In the desorption studies 0.1M HNO_3 was used as desorption agent. The polymer samples loaded with the maximum value of Ag^+ ions were placed in the desorption medium and the value of ions desorbed within 30 min determined. Fig. 6. Shows the data of repeated adsorption/desorption cycles for Ag^+ ions after 7 cycles. The data show that there is a slight decrease in the adsorption capacity of the polymer with progressing cycles. Hence, we can induce that adsorbent, CSMA-M, SMA–M-E and SMA–M-P polymers, can be used repeatedly without Vic timing its adsorption capacity towards Ag^+ ions.

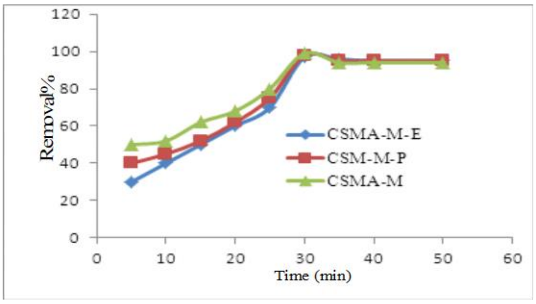


Fig. 6. Effect of time on desorption of silver (I) ion.

4. CONCLUSIONS

This method is very simple and cheaply and precise and used polymers recyclable to seven terms. In this study, the interaction between Ag^+ and polymers has been explored. The results indicated that several factors such as pH, adsorption time, Ag^+ concentration and acidic remedy affect the adsorption process. The physico-chemical characteristics of wastewaters from altering sources can be much more complex compared to the aqueous metal solution used in this study. Because of this, the effects of other blends of wastewaters on commercial metal adsorption process should be measured. Though, this work can be introduced a stickler study to evolve that CSMA-M, SMA–ME and SMA–MP, are proper and proficient material for the adsorption of Ag^+ from aqueous solution. Notwithstanding the fact that polymers have been extensively applied to the metal ion removal, the administration of the polymer produced in this work can be compared due to the lack of literature data, including interaction between the polymer and silver (I) ion in this way. Maximum adsorption capacity is SMA–MP> SMA–ME> CSMA-M. The resins were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, X-ray diffraction, and DSC (Differential Scanning Calorimetry), (Thermo Gravimetric Analysis) TGA analysis.

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