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حذف یون‌های منگنز(II) از محلول‌های آبی با به‌کار بردن مشتقات پلیمرپلی استایرن آلترناتیو مالئیک انیدرید

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Removal of Manganese Ions From Aqueous Solutions Using Polymers Derivations of Poly (Styrene-Alt- Maleic Anhydride)

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چکیده

در این مطالعه رزین‌های کیلیتی به‌عنوان مواد مناسبی برای بازیابی منگنز (II) از محلول‌های آبی مورد ارزیابی قرار گرفت. این رزین‌های اصلاح شده در حضور اشعه ماواربنفش با ۱و۲-دی آمینو اتان واکنش داد تا یک رزین سه بعدی در مقیاس نانو حاصل شود. رزین مورد استفاده در این کار کوپلیمری از پلی استایرن/مالئیک انیدرید بود که با روش جذب اتمی حذف یون‌های منگنز از محلول آبی مورد مطالعه قرار گرفت. روش ساده، حساس، ارزان و سریع می‌باشد. رفتار جذبی رزین در pH های مختلف ارزیابی شد که نشان داد حتی در pH های اسیدی نیز حذف یون‌های انتخاب شده انجام می‌شود. رزین مورد اشاره جهت حذف منگنز از نمونه‌های حقیقی نظیر آب فاضلاب‌های صنعتی به‌کار رفت که نتایج خوبی از حیث کارایی حاصل شد. معادلات سینتیکی نفوذ درون‌ذره‌ای، شبه مرتبه دوم و شبه مرتبه اول برای شبیه‌سازی داده‌های جذبی به‌کار رفت و نشان داد، داده‌ها با رفتار سینتیکی شبه مرتبه دوم مطابقت دارد. مشخصه‌یابی رزین با روش‌های FT-IR، SEM و XRD انجام شد.

واژه‌های کلیدی

حذف منگنز؛ پراش اشعه ایکس؛ رزین های کیلیت؛ میکروسکوپ الکترونی روبشی.

Abstract

In this study chelating resins have been considered to be suitable materials for the recovery of Manganese(II) ions in water treatments. These modified resins were further reacted with 1,2-diaminoethan in the presence of ultrasonic irradiation for the preparation of a tridimensional chelating resin on the Nano scale for the recovery of Manganese II) ions from aqueous solutions. In this work we used copolymers derivate resin of poly (styrene – Alternative - Maleic Anhydride) and Atomic Absorption Spectroscopy for removing and determining Manganese(II) ions .The method is simple, sensitive, inexpensive and fast. The adsorption behavior of Manganese(II) ions were investigated by the synthesis of chelating resins at various pH’s. The prepared resins showed a good tendency for removing the selected metal ions from aqueous solution, even at acidic pH. Also, the prepared resins were examined for the removal of Manganese(II) ions from real samples such as industrial wastewater and were shown to be very efficient at adsorption in the cases of Manganese(II) ions . The pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetics equations were used for modeling of adsorption data and it was shown that pseudo-second-order kinetic equation could best describe the adsorption kinetics. The intra-particle diffusion study revealed that external diffusion might be involved in this case. The resins were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, X-ray diffraction analysis.

Keywords

Removal of Manganese; X-ray Diffraction; Chelating Resins; Scanning Electron Microscopy.

1. INTRODUCTION

Metal ions are not only valuable intermediates in metal extraction, but also important raw materials for technical applications. Accordingly, complexation of metal ions is an important technique for recovering metals from various sources and for their removal from streams in municipal and industrial waste. As a consequence,

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*Corresponding Author: b.khodavirdilo@yahoo.com complexation, separation and removal of metal ions have become increasingly attractive areas of research and have led to new technological developments. Metal-chelating and ion exchange polymers were used in hydrometallurgical applications such as recovery of rare metal ions from seawater and removal of traces of radioactive metal ions from wastes [1]. Water pollution by heavy metals, through the discharge of industrial effluents, is a global environmental problem. The presence of heavy metal ions in municipal and industrial wastewater and their potential impact on the environment and human health have been a subject of scientific research for a long time because of their extreme toxicity even at low concentrations, and their tendency to accumulate in the food chain [2]. The removal of metal ions from aqueous solutions is a serious problem in many countries. On the one hand, soluble manganese presents a significant treatment challenge to many water utilities, causing operational concerns. While application of free chlorine to oxidize Manganese prior to filtration can be effective, this is not feasible for surface water treatment plants using ozonation followed by bio filtration because it inhibits biological removal of organics [3]. On the other hand, heavy metal removal, including Manganese removal, performed at a pH range in which a given metal undergoes an adsorption process, in industrial effluents by sequential adsorbent treatment, was set as a useful method for wastewater treatment [4]. Although dissolved Mn(II) ions are not known to be toxic and even block the toxic effect of hydrogen ions[5], they have undesirable effects on water use. An excess release of industrial effluent to natural water bodies causes heavy pollutant load to the aquatic environment. In line with this, the contamination of aquatic environment with heavy metal toxic ions is a serious concern because of its persistency and the level of toxicity occurring towards biological systems. Various industries, viz. electroplating, metal processing, textile, battery manufacturing, tanneries, petroleum refining, paint, pesticides, pigment manufacturing, printing, photographic industries, etc. are known to be culprit of releasing excessive amount of toxic metals, ultimately entering into the aquatic environment and leading to significant environmental imbalances [6]. The metal or metalloids of major environmental concern are arsenic, cadmium, chromium, cobalt, copper, lead, manganese, mercury, nickel and zinc [7]. Unlike organic pollutants, heavy metals are non biodegradable and are accumulated in living tissues, causing various diseases or biological disorders [8]. Therefore, water contaminated with heavy metal toxic ions requires a proper and adequate treatment prior to its discharge into the aquatic environment. Cadmium and manganese are known to be potential pollutants and showed several bio toxic effects once entered into the bio systems [9]. The permissible limit for Cd (II) and Mn(II) as demonstrated by WHO in potable water is 0.003 and 0.4 mg/L, respectively [10] Cadmium is regarded as a foreign metal to the human body and is basically known as nonessential ion for biological systems [11]. It has also been classified as a category 1 carcinogen (human carcinogen) by the International Agency for Research on Cancer (IARC) due to its potent behavior for lung cancer [12]. Prostate cancer and other hormone-related cancers were also associated with cadmium poisoning [13]. The mechanism of acute cadmium toxicity involves the depletion of glutathione and protein bound sulfhydryl groups, resulting in enhanced production of reactive oxygen species such as superoxide ion, hydrogen peroxide and hydroxyl radicals which in turn produces lipid peroxidation and results in DNA damage [14]. In addition, Cd^{2+} ions replace Zn^{2+} ions in some enzymes, thereby affecting enzyme activity [15]. The other toxic effects of cadmium include kidney damage, renal disorder, high blood pressure, bone fracture, and destruction of red blood cells [16]. On the other hand, manganese is naturally occurring and is an essential trace element for humans, plants, and animals [17]; however, adverse effect results from both deficiency and overexposure. The enhanced intake of manganese causes various toxic effects such as growth retardation, fever, sexual impotence, muscle fatigue, and blindness [18]. A specific study conducted on manganese toxicity reveals that manganese may provoke per oxidative damage in all the tissues and the gills of fish [19]. Therefore, there is a need and challenge for the development of efficient and cost-effective methods for the low-level removal of these two metal ions from aqueous solutions so as to meet stringent standards set by regulatory bodies. The commonly employed methods are precipitation, adsorption, ion exchange, membrane separation, reverse osmosis, etc. [20]. Among these methods, adsorption is recognized as a cost-effective and versatile method for the treatment of wastewaters contaminated with heavy metal toxic ions [21]. Moreover, flexibility in design and operation to produce high-quality treated effluent is an additional advantage employing the adsorption process [22]. Because of the high input cost involved with commercial activated carbons, research interest lies in introducing cheaper alternative soring materials having comparable efficiency and suitability which could ultimately replace the use of activated carbon in wastewater treatment methods [23]. The selection of materials with natural abundance makes it cost-effective and environmentally benign. In this regard, clay materials received greater interest in recent past because of their low cost, high adsorption capacities, and natural abundance. Manganese is an oligo-element, which is necessary for human survival, but becomes toxic when the concentration in the human body is too high [24]. According to World Human Organization, the maximum concentration of manganese admissible in drinking water is 0.05 mg L^{-1}[25]. Excess manganese in drinking water can cause problems in the nervous and respiratory systems and retard the intellectual development and normal growth of infants [26]. Chronically high manganese levels in the brain are neurotoxic and can result in a progressive, irreversible neurological disorder known as manganism. Manganese is a toxicant, causing a depletion of brain dopamine and a syndrome of motor dysfunction and memory loss resembling Parkinson disease [27].Prolonged exposure to high manganese concentrations can lead to impotence in men [28]. For these reasons it is necessary to treat the water contaminated by excess manganese so as to reduce its impact on the environment and human health. Several processes are used for water purification: coagulation–flocculation, adsorption on activated carbon, electrocoagulation, ion exchange, reverse osmosis, membrane filtration, bacterial treatment, bio sorption, etc. [29–32]. These techniques are highly effective, but very expensive in most cases [14]. In recent years the studies have been aimed towards water treatment methods using natural materials like zeolites, clays and agricultural waste materials such as saw dust of various plants, wheat bran, wheat husks, rice bran, rice husks, soybean hulls, bark of the trees, groundnut shells, coconut shells, waste tea leaves, sugarcane bagasse, sugar beet pulp, sunflower stalks, coffee beans and cotton stalks [15-17]. In this study, the usage of CSMA-M resin was demonstrated as an adsorbent for the removal of Mn (II) ions from aqueous solutions to investigate the equilibrium and kinetic parameters of the resin using the batch equilibration technique. To determine the performance of the CSMA-M it is important to get an accurate equilibrium relationship between the solid- and liquid phase concentrations of toxic metal ions. In this study, it is essentially required to test the equilibrium data obtained for removal of some toxic metal ions such as Mn(II) ions using CSMA-M resin for the adsorption studies, the kinetics investigations is important too, because it can predict the rate at which a toxic metal ion is removed from aqueous solutions and provides valuable data for understanding the mechanism of adsorption reactions [32]. The various parameters such as pH, contact time, concentrations of metal ion, mass of resin, and agitation speed were investigated on adsorption effect

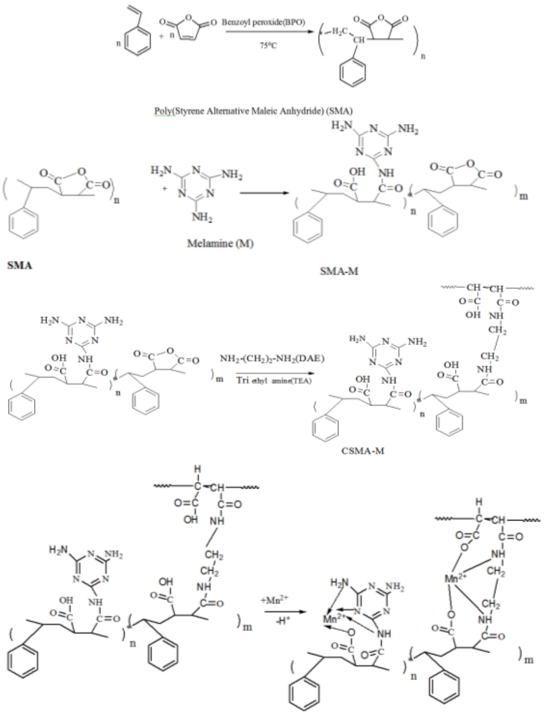
2. EXPERIMENTAL

2.1. Measurements and Chemicals

Atomic absorption spectrophotometer (AAS) (analytic jenanov AA 400) fitted with Manganese, hollow cathode lamps was used for determination of the Mn(II) ions concentration. The UV–Vis (200–800 nm) and IR (200–4000cm^{-1}) spectra were recorded on a Perkin Elmer (Lambda 25, Shelton, CT, USA) and a Perkin Mattson 5000 FTIR spectrophotometers, respectively, for the pH measurements, a digital pH meter (Metrohm 827 pH lab) was used. The pH value of each metal ion solution was adjusted with 0.1N HCl or NaOH solution purchased from Merck (Germany). The systems were shaken by horizontal bench shaker (Heidolph PROMAX 2020). The CSMA-M resin was prepared in polymer Lab of our department. The XRD spectra were recorded on an X'pert Philips X-ray photoelectron spectrometer using non monochromated Mg Ka radiation as the excitation source (The Netherlands). Stock solutions of Mn(II) was prepared by dissolution of reagent-grade $Mn(NO_3)_2$ (Merck) in deionized water, respectively Analytical-reagent grade and other inorganic chemicals, including HCl and NaOH were used without further purification. Melamine, styrene, maleic anhydride and the organic solvents and other necessary materials , such as Triethylamine(TEA), Tetrahydrofuran (THF) and normal Hexane, Oxalic acid, Butanedioic acid, Melamine etc, were also purchased from Merck and were used without further purification.

2.2. Synthesis of the grafted SMA copolymer by Melamine

The SMA copolymer was prepared by the free-radical polymerization of maleic anhydride and styrene at 75ºC in the presence of benzoyl peroxide as an initiator. For synthesis of the grafted SMA copolymer, 1.5 g (0.0075 mol) of SMA copolymer and 0.7875g (0.00375 mol) of Melamine at a ratio of 1 : 0.5 were poured into a flask. Then, 0.25 mL (0.002 mol) of Tri ethylamine (TEA) as a catalyst and 50 mL of THF 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 6 h at 95 ºC. 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 16 h at 65ºC (yield = 98%). The synthesis process of the chelating resins is shown in Scheme 1.



Scheme 1. Reaction and structural formulas of polymers (SMA, CSMA-M).

2.3. Adsorption Studies

Batch adsorption tests were enforced by mixing the CSMA-M (50 mg) and 50 mL of Manganese ions solution (50 ppm) in a 100 mL beaker. Asked value of toxic metal ions experiment solutions was prepared using suitable next dilutions of the present solution. The system was shaken (220 rpm) in measured time and after completing the adsorption the mixture was filtered and the metal ion concentration was measured in filtrate by AAS. In this study, all the tests were enforced at room temperature (25 ± 1)ºC. The gotten data were used to calculate the elimination percentage of Manganese ions applied the following mass balance relationship:

$$\%\text{Manganese ions removal} = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \qquad (1)$$

Where C_o and C_e are the first and equilibrium concentration (ppm) of the Manganese ion solution, respectively.

2.4. Effect of pH on Adsorption

The affect of pH was interrogated on the adsorption of Manganese ions by the CSMA-M resin. For this purpose, several Manganese ions olutions (50 mL, 50 ppm) was adjusted using 0.1N HCl or NaOH solutions at different pH between 2 and 8. Then measured value of CSMA-M resin was introduced to each sample and agitated in a horizontal bench shaker for 120 min. The mixture was filtered through Whatman [18] filter paper and the filtrate was analyzed by AAS. Each determination was repeated six times and the gotten outcome was their average contents.

2.5. Effect of Contact Time

Effect of contact time was interrogated with batch adsorption tests from 0.5 to 12 hour for Mn (II) ions concentration of 50 mg/L in 50 mL solution with the CSMA-M resin (50mg) at pH = 6. The samples were deleted at time respite for the analysis of remainder metal ion concentration in the aqueous solutions.

2.6. Effect of Adsorbent Dosage

Batch adsorption tests were administered at a various weight of CSMA-M resin (0.01–0.1 g) for uptake of Mn(II) ions from aqueous solutions (50 mL, 50 mg/L) at pH =6, for 120 min. The samples were filtered and the filtrates were analyzed by AAS.

2.7. Effect of Metal Ion Concentration.

The effect of metal ion concentration was interrogated on adsorption behavior of CSMA-M resin. For this purpose, each resin (50m g) was laved in Mn(II) ion solution with different concentration (50 mL, 10–400 ppm) at pH =6. The contents of the beakers were equilibrated on the shaker for 120 min. After adsorption, the samples were filtered and the Mn(II)ions was determined in filtrate by AAS.

2.8. Effect of Agitation Speed

To interrogated the effect of Effect of Agitation Speed on adsorption of Mn(II) ions, excited rate was altered from 100 to 300 rpm. Appropriate amount of the resin (50mg) was added to various beakers containing 50 mL of Mn(II)ions (50 mg/L, pH =6) and excited in a shaker for 2 h at room temperature of 25ºC. The volume of each solution was then filtered and analyzed by AAS after the excited time.

2.9. Desorption and Repeated Use

Desorption of Manganese ions were administered by 0.5M HCl solution. The CSMA-M– Mn(II) ion complexes were immersed in 0.2M HCl solution and the mixture was shaken until equilibrium was reached (60 min). Then the mixture was filtrated and the final concentrations of metal ion in the aqueous solution were measured by AAs. The desorption ratio (D%) of toxic metal ions from the (CSMA-M) resin was computed with following equation:

$$D\% = \frac{V_d C_d}{V(C_o - C_e)} \times 100 \qquad (2)$$

Where V is the volume of the solution (L); C_d is the concentration of the Mn(II) ions in the desorption solutions (mg/L); and V_d is the volume of the desorption solution (L).The assembled (CSMA-M) resin from the desorption process was washed thoroughly with deionized water and dried by vacuum pump at 65ºC for repeated use.

2.10. Determination of the Adsorption Capacity for Mn^{2+} Ions

Dynamic adsorption experiments were performed by the mixture of 50 mg of chelating resin with 50 mL of the Manganese ions solution (50 ppm) in a flask with a magnetic stirrer at 25ºC for 2 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 Mn^{2+}-ion concentration was determined by AAS. The adsorption capacities (q's; mmol Mn^{2+}/g resin) under various conditions were calculated as follows:

$$q = \frac{(C_o - C_f)V}{m} \qquad (3)$$

Where C_0 and C_f are the initial and final concentrations (mmol/L) of metal ions in the aqueous solution, respectively; V is the volume of the metal-ion solution (0.05 L); and m is the weight of the resin (0.05 g). The competitive adsorptions for mixtures of Mn^{2+} ions in the real sample under equal initial concentrations (5 ppm) were also studied according to the previous procedures (Table 1).

Table 1. Adsorption Capacity for Mn (II) Ions at Various pH's (2, 4, 6 and 8).

Resin	Adsorption			
	pH=2	pH=4	pH=6	pH=8
CSMA-M	0.197	0.584	0.792	0.885

2.11. Desorption of Metal Ions in Acidic Media

For desorption of metal ions, aqueous 0.2M HCl was used. The resin Manganese (II) - ion complexes in which adsorption was carried out at pH = 6 were immersed in the 0.5M HCl solution with a magnetic stirrer at 25ºC for 1 h. After filtration, the final Manganese (II) - ion concentration in the solution were estimated by AAS. The desorption ratio (D %) was calculated as follows:

$$D\% = \frac{\text{Millimoles of Mn(II)ions desorbed to the HCl solution}}{\text{Millimoles of Mn(II)ions adsorbed onto resin}} \times 100 \qquad (4)$$

2.12. Swelling Index

A known weight (0.5 g) of fully dried SMA–M was immersed in water. After a definite period of time, the polymer was filtered and blotted dry. The swollen polymer was weighed. The swelling index was determined by the ratio of the weight of the swollen polymer to the initial weight of the resin (Table 1):

$$x = \frac{\text{Mass of the wet resin} - \text{Mass of the dry resin}}{\text{Mass of the dry resin}} \qquad (5)$$

3. RESULTS AND DISCUSSION

Synthesis and Characterization of the SMA–M Copolymers. The SMA copolymer was prepared by the method mentioned in reference [19]. Fig. 1 shows the FTIR spectrum of the SMA copolymer.

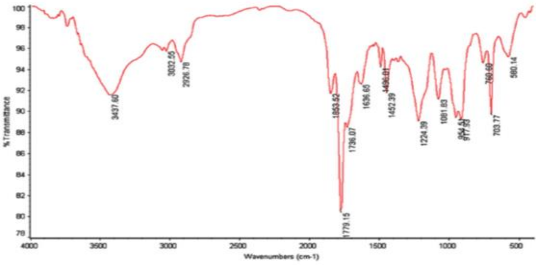


Fig. 1. FTIR spectrum of the SMA copolymer.

In this spectrum, the characteristic of anhydride bonds at 1735, 1784 and 1856 cm^{-1} are shown. The intrinsic viscosity of the resulting SMA copolymer was measured with an Ostwald viscometer at 25ºC in THF solvent, and it was determined to be 0.32 dL/g. The SMA–M was prepared 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 significantly resistant to hydrolysis, so the resulting copolymer was stable in acidic and basic media. To prepare the tridimensional SMA–M copolymer, the reaction was carried out with a step-by-step reaction of the SMA copolymer with melamine and modified melamine as a grafting agent and 1,2-diaminoethane as a crosslinking agent.

The comparison of the SMA–M spectrum with the SMA spectrum showed that the intensity of anhydride peaks decreased and the formation of amide groups took place at about 1676 cm^{-1}. In the case of the SMA and SMA–M copolymers, the FTIR spectra revealed that the grafting reaction was efficient and the anhydride peaks disappeared, and instead, the spectrum showed the characteristics of the absorption peaks of the carbonyl of amide at a lower frequency of about 1632 cm^{-1} and the carbonyl of carboxylate anion at about 1560 cm^{-1}.

The entire pendant carboxylic acids of the resins were converted to free carboxylate ions because of the existence of aminopyridine groups in the neighborhoods [20-21]. It is known that metal complexation to a certain polymeric ligand causes changes in the absorption spectra of the starting polymer [22]. FTIR spectroscopy has been used for the characterization of polymer–Mn(II) complexes because the frequency at which a characteristic group of the polymer absorbs is modified by Mn(II)-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 Mn^{2+} 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 [23-24]. The more covalent it was, the higher the frequency shift was for the free carbonyl bond absorption. 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 Manganese and appeared about 1690–1721 cm^{-1}The bands at 1632, 1560, 1454 and 1242 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 (1032, 914, 767 and 703 cm^{-1}) were not influenced by the metal complexation. The XRD patterns of the synthesized copolymers are depicted in Fig. 2.

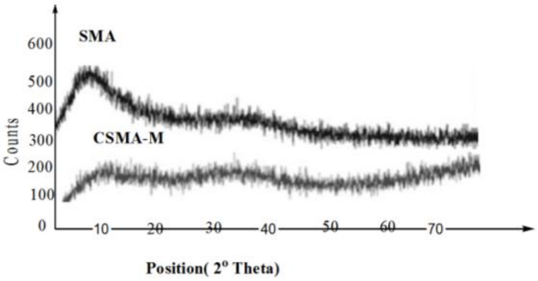


Fig. 2. X-ray diffraction patterns of the copolymer and polymeric adsorbent.

The diffraction patterns showed that the copolymers were amorphous. Indeed, there was only a broad diffraction hump at about 2θ= 20º; 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. Fig. 3 shows the SEM micrographs of typical SMA and SMA–M, in which the particles possessed an almost uniform distribution of size with spherical shapes. The diameter of the observed particles in the SEM images was estimated to be less than 100 nm.

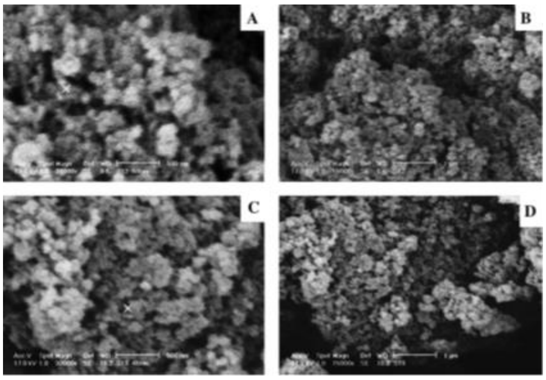


Fig. 3. SEM images of the chelating resin (A) SMA (scale = 500 nm), (B) SMA (scale = 1μm), and (C) SMA–M (scale = 500 nm) and (D) SMA–M (scale =1μm).

3.1. Sorption of Manganese(II) Ions as a Function of pH

The sorption behavior of any Manganese ion on the resins at different pH values was examined with a batch equilibration technique, and the results are summarized in Table 1 and 2.

Table 2. Adsorption Percentage for Mn(II) Ions at Various pH's (2, 4, 6 and 8).

Resin	Adsorption Percentage (%)			
	pH=2	pH=4	pH=6	pH=8
CSMA-M	25.84	44.82	98.6	89.44

The pH of the Mn(II) ion test solution was measured during the sorption process. After equilibration with the resin, a decrease in the pH of the solution was observed. This was attributed to the release of protons from the resin. In general, the adsorption of metal ions increased with increasing pH and reached a limiting value in each instance, which was followed by a decrease in adsorption beyond the limiting value. It is well known that the adsorption of Mn(II) ions by resins depends on the pH; this affects the chelation extremely as well as the physisorption processes. Thus, the effect of pH on the adsorption capacities needed to be further investigated. The SMA–M resin was dissolved completely in water at pH=8 because of its non cross linked nature, and its hydrophilicity was increased because of the deprotonation of its functional group. The effect of crosslinking on the sorption revealed that the sorption capacity increased in the cross linked samples by 1,2-diaminoethane compared to that in the non cross linked sample. There was an abrupt increase in the metal adsorption when the pH was raised from 2 to 8. The adsorption of the Mn(II) ions on the resin was more favorable at a pH value of 8. At low pH values, a high concentration of H could react with carboxylate ions (COO^-) and amine groups to form protonation. In other words, H could compete with Manganese(II) ions for adsorption sites and reduce the Manganese(II) ions adsorption capacity [25-27]. At the alkaline pH value, the carboxylate functional groups of the resin and the nitrogen of Melamine in the side chain of the resin formed a completely deprotonated form, so the Manganese uptake was intense.

3.2. Desorption of Manganese ions from the Chelating Resin

The desorption of the adsorbed Manganese ions from the chelating resin was also studied in a batch experimental setup. The chelating resin beads loaded to maximum amounts of the respective

Manganese(II) ions at pH =6 were placed within the desorption medium containing 0.5M HCl, and the amount of metal ions desorbed in 1 h was measured. The results in Table 2 show that for all of the Manganese(II) ions, the recorded desorption ratios were up to 98%.

3.3. Determination of the Equilibrium Distribution Coefficient (k_d)

k_d was determined according to eq. (6):

$$k_d = \frac{\text{Amount of Mn(II)ions on the absorbent}}{\text{Amount of Mn(II)ions in the solution}} \times \frac{V}{m} \qquad (6)$$

Where m is the weight of adsorbent (g). The k_d value can be used as a valuable tool to study Manganese(II) ions mobility. High values of k_d indicate that the metal has been retained by the solid phase, whereas low values of k_d indicate that a large fraction of the metal remains in solution. k_d was calculated with the previous equation [28]. Tables 3 and 4 show the k_d values for the adsorption of single Manganese(II) ions and the adsorption of Manganese(II) ions from a real sample, respectively.

Table 3. k_d Values of the Cross linked Copolymers for Mn(II)-Ion Adsorption.

Resin	Kd Mn2+ (mL/g)			
	pH=2	pH=4	pH=6	pH=8
CSMA-M	211	322	30110	41100

Table 4. k_d Values of the Cross linked Copolymers for Mn(II)-Ion Adsorption at pH=6 (optimized condition)in waste water.

Resin	K_d Mn^{2+} (mL/g)
CSMA-M	4.21×10^5

These findings proved that the k_d values were approximately high in the cases of Manganese(II) ions, so the prepared chelating resins were good candidates for the removal of Manganese(II) ions from aqueous solutions at pH=6.

3.4. Kinetic Study

For the kinetic studies, the resin (0.05 g) with 50 mL samples at the initial concentration of Manganese(II) ions (C_o) of 50 mg/L was agitated in a 100 mL beaker. The removal rate of Manganese(II) ions were investigated by measurement of Manganese(II) ions concentrations after predetermined time intervals by AAS method. The amount of adsorbed Manganese(II) ions at time t, q_t (mg/g), was calculated by following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \qquad (7)$$

Where the C_t is the concentration of Manganese(II) ions in solution at specified time (mg/L).

3.5. Adsorption Kinetic

The kinetic investigations are important for the adsorption studies because it can predict the rate at which Manganese(II) ions are removed from aqueous solutions and provide valuable data for understanding the mechanism of adsorption reactions. Three known kinetic models are used to investigate the adsorption mechanism.

3.6. Pseudo-First-Order Kinetic

Lagergren showed that the adsorption rate of ions on the adsorbent is based on the adsorption capacity. It followed a pseudo-first-order equation which is often used for estimating k_1 considered as mass transfer coefficient in the design calculations. The non-linear form of the pseudo-first-order equation is described by equation (8):

$$\frac{dq_t}{dt} = k_1 \ (q_e - q_t) \qquad (8)$$

Equation (8) can be expressed in linear form:

$$\log(q_e - q_t) \ = log q_t \ - \frac{k_1}{2.303}t \qquad (9)$$

Where q_e and q_t are the amounts of Manganese ions adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k_1 (1/min) is the rate constant of first-order adsorption. Values of k_1 are calculated from the plots of log (q_e - q_t) versus t [see Fig. 4] for sample Manganese(II) ions. The obtained R^2 values are relatively small and the experimental q_e values do not agree with the calculated values obtained from the linear plots. The data are listed in Table 5.

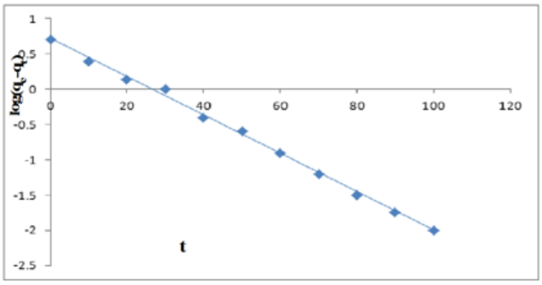


Fig. 4. Pseudo-first-order plot with AAS for Mn(II) ions.

Table 5. Kinetic Parameters for Mn(II) ions Using CSMA-M as Adsorbent (pH =6, Concentration of Mn(II) Ions = 50 mg/L, Resin Dose= 5 g/L).

Kinetic models	Parameters	Mn(II) by AAS
Pseudo-first order model	qe,exp (mg/g)	19.98
	q_e,cal (mg/g)	2.18
CSMA- M	k_1(1/min)	0.0320
	R^2	0.9670
	S.D. (%)	24.71
Pseudo-second order model	qe,exp (mg/g)	19.98
	q_e,cal (mg/g)	19.96
CSMA- M	k_1(1/min)	0.0479
	R^2	1
	S.D. (%)	0.03
Intra-particle diffusion model	Kp_1(mg/g min$^{1/2}$)	0.7036
CSMA- M	Kp_2(mg/g min$^{1/2}$)	0.0953
	C_1	15.683
	C_2	18.888
	$(R_1)^2$	0.9869
	$(R_2)^2$	0.9997

3.7. Pseudo-Second-Order Kinetic.

Ho developed a pseudo-second order kinetic expression for the adsorption system of divalent metal ions using the sphagnum moss peat. This model has since been widely applied to a number of metal/adsorbent adsorption systems. The adsorption of Manganese(II) ions onto the chelating resin at a short time scale may involve a chemical adsorption which implies the strong electrostatic interaction between the negatively charged surface and this metal ion. The second-order kinetics equation is described in the following form:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (10)$$

Equation (10) can be expressed in linear form:

$$\frac{1}{q_t} = \frac{1}{k_2\, q_e{}^2} + \frac{1}{q_e}t \qquad (11)$$

Where k_2 (g/mg min) is the rate constant of second-order adsorption. The activation energy of adsorption can be evaluated with the pseudo-second-order rate constants. The linear plot of t/q_t versus t is shown in Fig.5 and the obtained R^2 values are 1 for Manganese(II) ions. It also shows a good agreement between the experimental and the calculated q_e values (Table 5), indicating the applicability of this model to describe the adsorption process of Manganese(II) ions onto the CSMA-M.

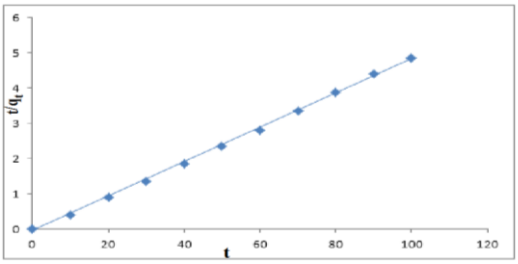


Fig .5. pseudo-second-order plot AAS for Mn (II) ions.

3.8. Intra-Particle Diffusion Kinetic.

As the above two kinetic models were not able to explain the diffusion mechanism, thus the kinetic model of intra-particle diffusion based on the theory or equation proposed by Weber and Morris is tested. It is an empirically functional relationship, common to the most adsorption processes. The adsorb ate uptake varies almost proportionally with $t^{1/2}$ rather than with the contact time t.

According to the following Weber–Morris's equation:

$$q_t = k_{pi}t^{1/2} + C_i \qquad (12)$$

Where k_{pi} is the rate parameter of i stage (mg/g h$^{1/2}$), calculated from the slope of the straight line of q_t versus $t^{1/2}$. C_i is the intercept of i stage, giving an idea about the thickness of boundary layer, that is, the larger the intercept, the greater the boundary layer effect is. For intra-particle diffusion, qt versus $t^{1/2}$ will be linear and if the plot passes through the origin, then the rate limiting process is only due to the intra-particle diffusion. Fig. 6 presents a linear fit of intra-particle diffusion model for adsorption of Manganese(II) ions onto CSMA-M. Such types of plots present multi linearity, indicating that two or more steps take place.

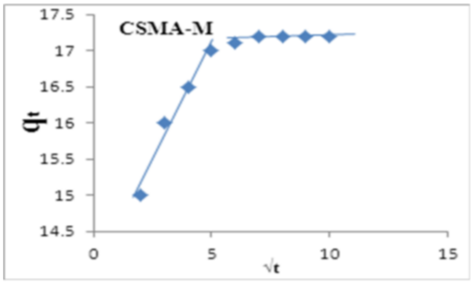


Fig. 6. Intra-particle diffusion plot for adsorption of Mn(II) ions with SMA–M.

It can be observed in Fig. 6 that the data points are related by two straight lines [28-31]. The first sharper portion is attributed to the adsorbate diffusion through the solution to the external surface of the adsorbent (external diffusion) and the second portion describes the gradual adsorption stage, corresponding to the adsorbate diffusion inside the pores of the adsorbent (intra-particle diffusion).

3.9. Validity of Kinetic Model.

Normalized-standard deviation, S.D.(%), is used to find the most applicable model that could describe the kinetic study of adsorption of Mn(II) ions on the CSMA-M. The normalized standard deviation S.D. (%) was calculated using the following equation:

$$S.D\% = 100 \times \{\sum \frac{[(q_{e,exp} - q_{e,cal})/ q_{e,\mathrm{exp.}}]^2}{N-1}\}^{1/2} \quad (13)$$

Where N is the number of data points, $q_{e,}$exp and q_e,cal (mg/g) are the experimental and calculated equilibrium adsorption capacity values, respectively. The results are summarized in Table 5. The values of S.D. obtained for the pseudo-first-order kinetic model, which were relatively high as compared to the S.D. values obtained for the kinetic model of pseudo-second order. Based on the highest R^2 values (for all the metal ions R^2=1) and the lowest S.D. values, the pseudo-second-order model was the most suitable equation to describe the adsorption kinetics of Manganese(II) ions using CSMA-M . This suggested that the overall rate of the adsorption process was controlled by chemisorption which involved valence forces through sharing or exchange of electrons between the adsorbent and adsorbate.

4. CONCLUSIONS

In this study, we synthesized CSMA-M resin, which uses for removing Manganese(II) ions from aqueous solutions. We were investigated AAS for measuring residual Manganese(II) ions in aqueous solution. These methods are simple, sensitive, inexpensive and fast. Adsorption of Manganese(II) ions is found to be effective in the pH range of 2–8 by resin. The removal percentage increases by increasing the adsorbent dose from 0.5 to4.0 g/L. The contact time studies in adsorption of Manganese(II) ions show that the removal percentage increases with time up to 30–40 min and after this time it remains constant. Three simplified kinetic models, pseudo-first-order, pseudo-second-order, and intra-particle diffusion were tested to investigate the adsorption mechanism. The pseudo-second-order kinetic model fits very well with the dynamical adsorption behavior of Manganese (II) ions based on the highest R^2 values . The results have shown that the CSMA-M is reusable resins with a good potential for adsorption of metal ions up to 20 cycles by maintaining performance. It can be said that the CSMA-M, resin has a good potential for removal of toxic metal ions such as Manganese(II) ions from aqueous solutions. Using these resins for the removal of toxic metal ions is simple, green, and clean technology method and has approximately high efficiency and maybe can provide a strategic approach to remove heavy metal ions from industrial sewage.

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