

Synthesis Of Some Polymers For The Elimination Of Heavy Metal Ions In Aqueous Solutions With Applied Poly (Styrene Alternative Maleic Anhydride) Modified With Melamine And Modified Melamine With Propanedioic And Butanedioic Acid

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Abstract— Synthesis of polymers such as CSMA-M, CSMA-MP and CSMA-MB that derivates from poly(styrene alternative maleic anhydride) SMA copolymer. Adsorption of Cd(II), Pb(II) and Zn(II) on modified SMA with melamine and modified melamine with propanedioic acid and butanedioic acid, modified poly (styrene alternative maleic anhydride) cross linked by 1,3-diamino propane as an ion substitution resin has been studied in aqueous solution. The dsorption behavior of these metal ions on the resins was studied by altering the characters such as pH (2–8), adsorbent dose (20-300 mg), contact time (0–600 min), and metal ion concentration (0-4g/L). Adsorption percentage was increased by increasing each of these parameters. Chelating resins have been proposed to be appropriate materials for the recovery of heavy metals in water remedies. The isotherm models such as: Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich were applied to explain adsorption equilibrium. The outcomes shown that the best match was accessed with the Langmuir isotherm equation, production maximum adsorption capacities of 83.21 ,82.12 and 78.98 mg/g with CSMA-M and 84.15 ,82.41, 79.03 mg/g with CSMA-MP resins for Pb (II), Cd (II), and Zn (II), respectively. The resins were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, X-ray diffraction analysis.

Keywords—CSMA-Mand CSMA-MP resins; modified melamine; isotherm models; Chelating resins

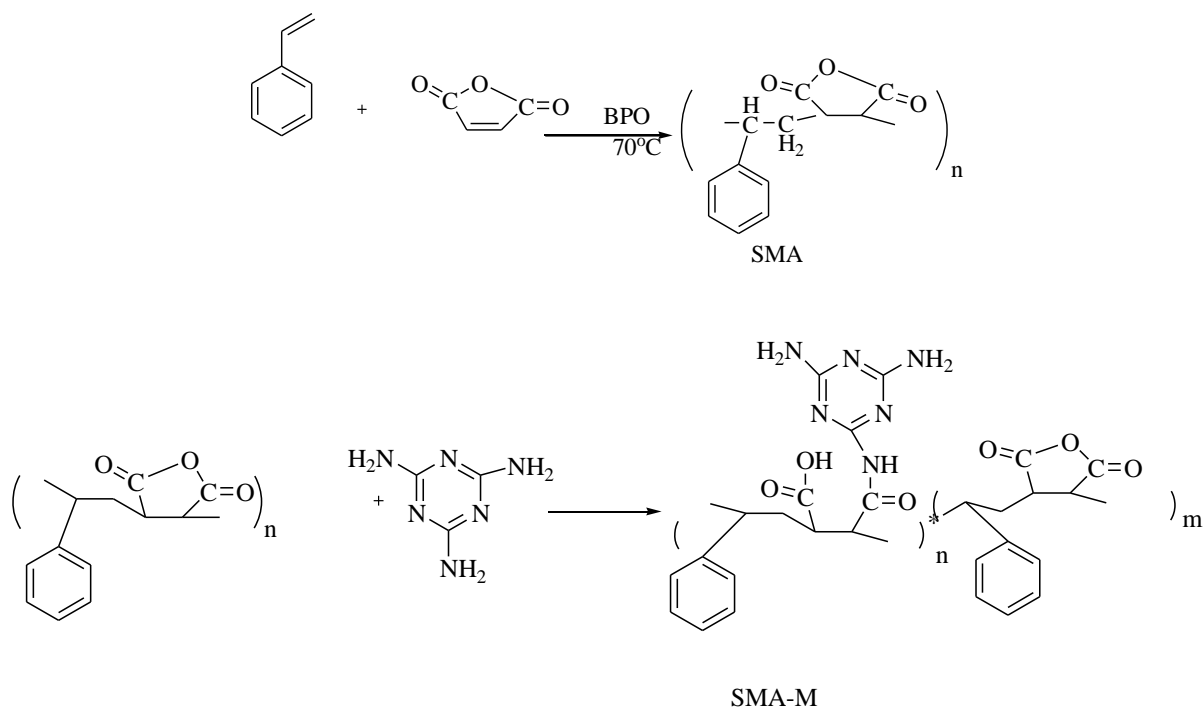
I. INTRODUCTION

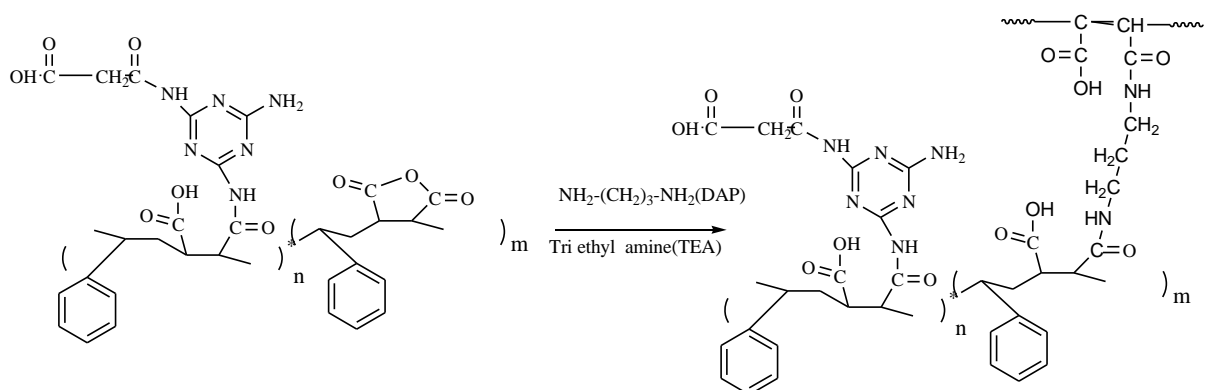
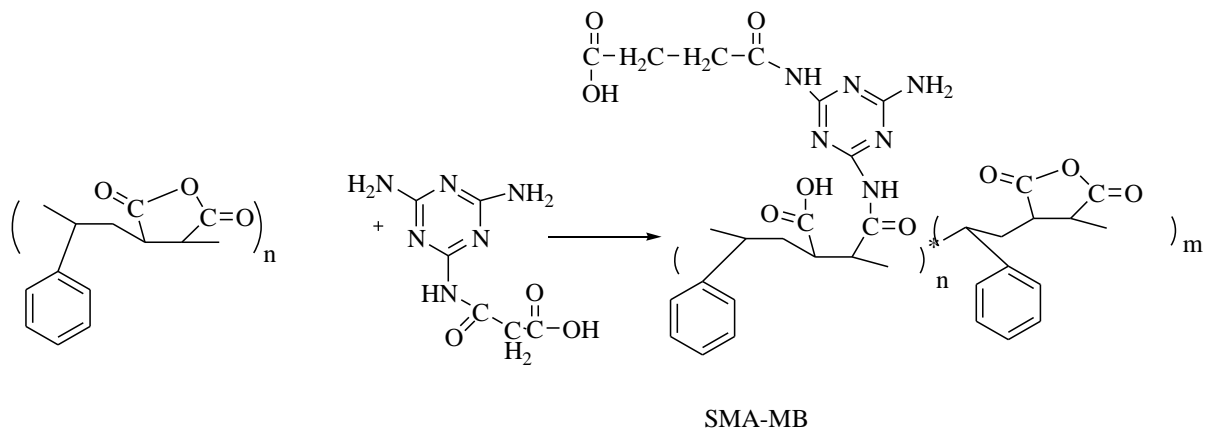
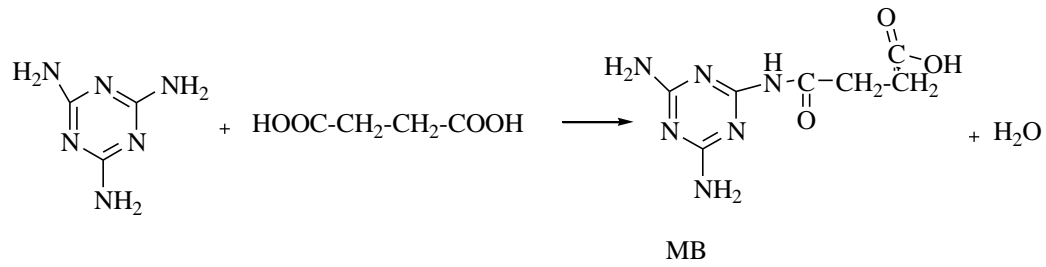
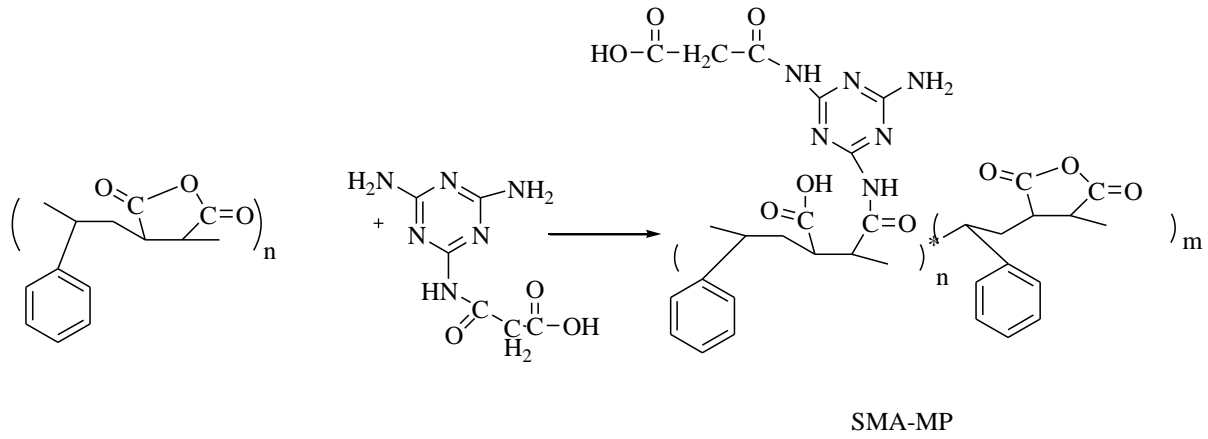
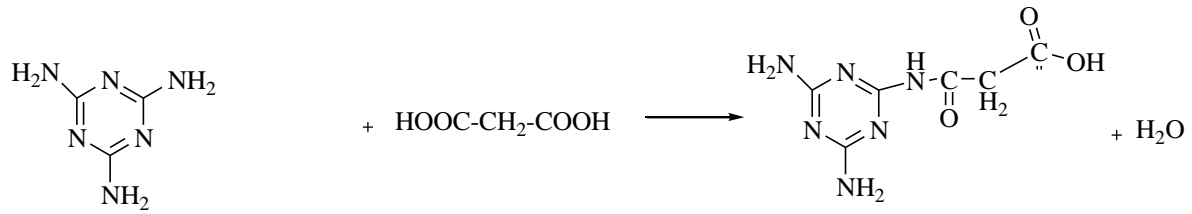
Water is one of the most important needs for living in the world. All plants and animals must have water to live. It is also necessary for the human activities. Water pollution is increasing worldwide because jumping improvement of

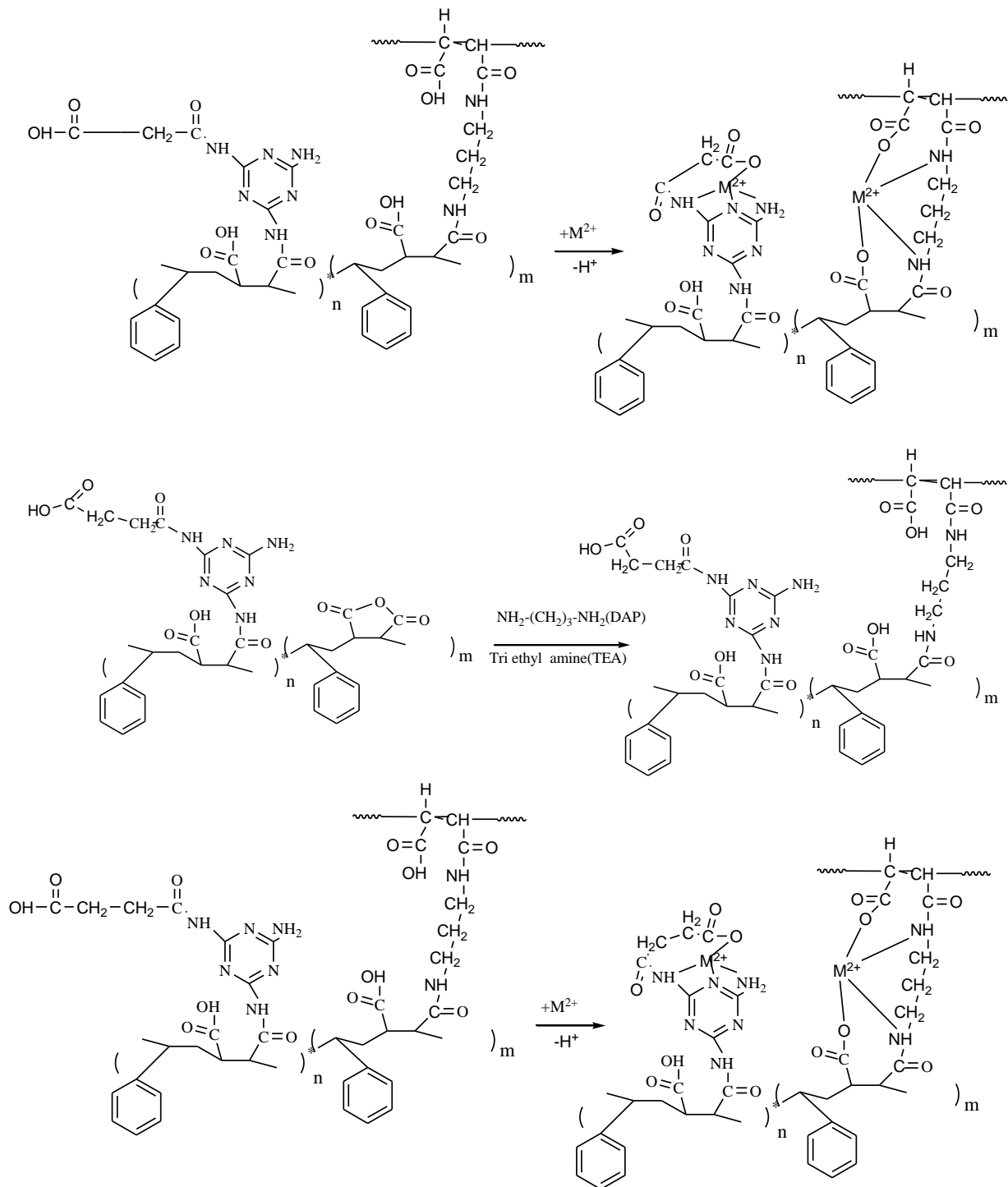
industry, increase human population, domestic and agricultural activities. Water pollution containing heavy metal ions such as cadmium, lead from industrial and domestic is becoming one of the most important environmental difficulties globally . Because of the low concentration of heavy metals in different resources could be several harms to the environment and contrary effecting the human health [1-4]. The treatment of heavy metals is so important owing to persistence in the environment. The world's zinc production is still rising. This basically means that more and more zinc ends up in the environment. Water is polluted with zinc, due to the presence of large quantities of zinc in the wastewater of industrial plants. This wastewater is not purified satisfactory. One of the consequences is that rivers are depositing zinc-polluted sludge on their banks. Zinc may also increase the acidity of waters. Some fish can accumulate zinc in their bodies, when they live in zinc-contaminated waterways [5-6]. When zinc enters the bodies of these fish it is able to bio magnify up the food chain. Large quantities of zinc can be found in soils. When the soils of farmland are polluted with zinc, animals will absorb concentrations that are damaging to their health. Water-soluble zinc that is located in soils can contaminate groundwater. Zinc cannot only be a threat to cattle, but also to plant species. Plants often have a zinc uptake that their systems cannot handle, due to the accumulation of zinc in soils. On zinc-rich soils only a limited number of plants have a chance of survival. That is why there is not much plant diversity near zinc-disposing factories. Due to the effects upon plants, zinc is a serious threat to the productions of farm lands. Despite of this zinc-containing manures are still applied. Finally, zinc can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms [7-9]. The breakdown of organic matter may seriously slow down because of this. Aquatic environment contamination by toxic metal ions, peculiarly as an outcome of industrialization, is increment being related to common health in an urban position, as toxic metals not only lead to pollution of aquatic life but also cause damage to human health, even at slight concentrations. In later years, there has been an increasing worry with environmental protection. This can be succeeded either by reduction of

pollutants offense to the environment or by their elimination from polluted solution. It is necessary to take up methods to slight their tendency in polluted media to harmless quantities, as lead, and cadmium are among the most toxic of elements. Among these toxic metals, cadmium and lead are of considerable environmental and health importance because of its increasing mobilization and human toxicity. The major sources for the introduction of cadmium in water are nonferrous metals smelting and refining, manufacturing processes related to chemicals and metals, and domestic wastewater. Cadmium and lead also expose human health to severe risks, as it can provoke cancer, kidney damage, mucous membrane destruction, vomiting, bone damage as well as affect the production of progesterone and testosterone. Several methods have been widely applied for the elimination of toxic metal ions such as precipitation, ion exchange, reduction, electrochemical treatment, reverse osmosis, solvent extraction, membrane filtration, and so forth. Most often, these methods have a high cost, generate secondary pollutants, or are simply incompetent, especially in removing toxic metal ions in trace quantities from aqueous solutions. Polymer analysis is often a challenging task, particularly when a polymer is made from new polymer chemistry, catalysis, or formulation process. Fortunately, a great number of analytical techniques are now available for polymer analysis. They include separation techniques [1 – 7], spectroscopic methods [8 – 11], NMR [12 – 14], X-ray [15 – 17], microscopy [18 – 21] and other surface characterization tools [22 – 24], and mass spectrometry (MS) [25 – 35]. For a given polymeric system, these techniques each having advantages and limitations over the others are often combined to provide a detailed

characterization of the system [33 – 41]. Among them, MS has become an indispensable tool for polymer analysis and has widely been used to study polymer structure, polymer composition, molecular mass and molecular mass distribution, bulk and surface properties, impurity contents, and so on. Of all the different methods, adsorption using slight-cost and cheap adsorbents is considered to be an economical and effective method for elimination of toxic metal ions from aqueous solutions. There are many types of adsorbents, including activated carbon fibers, resins, and biosorbents. Chelating materials are critically effective and chance adsorbents. Therefore, the most advanced technique for elimination of toxic metal ions is their adsorption on organic sorbents containing chelating functional groups. Among synthetic polymers, poly(styrene-alt-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 copolymer by melamine (M) and modified melamine with propanedioic acid (MP) and butanedioic acid (MB) as a grafting agent under various conditions by the amidation reaction of maleic anhydride repeating groups in the copolymer backbone. Also, the prepared resins were further reacted by 1,3 propylenediamin(DPA) as a crosslinking agent to form tridimensional resins. The preparation of the crosslinked resins in the presence of ultrasonic irradiation along with vigorous magnetic stirring gave rise to polymeric particles on the nanoscale. The adsorption behavior of Cd^{2+} and Pb^{2+} ions (M^{2+}) were investigated by synthesized chelating resins at various pH's. Structure formula was shown in scheme 1.







Scheme 1. the structure formula of various reactions and polymers for using this work 1

2. Experimental

2.1 Material

Analytical-reagent grade $\text{Cd}(\text{NO}_3)_2$, and $\text{Pb}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and other inorganic chemicals, including HCl and NaOH , were purchased from Merck (Germany) and were used without further purification. 1,3 Diamino propane (DAP), Styrene, Maleic anhydride, Melamine, propanedioic acid, butanedioic acid, benzoyl peroxide, triethylamine (TEA) and the organic solvents, such as tetrahydrofuran (THF) and normal hexane, 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 X-ray diffraction (XRD) spectra were recorded on an X'pert Philips X-ray photoelectron spectrometer (The Netherlands) with nonmonochromated $\text{Mg K}\alpha$ radiation as the excitation source. Atomic absorption spectrophotometry (AAS; Analytik jena novAA 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 25 °C in a thermostatic water bath. The elemental analysis of one of the resins 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).

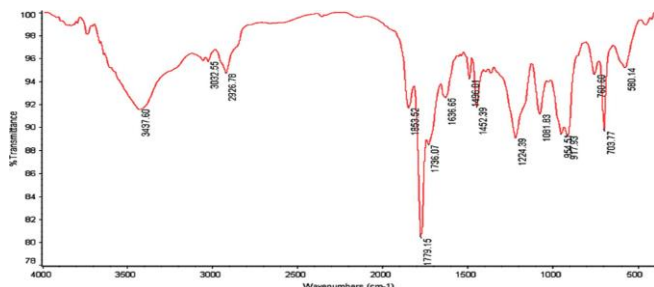


Figure 1. FTIR spectrum of the SMA copolymer

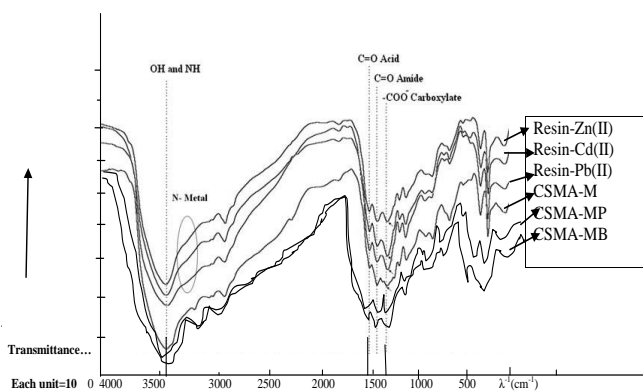


Figure 2. FTIR spectra of CSMA-M and CSMA-MP and CSMA-MB resins before and after complexation with Cd(II), Pb(II), and Zn(II).

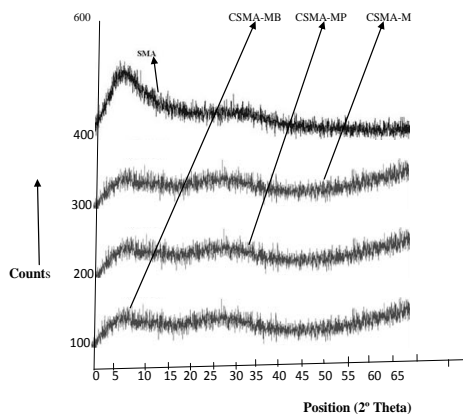


Figure 3. X-ray diffraction patterns of the copolymer and polymeric adsorbent

2.3 Synthesis of the grafted SMA copolymer by melamine

The SMA polymer was prepared by the free-radical polymerization of maleic anhydride and styrene at 75°C in the presence of benzoyl peroxide as an initiator. For a synthesis of the grafted SMA polymer, 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 triethylamine (TEA) as a catalyst and 50 mL of THF 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 6 h at 95 °C. 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 [41]. The product was dried in a vacuum oven for 16 h at 65°C (yield = 98%). This procedure was repeated for obtaining modified melamine with butanedioic acid and propanedioic acid. The synthesis process of the chelating resins is shown in Scheme 1.

2.4 Synthesis of the grafted SMA polymer by modifying melamine with propanedioic acid and butanedioic acid

For the synthesis of the grafted SMA polymer by modifying melamine 0.2g of melamine was solved in pH=4.34 of 15mL cold water that with adding 0.1 M of HCl adjusted pH in pH=4.34. Because dissolved melamine on pH=4.34 in cold water. In the other flask 1g of extra butanedioic acid was dissolved in 15mL of THF. Then the dissolved melamine was added slowly to flask contains butanedioic acid, that was clear at first and then it was formed turbid, produced mixture by along with vigorous magnetic stirring. The obtained product was filtered and the obtained under filter solution was concentrated by heater for vaporizing THF and receiving two half of the initial volume. It contains beaker was put in the refrigerator and crystal was formed and this procedure was repeated for obtaining modified melamine with propanedioic acid.

2.5 Preparation of CSMA-M and CSMA-MP, CSMA-MB

The Cross linked Melamine functioned SMA polymer (CSMA-M) was prepared by the simultaneous reaction of the SMA polymer with melamine and Modified melamine with 1,3 Diamino propane as cross linking agent. The reaction mixture was refluxed for 3 h under inert gas in the presence of ultrasonic irradiation along with vigorous stirring bar in THF. 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 nanoscale. The obtained product was filtered, washed thoroughly with THF, and dried by vacuum oven at 65°C for 16 h.

2.6 Adsorption Studies

Batch adsorption tests were enforced by mixing the CSMA-M (50 mg) and 50 mL of toxic metal ion solution (50 ppm) in a 100 mL beaker. Asked value of toxic metal ion 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 infiltrate by AAS. In this study, all the tests were enforced at room temperature (25 ± 1) °C. The gotten data were used to calculate the elimination percentage of toxic metal ions applied the following mass balance relationship:

$$\% \text{toxic metal ions removal} = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \quad (1)$$

Where C_0 and C_e are the first and equilibrium concentration (ppm) of the toxic metal ion solution, respectively.

2.7 Effect of pH on Adsorption

The effect of pH was interrogated on the adsorption of toxic metal ions by the (CSMA-M and CSMA-MP and CSMA-MB) resins. For this purpose, several metal ion solutions (50 mL, 50 ppm) were adjusted using 0.1N HCl or NaOH solutions at different pH between 2 and 8. Then measured value of CSMA-M and CSMA-MP and CSMA-MB) resins were introduced to each sample and agitated in a horizontal bench shaker for 120 min. The mixture was filtered through Whatman [43] filter paper and the filtrate was analyzed by AAS. Each determination was repeated six times and the gotten outcome was their average contents.

2.8 Effect of Contact Time.

The effect of contact time was interrogated with batch adsorption tests from 60 to 1080 min for toxic metal ion concentration of 50 mg/L in 50 mL solution with the (CSMA-M and CSMA-MP and CSMA-MB) resins (50mg) at pH = 6. The samples were deleted at time respite for the analysis of remainder metal ion concentration in the aqueous solutions.

2.9 Effect of Adsorbent Dosage.

Batch adsorption tests were administered at a various weight of (CSMA-M and CSMA-MP and CSMA-MB) resins (0.01–0.1 g) for uptake of toxic metal 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.

2.10 Effect of Metal Ion Concentration.

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

2.11 Effect of Excited Rate

To interrogate the effect of excited rate of adsorption of metal ions, excited rate was altered from 100 to 300 rpm. The appropriate amount of the resin (50mg) was added to various beakers containing 50 mL of heavy metal ions (50 mg/L, pH =6) and excited in a shaker for 2 h at room temperature of 25°C. The volume of each solution was then filtered and analyzed by AAS after the excited time.

2.12 Desorption and Repeated Use

Desorption of metal ions was administered by 0.5M HCl solution. The CSMA-M–metal ion, CSMA-M–metal ion, CSMA-M–metal ion, complexes were immersed in 0.2M HCl solution and the mixture were 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 and CSMA-MP and CSMA-MB) resins were computed by following equation:

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

Where V is the volume of the solution (L); C_d is the concentration of the toxic metal ions in the desorption solutions (mg/L); and V_d is the volume of the desorption solution (L).

The assembled (CSMA-M and CSMA-MP and CSMA-MB) resins from the desorption process was washed thoroughly with deionized water and dried by vacuum pump at 65°C for repeated use.

2.13 Equilibrium Isotherm

The interrogated of equilibrium isotherms was administered by agitating of 50mg (CSMA-M and CSMA-MP and CSMA-MB) resins in a solution containing different concentrations of metal ion for 120 min at pH =6. After filtration, the AAS was applied to measure the metal ion concentration in the filtrate. The amount of metal adsorbed q_e (mg/g) was measured using the following mass balance relationship:

$$q_e = \frac{V(C_o - C_e)}{m} \quad (3)$$

Where V is the volume of the solution (L); and m is the mass(g) of the adsorbent.

3. RESULTS AND DISCUSSION

3.1 Preparation and Morphology of CSMA-M and CSMA-MP and CSMA-MB

The SMA polymer was functionalized by melamine and modified melamine with propanedioic acid and butanedioic acid and cross linked by 1,3-diaminopropane. The morphology and average diameter of polymer network were shown at previous work by SEM image in two scales 1 μ m and 500 nm.³⁷ It was found that the SEM micro graphs of cross linked polymer in which particles possess almost uniform distribution of size [44]. The average diameter of the observed particles in SEM images can be conjectured under 100 nm with arguable monotony and granular schema. This outcome introduces that there might be various particle sizes in these polymer powders, although more of the grain size could be in nanometer-scale corrosion of the SEM. XRD determinations (Figure 3) introduce the dominantly chaotic nature of the SMA and CSMA-M, CSMA-MP, CSMA-MB.

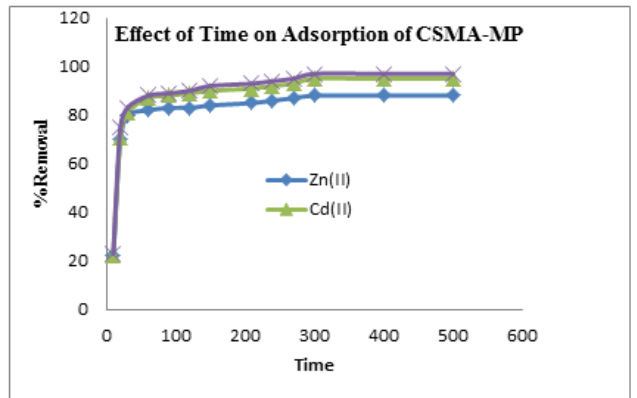
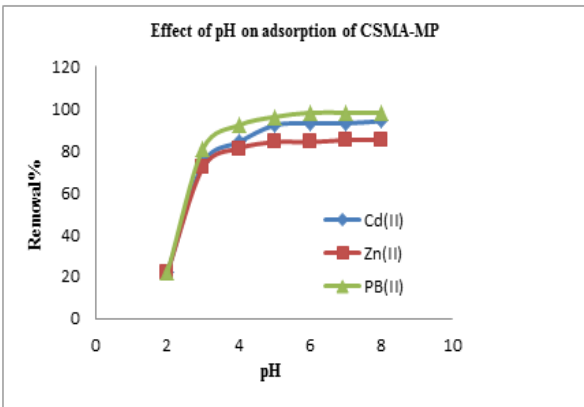
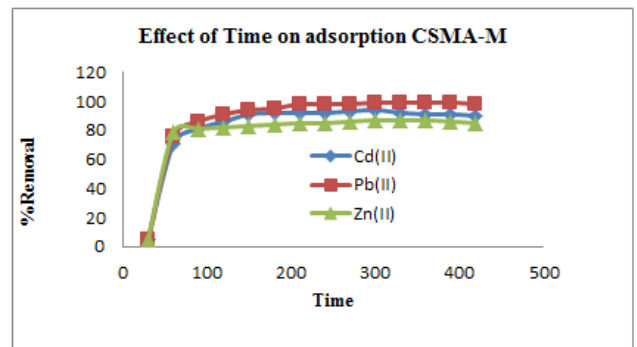
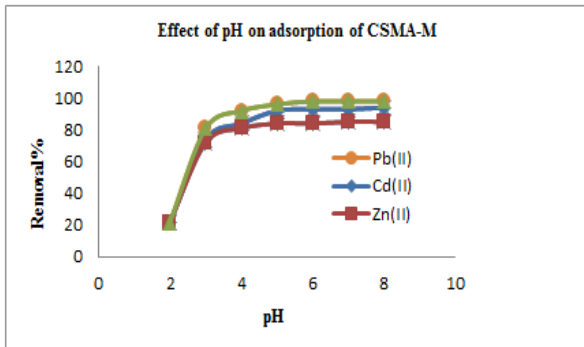


Figure 4. Effect of pH value on metal ions adsorption by CSMA-M and CSMA-MP and CSMA-MB resins. Effect of pH on CSMA-MP and CSMA-MB resins did not differ.

Figure 5. Effect of contact time (min) on metal ions adsorption by resins (effect of contact Time on CSMA-MP and CSMA-MB resins did not differ)

3.2 The Swelling Index

By stirring the resin in water, it was swelled without any dissolving. The swelling index of the polymers is shown in Figure 6. The outcome clearly introduced that the uptake of water depend on the structure inclination such as bores and the functional groups which can be increase or decrease the hydrophilicity of the resins. The swelling index was measured By the following equation:

$$x = \frac{\text{mass of wet resin} - \text{mass of dry resin}}{\text{mass of dry resin}} \quad (5)$$

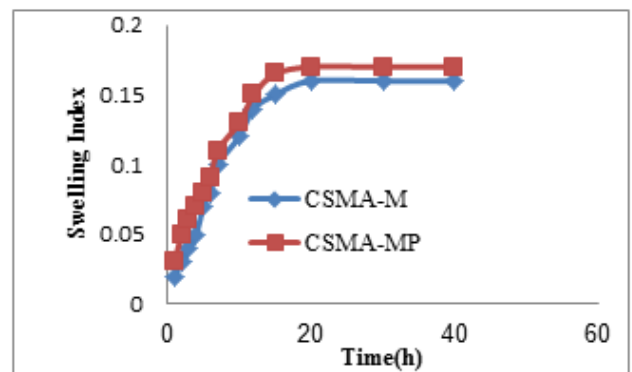


Figure 6. Swelling index of CSMA-M and CSMA-MP resins. (Effect of Time on CSMA-MP and CSMA-MB resins did not differ)

3.3 Effect of pH Value on Metal Ions Adsorption

The pH of aqueous solutions is one of the most significant controlling factors that effects the elimination percentage of toxic metal ions on adsorbent. The effect of pH on the adsorption of Cd(II), Pb(II), and Zn(II) ions was studied in different pH of the metal ion solution in the range of 2–8 because these metal ions could be sedimented by OH⁻ to form metal (II) hydroxide above pH 6. The outcome was shown in Figure 4. The extractability of the metal ions from the solution phase depends on the pH, because its affect on the solubility of the metal ions, concentration of the counter ions on the functional groups of adsorbent, and the degree of ionization of the adsorbate during reaction. The consequences shown that there is nearly no adsorption at pH = 2, and the removal percentage of CSMA-M and CSMA-MP and CSMA-MB for metal ions increases

significantly with the increase of the pH values. The maximum removal efficiencies of Cd(II), Pb(II), and Zn(II) ions were 97.2%, 98.67%, and 87.95% with CSMA-M and 98.3% ,98.7%, 88.4% with CSMA-MP , respectively(CSMA-MP and CSMA-MB adsorption are not different).In realy in acidic pH, the adsorbent surface will be completely covered with hydronium ions which compete strongly with toxic metal ions for adsorption sites at acidic pH, with an increase in pH, the concentration of H_3O^+ ions decreases facilitating the adsorption of metal ions by the adsorbent.

3.4 Effect of Contact Time on Metal Ions Adsorption

Contact time plays a significant obligation in the adsorption of metal ions with solid surface. Removal percentage of toxic metal ions are found to be commensurate to contact the time up to equilibrium received, after which it is free of time due to the verity that at equilibrium the rate of adsorption and desorption will be same. Affect of contact time for the elimination of Cd(II),Pb(II), and Zn(II) by the CSMA-M and CSMA-MP, CSMA-MB resins shown rapid adsorption of these metal ions in the first 100 min and, afterwards, the adsorption rate decreased gradually and the adsorption received equilibrium in about 300 min as shown in Figure 5. The relatively fast sorption of Cd (II), Pb (II), and Zn (II) ions on the CSMA-M and CSMA-MP and CSMA- MB resins maybe reflects the high success of the these metal ions to the ion substitution sites in the CSMA-M and CSMA-MP and CSMA- MB.

3.5 Effect of Adsorbent Dose on Metal Ions Adsorption

The effect of adsorbent dosage is a significant factor on the removal percentage of toxic metal ions from aqueous solutions, whereas it measures the capacity of an adsorbent for a given concentration. The adsorption efficiency for Pb (II),Cd (II), and Zn(II) ions as an accessory of adsorbent dosage was studied and the results can be observed in Figure7. The experimental data revealed that the elimination efficiencies of metal ions increased inchmeal with increasing amounts of CSMA-M and CSMA-MP and CSMA-MB. This may be imputed to the reality that increasing the adsorbent dose readied more adsorption sites for the metal ions. By increasing the adsorbent dose for Cd(II), Pb(II), and Zn (II) ions from 0.5 to 4.0 g/L, the adsorption of above-implicit ions were increased from 54.40% to 98.67%, 82.40% to 99.80%, and 74.60% to 90.39%, respectively, with CSMA-M and 77.40% to 98.80%, 79.40% to 99.90%, and 76.70% to 92.49%, respectively with CSMA-MP and no difference between CSMA-MP and CSMA-MB.

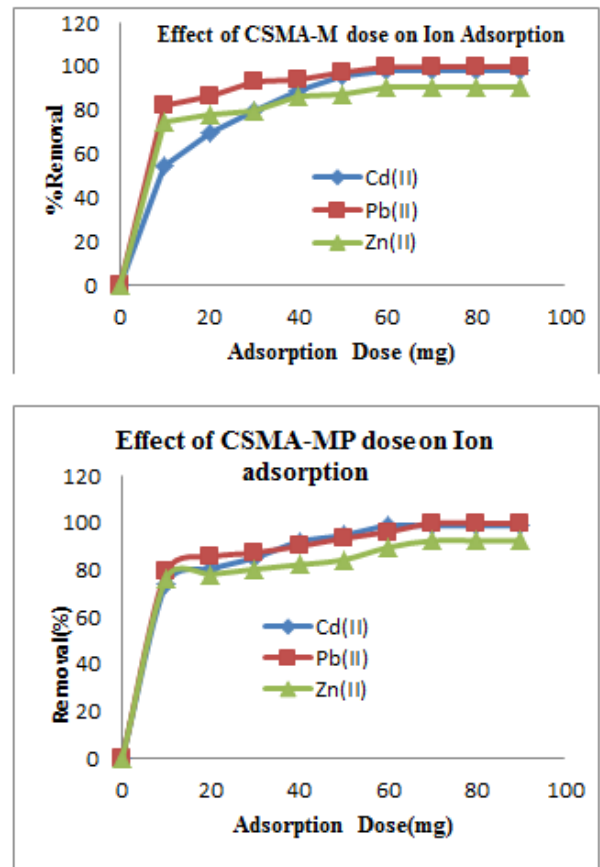


Figure 7 Effect of adsorbent dose on metal ions adsorption by CSMA-M and CSMA-MP.

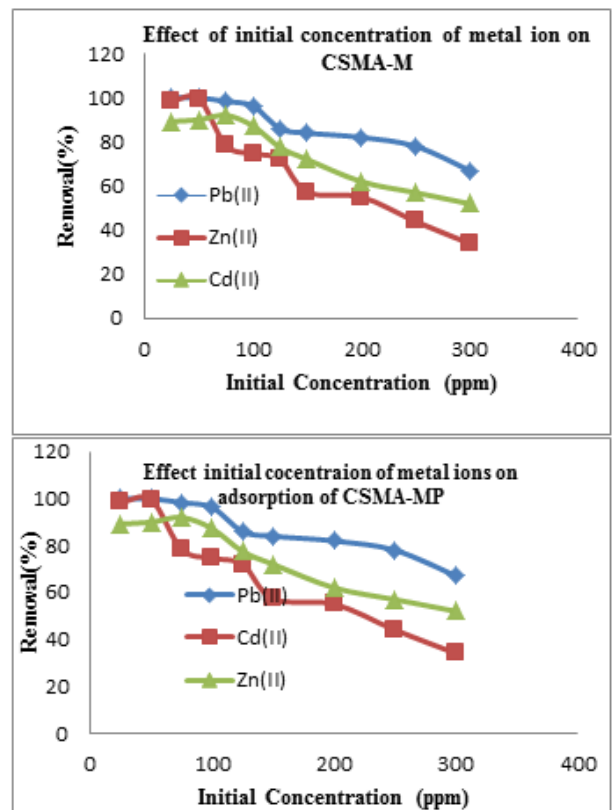


Figure 8 Effect of concentration of metal ion on metal ions adsorption by CSMA-M and CSMA- MP.

3.5 Effect of Concentration of Metal Ion on the Adsorption

The rate of adsorption is a function of the concentration of metal ions, which makes it a significant character to be supposed for efficient adsorption. The effect of metal ions concentration

was studied on the adsorption behavior of CSMA-M and CSMA-MP resins at various concentration (25–300 ppm), and the outcomes are exhibited in Figure 8. Totally, Figure 8 introduces that by increasing the metal ions concentration with a constant amount of the adsorbent, the metal ions adsorption was increased up to 50 ppm for Cd(II) and Pb(II) and 75 ppm for Zn(II). Further increases in the metal ion concentration were companionship by a reduction in the removal percentage. This phenomenon might be due to the glut of the active sites of the CSMA-M and CSMA-MP with the toxic metal ions at higher concentrations. The structure of polymer network was shown in Scheme 1. We can observe that these resins have so many active ion substitution sites for removing of heavy metal ions from aqueous solution.

FTIR Scan

FTIR spectroscopy has been applied to the characterization of polymer–metal complexes owing to of the repetition at which a functional group of the polymer absorbents is developed by metal ions complexation. As shown in Figure 2, after CSMA-M and CSMA-MP and CSMA-MB adsorbing metal ions, the band at 1625 cm^{-1} peaked and shifted to a lower frequency (at about 1464 cm^{-1}), introducing a stronger polymer–metal bond has wrought between metal ions and carboxyl oxygen in carboxylate salts. Moreover, a predominant peak was appeared at 3458 cm^{-1} expressing the N-H stretching vibrations of metal salts of amid[44].

3.6 Effect of Excited rate on Adsorption of Heavy Metal Ions

The effect of excited rate was investigated under the particular conditions (at optimum contact time of 1h, 0.05 g resin, 50 mL solution 50 ppm, pH =6, and at a room temperature of 25°C) with CSMA-M and CSMA-MP and CSMA-MB as adsorbent; it was observed that increase in excited rate from 50 to 300 rpm, the removal percentage of toxic metal ions (Cd, Pb, and Zn) increased up to 300 rpm as shown in Figure 6. Hence, at an agitation speed of 200 rpm, maximum recoveries were obtained for all the three metal ions, with 98.20% removal of Cd(II), 99.60% of Pb(II), and 82.28% removal of Zn (II) by CSMA-M and with 98.82% removal of Cd(II), 99.81% of Pb(II), and 84.32% removal of Zn(II) by CSMA-MP. Also Cd(II) attained maximum removal of 97.51% with CSMA-M and at a lower agitation speed of 150 rpm. The increase in agitation speed resting to increase in metal ions removal percentage was due to the fact that the increase in stirring rate sublimated the metal ions diffusion to the surface of the adsorbent; and also sake reduction in the film border layer environs the adsorbent.

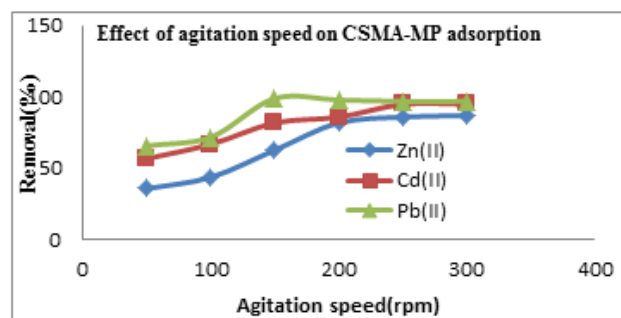
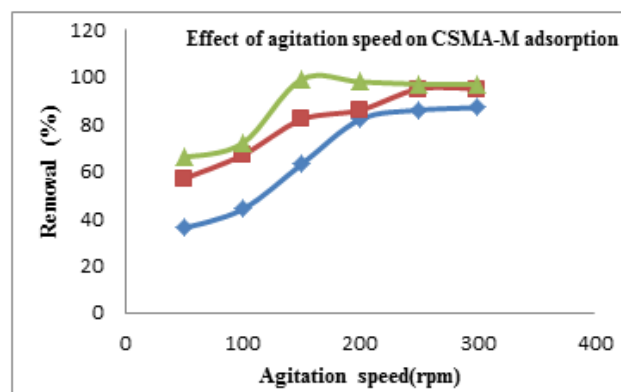


Figure 9. The effect of agitating speed on adsorption of heavy metal ions with CSMA-M and CSMA-MP.

3.7 Desorption and Repeated Use

For developed adsorbents recycling reproduced and repeated accessibility are significant factors. Such adsorbents not only possess more adsorption abilities, but also performance better desorption properties. Better desorption importantly reduces the wholly costs depend on adsorbate removal, particularly when expensive currently limit their potential apply. Inversely, after desorption, the metal ions can be recovered. Desorption of Cd(II), Pb(II), and Zn(II) ions from CSMA-M–metal ion and CSMA-MP–metal ion and CSMA-MB–metal ion complexes were displayed applied 0.5M HCl solution at room temperature. As stated pristinely, when the adsorption of the metal ions was desired to 0 at pH = 2, shown that, 0.1M H^+ (pH =1) could complete avoid the adsorptions of the Pb(II), Cd(II), and Ni(II) ions. Thus, in this work, the concentration of H1 was raised to 0.5M to improve the desorption efficiency. Figure 7(A) shows the effect of time on the desorption of Cd(II), Co(II), and Zn(II) ions from CSMA-M and metal CSMA-MP–metal ion and CSMA-MB–metal ion complexes. The desorption process received equilibrium at 300min and the desorption ratios were 96% for Cd(II), 98% for Pb(II), and 90% for Zn(II) CSMA-M and 97% for Cd(II), 99% for Pb(II), and 93% for Zn(II) with CSMA-MP. To examine the reusability of CSMA-M and CSMA-MP, reel adsorption desorption cycles were repeated times applied the same resins and the data are shown in Figure 10. The absorption capacity of the adsorbent did not importantly change during the repeated absorption–desorption turnovers for all metal ions. The outcomes were shown that the CSMA-M and CSMA-MP resins are good reusable adsorbent in the elimination of Cd (II), Pb (II), and Zn (II) from their single-metal ion solutions [45–48]

3.8 Determination of the Equilibrium Distribution Coefficient (k_d)

The distribution coefficient can be measured by the following equation:

$$K_d = \frac{\text{Amount of metal ion in adsorbent} \times \frac{V}{m}}{\text{Amount of metal ion in solution}} \quad (6)$$

Where V is the volume of the solution (mL) and m is the mass of adsorbent (g). The k_d value can be applied as an inestimable tool to investigate the metal cation mobility. High values of k_d indicated that the metal ion has been uptake by the solid phase, while low amounts of k_d introduced that a large fraction of the metal ion residual in solution. Table 1 shows the k_d amount for adsorption of toxic metal ions. These findings argument that the k_d amount is almost high in the case of Cd(II), Pb(II), and Zn (II) ions, so the CSMA-M and CSMA- MP resins had a good ability in the elimination of Cd (II), Pb (II), and Zn(II).

Table 1. Distribution Coefficient, k_d , of Toxic Metal Ions Adsorption by CSMA-M and CSMA-MP CSMA-MB Resins at pH =6 (Concentration of Metal Ions = 50 ppm, Resin Dose =50mg/L, Time = 300 min)

Resins	k_d (mL/g $\times 10^3$)		
	Pb(II)	Cd(II)	Zn(II)
CSMA-M	22.46	22.32	5.12
CSMA- MP	23.21	23.09	6.04
CSMA- MB	23.21	23.09	6.04

3.9 Adsorption Isotherm

The adsorption equilibrium is usually explained by an isotherm equation whose factor states the juncture of the adsorbent. To measure the representation of the resin, it is significant to get an accurate equilibrium dependence between the solid and liquid-phase concentrations of toxic metal ions. In this study, it is fundamentally needed to test the equilibrium data prepared for elimination of some toxic metal ions such as Cd (II),Pb(II), and Zn(II) applied CSMA-M and CSMA-MP resins with various isotherm models.

3.10 Langmuir Isotherm. Langmuir model has been widely used to some process of metal ions adsorption[54]. The fundamental supposition of the Langmuir theory is that uptake of metal ions happens on a monotonous surface by monolayer adsorption without any interplay between adsorbed metal ions that is all the adsorption sites have equal adsorbate continuity and that the adsorption at one site does not affect the adsorption at a neighbor site. So, the Langmuir isotherm is exact for monolayer adsorption onto a surface containing a determinate number of identical sites. The Langmuir adsorption isotherm model is given by:

$$q_e = \frac{q_m C_e K_L}{1 + C_e K_L} \quad (7)$$

Where C_e is the equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium (mg/g), q_m is the maximum adsorption capacity corresponding to the complete monolayer coverage (mg/g), and K_L is the Langmuir constant affiliated to the adsorption energy. The model of Langmuir adsorption isotherm can be rearranged as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (8)$$

The linear plot of Langmuir adsorption isotherm (C_e/q_e vs. C_e) demonstrated the applicability of Langmuir adsorption isotherm for this work that was shown in Figure 10. The values of q_m and K_L for Cd (II), Pb (II), and Zn(II) ions were calculated from the slope and the intercept of the linear plots C_e/q_e versus C_e . The results are listed in Table 2. The results showed that good fit was achieved with the Langmuir isotherm equation. 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 :

$$R_L = \frac{1}{1 + C_o K_L} \quad (9)$$

Where K_L is the Langmuir constant (L/mg) and C_o is the concentration of toxic 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 ($R_L = 0$). Figure 12 illustrated that adsorption of Cd (II), Pb (II), and Zn (II) increased continually with concentration of metal ion. The computed R_L values for this toxic metal ions adsorption illustrate that adsorption is desirable even for higher concentrations of metal ion.

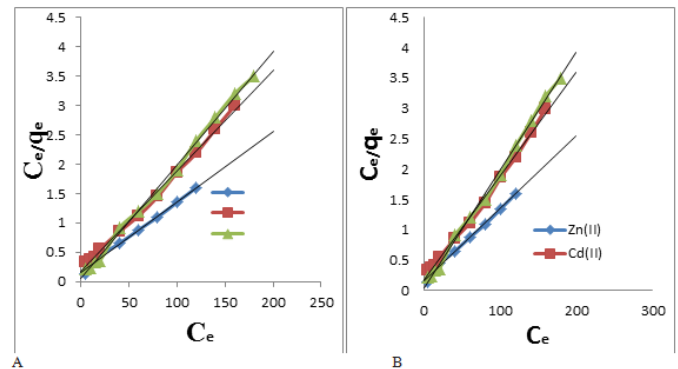


Figure 10. Langmuir isotherms for Cd(II), Pb(II), and Zn(II) adsorption onto CSMA-M (A) and CSMA-MP(B)

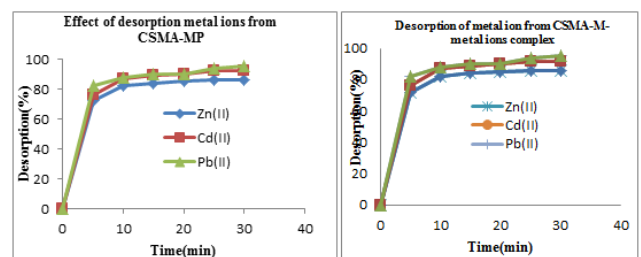


Figure 11. Desorption of metal ions from CSMA-M-metal ions and CSMA-MA-metal ions complex by 0.5M HCl solution

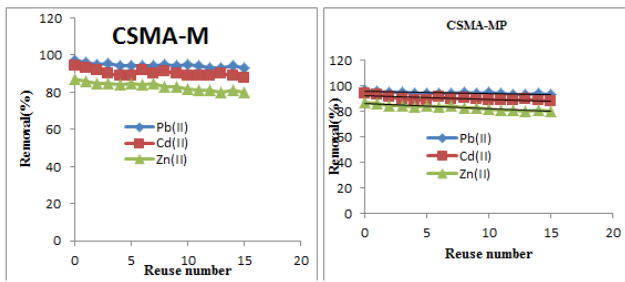


Figure 11 removal of metal ions after repeated adsorption-desorption operations at 25°C (concentration of metal ions = 50 ppm, adsorption time = 60 min, pH = 6, adsorbent dose = 5g/L).

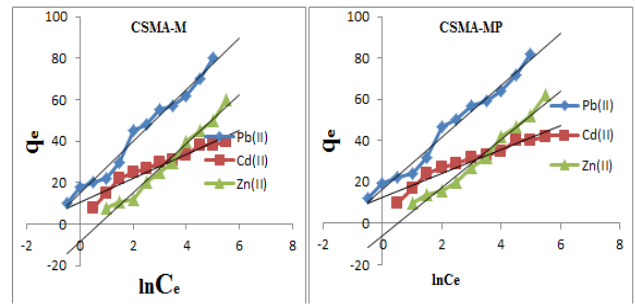


Figure 13. Temkin isotherms with CSMA-M and CAMA-MP resins.

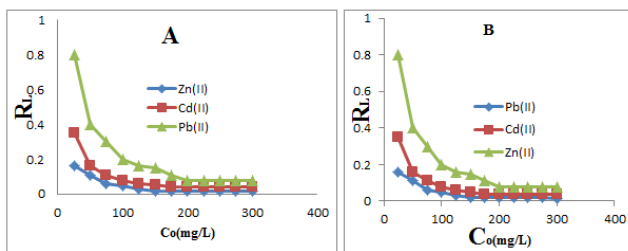


Figure 12. Separation factor (RL) profile for adsorption of Cd(II), Pb(II), and Zn(II) as function of concentration of metal ion by CSMA-M(A) and CSMA-MA (B) (pH = 6, time = 300 min, resin dose = 5 g/L).

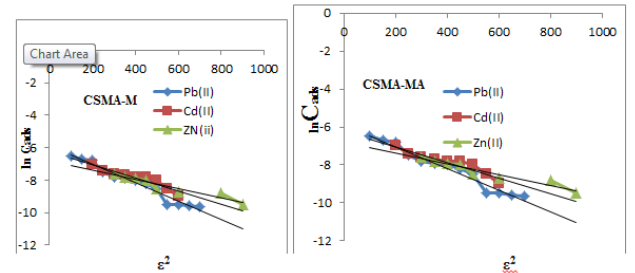


Figure 14. Dubinin-Radushkevich isotherms with CSMA-M and CAMA-MP resins

3.11 Freundlich Isotherm. The Freundlich isotherm theory said that the ratio of the amount of solute adsorbed onto a given mass of sorbent to the concentration of the solute in the solution is not constant at different concentrations. The heat of adsorption decreases in magnitude with increasing the extent of adsorption. The model of Freundlich adsorption isotherm, which is a demonstrator of surface heterogeneity of the sorbent, is given by following equation.

$$q_e = K_F C_e^{1/n} \quad (10)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (11)$$

Where K_F and $1/n$ are Freundlich constants depended on adsorption capacity and adsorption intensity, respectively. The values of n and K_L for Cd(II), pb (II), and Zn(II) ions were computed from the slope and the curve of the linear draws $\log q_e$ versus $\log C_e$ [Figure 13] with the correlation coefficients which were proved in Table 2. The resin shown better accordance for Langmuir isotherm than Freundlich isotherm.

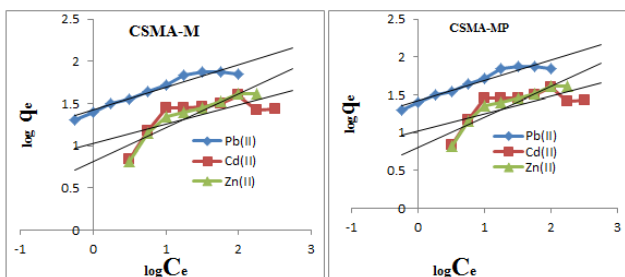


Figure 13. Freundlich isotherms with CSMA-M and CAMA-MP resins.

3.12 Temkin Isotherm. The model of Temkin adsorption isotherm contains a factor that explicitly takes into account adsorbent-adsorbate interactions[55]. This model assumes the following: (i) the adsorption heat of all molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm is applied in the following form:

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \quad (12)$$

The linear form of Temkin equation is

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (13)$$

where $B_T = RT/b_T$, T is the absolute temperature in K, and R is the universal gas constant (8.314×10^{-3} kJ/mol K). The constant b_T is related to the adsorption heat (kJ/mol), A_T is the constant of equilibrium binding (L/g) corresponding to the maximum binding energy. Thus, the constants can be obtained from the slope and intercept of a straight line plot of q_e versus $\ln C_e$ [Figure 13]. Temkin isotherm generates a satisfactory fit to the experimental data as indicated by correlation coefficients.

From Table 2, it can be seen that the value of A_T is larger for Pb(II) than Cd(II) and Zn(II), $Pb(II) > Cd(II) > Zn(II)$. This means in cation exchange processes using CSMA-M and CSMA-MP resins, adsorbent-adsorbate interactions are more effective for lead comparing with cadmium and zinc.

3.13 Dubinin-Radushkevich (D-R) Isotherm. Dubinin and Radushkevich have proposed another isotherm model[56] which is not based on the assumption of homogeneous surface or constant adsorption potential, but is applied to estimate the mean free energy of adsorption (E). The mean free energy of

adsorption per mole of the adsorbate, which is the energy required to transfer one mole of an adsorbate to the surface from infinity in solution, given by Hobson to evaluate the nature of interaction between metal ions and the binding sites. If the value of E is between 8 and 16 kJ/mol, the adsorption process can be assumed to involve chemical sorption. Conversely, values lower than 8 kJ/mol indicate that the adsorption process is of physical nature[57]. This adsorption model is given by:

$$C_{ads} = X_m e^{-\beta s^2} \quad (14)$$

The linear form of D–R isotherm equation is represented by the following equation:

$$\ln C_{ads} = \ln X_m - \beta s^2 \quad (15)$$

Where C_{ads} is the amount of toxic metal ions adsorbed per unit weight of the resin (mol/g), X_m is the adsorption capacity (mol/g), β is a constant related to adsorption energy (mol^2/kJ^2), and ϵ is the Polanyi potential, which can be calculated from equation :

$$s = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (16)$$

Where R is the universal gas constant (kJ/mol K), and T is the temperature (K). If $\ln C_{ads}$ is plotted against ϵ^2 , β , and X_m will be obtained from the slope and intercept, respectively. Figure14 indicated the experimental results. The straight lines obtained were useful in calculating the D–R isotherm constants, which are given in Table 2. The adsorption energy can also be worked out using the following relationship:

$$E = \frac{1}{\sqrt{2\beta}} \quad (17)$$

In this study, the E values obtained using the D–R constant were 14.13 kJ/mol for Pb(II), 11.30 kJ/mol for Cd(II), and 9.85 kJ/mol for Zn(II) and 15.11 kJ/mol for Pb(II), 12.45 kJ/mol for Cd(II), and 10.21 kJ/mol for Zn(II) , indicating that the adsorption of these ions onto CSMA-M CSMA-MP resins respectively , happen by chemical process.

Table2 . Isotherm Parameters and Regression Data for Cd(II), Pb(II),and Zn(II) Ions Using CSMA-M and CSMA-MP as Adsorbent (pH = 6, Time = 300 min, Resin Dose = 5 g/L, Concentration of Metal Ions = 50 ppm)

Isotherms	Parameters	Metal ions		
		Pb(II)	Cd(II)	Zn(II)
Langmuir	q_m (mg/g) (CSMA-M)	83.21	82.12	78.98
	q_m (mg/g) (CSMA-MP)	84.15	82.41	79.03
	K_L (L/mg) (CSMA-M)	0.221	0.208	0.074
	K_L (L/mg) (CSMA-MP)	0.241	0.210	0.078
	R_L (CSMA-M)	0.06	0.08	0.2
	R_L (CSMA-MP)	0.07	0.05	0.18
	R^2 (CSMA-M)	0.996	0.995	0.991
	R^2 (CSMA-MP)	0.997	0.996	0.994
Freundlich	K_F (CSMA-M)	19.54	19.32	7.92
	K_F (CSMA-MP)	19.74	19.53	8.02
	N (CSMA-M)	3.21	3.07	2.12
	N (CSMA-MP)	3.30	3.12	2.18
	R^2 (CSMA-M)	0.980	0.933	0.978
	R^2 (CSMA-MP)	0.981	0.933	0.977
Temkin	$b_T = \frac{RT}{B_T}$ (CSMA-M)	0.198	0.191	0.175
	$b_T = \frac{RT}{B_T}$ (CSMA-MP)	0.201	0.197	0.165
	A_T (CSMA-M)	4.54	3.21	0.85
	A_T (CSMA-MP)	4.67	3.34	0.798
Dubinin-Radushkevich (mol/g)	X_m (CSMA-M)	1.94×10^{-3}	5.12×10^{-3}	5.22×10^{-3}
	X_m (CSMA-MP)	1.98×10^{-3}	5.62×10^{-3}	5.57×10^{-3}
	β (kJ^2/mol^2) (CSMA-M)	0.0024	0.0038	0.0068
	β (kJ^2/mol^2) (CSMA-MP)	0.0028	0.0040	0.0069
	E (kJ/mol) (CSMA-M)	14.24	12.32	10.46
	E (kJ/mol) (CSMA-MP)	14.32	13.01	10.31
	R^2 (CSMA-M)	0.961	0.891	0.924
	R^2 (CSMA-MP)	0.961	0.892	0.924

4 CONCLUSION

Adsorption of Pb (II), Cd (II), and Zn(II) is found to be effective in the pH range of 3–6 by CSMA-AP resin. The elimination percentage increases by increasing the adsorbent dose from 0.5 to 4.0 g/L. The contact time studies in adsorption of selected metal ions exhibit that the elimination percentage increases with time up to 30–40 min and after this time it remains constant. The equilibrium data have been analyzed applying Langmuir, Freundlich,

Temkin, and Dubinin–Radushkevich isotherms. The characteristic factors for each isotherm and related correlation coefficients have been measured. The experimental data gained excellent matches within the following isotherms order: Langmuir >

Temkin > Dubinin–Radushkevich > Freundlich, based on its correlation coefficient values. From the Dubinin–Radushkevich isotherm, the adsorption energy was found 14.24, 12.32 and 10.46 kJ/mol with CSMA-M resin

and 14.32, 13.01 and 10.31 kJ/mol with CSMA-MP resin for Pb(II), Cd(II), and Zn (II), respectively, indicative of the removal of toxic metal ions was done by chemical adsorption phenomena [58-60]. The results have shown that the CSMA-M and CSMA-MP are reusable resins with a good potential for adsorption of metal ions up to 15 cycles by maintaining performance. It can be said that the CSMA-M and CSMA-MA resins have a good potential for removal of toxic metal ions such as Cd (II), Pb (II), and Zn(II) from aqueous solutions. Using this resin for the removal of toxic metal ions is simple, green, and clean technology method and has an approximately high efficiency and maybe can provide a strategic approach to remove heavy metal ions from industrial sewage [50-53].

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