



A suitable method for removing of heavy metal ions from aqueous solutions using proper copolymer and its derivations

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ABSTRACT: Synthesis of copolymers such as poly (styrene alternative maleic anhydride) (SMA), (SMA+ Melamine +1,3-diaminopropane) (CSMA-M), (CSMA-M + propanedioic acid) (CSMA-MP) and (CSMA-M + butanedioic acid) (CSMA-MB) for removing heavy metal ions from aqueous solutions. Adsorption of Cd (II), Pb (II) and Zn(II) on modified copolymers and adsorption behavior of these heavy metal ions on the adsorbents were studied by altering the characters such as pH, adsorbent dose, contact time, and heavy metal ions concentration. Adsorption percentage was increased by increasing each of these parameters. The isotherm models such as: Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich were applied to illustrate adsorption equilibrium. The outcomes shown that the best consistency was accessed with the Langmuir isotherm equation, production maximum adsorption capacities of these adsorbents are very suitable for removing heavy metal ions from aqueous solutions. The adsorbents were characterized by Fourier transform infrared spectroscopy scanning electron microscopy and X-ray diffraction analysis.

Key word: modified melamine; isotherm models; chelating resins; Langmuir isotherm

INTRODUCTION

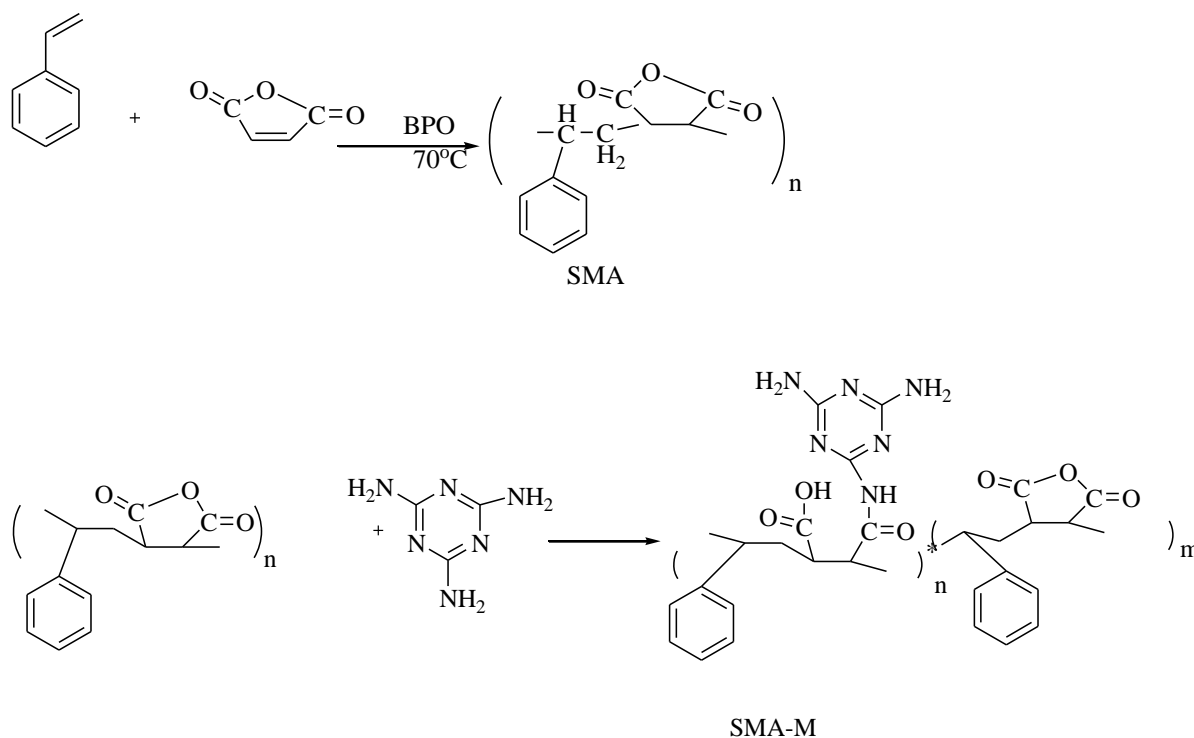
Water is one of the most important needs for living in the world. All plants, animals and human must have water to live [1-2]. It is also necessary for the human activities [3]. Water impurity is increasing worldwide because jumping improvement of industry, increase human population, and homelike and agricultural activities [4]. Water impurity containing heavy metal ions such as cadmium, lead from industrial and homelike is becoming one of the most important environment difficulties globally. Because of the low concentration of heavy metals in different resources could be several hurts to the environment and contrary affecting the human health [5-7]. The remedy of heavy metals is so important owing to perpetuity 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 impure with zinc, due to the presence of large quantities of zinc in the wastewater of industrial plants. This wastewater is not purified satisfactory [8-10]. 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 [11-14]. 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

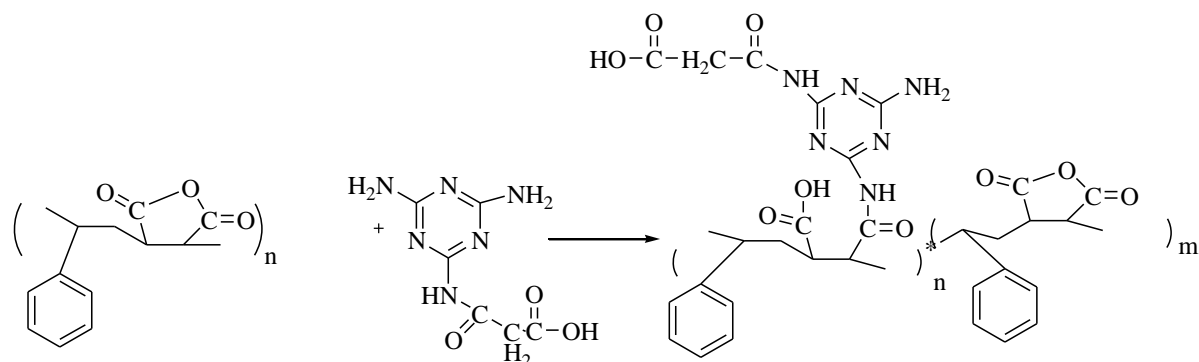
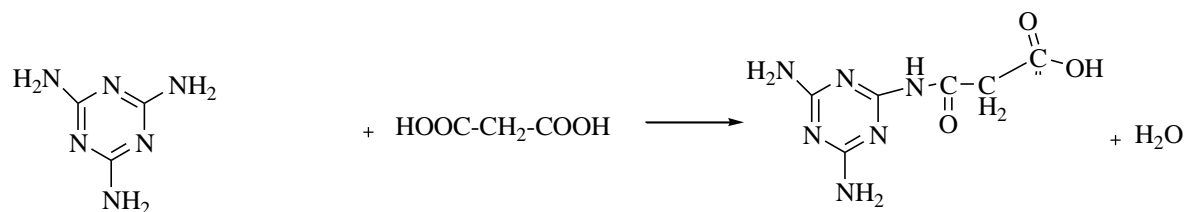


of plants have a chance of survival. That is why there is not much plant diversity near zinc-disposing factories. Due to the effects upon plants zinc is a serious threat to the productions of farmlands [15-18]. Despite of this zinc-containing manures are still applied. Finally, zinc can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms [19-22]. The breakdown of organic matter may seriously slow down because of this. Aquatic environments contamination by toxic heavy metal ions, peculiarly as an outcome of industrialization, is increment being related to common health in an urban position, as toxic heavy metals not only lead to pollution of aquatic life but also cause damage to human's 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 invasion 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 inoffensive quantities, as lead, and cadmium are among the most toxic of elements. Among these toxic heavy metals, cadmium and lead are of remarkable environmental and health importance because of its increasing mobilization and human toxicity [23-25]. The major sources for the introduction of cadmium in water are nonferrous metals smelting and refining, manufacturing processes related to chemicals and heavy metals, and homelike wastewater. Heavy metals such as 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. In biological systems, heavy metals have been reported to affect cellular organelles and components such as cell membrane, mitochondrial, lysosome, endoplasmic reticulum, nuclei, and some enzymes involved in metabolism, detoxification, and damage repair. Metal ions have been found to interact with cell components such as DNA and nuclear proteins, causing DNA damage and conformational changes that may lead to cell cycle modulation, carcinogenesis or apoptosis. Several studies from our laboratory have demonstrated that reactive oxygen species (ROS) production and oxidative stress play a key role in the toxicity and carcinogenicity of metals such as mercury, arsenic, cadmium, lead, and Zinc. Because of their high degree of toxicity, these five elements rank among the priority metals that are of great public health significance. They are all systemic toxicants that are known to induce multiple organ damage, even at lower levels of exposure. According to the United States Environmental Protection Agency (U.S. EPA), and the International Agency for Research on Cancer (IARC), these metals are also classified as either "known" or "probable" human carcinogens based on epidemiological and experimental studies showing an association between exposure and cancer incidence in humans and animals. In biological systems, heavy metals have been reported to affect cellular organelles and components such as cell membrane, mitochondrial, lysosome, endoplasmic reticulum, nuclei, and some enzymes involved in metabolism, detoxification, and damage repair. Metal ions have been found to interact with cell components such as DNA and nuclear proteins, causing DNA damage and conformational changes that may lead to cell cycle modulation, carcinogenesis or apoptosis. Several studies from our laboratory have demonstrated that reactive oxygen species (ROS) production and oxidative stress play a key role in the toxicity and carcinogenicity of metals such as arsenic, cadmium, lead, and zinc [26-28]. Because of their high degree of toxicity, these five elements rank among the priority metals that are of great public health significance. They are all systemic toxicants that are known to induce multiple organ damage, even at lower levels of exposure. According to the United States Environmental Protection Agency (U.S. EPA), and the

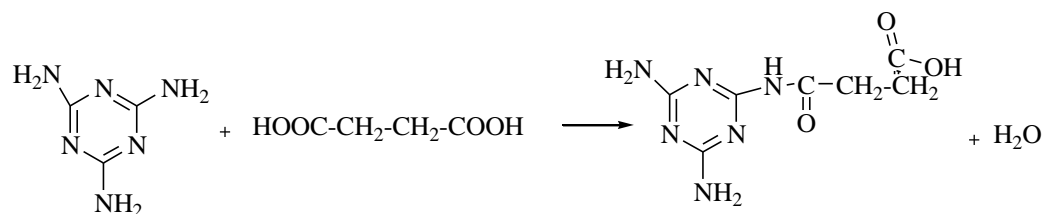


International Agency for Research on Cancer (IARC), these metals are also classified as either “known” or “probable” human carcinogens based on epidemiological and experimental studies showing an association between exposure and cancer incidence in humans and animals. Of all the different methods, adsorption using slight-cost and cheap adsorbents is considered to be an economical and effective method for elimination of toxic heavy metal ions from aqueous solutions [29], There are many types of adsorbents, including activated carbon fibers, resins, and bio sorbents. Chelating materials are critically effective and chance adsorbents [30-34]. Therefore, the most advanced technique for elimination of toxic heavy 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 propylene di-amin (PDA) as a crosslinking agent to form tridimensional adsorbents[35-38]. The preparation of the cross linked resins in the presence of ultrasonic irradiation along with vigorous magnetic stirring gave rise to polymeric particles on the Nano scale. 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.

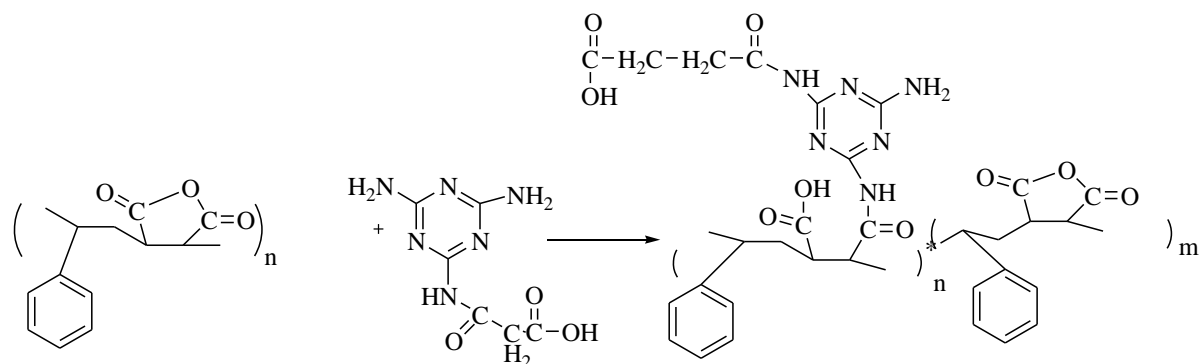




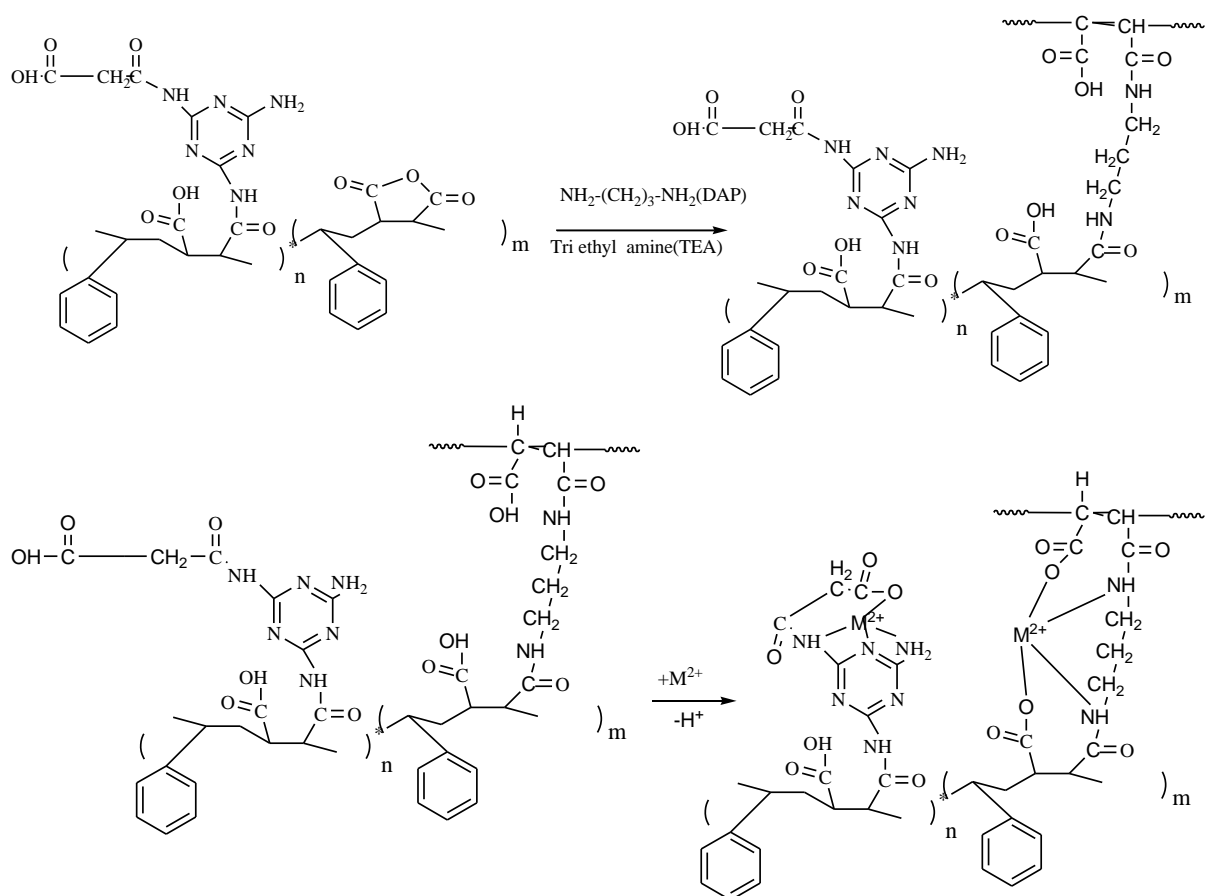
SMA-MP

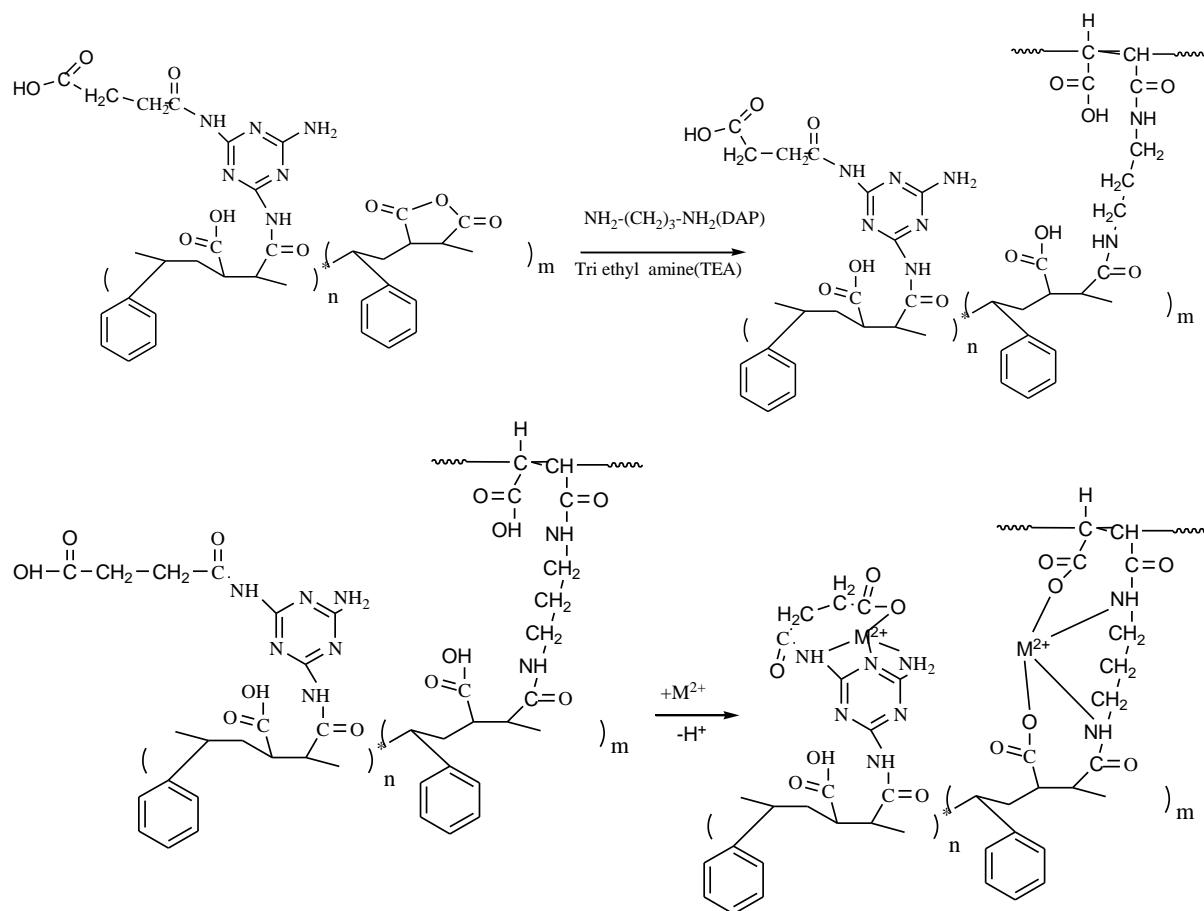


MB



SMA-MB





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

Experimental

Material

Analytical-reagent grade $Cd(NO_3)_2$, and $Pb(NO_3)_2$, $Zn(NO_3)_2 \cdot 6H_2O$ and other inorganic chemicals, including HCl and NaOH, were purchased from Merck (Germany) and were used without further purification. 1,3 Di amino propane (DAP), Styrene, Maleic anhydride, Melamine, propanedioic acid, butanedioic acid, benzoyl peroxide, tri ethyl amine (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.

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 Mg Ka radiation as the excitation source. Atomic absorption spectrophotometry (AAS; Analytik jena novAA 400, Germany) was used to determine the heavy metal-ion concentrations in aqueous solutions. The inherent viscosity of the resulting SMA copolymer 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).

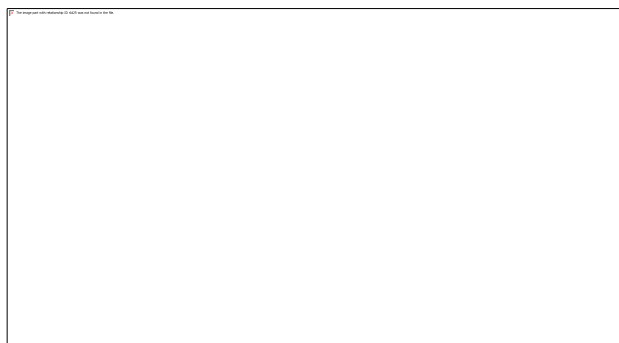


Figure 1. FTIR spectrum of the SMA copolymer

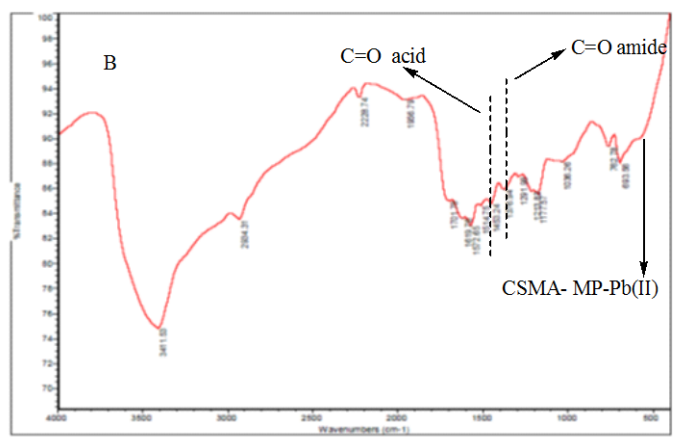
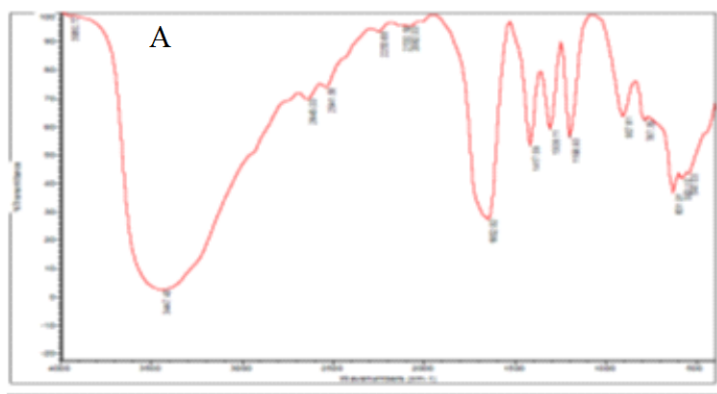




Figure 2. FT-IR spectra of CSMA-MP copolymer, A: before complexation and B: after complexation with Pb(II) ions

Synthesis of the grafted SMA copolymer by melamine

The SMA copolymer was prepared by the free-radical polymerization of maleic anhydride and styrene at 75°C in the presence of benzoyl peroxide as an initiator. 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 5 h at 93 °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 [39-43]. The product was dried in a vacuum oven for 14 h at 65°C (yield = 98%). and 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.

Synthesis of the grafted SMA copolymer by modified melamine with propanedioic acid and butanedioic acid

For the synthesis of the grafted SMA copolymer by modified 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 cleared at first and then it was formed turbid, produced mixture by along with vigorous magnetic stirring ²¹. The obtained product was filtered and the obtained under filter solution was concentrated by heater for vaporizing THF and receiving to half of the initial volume [44-46]. It contains beaker was putted in refrigerator and crystal was formed and this procedure was repeated for obtaining modified melamine with propanedioic acid.

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

The Cross linked melamine functionalized SMA copolymer (CSMA-M) was prepared by simultaneous reaction of the SMA copolymer with melamine and Modified melamine with 1,3 Di amino propane as cross linking agent. The reaction mixture was refluxed for 3 h under inert gas in 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 Nano scale. The obtained product was filtered, washed thoroughly with THF, and dried by vacuum oven at 65°C for 16 h.

Adsorption Studies

Batch adsorption tests were enforced by mixing the CSMA-M (50 mg) and 50 mL of toxic metal 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 (210 rpm) in measured time and after completing the adsorption the mixture was filtered and the metal ion concentration was measured in filtrate by AAS [47-48]. In this study, all the tests were enforced at room temperature (25 ± 2)°C. The gotten data were used to calculate the elimination percentage of toxic heavy metal ions applied the following mass balance relationship:

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



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

Desorption and repeated use

Desorption of heavy metal ions was administered by 0.5M HCl solution. The CSMA-M– heavy metal ion, CSMA-M–heavy metal ion, CSMA-M– heavy metal 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 heavy metal ion in the aqueous solution were measured by AAs. The desorption ratio (D%) of toxic heavy metal ions from the (CSMA-M and CSMA-MP and CSMA-MB) resins were computed with following equation:

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

Where V is the volume of the solution (L); C_d is the concentration of the toxic heavy 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 desorption process was washed thoroughly with deionized water and dried by vacuum pump at 65°C for repeated use.

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 heavy metal ion for 120 min at pH =6. After filtration, the AAS was applied to measure the heavy metal ion concentration in the filtrate. The amount of heavy metal adsorbed q_e (mg/g) was measured using the following mass balance relationship:

$$q_e = \frac{V(C_i - C_e)}{S} \quad (3)$$

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

RESULTS AND DISCUSSION

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

The SMA copolymer 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 copolymer network were shown at previous work by SEM image in two scales 1 μ m and 500 nm. It was found that the SEM micrographs of cross linked copolymer in which particles possess almost uniform distribution of size [50]. 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 size in these copolymer powders, although more of the grain size could be in nanometer-scale corrosion of the SEM (Figure 3). XRD determinations (Figure 4) introduce the dominantly chaotic nature of the SMA and CSMA-M, CSMA-MP, CSMA-MB.

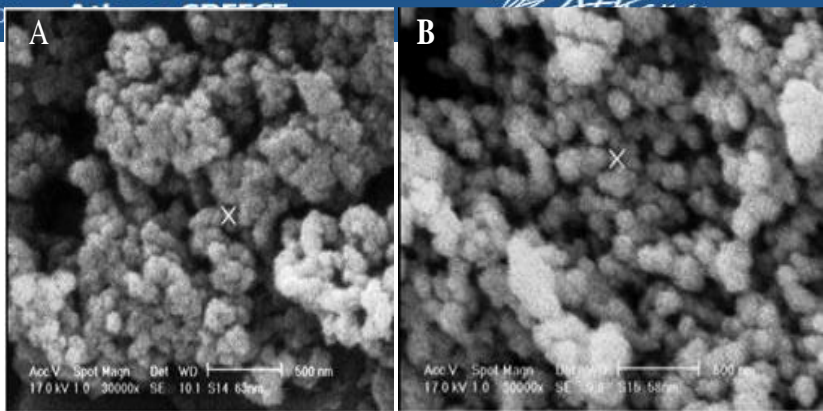
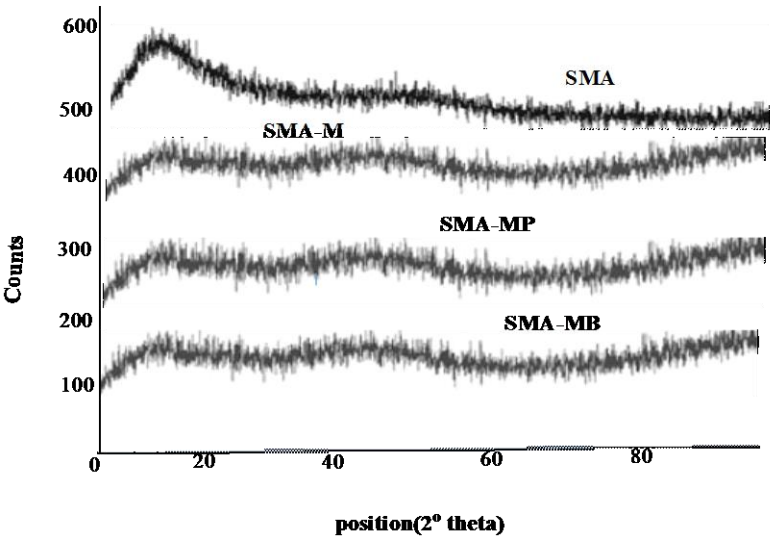


Figure 3. SEM images of chelating adsorbents A: CSMA-MP (scale: 500 nm), B: CSMA-MB (scale: 500 nm)

Figure. 4. X-ray diffraction patterns of the copolymer and polymeric adsorbent



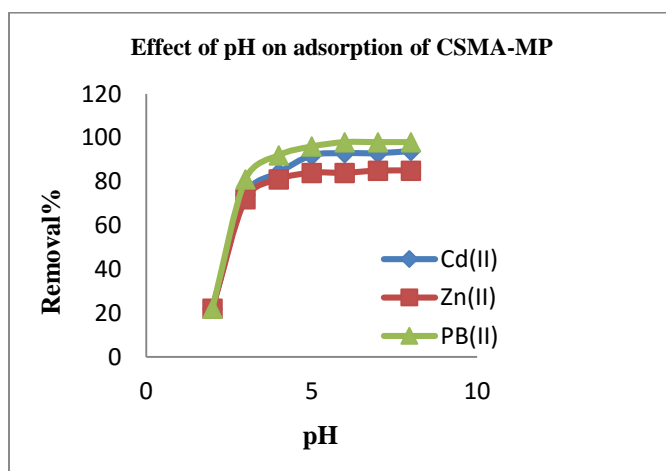
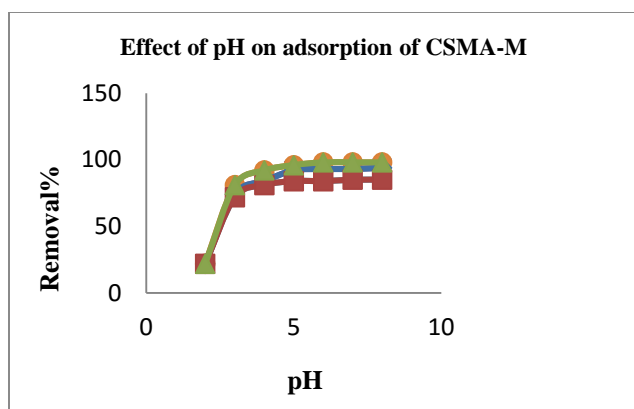


Figure 5. Effect of pH value on metal ions adsorption by CSMA-M and CSMA-MP and CSMA-MB resins
 Effect of pH on CSMA-MP and CSMA-MB resins did not different.

The Swelling Index

By stirring the resin in water, it was swelled without any dissolving. The swelling index of the copolymers is shown in Figure 7. 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 hydrophobicity of the resins. The swelling index was measured with the following equation:

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

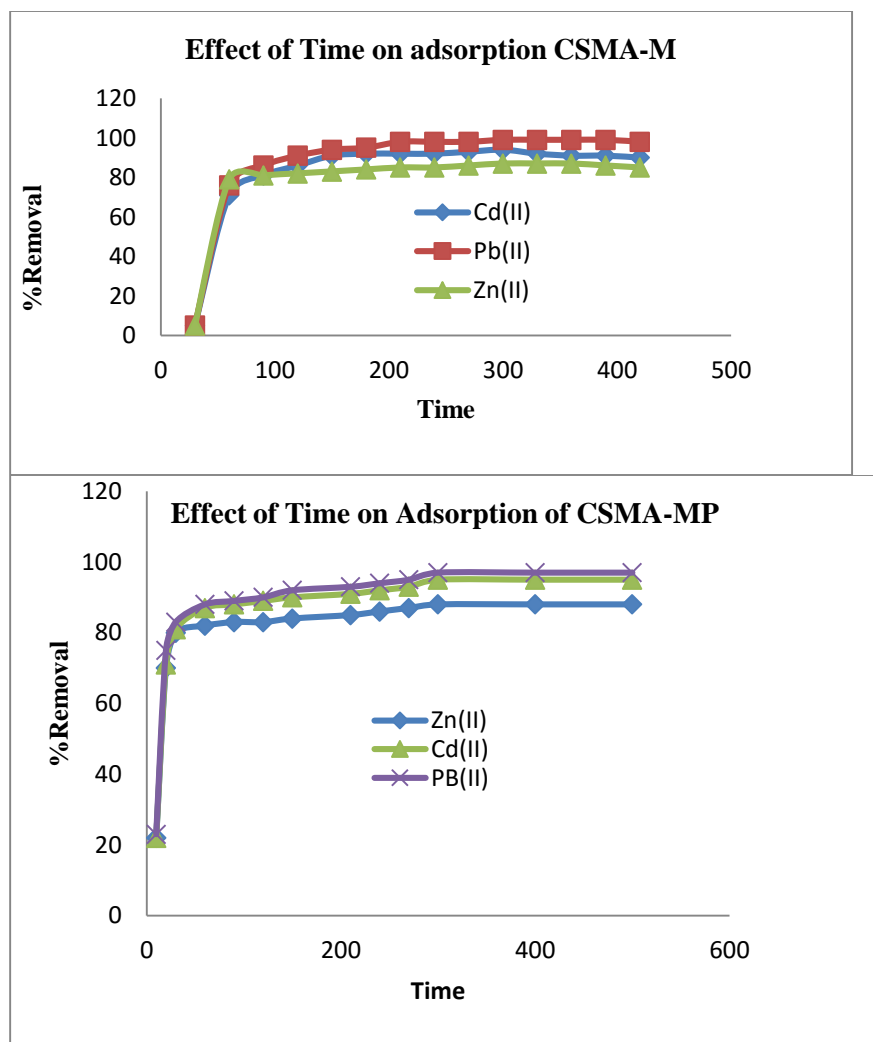


Figure 6 .Effect of contact time (min) on heavy metal ions adsorption by resins (effect of contact Time on CSMA-MP and CSMA-MB resins did not different)

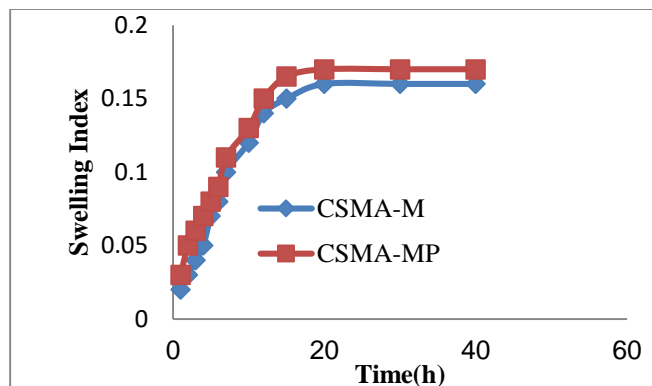


Figure 7. Swelling index of CSMA-M and CSMA-MP resins. (effect of Time on CSMA-MP and CSMA-MB resins did not different)

Effect of pH value on heavy metal ions adsorption

The pH of aqueous solutions is one of the most significant controlling factor that effects the elimination percentage of toxic heavy 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 heavy metal ion solution in the range of 2–8 because these heavy metal ions could be residue by OH⁻ to form heavy metal (II) hydroxide above pH 6. The outcome was shown in Figure 5. The extractability of the metal ions from the solution phase depends on the pH, because its affect on the solubility of the heavy metal ions, concentration of the counter ions on the functional groups of adsorbent, and the degree of ionization of adsorb ate 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 heavy 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 aren't different).In fact in acidic pH, the adsorbent surface will be completely covered with hydronium ions which compete strongly with toxic heavy metal ions for adsorption sites at acidic pH, with an increase in pH, the concentration of H₃O⁺ ions decreases facilitating the adsorption of heavy metal ions by the adsorbent.

3.4 Effect of contact time on heavy metal ions adsorption

Contact time plays a significant obligation in the adsorption of heavy metal ions on solid surface. Removal percentage of toxic heavy metal ions is found to be commensurate to contact 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. Effect 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 heavy 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 6. 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 high success of the these heavy metal ions to the ion substitution sites in the CSMA-M and CSMA-MP and CSMA- MB.

Effect of Adsorbent Dose on metal ions adsorption

The influence of adsorbent dosage is a significant factor on the removal percentage of toxic heavy 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 a accessory of adsorbent dosage was studied and the results can be observed in Figure 8 . The experimental data revealed that the elimination efficiencies of heavy 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 heavy 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 was 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.

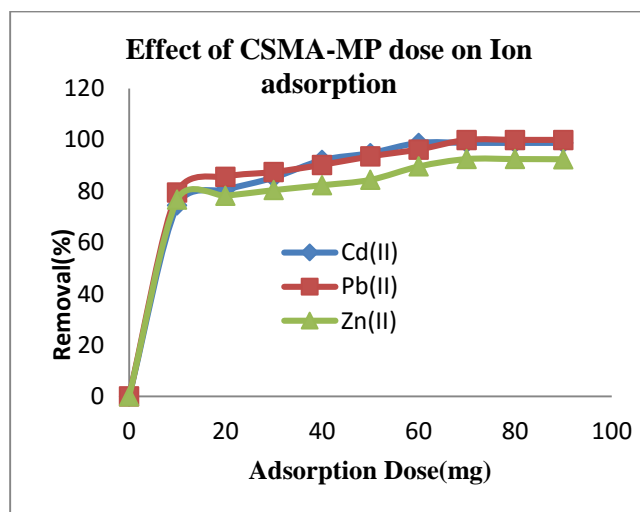
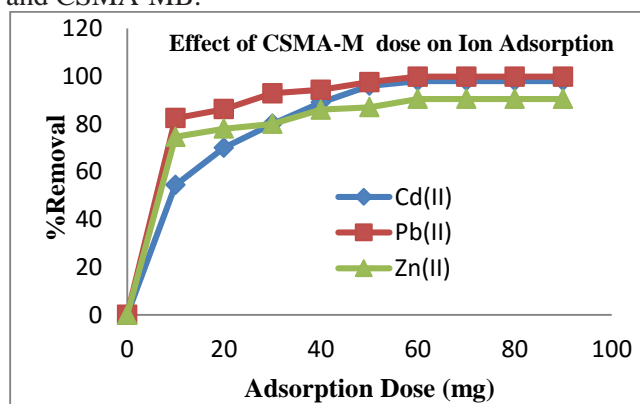


Figure 8. Effect of adsorbent dose on heavy metal ions adsorption by CSMA-M and CSMA-MP.

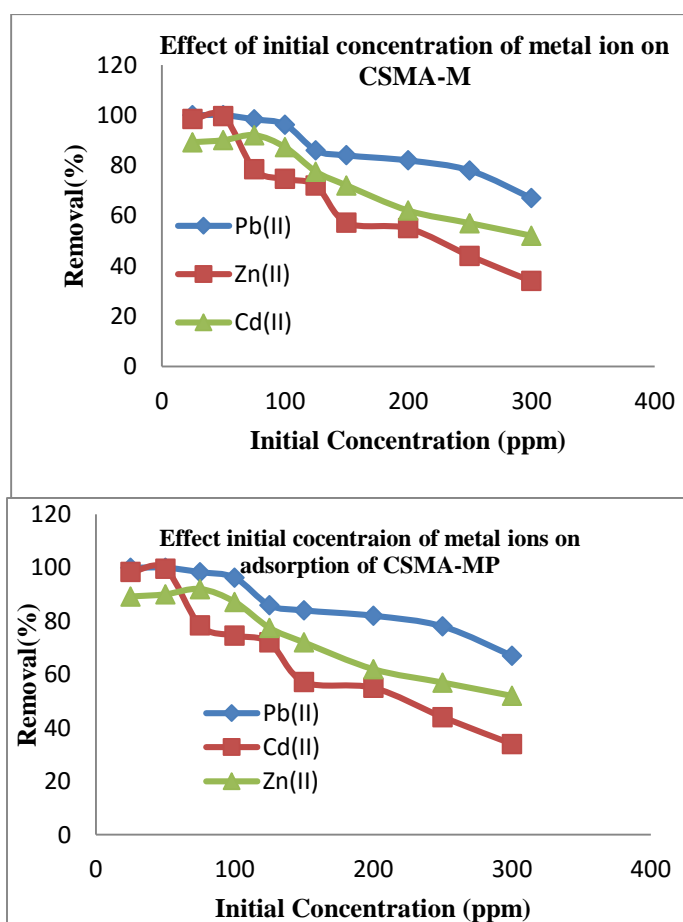


Figure 9. Effect of concentration of heavy metal ion on heavy metal ions adsorption by CSMA-M and CSMA- MP.

3.5 Effect of concentration of heavy metal ion on the Adsorption

The rate of adsorption is a function of the concentration of heavy metal ion, which makes it a significant character to be supposed for efficient adsorption. The affect of metal ions concentration was studied on the adsorption behavior of CSMA-M and CSMA-MP resins at various concentrations (25–300 ppm), and the outcomes are exhibited in Figure 8. Totally, Figure 9 introduces that by increasing the heavy metal



ions concentration with constant amount of the adsorbent, the heavy 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 reduction in the removal percentage. This phenomenon might be due to glut of the active sites of the CSMA-M and CSMA-MP with the toxic metal ions at higher concentrations. The structure of copolymer network was shown in Scheme 1. We can observe that these resins have so many active ion substitution sites for elimination of heavy metal ions from aqueous solution.

FTIR Scan

Fourier transform spectroscopy (FT-IR) (KBr): 3250-3560(acidic OH+NH amide), 3030-3065 (aromatic CH), 2880-2991(aliphatic CH), 1866(C=O anhydride), 1789(C=O anhydride), 1724 (C=O acid), 1695 (C=O amide), 1560, 1600(NH), 1495(C=C substituted benzene), 1460, 1383(C-N), 1245(C-N-H), 1220(C-OH), 1189(C-O anhydride), 1070(C-H mono substituted benzene), 920(C-H alkane), 660(N-H amino Melamine), 560(H-C-C and C-C-C skeletal) cm^{-1} . FTIR spectroscopy has been applied for the characterization of copolymer-heavy 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 heavy metal ions, the band at 1625 cm^{-1} piked and shifted to lower frequency (at about 1464 cm^{-1}), introducing a stronger copolymer-metal bond has wrought between heavy 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 heavy metal salts of amid [49-50].

Effect of agitation 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 heavy 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-MA. Also Cd(II) attained maximum removal of 98.51% with CSMA-M and at a lower agitation speed of 210 rpm. The increase in agitation speed resting to increase in heavy metal ions elimination percentage was due to the fact that increase in stirring rate sublimated the heavy metal ions diffusion to the surface of the adsorbent; and also sake reduction in the film border layer environs the adsorbent.

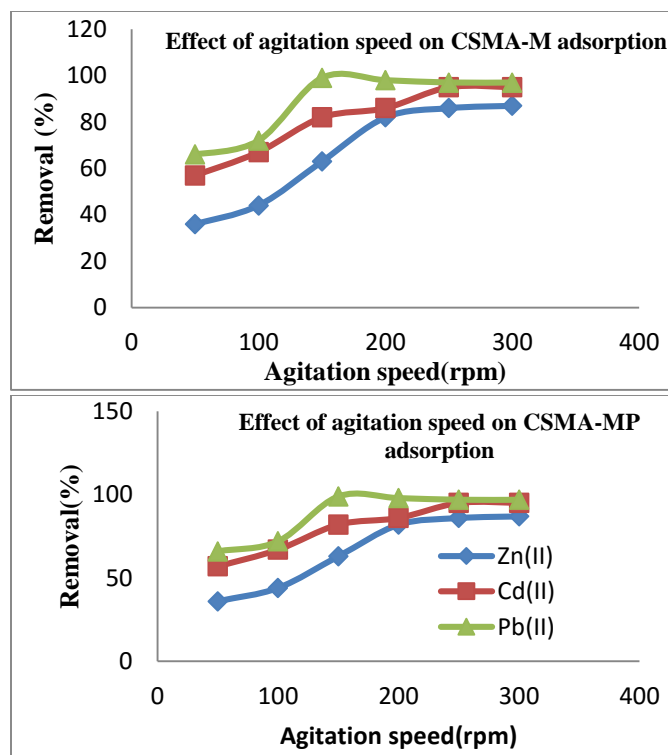


Figure 10. Effect of agitation speed on adsorption of heavy metal ions with CSMA-M and CSMA-MP.

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 heavy metal ions can be recovered. Desorption of Cd(II), Pb(II), and Zn(II) ions from CSMA-M– heavy metal ion and CSMA-MP–metal ion and CSMA-MB– heavy 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), Pb(II), and Zn(II) ions from CSMA-M and heavy metal CSMA-MP–metal ion and CSMA-MB– heavy 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 Figure10. 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 elimination of Cd(II), Pb(II), and Zn(II) from their single-metal ion solutions²⁵.

3.8 Determination of the Equilibrium Distribution Coefficient (k_d)

The distribution coefficient can be measured with the following equation:

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

Where V is the volume of the solution (mL) and S is the mass of adsorbent (g). The k_d value can be applied as a 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 augment 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 heavy metal ions Adsorption by CSMA-M and CSMA-MP CSMA-MB Resins at pH=6 (Concentration of heavy metal ions = 50 ppm, Resin Dose =50mg/L, Time = 300 min)

Resins	$k_d \text{ (mL/g} \times 10^3)$		
	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 accurate equilibrium dependence between the solid and liquid-phase concentrations of toxic heavy 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 models²⁵.

3.10 Langmuir Isotherm.

Langmuir model has been widely used to some process of metal ions adsorption [50]. 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 11. 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 dimensionless separation factor (R_L), which has been defined as below :

$$R_L = \frac{1}{1 + C_0 K_L} \quad (9)$$

Where K_L is the Langmuir constant (L/mg) and C_0 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 ($R_L = 0$). Figure 14 illustrated that adsorption of Cd(II), Pb(II), and Zn(II) increased continually with concentration of heavy metal ion. The computed R_L values for this toxic heavy metal ions adsorption illustrate that adsorption are desirable even for higher concentrations of metal ion.

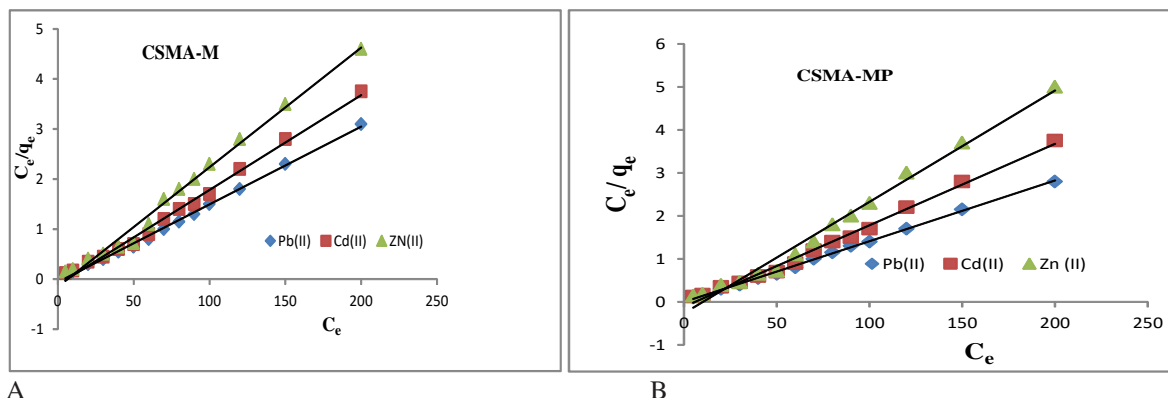


Figure 11. Langmuir isotherms for Cd(II), Pb(II), and Zn(II) adsorption onto CSMA-M (A) and CSMA-MP(B)

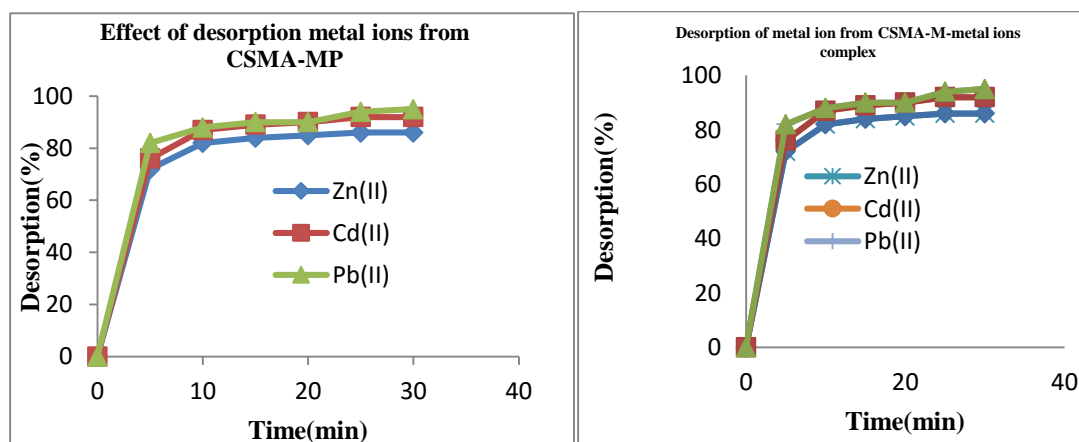


Figure 12. Desorption of heavy metal ions from CSMA-M– heavy metal ions and CSMA-MA– heavy metal ions complex

by 0.5M HCl solution

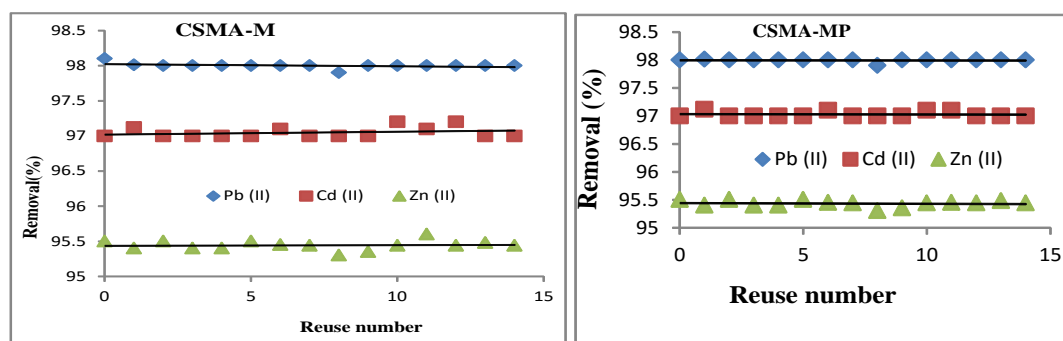


Figure 13. removal of metal ions after repeated adsorption-desorption operations at 25°C (concentration of metal ions = 50 ppm, adsorption time = 60 min, pH = 6, adsorbent dose = 5g/L).

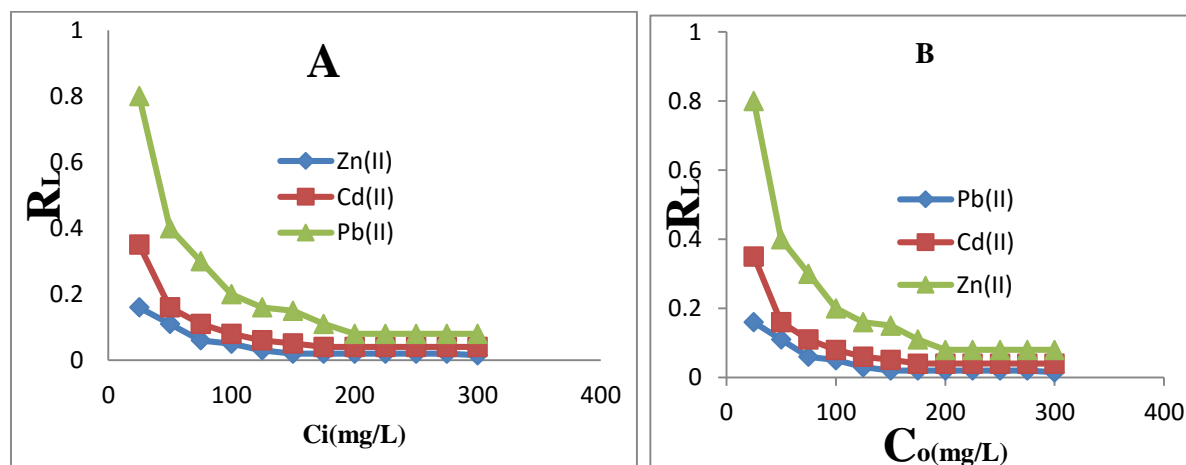


Figure 14. Separation factor (RL) profile for biosorption of Cd(II), Pb(II), and Zn(II) as function of concentration of metal ion by CSMA-M(A) and CSMA-MA (B) (pH = 6, time = 300 min, resin dose = 5 g/L).

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 17] with the correlation coefficients which were showed in Table 2. The resin shown better accordance for Langmuir isotherm than Freundlich isotherm.

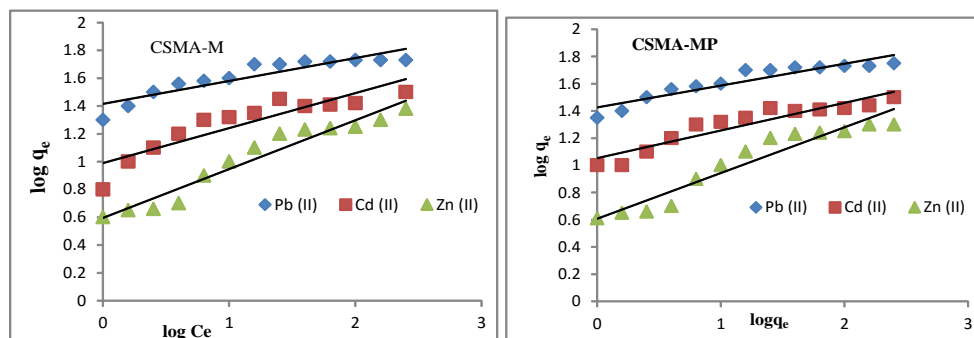


Figure 15. Freundlich isotherms with CSMA-M and CAMA-MP resins.

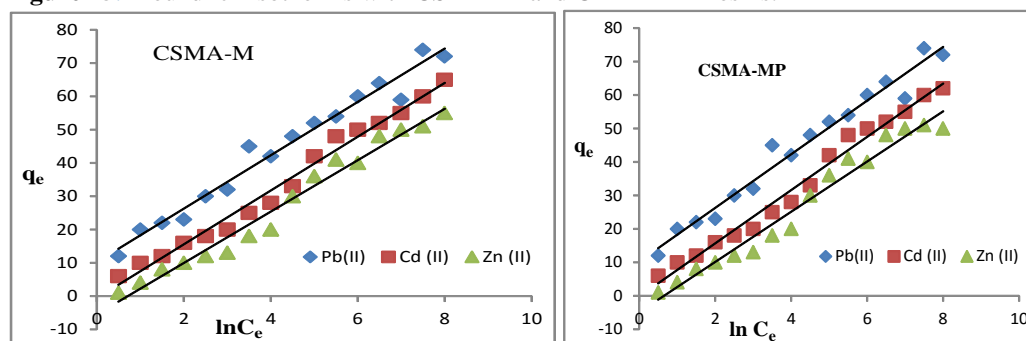


Figure 16. Temkin isotherms with CSMA-M and CAMA-MP resins.

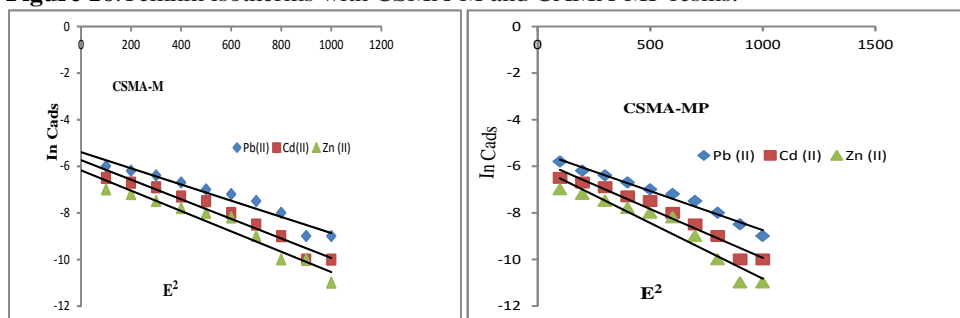


Figure 17. Dubinin–Radushkevich isotherms with CSMA-M and CAMA-MP resins

3.12 Temkin Isotherm. The model of Temkin adsorption isotherm contains a factor that explicitly takes into account adsorbent–adsorbate interactions [51-56]. 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 16]. Temkin isotherm generates a satisfactory accord to the experimental data as indicated by correlation coefficients.

From Table 2, it can be seen that 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 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). Mean free energy of adsorption per mole of 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 heavy 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. 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. Figure 17 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 [57-60].



Table 2 . 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 =0.05 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	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

CONCLUSIONS

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 heavy 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 consistencies 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 heavy metal ions was done by chemical adsorption phenomena [61–64]. 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 8 cycles by maintaining performance. It can be said that the CSMA-M and CSMA-MP resins have a good potential for removal of toxic heavy metal ions such as Cd(II), Pb(II), and Zn(II) from aqueous solutions. Using these resins for the removal of toxic heavy 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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