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Synthesized nanoparticles of poly (Styrene–alternative-maleic anhydride) and prunus cerasus rock used for removing Cadmium (II) ions from aqueous solutions

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ABSTRACT

Chelating adsorbents have been considered to be suitable materials for the
recovery of cadmium in water treatments. Adsorption of Cadmium (II) ions
on melamine-butanedioic acid, modified poly (Styrene-alternative-maleic
anhydride) cross-linked by 1, 2-diaminobutane (CSMA-MB) and pit shell of
sour cherry (Prunus cerasus rock) (PCR) as an ion exchange adsorbents have
been investigated in aqueous solution. The adsorption behavior of these
Cadmium (II) ions on the adsorbents was studied by varying the parameters
such as pH (2-8), adsorbent dose (0-4.0 g/L $^{-1}$), contact time (0–240 min), and
Cadmium (II) ion concentration (20-300 mg/L ⁻¹). Adsorption percentage was
increased by increasing each of these parameters. The isotherm models such
as Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich were used to
describe adsorption equilibrium. The results showed that the best fit was
achieved with the Langmuir isotherm equation, yielding maximum
adsorption capacities of 81.30, 80.42 mg/g ⁻¹ for Cd (II) with CSMA-MB and
PCR respectively. Both adsorbents, CSMA-MB and PCR, are very suitable for
the removal Cadmium (II) ions from aqueous solutions. The adsorbents were
characterized by fourier transform infrared spectroscopy (FT-IR), scanning
electron microscopy (SEM), x-ray diffraction analysis (XRD).

Graphical Abstract



Introduction

Heavy metal pollution is a significant problem to the aquatic ecosystems since these heavy metals are potentially toxic even in very trace amounts [1]. Heavy metals are more perilous because they tend to bio accumulate. Due to these reasons, there is a great interest in the removal of heavy metals from wastewater effluents. Exposure to heavy metals, even at trace levels, is harmful to human beings [2]. An increase in the application of heavy metals in the industrial activity results in the production of wastewater that contains high values of toxic heavy metals and their presence thus causes environmental risks. Dissolved and liberated metals in the environment may accumulate in live tissues through the food chains [3]. Heavy metal poisoning is the accumulation of heavy metals, in toxic amounts, in the soft tissues of the body. Symptoms and physical findings associated with heavy metal poisoning vary according to the metal accumulated. Many of the heavy metals, such as zinc, copper, chromium, iron, and manganese, are essential to body function in very small amounts. But, if these metals accumulate in the body in concentrations sufficient to cause poisoning, then serious damage may occur. The heavy metals most commonly associated with poisoning of humans are lead, mercury, arsenic, and cadmium. Heavy metal poisoning may occur as a result of industrial exposure, air or water pollution, foods, medicines, improperly coated food containers, or the ingestion of leadbased paints. Cadmium is an extremely toxic metal commonly found in industrial workplaces. Due to its low permissible exposure limit, overexposures may occur even in situations where trace quantities of cadmium are found [4, 5].

Cadmium is used extensively in electroplating, although the nature of the operation does not generally lead to overexposures. Cadmium is used for many items, including electroplating, storage batteries, and vapor lamps and in some solders [6]. The onset of symptoms may be delayed for two to four hours after exposure [7–9]. Overexposure may cause fatigue, headaches, nausea, vomiting, abdominal cramps, diarrhea, and fever. In addition, progressive loss of lung function (Emphysema), an abnormal buildup of fluid in the lungs (Pulmonary edema), and breathlessness (Dyspnea) may also be present. Cadmium is also found in some industrial paints and may represent a hazard when sprayed. Operations involving removal of cadmium paints by scraping or blasting may pose a significant hazard. Cadmium is also present in the manufacturing of some types of batteries. Exposures to cadmium are addressed in specific standards for the general industry, shipyard employment, construction industry, and the agricultural industry [10–14]. The buildup of cadmium levels in the water, air, and soil has been occurring particularly in industrial areas. Environmental exposure to cadmium has been particularly problematic in Japan where many people have consumed rice that was grown in cadmium contaminated irrigation water. This phenomenon is known under the name itai-itai disease [15].

Aside from tobacco smokers, people who live near hazardous waste sites or factories that release cadmium into the air have the potential for exposure to cadmium in the air. However, numerous state and federal regulations in the United states control the amount of cadmium that can be released to the air from waste sites and incinerators so that properly regulated sites are not hazardous. The general population and people living near hazardous waste sites may be exposed to cadmium in contaminated food, dust, or water from unregulated releases or accidental releases. Numerous regulations and use of pollution controls are enforced to prevent such releases [16, 17]. Heavy metals released from industrial activities pose a significant threat to the environment and public health due to their reported toxicity even at trace levels. Although there are several available methods to treat or remove heavy metals from water and wastewater, the research focuses on the development of technological solutions which sound environmental friendly and economically feasible, able to reduce the costs and maximize the efficiency. In this framework, the absorption process, which uses cheap and non-pollutant materials, may be considered as an alternative, viable and promising, technology for heavy metal and metalloid ion sequestration and ultimately removal technology in the wastewater treatment. However, there is as yet little data on full-scale applications for the design and testing of adsorption units using single biosorbents and their combinations to sequester heavy metal ions from a multi-metal system [18–21].

Immediate research and development are hence earnestly required in this specific direction to further make progress this blooming technology and widen its scope of application to real situations

needing heavy metal pollution remediation [22–24]. This review provides a comprehensive appraisal of the equilibrium modeling of a number of bio svation of biosorbents. Further, the relative merits of the methods used to recover sequestered heavy metal ions and regenerate bio sorbents through desorption routes and their future applications are discussed. Among various methods of heavy metal removal such as liquid-liquid extraction, precipitation, electrolytic concentration, membrane filtration, ion exchange and adsorption, the last are generally preferred because of its high efficiency, ease of handling and availability of different sorbents. Although in using methods such as chemical precipitation and reverse osmosis for the removal of metal ions from wastewaters, metal removal is incomplete, and moreover, these processes have high reagent and energy requirement, the toxic sludge produced requiring careful disposal. Therefore, the most promising technique for the removal of metal cations is their adsorption on organic sorbents containing chelating functional groups [25–27]. An organic chelating sorbent consists of two main parts: chelating functional group(s) and the polymer matrix or support. The structure of the polymer matrix and of the chelating groups, on one side, and the interaction model between the support and functional group, on the other side, determine the specific applications of the chelating sorbents. Through their high selectivity in binding metal ions and metal complex ions, organic chelating sorbents have a major implication in concentration control and in inorganic analytical chemistry [28–31].

In this work, a new type of reactive polymer has been synthesized by the modification of a linear polymer of poly (Styrene-alternative-maleic anhydride) by melamine. The prepared resin has a good potential for cross-linking by 1, 4–diaminobutane for the preparation of porous resin beads. All of the reaction can be carried out as one pot reaction. The melamine grafted linear polymer is expected to take a flexible motion on metal complex formation inside the actual pore of the bead and the prepared chelating resin and Plant material applicable as biosorbent should be classified in the grain size between 0.1 and 3 mm. Better functionality and applicability of the biosorbent in the process of biosorption should be ensured by its chemical treatment. Biosorbent is then immediately capable of biosorption of ions from metals in aqueous solutions. Biosorbent should be cheaply and easily available in large quantities. Moreover, it should contain reactive groups in its structure, which are responsible for the isolation of metals from solutions. This implies that it is convenient to be aware of the chemical composition of a cell wall of the applied bio sorbent. Furthermore, sour cherry (Prunus cerasus) rock (CPR) has been examined to the loading behavior of Cadmium (II) ions.

Experimental

Materials and methods

Analytical-reagent grade Cd $(NO_3)_2$ and other inorganic chemicals, including HCl and NaOH, were purchased from Merck (Germany) and were used without further purification. 1, 4-diamino butane (DAP), styrene, maleic anhydride, melamine, 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 cadmium salts in deionized water. Shells of the Iranian pit shell (Sour cherry or prunus cerasus rock) (PCR) were used as bio sorbent. IR spectra were measured with a Fourier transform infrared spectrophotometer (Nexus-670, Thermo Nicolet, USA). The X-ray diffraction (XRD) spectra were recorded on a X'pert Philips X-ray photo electron spectrometer (The Netherlands) with non-mono-chromated Mg Ka radiation as the excitation source. Atomic absorption spectrophotometry (AAS; Analytik jenanov AA 400, Germany) was used to determine the metal-ion concentrations in aqueous solutions. The inherent viscosity of the resulting SMA polymer was obtained with an Ostwald Viscometer at 25 °C in a thermostated water bath. The elemental analysis of one of the adsorbents 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).

Biosorbent characteristics

Shells of the iranian pit shell (Sour cherry or prunus cerasus) (PCR) were used as bio sorbent. The PC of the iranian pit shell is very hard, chemically inert, nontoxic and largely available plant material. A shell of the prunus cerasus pit is formed by three basic substances, namely cellulose (42.58%), hemicellulose (24.7%) and lignin (22.3%). The element content of elements determined in a shell of the Prunus Cerasus pit is as follows: 62.4% carbon; 6.6% hydrogen; 0.12% nitrogen; 0.12% sulfur; 0.26% phosphorus; 0.42% potassium; 0.14% calcium and 0.18% magnesium and a low quantity of mineral compounds, which are labeled as ash content in the prunus cerasus pit rock (1.1%). On the iranian pit shell cell wall surface, there is a large quantity of various functional groups that are able to trap and bond more metals from solutions. The reactive groups in the bio sorbent formulas significant for the metal bonds were determined using the method of fourier transform onto the absorption infrared spectrum (FT-IR). All bio sorbent samples showed similar FT-IR spectra development; therefore, individual reactive (Functional) groups in the structure of sour cherry shell were determined by FT-IR spectrum sample of the bio sorbent activated by NaOH (Figure 1). With this sample, it came to the highest efficiency of Cadmium removal during kinetics and equilibrium studies. In the infrared spectrum shown in Figure 1, there is an apparent wide band with a maximum of 3420 cm⁻¹ in the area 3060-3660 cm⁻¹. This spectrum sphere is characteristic of the –OH group

(Alcohols). Alcohols also have an apparent intensive absorption band of valence vibration of C–O bond around 1060 cm⁻¹. A characteristic band of valence vibrations of C–H bond at 2 850-3050 cm⁻¹ is typical for the absorption bands of C-H in methyl compounds and a methylene group in the lignin structure. In the sour cherry rock cell wall structure, there are also carboxylic groups, for which there is a characteristic band in the area 1682 to 1780 cm⁻¹). In the area 1460 to 1650 cm⁻¹, there are a number of bands of medium intensity, which are caused by complex vibration movements of an aromatic ring and characterize aromatic compounds.

Synthesis of grafted SMA polymer by melamine

The SMA polymer was prepared by the free-radical polymerization of maleic anhydride and styrene at 75 °C in the presence of di-benzoyl peroxide as an initiator. For a synthesis of the grafted SMA polymer, 1.5 g (0.0075 moles) of SMA polymer and 0.7875 g (0.00375 moles) of melamine at a ratio of 1:0.5 were poured into a flask. Then, 0.25 mL (0.002 moles) of triethylamine (TEA) as a catalyst and 50 mL of THF as a solvent was charged into 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 an insolvent and were separated by filtration and washed by *n*-hexane several times. 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. The synthesis processes of the chelating resin are shown in Scheme 1 and Figures 2 and 3.



Figure 1. FT-IR spectrum of the iranian pit shells (Sour cherry rock) (PC)



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



Figure 2. FT-IR spectrum of the SMA polymer



Figure 3. The FT-IR spectrum of the SMA modified with melamine + butanedioic acid

Synthesis of grafted SMA polymer by modifying mmelamine with butanedioic acid

For the synthesis of the grafted SMA polymer by modifying melamine 0.2 g of melamine was solved in pH = 4.34 of 15 mL 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 1 g of extra butanedioic acid was dissolved in 15 mL 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 [32]. The obtained product was filtered and the obtained under filter

solution was concentrated by the heater for vaporing THF and receiving two half of the initial volume. It contains beaker was put in the refrigerator and crystal was formed (Figure 3) shown the FT-IR spectra.

Preparation of CSMA-MB

The cross-linked melamine functioned SMA polymer (CSMA-MB) was prepared by the simultaneous reaction of the SMA polymer with melamine and modified melamine with 1,4 diamino butane as cross-linking agent. The reaction mixture was refluxed for 3 h under inert gas in the presence of ultrasonic irradiation along with a vigorous stirring bar in THF. It can be said that the preparation of cross-linked resin in the 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.

Biosorbent treatment

The PC of the iranian pit shell (Sour cherry rock) was first cleaned from the kernel. For better applicability in grinding, shells were crushed to the size of about 0.5–2 cm.

Thermal treatment of biosorbent surface

The pre-treated shells of the iranian pit shell (Crushing) were first dried at the laboratory temperature for 36 h prior to grinding. To prevent a sticky effect in screening, the samples are dried at the temperature of 110 °C till constant mass for 3 h prior to screening. The iranian pit shell samples were also thermally treated at 110 °C till constant mass for 3 h before and after activation of the sorbent by activating agents.

Grain-size treatment of biosorbent

Crushed and dried shells of the iranian pit shells of sour cherry (Collected urmia gardens) were screened into grain-size classes 1–2 mm.

Chemical activation of biosorbent

The chemical activating agent was 0.1 M HCl and 0.1 M NaOH. The chemical activation by 0.1 M HCl took 120 min at 200 rpm with bio sorbent concentration of 10 g/L⁻¹. In the case of activation by 0.1 M NaOH, the process lasted 15 min at 200 rpm with bio sorbent concentration of 10 g/L⁻¹. Then, each material was washed four times with redistilled water to avoid any trace of the used activating agent. As a standard for adsorption tests, we used iranian pit shells which underwent identical

physical and thermal treatment, but the redistilled water was used instead of the activating agent. In order to identify the most suitable method of activation for the given bio sorbent and determination of limits when the sorption is already insignificant and when it does not take place, the further conditions of iranian pit shell biosorption were studied but activated by a more suitable activating agent of sodium hydroxide. Apart from the original concentration of NaOH 0.1 mol/L⁻¹ also the concentration of 0.01, 1, and 2 mol/L⁻¹ were used. The original time of activation of 15 min was

Effects of pH on adsorption

expanded to 5, 30, 45, and 60 min.

For the study of the pH value effect on biosorption, we chose the observed range of pH values 2-8 (That is, 2, 3, 4, 5, 6, and 8). The input concentration of the model Cadmium (II) ion solution was 200 mg/L⁻¹ and biosorbent and CSMA-MB concentration in the Cadmium (II) ion solution was 20 g L⁻¹. Adding nitric acid of concentration 0.1 mol/L⁻¹ or sodium hydroxide of concentration 0.1 mol/L⁻¹ always achieved the required pH value. Acid or alkali were added in such amounts so as not to alter the solution volume. The treated samples of model Cadmium (II) ion solutions with sorbent were agitated in a shaking incubator at 200 rpm. Then, the biosorbent samples were filtered, and the input and steady state (Residual final) concentrations of the studied Cadmium (II) ions were analyzed using the method of atomic absorption spectrometry (Table 1).

Swelling index

A known weight (0.5 g) of fully dried SMA–MB and CPR were immersed in water separately. 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 adsorbent (<u>Table 2</u>).

Modeling of adsorption isotherms

For the modeling of adsorption isotherms, we used the working solutions with Cadmium contents in 40, 60, 80, 120, and 200 mg/L⁻¹. A standard Cd $(NO_3)_2$ was used for the preparation of model Cadmium samples. The model Cadmium samples with biosorbent of concentration 10 g L⁻¹ were agitated in a shaking incubator at 200 rpm till the uptake equilibrium was stabilized. At the time of establishing the uptake equilibrium which was set on the basis of kinetics study (6 h), samples were

		Adsorption			
Adsorbent	рН =	2	4	6	8
CSMA-MB		0.187	0.574	0.882	0.865
PCR		0.181	0.571	0.878	0.811

Table 1. Adsorption capacity (mg g⁻¹) for Cadmium (II) ions at various pH's (2, 4, 6, and 8)

Table 2. Polymer synthesized for index swelling

CSMA	A-MB	PCR		
Adsorbent	Time (h)	Adsorbent	Time (h)	
0.0030	0.05	0.032	0.05	
0.0044	1	0.055	1	
0.056	2	0.099	2	
0.072	4	0.111	4	
0.088	6	0.121	6	
0.112	8	0.141	8	
0.016	10	0.191	10	
0.181	12	0.214	12	
0.192	24	0.224	24	
0.0192	48	0.224	48	
0.0193	72	0.225	72	

drawn, filtered and analyzed using the method of atomic absorption spectrometry. Based on the acquired values, Cadmium adsorption was calculated according to the following equation I:

$$q = \frac{V(C_i - C_f)}{W} \tag{1}$$

Where q is the equilibrium metal uptake (mg/g⁻¹), V the volume of metal solution (l); C_i and C_f are the initial and final metal concentration (mg/L⁻¹) and W is the weight of biosorbent (g). The best treatment to express Cadmium biosorption from model solutions in all the biosorbent samples was the relation for modified Langmuir isotherm of the first type equation II:

$$\frac{C_f}{q} = \frac{C_f}{q_{max}} + \frac{1}{q_{max} b} \tag{II}$$

Where *q* is the equilibrium metal uptake (mg/g), q_{max} is the maximum equilibrium metal uptake (mg/g⁻¹), *b* is the Langmuir constant and C_f is the final Cadmium concentration (mg/L⁻¹). Adsorption Cadmium isotherms were graphically created with the help of the "Origin Lab" programed [33].

Results and discussion

Synthesized and characterization of SMA-MB polymer

The SMA polymer was prepared by the method mentioned in reference [34]. Figure 2 shows the FT-IR spectrum of the SMA polymer. In this spectrum, the characteristic of anhydride bonds at 1745, 1785, and 1856 cm⁻¹ are shown. The intrinsic viscosity of the resulting SMA polymer was measured with an ostwald viscometer at 25 °C in THF solvent, and it was determined to be 0.42 dL/g⁻¹.

The SMA–MB was prepared with the amidation of anhydride moieties of the SMA polymer. The amine group of MP reacted with maleic anhydride repeating groups in the SMA polymer backbone to form an alkyl amide linkage and a carboxylic acid group. Amide bonds are significantly resistant to hydrolysis, so the resulting polymer was stable in acidic and basic media. To prepare the tridimensional SMA-MB polymer, the reaction was carried out with a step-by-step reaction of the SMA polymer with melamine and modified melamine with oxalic acid and butanedioic acid as a grafting agent and 1, 2-diaminobutane as a cross-linking agent.

Figure 3 and displays the FT-IR spectra of the SMA-MB polymer. 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 1679 cm⁻¹. In the case of the SMA-MB polymer, the FT-IR 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 1570 cm⁻¹. All of the pendant carboxylic acids of the resins were converted to free carboxylate ions because of the existence of aminopyridine groups in the neighborhoods [35]. It is known that metal complexation to a certain polymeric ligand causes changes in the absorption spectra of the starting polymer [36]. FT-IR spectroscopy has been used for the characterization of polymer-Cd (II) complexes because the frequency at which a characteristic group of the polymer absorbs is modified by Cd (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 chelate resin with Cd²⁺ was provided by the FT-IR 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 [37]. The more covalent it was, the higher the frequency shift was for the free carbonyl bond absorption.

Figure 4 represents the FT-IR spectra of the four kinds of Cd²⁺ ions adsorbed in the resins. In this study, the absorption band for C=O in the chelating group shifted to higher frequencies with the increasing covalent nature of the carbonyl band in the results of complexation with ionic cadmium and appeared about 1695-1725 cm⁻¹. The bands at 1642, 1569, 1458, and 1252 cm⁻¹ shifted to a lower frequency; this indicated that the metal coordination through the chelating ligands was done in the polymer network. Also, the absorption bands characteristic of the aromatic parts of the matrix (1042, 924, 769, and 712 cm⁻¹) were not influenced by the metal complexation.

The XRD patterns of the synthesized polymers and bio sorbent are depicted in Figure 5. The diffraction patterns showed that the polymers were amorphous. Indeed, there was only a broad diffraction hump at about 2θ =20°; this indicated the amorphous nature of the polymers. So, the presence of the grafting and cross-linking agent in the polymer backbone did not affect the amorphous structure of the polymer Figure 5 shows the SEM micrographs of typical CPR and SMA–MB, 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.

Sorption of cadmium (II) ions as a function of pH

The sorption behavior of any Cadmium ions on the resin at different pH values was examined with a batch calibration technique, and the results are summarized in Table 1. The pH of the Cadmium ion test solution was measured during the sorption process. After calibration 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 heavy metal ions by resin depends on the pH; this affects the chelation extremies as well as the physisorption processes. Thus, the effect of pH on the adsorption capacities needed to be further investigated. The SMA–MB 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-diaminobutane compared to that in the non-cross-linked sample. Figure 6 shows the metal binding onto the chelating resin. There was an abrupt increase in the metal adsorption when the pH was raised from 2 to 8. The adsorption of



Figure 4. FT-IR spectrum of the CSMA-MB-Cd (II) ions



Figure 5. X-ray diffraction patterns of the polymer (SMA), polymeric adsorbent (CSMA-MB) and Biosorbent Pit of sour cherry shell (CPR)



Figure 6. SEM images of the chelating resin SMA–MB (with ×) and sour cherry rock (PCR) (without ×) (scale = 500 nm)

the Cd (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 Cadmium ions for adsorption sites and reduce the Cadmium ion adsorption capacity [38]. 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 Cadmium ion uptake was intense.

Desorption of metal ions in acidic media

For desorption of metal ions, aqueous 0.2 M HCl was used. The adsorbent–Cadmium (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 25 °C for 1 h. After filtration, the final Cd (II) ion concentration in the solution were estimated by AAS (Table 3). The desorption ratio (D%) was calculated as follows:

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

Determination of the equilibrium distribution coefficient (k_d)

k_d was determined according to equation (5):

$$k_d = \frac{\text{Amount of Cd(II)ions on the adsorbent}}{\text{Amount of Cd(II)ions in the solution}} \times \frac{V}{m}$$
(5)

where m is the weight of adsorbent (g). The k_d value can be used as a valuable tool to study metalcation 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 [39]. Tables 3 and 4 show the k_d values for the adsorption of single, cadmium ions and the adsorption of Cadmium ions from a real sample, respectively. These findings proved that the k_d values were approximately high in the cases of Cd^{2+} ions, so the prepared chelating resins were good candidates for the removal of cadmium ions from aqueous solutions at pH = 6 (Table 4, 5, and 6).

Table 3. Percer	ntage of desc	orption for	Cd (II) ions
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Adsorbent	Percentage of desorption (Cd ²⁺)	
CSMA-MB	98.60	
PCR	98.10	

Table 4. kd Values of the cross-linked copolymers for cadmium-ion adsorption

		$K_d Cd^{2+} (mL/g)$			
Adsorbent	pH=	2	4	6	4
CSMA-MB		210	320	30100	41000
PCR		41	31	3600	51000

Table 5. k_d Values of the cross-linked copolymers for cadmium-ion adsorption at pH = 6 (Optimized condition) in waste water

Adsorbent	$K_{d} C d^{2+} (mL/g^{-1})$
CSMA-MB	4.44×10 ⁵
PCR	4.43×10 ⁵

Table 6. Adsorption percentage for Cadmium (II) ions at various pH's (2, 4,6 and 8)

		Adsorption			
Adsorbent	pH=	2	4	6	8
CSMA-MB		1.49	58.42	100	100
PCR		1.2	68.44	99.42	97.4

Adsorption studies

Batch adsorption tests were enforced by mixing the CSMA-MB and CPR (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 (200 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:

%Cadmium ion removal =
$$\left(\frac{C_o - C_e}{C_o}\right) \times 100$$
 (1)

C_o and C_e are initial and equilibrium concentration (ppm) of the Cadmium ion solution, respectively.

Effect of contact time

The effect of contact time was interrogated with batch adsorption tests from 60 to 360 min for Cadmium (II) ion concentration of 50 mg/L⁻¹ in 50 mL solution with the (CPR and CSMA-MB) adsorbents (50 mg) at pH = 6. The samples were deleted at time respite for the analysis of remainder Cadmium (II) ion concentration in the aqueous solutions.

Effect of adsorbent dosage

Batch adsorption tests were administered at a various weight of (CPR and CSMA-MB) adsorbents (0.01-0.1 g) for uptake of Cadmium (II) ions from aqueous solutions (50 ml, 50 mg/L⁻¹) at pH = 6, for 120 min. The samples were filtered and the filtrates were analyzed by AAS.

Effect of metal ion concentration

The effect of metal ion concentration was interrogated on the adsorption behavior of (CPR and CSMA-MB) adsorbents. For this purpose, each adsorbent (50 mg) was levied in Cadmium (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 Cadmium (II) ions were determined infiltrate by AAS.

Effect of agitated speed

To interrogate the effect of agitated speed on adsorption of Cadmium (II) ions, agitated speed was altered from 100 to 350 rpm. An appropriate amount of the resin (50 mg) was added to various

beakers containing 50 ml of cadmium (II) ions (50 mg/L⁻¹, pH = 6) and excited in a shaker for 2 h at 25 °C. The volume of each solution was then filtered and analyzed by AAS after the excited time.

Langmuir isotherm

Langmuir model has been widely used to some process of Cadmium (II) ions adsorption [40]. The fundamental supposition of the Langmuir theory is that uptake of metal ions happens on a monotonous surface by mono-layer 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 exactly for mono-layer adsorption onto a surface containing a determinate number of identical sites. The Langmuir adsorption isotherm model is given by:

$$q_e = \frac{q_m c_e \kappa_L}{1 + c_e \kappa_L} \tag{7}$$

where C_e is the equilibrium concentration (mg/L⁻¹), q_e is the amount adsorbed at equilibrium (mg/g⁻¹), q_m is the maximum adsorption capacity corresponding to the complete mono-layer coverage (mg/g⁻¹), and K_L is the Langmuir constant affiliated to the adsorption energy. The model of Langmuir adsorption isotherm can be rearranged as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{8}$$

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 7. The values of q_m and K_L for Cd (II) and 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 7. 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 free of dimension separation factor (R_L), which has been defined as below:

$$R_L = \frac{1}{1 + C_o K_L} \tag{9}$$

where K_L is the Langmuir constant (L/mg⁻¹) and C_0 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 8 illustrated that adsorption of Cadmium (II) ions increased continually with the concentration of Cadmium (II) ions. The computed R_L value for this Cadmium (II) ions adsorption illustrates that adsorption is desirable even for higher concentrations of Cadmium (II) ions.

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 absorption. The model of the Freundlich adsorption isotherm, which is a demonstrator of surface heterogeneity of the sorbent, is given by the following equation.

$$q_e = K_F \ C_e^{1/n} \tag{10}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{11}$$

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) ions were computed from the slope and the curve of the linear draws the log q_e versus log C_e (Figure 9) with the correlation coefficients which were shown in Table 7. The resin showed better accordance for Langmuir isotherm than Freundlich isotherm.

Temkin isotherm

The model of Temkin adsorption isotherm contains a factor that explicitly takes into account adsorbent–adsorbate interactions. 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 the heat of adsorption (A 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:

$$q_e = \frac{RT}{b_T} \operatorname{Ln} \left(A_T C_e \right) \tag{12}$$

The linear form of Temkin equation is

$$q_e = B_T LnA_T + B_T LnC_e$$
(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⁻¹/K⁻¹). But the constant is related to the adsorption heat (KJ/mol⁻¹), A_T is the constant of equilibrium binding (L/g⁻¹) 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 LnC_e (Figure 7).

		Adsorption			
Adsorbent	pH=	2	4	6	8
CSMA-MB		1.49	58.42	100	100
PCR		1.2	68.44	99.42	97.4

Table 7. Adsorption percentage for Cadmium (II) ions at various pH's (2, 4, 6 and 8)

Table 8. Isotherm parameters and regression data for Cd (II) ions using CSMA-MB and CPR as adsorbent (pH = 6, Time = 120 min, Resin dose = 5 g/L^{-1} , Concentration of Cadmium (II) ions = 50 ppm)

Isotherms	Parameters	Cd(II)
Langmuir	$q_m (mg g^{-1})$ (CSMA-MB)	83.21
	$q_m (mg g^{-1})$ (CPR)	84.15
	K_L (L mg ⁻¹) (CSMA-MB)	0.221
	K_L (L mg ⁻¹) (CPR)	0.241
	R _L (CSMA-MB)	0.06
	R _L (CPR)	0.07
	R ² (CSMA-MB)	0.996
	R ² (CPR)	0.997
Freundlich	K _F (CSMA-MB)	19.54
	K _F (CPR)	19.74
	N (CSMA-MB)	3.21
	N (CPR)	3.30
	R ² (CSMA-MB)	0.980
	R ² (CPR)	0.981
Temkin	$b_T = \frac{RT}{B_T}$ (CSMA-MB)	0.198
	$b_T = \frac{RT}{B_T}$ (CPR)	4.54

	A _T (CSMA-MB)	4.67
	A _T (CPR)	1.94×10-3
Dubinin-radushkevich (mol g-1)	X _m (CSMA-MB)	1.98×10 ⁻³
	X _m (CPR)	0.0024
	B (kJ ² mol ⁻²)(CSMA-MB)	0.0028
	B (kJ ² mol ⁻²)(CPR)	14.24
	E (kJ mol ⁻¹) (CSMA-MB)	14.32
	E (kJ mol ⁻¹) (CPR)	0.961
	R ² (CSMA-MB)	0.962
	R ² (CPR)	



Figure 7. Temkin isotherms for Cd (II) adsorption onto CSMA-MB and CPR

Temkin isotherm generates a satisfactory fit to the experimental data as indicated by correlation coefficients.

Dubinin-radushkevich (D-R) isotherm



Figure 8. Langmuir isotherms for Cd(II) adsorption onto CSMA-MB and CPR



Figure 9. Freundlich isotherms for Cd (II) adsorption onto CSMA-MP and CPR

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). 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 the interaction between metal ions and the binding sites. If the value of E is between 8 and 16 kJ mol⁻¹, the adsorption process can be assumed to involve chemical sorption. Conversely, values lower than 8 kJ mol⁻¹ indicate that the adsorption process is of physical nature [28–34]. This adsorption model is given by:

$$C_{ads} = X_{\rm m} e^{-} \beta E^2 \tag{14}$$

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

$$LnC_{ads} = LnX_m - \beta E^2$$
⁽¹⁵⁾

where C_{ads} is the amount of Cadmium (II) ions adsorbed per unit weight of the resin (mol/g), X_m is the adsorption capacity (mol g⁻¹), β is a constant related to adsorption energy (mol² kJ⁻²), and E is the Polanyi potential, which can be calculated from the equation:



$$E = RTLn (1 + \frac{1}{c_e})$$
(16)

Figure 10. Dubinin-radushkevich isotherms for Cd (II) adsorption onto CSMA-MB and CPR

where R is the universal gas constant (kJ mol⁻¹ K⁻¹), and T is the temperature (K). If Ln C_{ads} is plotted against E^2 , β , and X_m will be obtained from the slope and intercept, respectively. Figure 10 indicated the experimental results. The straight lines obtained were useful in calculating the D–R isotherm constants, which are given in Table 8. The adsorption energy, can also be worked out using the following relationship:

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

In this study, the E values obtained using the D–R constant were 13.14 kJ mol⁻¹ for Cd (II) indicating that adsorption of these ions onto CPR and CSMA-MB adsorbents respectively, happen by a chemical process.

Conclusion

Adsorption of Cd (II) is found to be effective in the pH range of 2–8 by CSMA-MB resin and pit shells of Sour Cherry. The elimination percentage increases by increasing the adsorbent dose from 0.5 to 4.0 g/L⁻¹. The contact time studies in the adsorption of selected Cadmium (II) 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 kJ/mol⁻¹ with CSMA-MB resin and 14.32 kJ/mol⁻¹ with CPR for Cd (II) respectively, indicative of the removal of toxic metal ions was done by chemical adsorption phenomena. The results have shown that the CSMA-MB and CPR 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-MB and CPR adsorbents have a good potential for removal of toxic metal ions such as Cd (II) ion from aqueous solutions. Using these adsorbents 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.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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