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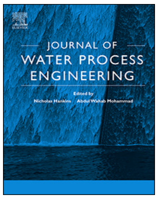

Preparation and characterization of novel bio ion exchanger from medicinal herb waste (chicory) for the removal of Pb^{2+} and Cd^{2+} from aqueous solutions

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ABSTRACT

The ion exchange method has great potential for the removal of heavy metal ions from aqueous solutions. In this study, after the pre-selection experiments among 14 medicinal herb wastes, the ion exchange capacity of the raw chicory waste and its modified forms were evaluated for the removal of Pb^{2+} and Cd^{2+} from aqueous solutions. Furthermore, kinetics, equilibrium isotherms, and column studies were conducted. Modification of the raw chicory waste by $CaCl_2$ increased the cation exchange capacity as well as the Pb^{2+} and Cd^{2+} removal efficiency. The maximum adsorption capacities were increased from 103.1 and 53.8 mg g^{-1} by raw chicory waste to 123.5 and 64.5 mg g^{-1} by modified chicory waste for Pb^{2+} and Cd^{2+}, respectively. Exchange of Pb^{2+} and Cd^{2+} ions with alkali metals (Na^+ and K^+) and alkaline earth metals (Ca^{2+} and Mg^{2+}) onto the waste surface during the removal experiments indicated that the ion exchange could be the dominant mechanism for the removal of Pb^{2+} and Cd^{2}. In addition, the regeneration of raw and modified chicory waste loaded by Pb^{2+} and Cd^{2+} with distilled water was not possible, while eluting the waste using $CaCl_2$, NaCl and HNO_3 could effectively recover both metals. It was concluded that the prepared bio ion exchanger from chicory waste could be a promising and low-cost alternative to synthetic resins for the removal of heavy metals from the water and wastewater.

1. Introduction

Heavy metals (HMs) are amongst the most crucial water pollutants in the environment and thus limit natural water usage. Unlike organic compounds, HMs are not decomposable through chemical and biological processes in the environment; they are highly toxic, and also can be accumulated in plants, animals, and humans [1,2]. Among HMs, lead (Pb) and cadmium (Cd), listed as priority pollutants by the United States Environmental Protection Agency (USEPA) [3], are of such high concern that they are considered to be toxic and dangerous even in low concentrations. Therefore, they are of critical importance and must be removed from the aquatic environment [4]. The major sources of Pb and Cd pollution are industrial wastewaters, including wastewaters of mining, paint, pigments, electroplating, metal smelting, wood preservation, manufacturing of batteries, and agricultural activities through the application of fertilizers and pesticides and urban wastewaters [5,6].

The ion exchange process is a very efficient method due to its high capacity, efficiency, speed, selectivity and low amount of sludge production [7]. In this process, the cations and anions are separated from the solution and enter the exchanger surface; at the same time, different ions with the same charge are released from the exchanger to the solution [8,9]. There are several types of materials that can exchange ions and hence be used for the purification of polluted aqueous solutions and the softening of hard waters. These ion exchangers can be natural-based (e.g., zeolite, vermiculite, polysaccharide, protein, and carbonaceous materials) or synthetic (e.g., zeolites, titanates and silicotitans, polystyrene divinylbenzene, phenol, and acrylic) [10,11]. Resins are among the most practical cation and anion exchangers. Most of the resins are synthetic materials, and despite their excellent performance in the removal of HMs, they are costly. On the other hand, the synthetic ion exchangers may have harmful effects on the environment due to the high use of chemicals in their production process. For instance, Bisphenol-A is used as a basic raw chemical for the production of epoxy resins [12,13] but can mimic the hormones of humans and animals and cause a detrimental effect on human health, reproduction of wildlife, embryonic development and the induction of genetic aberrations [14]. Furthermore, exposure to epichlorohydrin, another

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known compound used for production of ion exchangers, has shown skin tumors [15], genetic damage on male reproductive function and animal infertility [16], as well as possible carcinogenic effects [17], mutagenic effects on fungi, bacteria and plant [18] and respiratory and dermal toxicity in animals and humans [19].

The use of natural materials can not only decrease the production costs by as much as one-tenth of the synthetic ones but also reduce the hazards of chemicals significantly [20]. Natural wastes and by-products have the great potential to remove the HMs from aquatic environments. They are renewable, low-cost, biodegradable, environmentally friendly, and highly efficient [21]. Medicinal herb wastes are by-products of distillation factories which can be used in this regard. *Cichorium intybus* L. commonly known as chicory, as a medicinal herb, belongs to the *Asteraceae* family. It is a native plant of Europe, West Asia, and North Africa [22,23]; however, it has a broad geographic distribution all over the world with many commercial uses, e.g., medicinal herb, coffee substitute, vegetable crop, and occasionally for animal forage and for ethanol production by direct fermentation [24]. The Food and Agriculture Organization (FAO) reported that the world production of lettuce and chicory was about 26.8 million tons in 2016, an estimated 530 000 tons of which were produced in Iran.[25]. Because of its particular chemical compositions and physiological bioactivities, extracts of chicory are used as salubrious beverages, functional foods, additives and as natural medicine (drugs) for the treatment of diabetes mellitus, coronary heart disease, chronic liverish disease, allergic or infective disease, inflammation, and even types of cancer [24]. Generally, a large amount of chicory waste is produced in essence extraction factories, of which its management is very important, particularly in Iran as one of the leading producers of medicinal plants in the world. At the moment, most of these waste materials are disposed of at considerable expense. Consequently, their valorization is of great importance for sustainable waste management. In this regards, synthesis of an ion exchanger with high added value from chicory wastes as cheap and available materials for the removal of heavy metals from water is justifiable both from the environmental and the economic perspectives.

Although most of the natural materials used to remove HMs have been considered as an adsorbent in the biosorption process [26], less attention has been paid to their application as an ion exchanger. Additionally, the few published studies concerning the production of bio ion exchangers have often focused on the use of marine macroalgae such as *Laminaria Hyperborea, Fucus spiralis, Pelvetia caniculata* and *Ascophyllum nodosum* [20]. Therefore, this work aimed to investigate the possibility of using raw and modified chicory waste (CW) generated in essence extraction factories as a new cationic bioexchanger for the removal of Pb^{2+} and Cd^{2+} from aqueous solutions. According to our knowledge, these medicinal plant wastes have not been used as ion exchangers before. We hypothesize that the material characteristics, such as surface functional groups, could act as active sites for Pb and Cd cation removal through the ion exchange mechanism. It seems that the surface modification of the CW via different chemical treatments may improve their ion exchange efficiency. In this regard, the raw and modified chicories were characterized using different methods.

2. Materials and methods

2.1. HM solutions

The stock solutions of Pb^{2+} and Cd^{2+} ($1000\ mg\ L^{-1}$) was prepared by dissolving 160 mg and 180 mg of $Pb(NO_3)_2.4H_2O$ and $CdCl_2.H_2O$, respectively in 1 L of distilled water. Different concentrations of Pb^{2+} and Cd^{2+} were obtained by diluting the stock solution. The pH of the solutions was adjusted at 5 using 0.1 M solutions of HCl and NaOH. All the chemicals used were of the analytical grade obtained from Merck Company (Germany).

2.2. HM measurement

The HM removal efficiency (R), adsorption capacity (q_e) by medicinal herb wastes and distribution coefficient (K_d) of Pb^{2+} and Cd^{2+} in the experiment were calculated as follows [27,28]:

$$R = \frac{C_i - C_e}{C_i} \times 100 \tag{1}$$

$$q_e = \frac{V(C_i - C_e)}{M} \tag{2}$$

$$K_d = \frac{C_i - C_f}{C_f} \times \frac{V}{M} \tag{3}$$

where R is Pb^{2+} and Cd^{2+} removal efficiency (%), q_e is the metal concentration in the solid phase (mg g^{-1} medicinal herb wastes), K_d is the distribution coefficient (L g^{-1}) of Pb^{2+} and Cd^{2+}, C_i, C_e and C_f are the initial, equilibrium and final HM concentration in the solution phase (mg L^{-1}), respectively, V is the volume of HM solution (L) and M is the dry weight of medicinal herb wastes (g).

2.3. Bio ion exchangers preparation and characterization

Fourteen different medicinal herb wastes, used as bio ion exchangers in this study, were obtained from Rana Factory located in Kashan, Isfahan Province, Iran. The samples were washed several times with distilled water to decrease their electrical conductivity (EC) and remove any impurities. Then, they were dried in an oven at a temperature of 60 °C for 24 h [29,30]. The dried materials were further crushed by a Moulinex mill and sieved with mesh 40.

The chicory waste which showed a higher effect on the HM removal efficiency in comparison to the other medicinal herbs was chosen for the next set of experiments and is called RCW (raw chicory waste) in this text.

Proximate analysis was done by weighing 1 g of RCW into a crucible. Based on ASTM D 1102 ± 84, the crucible was placed in the furnace (Godaze Saz, A 10) at a constant temperature of 600 °C for 3 h and the ash content was measured (Eq. 4) [31].

$$Ash\ content\ \% = \left(\frac{W_1}{W_2}\right) \times 100 \tag{4}$$

where W_1 is the weight of ash (g), and W_2 is the weight of the oven-dry sample. The determination of moisture content was done by drying the samples at 103 °C for 3 h according to ASTM E 871 ± 82 (Eq. 5) [31].

$$Moisture\ content\ \% = \left(\frac{W_i - W_f}{W_i - W_c}\right) \times 100 \tag{5}$$

where W_c is the container weight (g), W_i is the initial weight (g) and W_f is the final weight (g). The percentage of volatile matter was measured based on ASTM E872 ± 82 at 900 °C for 7 min (Eq. 6).

$$A = Weight\ loss\ \% = \left(\frac{W_i - W_f}{W_i - W_c}\right) \times 100$$

B = moisture%

$$\text{Volatile matter\%} = A - B \tag{6}$$

The fixed carbon content was calculated using the following equation (Eq. 7) [32]:

$$\text{Fixed carbon\%} = 100 - [\text{moisture\%} + \text{volatile matter\%} + \text{ash\%}] \tag{7}$$

Contents of neutral detergent fiber (NDF), acid detergent fiber (ADF) and acid detergent lignin (ADL) were analyzed in the sample using an ANKOM 220 Fiber Analyzer (ANKOM Technology Corporation), according to the methods of Van Soest et al. (1991) [33].

Hemicellulose and cellulose were calculated considering the Eqs. 8 and 9 [34]:

$$\text{Hemicellulose\%} = \text{NDF} - \text{ADF} \quad (8)$$

$$\text{Cellulose\%} = \text{ADF} - \text{ADL} \quad (9)$$

The sample was mixed with KBr to prepare the pellet and analyzed by Fourier transform infrared (FT-IR) spectroscopy (Bruker, Tensor27) in the range of 400–4000 cm^{-1} to characterize its functional groups. To study the morphology of bio ion exchanger, Scanning Electron Microscopy (SEM) in a Philips XI30 microscope at 30 kV voltage, equipped with an energy dispersive X-ray spectrometer (EDX) (Seron AIS 2300) were used. To obtain the cation exchange capacity (CEC), 0.5 g of CW were mixed with 16 mL of 1 N sodium acetate solution for five minutes and then separated by centrifugation (Hettich, Rotina 380) for 5 min at 3000 rpm. This step was repeated three times. The same process was then performed using 96% ethyl alcohol instead of sodium acetate. Consequently, ammonium acetate 1 N was used as an extractant and the solution was then centrifuged. This step was repeated three times, and the supernatant solutions were collected in each time in 50 mL volumetric flask and then mixed with ammonium acetate solution to reach 50 mL. The concentration of sodium in this solution was measured by a flame photometer (Cole-Parmer, PFP7) and then CEC was calculated. The concentrations of HMs (Pb^{2+} and Cd^{2+}), alkali metals (Na^+ and K^+) and alkaline earth metals (Ca^{2+} and Mg^{2+}) in dry samples of RCW were measured using dry ash method [35]. One gram of exchanger was converted to ash in a furnace at 550 °C for 4 h. Next, the ash was digested by 5 mL of HNO_3 (25% v/v) and the volume reached to 25 mL. The amount of Pb^{2+}, Cd^{2+}, Ca^{2+} and Mg^{2+} in acid-digested solutions were measured using flame atomic absorption spectroscopy (FAAS) (PerkinElmer, AAnalyst700). A flame photometer was used to measure the concentration of Na^+ and K^+ in these solutions. The pH of the RCW was measured using pH meter (JENWAY 3330). 1 g of biomass was placed in an Erlenmeyer flask containing 100 mL of distilled water and boiled for 5 min. The solution was diluted to 200 mL by adding distilled water and cooled at room temperature. Then it was stirred and the pH was determined [31].

2.4. Bio ion exchanger modification

To find out the most efficient form of CW for removal of Pb^{2+} and Cd^{2+} from aqueous solutions, different types of (particle size, number of washing and using hot water) and chemical (basic, acidic, salts, surfactant and organic agents) pretreatment of CW were performed.

2.4.1. Particle sizes

The dried RCW was grinded by a Moulinex and sieved to different particle sizes < 500 μm, 500 μm –1000 μm and > 1000 μm, using standard sieves.

2.4.2. Washing

0.5 g of RCW was added to a beaker containing 250 mL distilled water and placed on a shaker with 150 rpm for 2 h. The old solution was then replaced by 250 mL of new distilled water and the replacement process was repeated for three times. Next, the biomass was filtered and dried at 60° C for 24 h.

2.4.3. Hot water

0.5 g of RCW was added into 250 mL flasks poured with distilled water with different temperatures 50° C, 70° C, and 100° C and kept for 30 min in these conditions. Then, the solutions were filtered by Whatman filter paper (No. 42) and biomasses were dried in an oven at 60° C for 24 h.

2.4.4. Dry heating (Oven)

0.5 g of RCW was placed onto 3 glass plates, separately. The glass plates were kept in an oven at 50° C, 70° C and 10° C for 4 h and then cooled at room temperature.

2.4.5. Wet heating (Autoclaving)

0.5 g of RCW was added into 250 mL beakers, separately. The beakers were put in an autoclave under pressure of 15 bars at 50° C, 70° C and 100 ° C for 2 h. After the autoclaving process and cooling, the samples were removed and used for the experiments.

2.4.6. Chemical modification

To improve the cation exchange capacity of RCW, modification of biomass were performed in calcium, sodium, and hydrogen forms. 250 mL (1 M) of various solutions including Ca^{2+} solution ($CaCl_2$), Na^+ solutions (NaCl, Na_2SO_4, CH_3COONa, $NaC_{12}H_{25}SO_4$ and NaOH) and H^+ solutions (HNO_3, HCl, H_2SO_4, H_3PO_4, $C_6H_8O_6$ and CH_3COOH) were separately poured in 500 mL flasks. In each container, 2 g of biomass was added and the containers were then placed at 25 ± 2 °C for two 12-hour cycles at an incubator shaker at 150 rpm. After each cycle, the old solution was replaced with a new one [30]. The solutions were passed through Whatman filter paper (No. 42) and washed several times with distilled water to decrease the EC and the pH of the outlet solution to the neutral value.

2.4.7. RCW/sodium alginate bead

Immobilized beads was prepared by mixing sodium alginate and RCW in different ratios of 1:1, 1:3 and 1:6 (biomass (g)/ sodium alginate (g)). Different amounts of sodium alginate were completely dissolved in 50 mL distilled water by stirring. Then, 1.5 g of biomass was added to the solution and they were mixed to provide a homogenized suspension. It was shaken for about 1 h to eliminate the resulting bubbles and slowly poured into 1 M solution of $CaCl_2$ by syringe. The prepared beads were kept in the $CaCl_2$ solution for 24 h for hardening and then they were filtered, washed with distilled water several times, and dried at ambient temperature for 24 h.

2.5. Batch experiments

2.5.1. Medicinal herb waste selection

0.05 g of each medicinal herb waste was placed in 100 mL flasks separately in contact with 50 mL of 50 mg L^{-1} Pb^{2+} and Cd^{2+} solution, separately (equivalent to 0.48 meq L^{-1} Pb^{2+} and 0.89 meq L^{-1} Cd^{2+}) at pH = 5 for 60 min on a rotary shaker at 300 rpm. Metal solutions were filtered by centrifuging at 3000 rpm for 5 min, and the residual Pb^{2+} and Cd^{2+} concentrations were measured using FAAS. All the experiments were performed in duplicate and the mean value of the results was reported.

2.5.2. Modification selection and optimization

Batch experiments were also performed to determine the effect of $CaCl_2$ modifications on Pb^{2+} and Cd^{2+} removal efficiency from aqueous solutions. For this purpose, the removal experiments (as described in the previous section) were performed with 0.05 g (1 g L^{-1}) of each pretreated CW. The pretreated sample with highest efficiency of Pb^{2+} and Cd^{2+} removal was selected for further experiments to optimize the effect of temperature (25, 50 and 100 °C) and the modifier solution concentration (0.1, 0.2, 0.5, 1, 2 M). The biomass modified in the optimum conditions was called MCW (modified chicory waste). MCW was characterized using FT-IR and SEM-EDAX analyses.

2.5.3. Ion exchange process

Before doing the experiment, the ion exchangers were washed several times to decrease the EC to an acceptable level, to prevent the interferences of the ions (in washing the extracts of the biomass structure) with Pb^{2+} and Cd^{2+}exchange.

The ion exchange experiments by RCW and MCW were done using the same removal method as described in the section of 2.5.1. Next, the concentration of HMs (Pb^{2+} and Cd^{2+}), alkali metals (Na^{+} and K^{+}) and alkaline earth metals (Ca^{2+} and Mg^{2+}) were measured in the solution phase. Simultaneously, the concentration of these metals in the solid phase (bio ion exchanger) were calculated for mass balance study using dry ash method [35]. Accordingly, the mechanism of heavy metals removal through ion exchange was investigated by comparing the amount of HMs, alkali and alkaline earth metals in solid and solution phases.

As the matrix effect is an important problem in the removal of metal ions in real samples, the effect of interference was studied in the synthetic solutions and industrial wastewater sample for selected MCW. Standard solutions of Ni, Mo, Ag, Mn, As, Al, Cu, K, Cd, Pb, Mg, PO4, Zn and Cr were added separately to 50 mg L^{-1} of Pb^{2+} or Cd^{2+} solutions in binary model and the proposed batch procedure was applied to determine the effects of the competition between the ions on the metal removal. To evaluate the efficiency of the bio ion exchanger in wastewater treatment, an industrial wastewater obtained from a local galvanizing company (the process of applying a protective zinc coating to steel or iron) was used. The wastewater pH and EC was 6.0 and 3.8 mS cm^{-1}, respectively. The Pb and Cd concentration was less than the instrumental detection limit (15 and 0.8 μg L^{-1}), whereas the concentrations of Ni, Cu and Cr were 0.069, 0.065 and 0.072 mg L^{-1}, respectively. The pH of the wastewater sample was adjusted to 5.0 using 0.1 M HCl and 0.1 M NaOH solutions before the experiments. Furthermore, the initial concentrations of Pb^{2+} and Cd^{2+} in the wastewater were increased to 10, 30 and 50 mg L^{-1} by adding the metal solutions and the removal experiments were carried out under the same conditions for the synthetic solutions.

2.6. Regeneration experiments

0.05 g of saturated bio ion exchangers (RCW and MCW) containing Pb^{2+} and Cd^{2+} were separately shaken in contact with 50 mL eluent solutions of 1 M NaCl, $CaCl_2$, HNO_3, and distilled water. In the end, the concentrations of the recovered Pb^{2+} and Cd^{2+} in the solutions were measured. The recovery efficiency (%) of Pb^{2+} and Cd^{2+} was calculated using the following equation:[36].

$$D(\%) = \left(\frac{q_{e,recovery}}{q_{e,\,sorption}}\right) \times 100 \tag{10}$$

where, D is the HM recovery efficiency (%), $q_{e,\ recovery}$ and $q_{e,\ sorption}$ are the HM recovery and sorption capacity (mg g^{-1}), respectively. The HM recovery capacity was calculated as follows:

$$q_{e,\,recovery} = \frac{V(C_f)}{M} \tag{11}$$

where, $q_{e,\ recovery}$ is the amount of HM recovered from one gram of saturated ion exchanger (mg g^{-1}), C_f is the HM concentration in the recovery solution (mg L^{-1}), V is the recovery solution volume (L), and M is the HM saturated ion exchanger weight (g).

50 mL of different concentrations (0.05, 0.1, 0.5, 1 and 2 M) of the eluent solution were placed in contact with the saturated bio ion exchangers (containing Pb^{2+} and Cd^{2}), to examine the optimum concentration of the eluent for the regeneration process.

2.7. Column experiments

A continuous-flow ion exchange experiment was conducted using a Teflon column (150 height × 30 diameter mm). To avoid biomass loss, a small amount of glass wool was plugged at the bottom of the column. Then, the column was packed with 0.1 g of MCW. Before loading the Pb^{2+} and Cd^{2+} solutions, the column was washed with distilled water. The continuous experiments were carried out by separately pumping 500 mL of Pb^{2+} and Cd^{2+} solution (50 mg L^{-1}) into the column using a peristaltic pump (Sina Lab Equipment, SP15, Iran) with 1.5 mL min^{-1} flow rate. Each experiment ran for approximately 430 min. to ensure the formation of a complete breakthrough curve and 21 samples were taken at different time intervals during this period.

2.8. Kinetic and isotherm models

Kinetic experiments were conducted using the batch equilibrium technique obtained by mixing a known amount of RCW and MCW with 50 mL of Pb^{2+} and Cd^{2+} solutions in a rotary shaker at 300 rpm and 25 ± 2 °C, which was sufficient to reach the equilibrium in a 100 mL conical flask. In order to evaluate the kinetic data, separate flasks were prepared for 0–180 min time intervals. For each adsorption isotherm experiment, known amounts of RCW and MCW were separately added to 50 mL of Pb^{2+} and Cd^{2+} solutions in a concentration range from 1 to 150 ppm. The mixture was shaken in a rotary shaker at 300 rpm for 1 h at 25 ± 2 °C. Two kinetic models namely pseudo-first-order and pseudo-second-order were used to investigate the ion exchange kinetic modeling of the experimental data. Langmuir, Freundlich and Temkin models, widely used for the liquid-solid systems, were employed for the sorption isotherm modeling of the equilibrium data.

2.9. Statistical analysis

The data in this study were analyzed using the SPSS software package (Version 21). The One- way ANOVA was used to analyze the significant effects of various parameters.

3. Results and discussion

3.1. Comparison of different medicinal herb wastes

The removal efficiency (R%), adsorption capacity (q: mg g^{-1}) and distribution coefficient (K_d: mL g^{-1}) of 14 different medicinal herb wastes were investigated. According to the results presented in Table S1 and S2 of supplementary file. The removal efficiency and the affinity of Pb^{2+} to the binding groups (K_d) had the highest value for *Coriandrum sativum*, *Cichorium intybus*, *Coriandrum sativum,* and *Achillea millefolium. Cichorium intybus* also showed the most removal efficiency and adsorption capacity for Cd^{2+} ions. Higher K_d in *Cichorium intybus* waste than in other medicinal herb wastes indicated that more amount of Pb^{2+} was adsorbed on its surface in comparison to the concentration of Pb^{2+} in the aqueous phase.

Since *Cichorium intybus* is the most abundantly used medicinal herb in Iran and since it showed a higher Pb^{2+} and Cd^{2+} removal in comparison to the other plants, all further experiments were conducted using its waste.

3.2. Characteristics of raw chicory waste (RCW)

The physicochemical parameters of RCW are shown in Table 1. The values of proximate analyses of the waste are in accordance with the literature [37,38]. The pH of RCW was neutral (about 6) which indicates that using chicory for removal of Pb^{2+} and Cd^{2+} do not change the pH of the solution to acidic or basic pH, so it does not have any adverse effects on exchanging of Pb^{2+} and Cd^{2+} with the surface ions of chicory. Cation exchange capacity (CEC) of chicory was about 98 Cmol(+) kg^{-1} (equal to 98 meq $100g^{-1}$) which is high enough for the ion exchange. The elemental analysis of chicory showed that there were not any Pb^{2+} and Cd^{2+} ions in the structure of the biomass and that the Ca^{2+} amount was the highest (0.974 meq g^{-1}) among the exchanging ions.

3.3. Electrical conductivity

Initial EC of chicory was 1599 μS cm^{-1}. Therefore, usage of unwashed chicory as ion exchanger may cause some interferences. The

Table 1
Characteristics of raw chicory waste (RCW).

Properties	Unit	Measurement	Properties	Unit	Measurement
Proximate analysis			Pb^{2+}	meq g^{-1}	nd
Moisture	%W	4.8	Cd^{2+}	meq g^{-1}	nd
Ash	% DW[1]	4.13	**Chemical analysis**		
Volatile matter	% DW	89.5	pH	–	6
Fixed carbon	% DW	1.57	CEC[2]	Cmol(+) kg^{-1}	98
Exchangeable ions			NDF[3]	% DW	44.37
Na^+	meq g^{-1}	0.032	ADF[4]	%DW	34.94
K^+	meq g^{-1}	0.017	Cellulose	% DW	28.59
Ca^{2+}	meq g^{-1}	0.974	Hemicellulose	% DW	9.43
Mg^{2+}	meq g^{-1}	0.126	Lignin	% DW	6.35

released alkali and alkaline earth ions, particularly Ca^{2+}, having a high content in the chicory structure, may compete with Pb^{2+} and Cd^{2+} to be exchanged and consequently reduce the exchange rate of the metal ions. Therefore, it is necessary to reduce the negative impact of the ions in the extracted biomass as much as possible. For this purpose, the raw and modified biomass were rinsed with distilled several times. The most significant changes in EC happened during the first and the second rinsing stages and there were fewer changes were in the next rinsing rounds. Therefore, two stages of washing could be sufficient for reducing the interference effect of the ions in the biomass.

3.4. Effect of physical and chemical modification

It has been reported in various studies that the modification processes may increase or decrease the efficiency of the sorbents. In order to evaluate the effect of different modifications on Pb^{2+} and Cd^{2+} removal efficiency of chicory waste, various physical and chemical modification methods were investigated. Four different physical pretreatment methods including using different particle sizes, boiling in water, heating by oven and autoclaving were investigated. According to the results presented in Table S3, increasing the size of particles (> 500 μm) decreased the sorption efficiency and capacity of CW. Chicory waste with particle sizes less than 500 μm showed the highest adsorption capacity of Pb^{2+} and Cd^{2+} which can be attributed to the higher surface area of the small particles, providing the more total area for interacting with HM ions.

Washing the biomass enhanced the Pb^{2+} and Cd^{2+} removal efficiency, due to the removal of dust and other materials which could interfere with the metals. However, boiling the biomass in hot water at 70°C and 100°C significantly decreased the HM sorption (Table S3). Boiling can dissolve the mineral matter, decompose the organic matter [39], rupture the biomass cells and cause unavailability of binding sites for HM ions [40]. Dry heating did not show any significant effect on the removal capacity of chicory waste, a finding which was in accordance with the previous reports in the literature [39].

Chicory waste autoclaved at different temperatures and pressure of 15 bar did not have a significant effect on HM sorption in comparison to the untreated waste, while contradictory results are reported by other researches. Daneshvar et al. [39] indicated that autoclaving of macroalgae biomass reduced the methylene blue biosorption due to the physical and morphological changes in the biomass structure, including the destructive effect of dry heating on functional groups of algae cell walls. On the other hand, Abdollah and Taha [41] represented that autoclaving of the fungal biomass might increase the porosity and surface area, which can increase the ion removal efficiency of the biomass. This statement confirms that depending on the biomass type and its reactions under high pressure and heat, dry heating can have different effects on its sorption capacity.

The chemical modification of CW was carried out using various chemical reagents. The results of the Pb^{2+} and Cd^{2+} removal experiment showed that modification with Na^+ and H^+ solutions reduced the ion exchange capacity of CW. However, the $CaCl_2$ modification could significantly increase the removal efficiency of Pb^{2+} and Cd^{2+}. The distribution coefficient of Ca^{2+} treated CW was at the highest for Pb^{2+} and Cd^{2+} in comparison to the other treated ones, indicating that the most amount of Pb^{2+} and Cd^{2+} ions in aqueous phase could be adsorbed on the Ca^{2+} treated biomass surface ($p\text{-value} < 0.01$) (Table S3). Calcium ion with a higher positive charge than Na^+ and H^+ ions could be more efficient for removing the intended ions and exchange with them. In some articles, Ca^{2+} was introduced as the main cation for the removal of HM ions through ion exchange process [42,43]. Calcium can bind to functional groups and improve CEC. In this study, biomass pretreatment with Na^+ solutions decreased the removal efficiency of chicory waste, a finding which was similar to the results reported by Daneshvar et. al. [39] who mentioned that the adverse effect of NaOH in pretreatment might be attributed to biomass agglomeration and reduction of the effective number of binding sites for HM cations. In some other studies, the efficiency of HM removal by NaCl treated algae was slightly better than $CaCl_2$ treated one [30]. Decreasing the removal efficiency and capacity of H^+ modified chicory treated using acids (e.g., hydrochloric acid and nitric acid) could be due to the reduction of chicory surface electronegativity [39]. By changing the surface charge of the biomass from negative to positive, electrostatic attraction between chicory biomass and HM cation might be decreased [41]. These results might also be due to the destruction of binding sites, responsible for ion exchange after the biomass was exposed to acids [29]. The surface chemical groups of chicory are protonated by pretreatment with strong acids, and hence the residual H^+ in the cell wall may compete with the Pb^{2+} and Cd^{2+} for the surface active sites of the ion exchangers [39]. As previously mentioned, light metals (LMs) can bond to biomass through electrostatic interactions and play a significant role in the ion exchange of Pb^{2+} and Cd^{2+}, metal complex formation, coordination interaction, and other processes [42]. Therefore, Ca^{2+}, Mg^{2+}, Na^+, and K^+, present in the biomass structure, are washed away from the biomass as a result of the acid treatment, which reduces the exchange rate of Pb^{2+} and Cd^{2+}. Moreover, the washed LMs (Ca^{2+}, Mg^{2+}, Na^+, and K^+) are replaced by H^+ and the biomass surface is protonated consequently. The HM ions are then replaced by these protons which decreases the pH of the solution and leads toa reduction of the HMs removal due to competition between H^+ and the Pb^{2+} and Cd^{2+} [20,44]. Maximum Pb^{2+} and Cd^{2+} adsorption capacity (mg g^{-1}) was observed for Ca^{2+} treated ion exchanger, so further experiments were conducted on optimization of CW (with the particle size less than 500 μm) by $CaCl_2$ modification (1M).

3.4.1. Effect of $CaCl_2$ concentration

Fig. 1a demonstrated the effect of different concentrations of $CaCl_2$ on the removal efficiency of the CW modification process. As it is clear, by increasing the $CaCl_2$ concentration from 0.01 to 1 M, the removal efficiency for Pb^{2+} and Cd^{2+} increase from 29 to 92% and from 26 to 74%, respectively. Increasing the concentration of $CaCl_2$ from 1 to 2 M did not affect the Pb^{2+} adsorption capacity, significantly; however, it

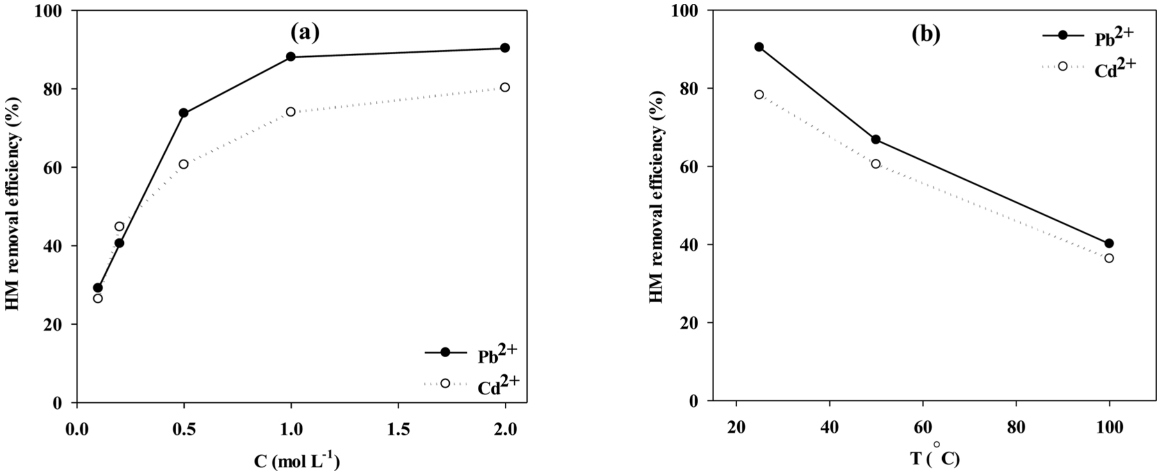

Fig. 1. Effect of $CaCl_2$ concentration (a), and reaction temperature (b) on the sorption capacity of chicory waste for removing $Pb^{2+}$and Cd^{2+} from the solution. Conditions: pH, 5.0; biomass dosage, 1 g L^{-1}; $Pb^{2+}$and Cd^{2+} solution concentration, 50 mg L^1; contact time, 60 min; agitation speed, 300 rpm.

slightly increased the capacity of Cd^{2+} sorption. Therefore, the 1M solution of $CaCl_2$ was selected for modification of CW for both metals and the modified chicory waste (MCW).

3.4.2. *Effect of temperature*

Results revealed that by increasing the temperature from 25 °C to 100 °C, the removal efficiency of Pb^{2+} and Cd^{2+} by the CW was reduced from 90 to 40% and from 78 to 36%, respectively (Fig. 1b). Hence, it is better to modify the CW at the lower temperature. The reason could be attributed to the fact that some part of the structure of the ion exchanger might be decomposed at higher temperatures which could lead to the loss of a portion of porosity on the surface of the sorbent [45]. Besides, increasing the temperature could lead to the conversion of some the functional groups to others with less exchange potency.

3.5. *Surface analysis of row and modified chicory waste*

The SEM micrograph of the RCW and MCW are shown in Fig. 2. Overall, the samples show a similar morphology, which consists of a smooth and fibrillary structure without a defined geometry. It was observed that the structure was not damaged or destroyed after the $CaCl_2$ modification.

The FTIR spectroscopic analysis of RCW and MCW revealed the functional groups of the exchanger's surface and the possible interactions of these functional groups with the Pb^{2+} and Cd^{2+} in the solution. The broad and strong band between 3600 and 3200 cm^{-1} seen in the spectra (Fig. 3) are associated with hydroxyl (−CHOH) stretching and amino groups (N−H) [20]. These groups are associated with cellulose and proteins of chicory cell wall. A small shift in the MCW band compared to RCW indicates changes in the amino group, as a result of the $CaCl_2$ modification. The shift also suggests that Ca^{2+} competes with the hydrogen bonding between the −OH groups [46]. The peak observed between 3000 and 2800 cm^{-1} can be attributed to −CH groups [43,47] and those at 1650 cm^{-1} and 1480 cm^{-1} could be assigned to the carboxylic functional group (C=O) [20]. Moreover, the bond between 1050 and 1100 cm^{-1} might be attributed to C–O stretching of alcohol and carboxylic acid [48].

3.6. *The concentration of ions in solid and solution phases*

The acid digestion results of RCW showed that the concentration of Ca^{2+} (0.97 meq g^{-1}) was higher than that of Mg^{2+} (0.12 meq g^{-1}), Na^+ (0.03 meq g^{-1}) and K^+ (0.02 meq g^{-1}). When RCW was modified with $CaCl_2$ solution, the concentration of Mg^{2+}, Na^+, and K^+ in biomass decreased to 0.07, 0.005 and 0.002 meq g^{-1}, respectively, while Ca^{2+} concentration increased significantly to 1.18 meq g^{-1} (p-value < 0.01). This was because the Ca^{2+} concentration was very high in $CaCl_2$ solution, hence when these ions were in contact with RCW exchanger, Na^+, K^+, and Mg^{2+} could be replaced and exchanged by the Ca^{2+}. The results indicated that these wastes could react with Ca^{2+} and the functional groups on the surface might be saturated with Ca^{2+}. Hence, they showed a higher ability for removing Pb^{2+} and Cd^{2+} ions via the ion exchange process Figs. 4b and 5 b). The concentration of sum of LMs (Na^+, K^+, Ca^{2+} and Mg^{2+}) increased from 1.150 in RCW (Figs. 4a and 5 a) to 1.258 meq g^{-1} in MCW (Figs. 4b and 5 b).

Comparison of the elemental constitution of RCW and MCW by using elemental microprobe analysis of EDAX (Fig. S1) approved these results. The signals of Ca^{2+}, Na^+, K^+, and Mg^{2+} can be observed in Fig. S1a which are known as the principal elements of CW. Considering the exchange of Ca^{2+} with other LMs during $CaCl_2$ modification, no signals of other LMs (Na^+, K^+, and Mg^{2+}) were found in the EDAX results for MCW (Fig. S1b), where it is shown that Ca^{2+} is the principal element of the MCW.

Due to the increase of Ca^{2+} concentration on the surface of modified exchangers (from 0.974 meq g^{-1} in RCW to 1.182 meq g^{-1} in MCW), the CEC values significantly increased (p-value < 0.01) from 98 meq $100g^{-1}$ in RCW to 118 meq $100g^{-1}$ in MCW, which caused an increase in HM ion exchange efficiency of MCW.

After the exchange, an experiment in a solution with 50 mg L^{-1} of the Pb^{2+}, the loaded Pb^{2+} concentration on the RCW and MCW surfaces were 0.30 and 0.42 meq g^{-1}, respectively (Fig. 4). Also, in a solution with 50 mg L^{-1} of the Cd^{2+}, 0.59 meq g^{-1} of Cd^{2+} was removed by the RCW while the MCW could remove 0.7 meq g^{-1} of Cd^{2+} (Fig. 5). Moreover, the amount of Ca^{2+} on RCW and MCW decreased through the HM ion exchange process. So, 0.24 and 0.47 meq g^{-1} of Ca^{2+} in RCW and MCW exchanged with Pb^{2+} (Fig. 4), while 0.38 and 0.61 meq g^{-1} of Ca^{2+} in RCW and MCW exchanged with Cd^{2+}, respectively (Fig. 5).

This decrease was well-aligned with the amount of Ca^{2+} released to both the Pb^{2+} and the Cd^{2+} solutions after the ion exchange process by RCW and MCW, which were respectively 0.26 and 0.45 meq L^{-1} into Pb^{2+} solution and 0.410 and 0.58 meq L^{-1} into Cd^{2+} solution. The comparison of Pb^{2+} and Cd^{2+} concentrations in the solution phase before and after the ion exchange process confirmed these results (Figs. 4 and 5). After the removal experiment by RCW, the concentrations of unexchanged Pb^{2+} and Cd^{2+} in the solutions were 0.12 and 0.31 meq L^{-1} and after the using MCW, the figures were 0.03 and 0.21 meq L^{-1}, respectively. The sum of LM concentrations (Na^+, K^+, Ca^{2+} and Mg^{2+}) in RCW (1.15 meq g^{-1}) decreased to 0.84 and 0.69 meq g^{-1} after the Pb^{2+} and Cd^{2+} exchange process, respectively

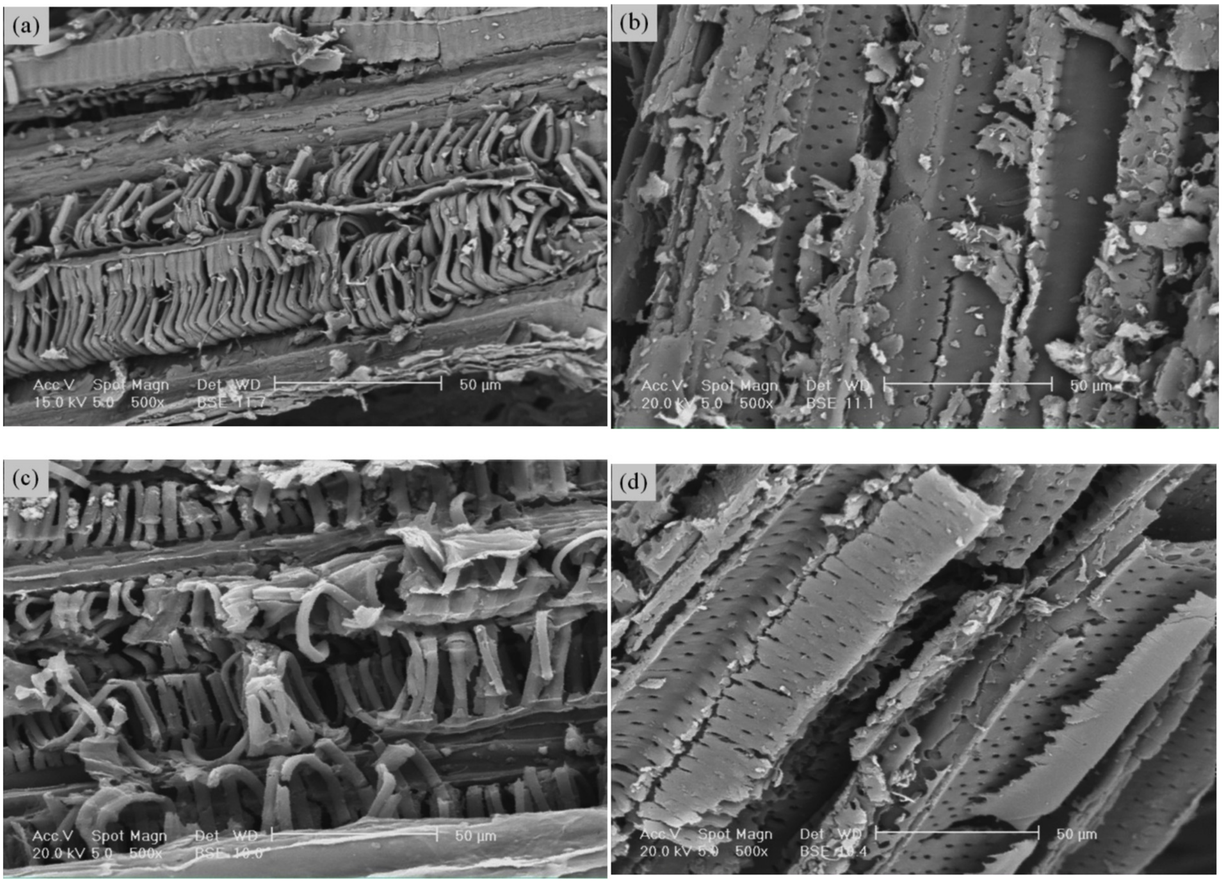

Fig. 2. SEM image of raw chicory waste (RCW) (a, b) and modified chicory waste (MCW) (c, d) (× 500 magnification).

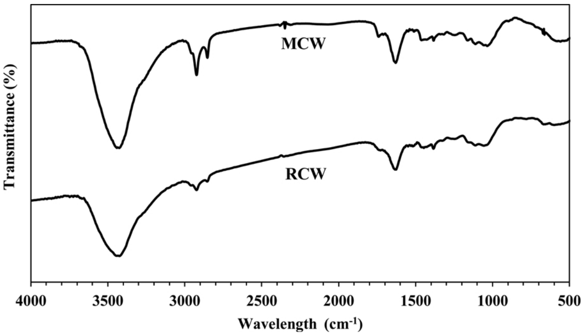

Fig. 3. FTIR spectra of raw (RCW) and modified chicory waste (MCW).

(Figs. 4a and 5 a). Therefore, the removal efficiency was about 78.3% for Pb^{2+} and 64.7% for Cd^{2+}. Also, the sum of LM concentrations in MCW was 1.258 meq g^{-1} before the ion exchange, which decreased to 0.779 and 0.621 meq g^{-1} respectively after the exchange of Pb^{2+} and Cd^{2+}. These results indicated that 0.479 meq g^{-1} of these LMs were exchanged with Pb^{2+} and 0.637 meq g^{-1} of LMs exchanged with Cd^{2+} (Figs. 4b and 5 b) (1 g L^{-1} of CW is applied in Pb^{2+} and Cd^{2+} solution, hence meq g^{-1} is equivalent to meq L^{-1}). Therefore, the removal efficiency of Pb^{2+} and Cd^{2+} were 95.3 and 73.3%, respectively. Furthermore, EDAX spectra of RCW (Fig. S1d) after Pb^{2+} the removal process illustrated the reduction of LMs weight and the increase of Pb weight, compared to their spectra before removal process. The spectra of RCW and MCW after Cd^{2+} removal which is shown in Fig. S1 (e and f) revealed a similar trend of Cd and LM signals confirming the occurrence of the ion exchange.

In another study [29] on the efficiency of algae as an ion exchanger, it was also stated that the concentration of Ni^{2+} bonded to biomass is proportional to the sum of LM concentrations (Na^{+}, K^{+}, Ca^{2+}, and Mg^{2+}) released from its surface. Based on the ions concentrations in acid-digested RCW and MCW solutions (before and after Pb^{2+} and Cd^{2+} exchange experiment), reduction of Ca^{2+} concentration and increasing of Pb^{2+} and Cd^{2+} concentration in the solid phase confirmed the exchange of the Pb^{2+} and Cd^{2+} with Ca^{2+} on the surface of RCW and MCW samples. Besides, increasing the Ca^{2+} concentration and reduction of the Pb^{2+} and Cd^{2+} concentrations in the solution phases clearly proved these results. Among the ions, Pb^{2+} and Cd^{2+} showed a higher potential to be exchanged on the surface of RCW and MCW. The high concentration of Pb^{2+} and Cd^{2+} in the solution phase, greater electrical charge (for Pb^{2+}, Cd^{2+} is twice that of Na^{+} and K^{+}) and greater electronegativity of Pb^{2+} and Cd^{2+} than Mg^{2+}, Ca^{2+}, Na^{+} and K^{+} could be the main reasons for superiority of Pb^{2+} and Cd^{2+} for exchanging with listed LMs [49,50].

The exchange experiment of RCW and MCW showed that the removal efficiency of Pb^{2+} was 78.3 and 95.3% and of Cd^{2+} were 64.7 and 73.3%, respectively. These results indicated an increase in RCW removal efficiency after the modification process. It could be due to the increase in CEC after modification of RCW. These findings are consistent with various studies indicating that the modification of natural ion exchanger with alkali and alkaline earth chloride salts increased the adsorption capacity of HMs [29]. It might be due to the trapping of Pb^{2+} and Cd^{2+} on a NaCl treated algae and releasing of Na^{+} which was attributed to the ion exchange process [20,29]. Furthermore, Bhatnagar et al. in their study of Ni^{2+} biosorption, stated that the adsorption of the metal ions on the treated biomass was accompanied by the release of Na^{+} from the exchanger [29]. The results also indicated that the ion exchange selectivity by RCW and MCW was higher for Pb^{2}than Cd^{2+}. In other words, the relative exchanging strength of Pb^{2+} was greater than that of Cd^{2+}. This preference could be attributed to hydrated radius

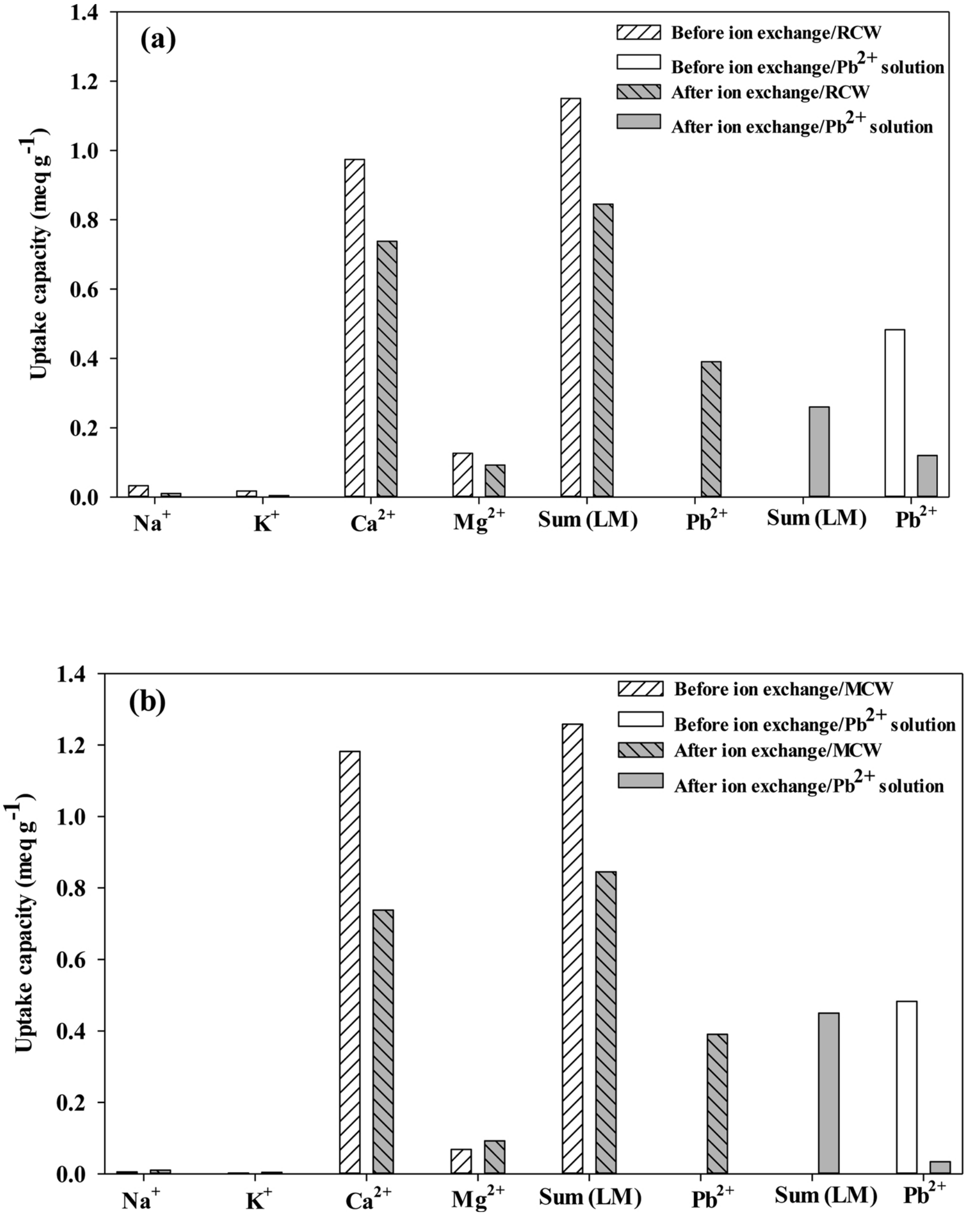

Fig. 4. Changes in cations concentration in solid and solution phases, during Pb^{2+} exchange process before and after ion exchange by raw chicory waste (RCW) (a) and modified chicory waste (MCW) (b).

(Pb^{2+} = 0.401 and Cd^{2+} = 0.426 nm), electronegativity (Pb^{2+} = 2.10 and Cd^{2+} = 1.69), E_h (hydration energy; –1481 and −1807 kJ mol^{-1} for Pb^{2+} and Cd^{2+}, respectively) and pK_H (negative log of hydrolysis constant; 7.78 and 11.70 for Pb^{2+} and Cd^{2+}, respectively). Higher electronegativity and lower hydrated radius, E_h and pK_H led to a growing tendency of the Pb^{2+} than Cd^{2+} for both RCW and MCW [50–52]. Coles et al. studied the removal of Pb^{2+} and Cd^{2+} by kaolinite in the ion exchange process. They indicated that the affinity of Pb^{2+} to kaolinite was greater than that of Cd^{2+} [49]. Similar results were reported in other researches [53–55].

According to the above results, it can be stated that the main process for the removal of HMs in this study was ion exchange. In similar articles, it was pointed out that the functional groups on the exchanger's surface were able to exchange protons and/or alkali ions (Na^+ and K^+) and alkaline earth ions (Ca^{2+} and Mg^{2+}) with HM cations [56,57]. It was reported in other researches that $CaCl_2$ treated natural exchanger could properly exchange ions in the removal processes, removing various types of HMs from aqueous solutions by exchanging them with Ca^{2+} [29,30].

3.7. Ion exchange modeling

3.7.1. Kinetic models

The values of kinetic constants for Pb^{2+} and Cd^{2+} sorption onto RCW and MCW are presented in Table 2. The correlation coefficient obtained for the pseudo-second-order kinetic model was higher than 0.99 was (Fig. S2), which showed that the adsorption process followed the pseudo-second-order rate expression for removal of Pb^{2+} and Cd^{2+}. The results also indicated higher Pb^{2+} and Cd^{2+} sorption capacity (q_e) of MCW than of RCW.

3.7.2. Isotherm models

Isotherm parameters for Pb^{2+} and Cd^{2+} sorption by RCW and MCW are given in Table 3. It is assumed that in the Langmuir model there is no significant competition between the adsorbate and the solvent to occupy the adsorption sites. The equilibrium data were also subjected to the Temkin isotherm model in which the interactions between HM-ion exchanger is based on the assumption that the free energy of sorption is a function of the surface coverage.

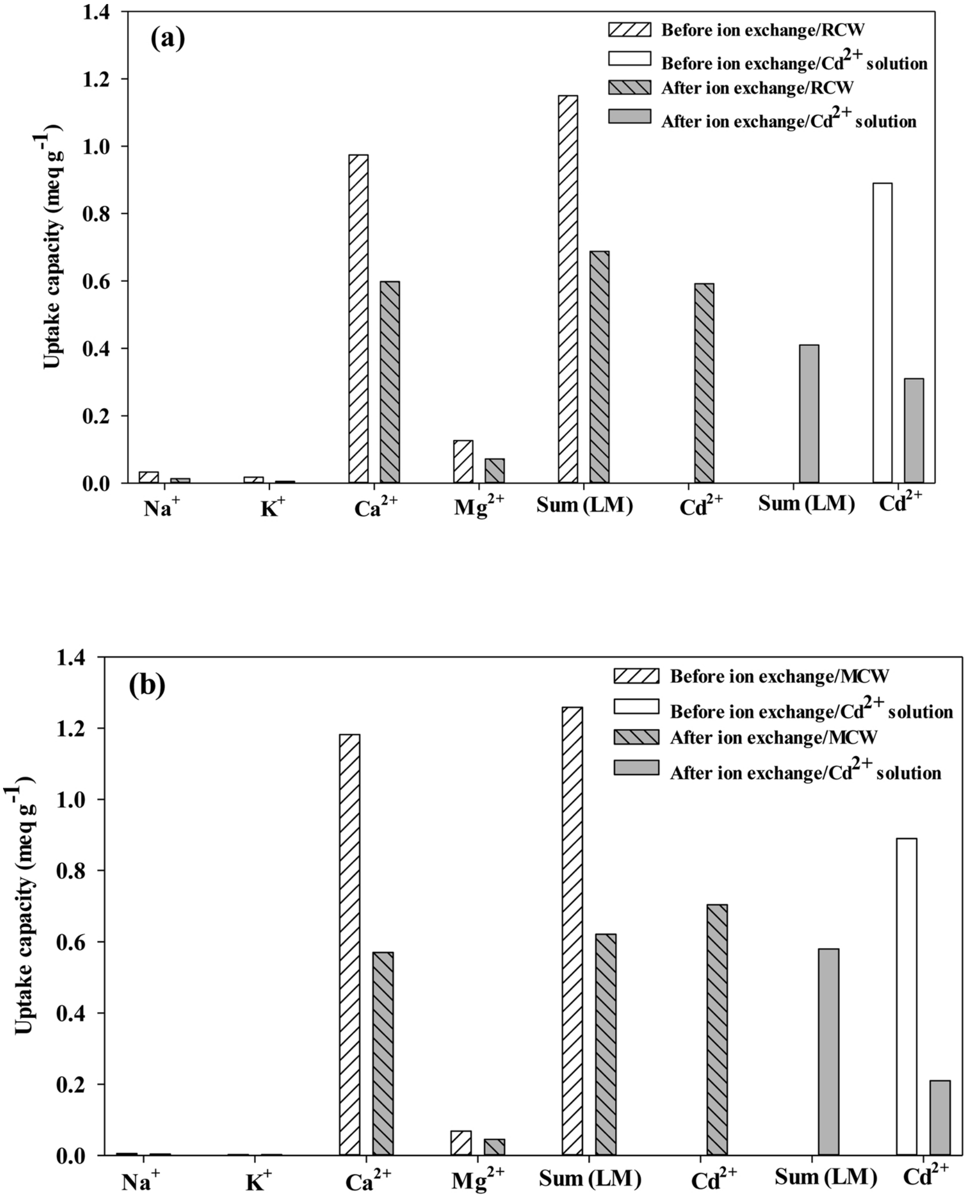

Fig. 5. Changes in cations concentration in solid and solution phase, during Cd^{2+} exchange process before and after ion exchange by raw chicory waste (RCW) (a) and modified chicory waste (MCW) (b).

Table 2
Kinetic parameters for the removal of Pb^{2+} and Cd^{2+} by the raw and modified chicory waste (RCW and MCW, respectively).

Model	Parameter	RCW		MCW	
		Pb	Cd	Pb	Cd
Pseudo-first-order	q_e	10.68	11.69	9.44	20.54
	K_1	0.029	0.024	0.031	0.032
	R^2	0.69	0.76	0.69	0.94
Pseudo-second-order	q_e	39.37	29.32	46.94	36.36
	$K_2 \times 10^2$	0.11	0.98	1.55	0.49
	$K_2 q_e$	0.046	0.289	0.731	0.181
	R^2	0.999	0.998	0.999	0.994

Table 3
Isotherm parameters for the removal of Pb^{2+} and Cd^{2+} by raw and modified chicory waste (RCW and MCW, respectively).

Model	Parameter	RCW		MCW	
		Pb	Cd	Pb	Cd
Langmuir	q_m	103.11	53.76	123.45	64.51
	K_L	0.138	0.156	0.199	0.141
	R_L	0.126	0.113	0.091	0.123
	R^2	0.991	0.991	0.990	0.991
Freundlich	n	1.77	2.43	1.67	2.22
	K_F	12.44	9.36	17.33	9.81
	R^2	0.944	0.965	0.930	0.982
Temkin	b_T	146.19	302.73	118.84	252.85
	K_T	3.06	4.33	4.16	3.94
	R^2	0.961	0.973	0.978	0.950

The R^2 value of the Langmuir model was higher than that of Freundlich and Tempkin isotherms (Fig. S3). Based on Langmuir theory, the Pb^{2+} and Cd^{2+} sorption could take place at specific homogenous sites on the surface of RCW and MCW. Value of q_m, which is assumed as the maximum capacity of sorbent, has been calculated from the Langmuir plots. The maximum adsorption capacities of Pb^{2+} and Cd^{2+} have been increased from 103.11 and 53.76 mg g^{-1} by RCW to 123.45 and 64.51 mg g^{-1} by MCW, respectively. In the Langmuir

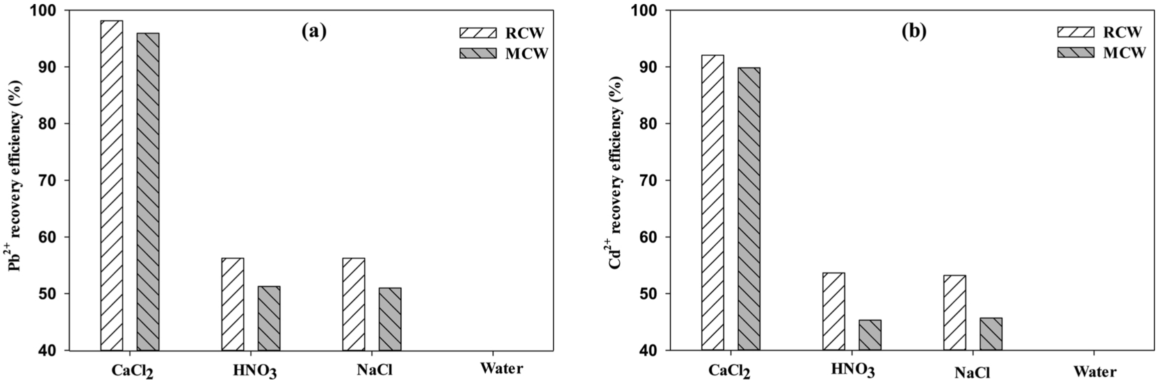

Fig. 6. Pb^{2+} (a) and Cd^{2+} (b) recovery efficiency of raw and modified chicory wastes (RCW and MCW, respectively) using HNO_3, $CaCl_2$ and NaCl (1 M) in comparison to distilled water.

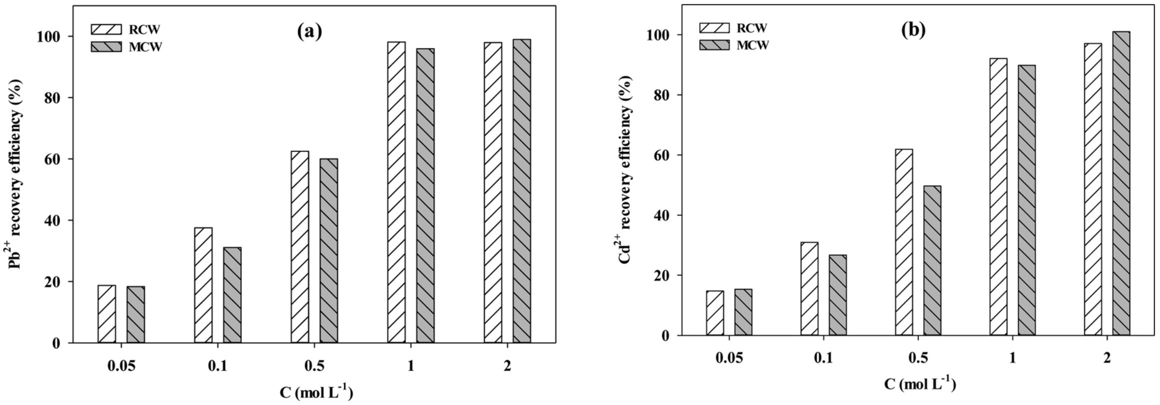

Fig. 7. Effect of $CaCl_2$ concentration on Pb^{2+} (a) and Cd^{2+} (b) recovery efficiency of raw and modified chicory wastes (RCW and MCW, respectively).

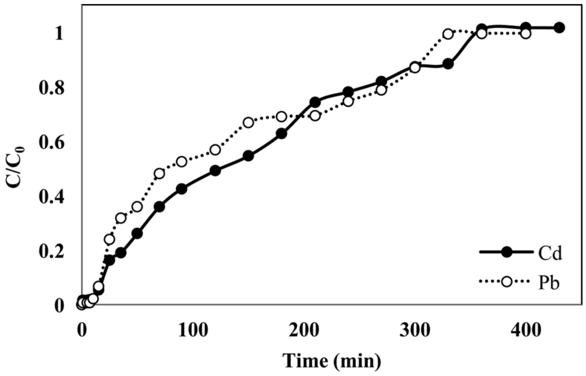

Fig. 8. The breakthrough curve of Pb^{2+} and Cd^{2+} removal by modified chicory wastes (MCW).

isotherm, the dimensionless separation factor (R_L) can be used as an indicator of the favorability of adsorption. Based on the Langmuir isotherm the adsorption is either irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$) [58]. The second situation was true for all the conditions of the current experiment, therefore the exchange of Pb^{2+} and Cd^{2+} with surface alkali and alkaline earth ions of RCW and MCW were favorable.

3.8. Regeneration of the ion exchanger

Ion exchanger recovery plays an important role in reducing wastewater treatment costs. It not only makes the reuse of the exchanger in several cycles possible but also provides the recovery of HMs [20]. The results of the RCW and MCW cation exchanger recovery process are shown in Fig. 6. According to the results, distilled water could not recover HMs from the solid phase, while $CaCl_2$, NaCl and HNO_3 could recover metals with different efficiencies. Another study [59] reported the same result with distilled water and NaCl. Among the rinsing solutions, $CaCl_2$ had the highest ability to recover HMs. Also, increasing the concentration of the $CaCl_2$ solution from 0.05 to 1 M significantly increased the Pb^{2+} and Cd^{2+} recovery due to the higher amount of Ca^{2+} ions in the eluent solution (sig < 0.05). The eluent with the concentration of more than 1 M did not show any significant effect on the recovery of HMs (Fig. 7). It should be noted that the regeneration efficiency is an important parameter to scale up the process. In this study, the possibility of the Pb and Cd desorption from saturated bio ion exchanger by $CaCl_2$ solution was examined without considering the stoichiometric calculations. In general, the regeneration experiments were conducted in the same method [30].

Table 4
Removal efficiency of Pb^{2+} and Cd^{2+} from the galvanic wastewater using modified chicory waste (MCW).

Metal concentration (mg L^{-1})	Remova1 (%)	
	Pb	Cd
10	85.89	68.03
30	73.02	51.30
50	72.88	43.05

The Pb^{2+} recovery rate for RCW and MCW using $CaCl_2$ solution was 98% and 95.9%, and was 92% and 89.8% for Cd^{2+}, respectively, which was approximately twice than that of HNO_3 and NaCl (Fig. 6). These results can be related to the charge of the existing ions in the rinsing solution. Since Ca^{2+} has two positive charges in comparison to Na^+ and H^+ with only one positive charge, its tendency and ability to be exchanged by Pb^{2+} and Cd^{2+} is higher than Na^{+} and H^{+}. Moreover, the results demonstrated that Ca^{2+} have more affinity to be exchanged with Pb^{2+} than Cd^{2+}. Therefore, the amount of the released Pb^{2+} to the $CaCl_2$ solution was higher than that of Cd^{2+}.

3.9. Ion exchange column studies

The breakthrough curve, showing the relative concentrations versus time for the exchange of Pb^{2+} and Cd^{2+} on MCW bed are depicted in Fig. 8. For the initial minutes, the effluent from the bottom of the bed was almost free of Pb and Cd ions due to the high availability of active sites on MCW, indicating that the column was performing at a maximum efficiency during that period. As the solution continued to flow, the available active sites were gradually occupied and accordingly, the outlet concentration of Pb and Cd ions began to increase. However, more than 50% of Pb^{2+} and Cd^{2+} could be removed after 90 and 120 min, respectively. The biomass exhaustion occurred at approximately 330 and 360 min after Pb and Cd removal, respectively.

3.10. Interference study

To assess the suitability of the proposed method in Pb^{2+} and Cd^{2+} removal, the interference of several ions was determined. The results showed that Mo^{2+}, Ag^{+}, K^{+}, and PO_4^{3-} did not affect the efficiency of the ion exchanger for Pb^{2+}. Besides, Ag^{+}, K^{+}, and PO_4^{3-} did not interfere with Cd^{2+} removal. However, 50 mg L^{-1} concentration of Cu^{2+}, Zn^{2+}, As^{2+}, and Mg^{2+} were found to reduce the removal efficiencies of both Pb^{2+} and Cd^{2+}.

3.11. Removal of HMs from industrial wastewater

The proposed method was applied to determine the heavy metal ion removal using MCW in real industrial wastewater sample. The results (Table 4) indicated the considerable efficiency of the synthesized ion exchanger for removal of Pb^{2+} and Cd^{2}, which was in the range of 72–85% and 43–68%, respectively in various initial concentrations.

4. Conclusions

In this study, we investigated the potential application of various medicinal wastes to exchange Pb^{2+} and Cd^{2+} ions from aqueous solutions. Among the used wastes, chicory waste showed an excellent ability to exchange the metal ions with its surface elements. Modification of CW using $CaCl_2$ solution in ambient temperature could increase CEC from 98 to 118 Cmol (+) kg^{-1} (equal to 98 to 118 meq 100 g^{-1}) and enhance its efficiency in the ion exchange process. The maximum Pb^{2+} and Cd^{2+} adsorption capacity by MCW reached to about 123.5 and 64.5 mg g^{-1}, respectively while the corresponding amounts for raw materials were 103.1 and 53.8 mg g^{-1}, respectively, indicating an increase in HM adsorption capacity after the modification process. Because of releasing of alkali and alkaline earth ions, particularly Ca^{2+}, from RCW and MCW into the solution and removing of Pb^{2+} and Cd^{2+} from the solutions, it was found that the main mechanism for the removal of the metals by RCW and MCW was the ion exchange. Recovery of the metals by $CaCl_2$, NaCl and HNO_3 and the lack of recovery by distilled water reinforced the ion exchange mechanism. Further researches are needed to evaluate the robustness and degradation of the chicory waste during the application as well as to develop the scale up of the process considering the economic aspects.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jwpe.2019.01.007.

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