JOURNAL OF Applied Polymer SCIENCE

Removal of Pb^{2+} and Cd^{2+} from drinking water using polysaccharide extract isolated from cactus pads (*Opuntia ficus indica*)

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ABSTRACT: The use of a polysaccharide extract isolated from cactus pads (*Opuntia ficus indica*) as a low-cost adsorbent for the removal of Pb^{2+} and Cd^{2+} from water was investigated. The Brunauer–Emmett–Teller study showed that the surface area of the extract powder was approximately 2.373 m^2/g. Inductively coupled plasma optical emission spectrometry was used to monitor changes in ion concentrations during the adsorption. The adsorption mechanism was studied as a function of physicochemical variables such as initial metal ion concentration, adsorbent dosage, contact time, and pH of the solution. The results indicated that the adsorption percentage of the two cations increased with contact time, attaining equilibrium at 150 and 120 min for Cd^{2+} and Pb^{2+}, respectively. At these optimal times, the adsorption capacity of Pb^{2+} and Cd^{2+} increased with increasing pH. Langmuir, Freundlich, Toth, Dubinin–Radushkevich, Sips, and Redlich–Peterson isotherm models were thereafter applied to understand the adsorption mechanism. The qe plot against C_e for the Toth isotherm model had the best fit with low error values and the highest correlation coefficient (R^2) values of 0.9973 and 0.9953 for Pb^{2+} and Cd^{2+}, respectively. Therefore, the isotherm study reveals that the adsorption mechanism involved is complex because of the presence of different interactions (such as ionic exchange and coagulation), yielding maximum adsorption capacities of 256 and 151 gm/L for Pb^{2+} and Cd^{2+}, respectively. Generally, the polysaccharide extract exhibited higher adsorption capacity of Pb^{2+} than of Cd^{2+} under similar conditions. Besides the removal capacities reported in this study, the adsorbent regeneration and its reusability was also investigated. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43913.

KEYWORDS: adsorption; biopolymers & renewable polymers; polysaccharides

Received 7 February 2016; accepted 12 May 2016
DOI: 10.1002/app.43913

INTRODUCTION

The contamination of water as a result of various toxic derivatives (such as trace metal ions, dyes, aromatic compounds, and pesticides) is a serious environmental matter worldwide.[1] Trace metal ions, particularly Pb^{2+} and Cd^{2+}, are known to be among the most highly toxic, causing hormonal, nervous, muscular, and skeletal anomalies in humans. Hence, their removal from water bodies has been a priority in water-treatment plants.[2] Although several procedures (such as precipitation, membrane filtration, and ion exchange) have been popularly employed for this purpose,[3] the adsorption of metals on natural polymers is possibly one of the most natural procedures for water decontamination.[4] Generally, adsorption involves the binding of molecules or particles (the adsorbate) to a surface (the adsorbent).[5] Adsorbents (such as activated charcoal, silica gel, and zeolites) are commonly used in industries for the removal of water pollutants, which include toxic metals.[6] Most of these adsorbents are synthetic and have been popularly used in water-treatment processes. However, investigations into the use of biosorbents have recently gained momentum because of environmental and cost considerations.[7] Common biopolymers that are chief constituents of plant cell walls (including cellulose, hemicellulose, pectins, and lignin) are the most abundant renewable sorbents.[8] They are the most abundant renewable resources that can be isolated from biomass via chemical processes. The literature reveals that biopolymers are mainly made up of polysaccharides that bear —COOH, —OH, and —SH functional groups. These groups are capable of ionizing in suitable solvents, thereby providing charged functionalities that could scavenge toxic metal ions through cation exchange.[9]

It is worth noting that the ability to bind trace metal ions is also dependent on the chemical structures of these

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biopolymers.[10,11] For this reason, the role of biopolymers in the removal of trace metal ions has inspired numerous research activities in the water-treatment sector. For instance, a study on the simultaneous removal of Pb^{2+}, Cu^{2+}, Cd^{2+}, and Zn^{2+} using polysaccharides such as hemicellulose has shown preferential adsorption toward Pb^{2+}.[12] It has been found that such adsorptions are driven by parameters such as pH of the solution, the metal ion concentration, sorbent dosage, temperature, and contact time.

Several cactus plant species, in particular, grow in almost all types of climatic conditions in the world, especially in arid and semi-arid regions. The *Opuntia ficus indica* species is thought to be indigenous to Mexico and is now domesticated in many parts of the world.[13] These various types of cactus have been subjected to chemical extractions in order to obtain natural sugars, which are functionalized and applied in various industries. Previous extraction works on cactus pads by Young[14] and Cardenas *et al.*[15] revealed the presence of mucilage and pectins. Their utilization for the removal of trace metals such as arsenic and bacteria from water have also been reported by other researchers.[16,17] However, the potential applications of other constituent polysaccharides are not well detailed in the literature.

In the present study, a polysaccharide sorbent isolated from wild cactus was applied for the removal of Pb^{2+} and Cd^{2+} from water. To identify the optimal conditions for the adsorption process, determining factors such as the point of zero charge (pH_{pzc}), sorbent dosage, contact time, and metal ion concentration were investigated as variables. In addition, an adsorption isotherm study was carried out in order to understand the adsorption mechanism as well as determine the modeled adsorption capacity of the polysaccharide extract. The adsorption equilibrium data were fitted into Langmuir (L), Freundlich (F), Toth (T), Dubinin–Radushkevich (DR), Sips (S), and Redlich–Peterson (RP) models, which were selected based on the literature review. Finally, desorption studies of these metal ions were performed to assess regeneration of the sorbent material and therefore their possible reusability. The novelty of this study lies in the extraction of a hemicellulose-rich polysaccharide and its application for the removal of metals in contaminated water.

EXPERIMENTAL

Materials

The cactus pads used in the study were harvested during the dry winter season from a field neighboring the University of Johannesburg, South Africa, located at 1767 m above sea level (latitude: 26°12′08″ S; longitude: 28°02′37″ E). The chemical reagents used in the isolation and purification of the polysaccharide extract included sodium hydroxide (NaOH), hydrochloric acid (HCl), and absolute ethanol (C_2H_5OH). The resulting polysaccharide powder was finally used as an adsorbent for the target cations. Other reagents (such as $Pb(NO_3)_2$, $CdSO_4{\cdot}H_2O$, HNO_3, and KOH) were supplied by Sigma-Aldrich (Pty) Ltd and Merck (Pty) Ltd, both Johannesburg South Africa and were used as received. Ultrapure water used for the preparation of all aqueous solutions was obtained from a Direct Q 3UV-R (Molsheim, France) purification system.

Isolation and Characterization of the Polysaccharide Extract

First, the spines were removed from the pads using a scalpel, followed by copious washing with tap water and further with deionized water. The precleaned pads were cut into small pieces, weighed, and immediately heated at 80 °C for 20 min (in order to prevent enzymatic degradation). The obtained parboiled sample was then used for isolation of the polysaccharide. The isolation procedure included the continuous heating of the resulting paste in a solvent mixture of 70% C_2H_5OH and 2 *M* NaOH (2:1 v/v) at 75 °C. This was followed by mixing the solid residue with a 10% NaOH solution for 3 h at 50 °C so as to solubilize the polysaccharide extract.[18] The mixture was centrifuged at 7500 rpm for 20 min (using Eppendorf model 5702 (Hamburg, Germany)). The pH of the obtained supernatant was adjusted to 5.3 by dropwise addition of 50 mL 0.5 *M* HCl before mixing with 95% C_2H_5OH in the ratio 1:4 (v/v). The mixture was left to stand overnight to allow the precipitation of the polysaccharide extract. The obtained precipitate was separated by centrifugation followed by washing with 70%, 90%, and 98% C_2H_5OH (% by volume), in order to ensure complete removal of any residual proteins and oligomers likely to be present. Finally, the extract was redispersed in water and freeze-dried at −40 °C for 4 days using a VirTis BenchTop K (model 2K BTES) (New York, USA) freeze drier.

The functional groups of the freeze-dried polysaccharide extract were identified with the aid of a Fourier transform infrared spectrometer (FTIR; Perkin Elmer version 6.3.5) equipped with an attenuated total reflectance crystal accessory. A frequency range of 600 to 4000 cm^{-1} was used. All spectra were obtained after 10 consecutive scans at a resolution of 4 cm^{-1}. A scanning electron microscope (SEM) bearing Vega TC3 software (TESCAN performance in nanospace) was used to examine the surface morphology of the test samples. Each sample was mounted directly onto the aluminum sample stub with the aid of black double-sided conductive tape, followed by coating with a carbon sputter prior to examination. The average particle size of the polysaccharide was calculated using ImageJ software (free download available at publisher.brothersoft.com).

Determination of pH_{pzc}

The pH at the point of zero charge (pH_{pzc}) is the point at which the surface functional groups of the adsorbent do not affect the pH of the solution during adsorption. The pH_{pzc} value was determined using the solid addition method.[19,20] Accordingly, molar solutions of HNO_3 and KOH were mixed in six different vials at varied proportions to adjust the initial pH (pH_i) values to 2, 4, 6, 8, 10, and 12. Twenty grams of the polysaccharide extract was added to each solution in the ratio of 1:5 w/v and shaken on an orbital platform shaker at 1300 rpm for 24 h. The resulting solutions were left to settle for 5 min before the final pH (pH_f) was measured. From a plot of pH_f against pH_i, the pH_{pzc} was obtained as the plateau along the pH_i axis.

Specific Surface Area and Porosity Analysis

The Brunauer−Emmett−Teller (BET) surface area of the polysaccharide extract was obtained by N_2 adsorption/desorption measurements using a Micromeritics ASAP 2020 analyzer. Approximately 0.3 g of freeze-dried isolate was weighed and transferred into the sample tube. It was degassed under vacuum at 120 °C for 12 h to eliminate residual moisture and

contaminants adsorbed on the surface prior to the analysis. By automation, liquid nitrogen was passed through the surface until saturation was observed. The quantities of N_2 adsorbed onto and desorbed from the solid surface at equilibrium were measured. The sample's specific surface area, pore width, and pore volume were obtained from the N_2 adsorption/desorption curves using BET theory.[21] In addition, the adsorption and desorption cumulative volume and average pore diameter were determined using a Barrett, Joyner, and Halenda (BJH) analysis.[22]

Determination of Adsorption Capacity

Adsorption experiments were performed using Cd^{2+} and Pb^{2+} solutions with concentrations in the range of 100–450 mg/L. First, 0.01 g of polysaccharide extract was added into 50 mL of the single-metal standard solutions. Each test mixture was homogenized in a shaker at room temperature and left to equilibrate for 2 h. After equilibration, the solution was centrifuged and filtered through a 0.45 μm polyether sulfone (PES) filter disk. The residual metal ion concentration (in the filtrate) was determined using inductively coupled plasma optical emission spectroscopy (ICP-OES). The adsorption experiment was repeated at varied concentration, contact time, temperature, and initial pH. In order to distinguish between possible metal precipitation and actual metal sorption as a means of quality control, control solutions (i.e., solutions without contact with the biosorbent) were also analyzed and blank corrections made. The % removal of the trace metals was estimated using eq. 1:

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

where C_o and C_e are the initial and final metal ion concentrations, respectively.

Effect of the Initial pH of Solution on the Metal Ion Uptake by the Cactus Polysaccharide

The initial pH of the metal solutions is considered to be a major parameter in the adsorption process. This is because the pH has an impact on the ionization of the functional groups present on the surfaces of the adsorbent and the chemical speciation of the metal ions. In order to study the effect of pH on adsorption, standard solutions (100 mg/L) of both Pb^{2+} and Cd^{2+} were prepared. Solutions with a pH range of 5–8 were prepared using 0.01 *M* NaOH and 0.01 *M* HNO_3. This was to cover the range for normal drinking water as well as avoid the possible precipitation of target cations as hydroxides. Then, ~0.01 g of the extract was added to 25 mL of each metal solution (in a stoppered 50 mL bottle). The solutions were then shaken at 160 rpm for 1 h using an orbital platform shaker, after which they were left to equilibrate for 2 h. This was followed by centrifugation to separate the bulk sorbent from the solution (before filtering) prior to subsequent analysis. The measurements were done in triplicate, and the average values of metal concentrations were calculated using eq. 2:

$$qe = \frac{(C_o - C_e)}{m} V \quad (2)$$

where qe is the equilibrium concentration; C_o and C_e are the initial and final metal ion concentrations (in mg/L), respectively; V is the volume of metal ion solution adsorbing to the polysaccharide extract (in liters), and m is the mass of the sorbent (in grams).

Effect of Dosage on the Sorption Process

A known amount of the adsorbent (between 0.01 and 0.05 g) was added to 50 mL of the metal ion solutions of known concentration, usually 100 mg/L. The mixture was agitated for 1 h and left to equilibrate for another 2 h before centrifugation at 7500 rpm for 15 min. The resulting supernatant was then filtered, and the metal ion concentrations remaining in the solution were determined by ICP-OES.

Effect of Contact Time on the Sorption Process

In this case, the effect of time on the interaction of the polysaccharide with the metal ions was performed at optimum pHs of 6 and 7 for Pb^{2+} and Cd^{2+}. Exactly 0.01 g of the sorbent was added to 50 mL of a standard metal ion solution (100 mg/L) in a water bath shaker. The contact time for adsorption was varied from 10 to 240 min and immediately centrifuged for 15 min. Then, the concentrations of the metal cations in the supernatants were measured by ICP-OES.

Effect of Initial Metal Concentration on Adsorption of Metal Ions

The initial concentration of the metal ions was varied between 100 and 450 mg/L. A known amount (0.01 g) of the polysaccharide extract was put into a 50 mL bottle containing Pb^{2+} or Cd^{2+} solution, and the mixture was shaken in a water bath for 150 min (optimized contact time) to ensure removal equilibrium was reached. The adsorbent was removed after centrifugation (10 min) for easy filtration. Finally, the cation concentrations were determined by ICP-OES. All of the adsorption experiments were conducted in triplicate, and the average results are reported.

Adsorption Isotherm Study

Adsorption equilibrium isotherms usually provide information on the mechanism and strength of the interaction between sorptives (such as metal ions) and a sorbent (polysaccharide extract in this case). The experiments were carried out for an optimized contact time with metal concentrations ranging from 100 to 450 mg L^{-1}. Therefore, adsorption isotherms at the optimum conditions were used to determine the maximum adsorption capacities of the polysaccharide extracts. One of the most feasible and easy-to-use tools for identifying and describing the best-fitting relationship in adsorption systems is linear regression.[23] However, because of the biases resulting from the transformation accorded to the values on the abscissa and ordinate, nonlinearized fitting has been statistically found to be more reliable. In this study, both two-parameter (Langmuir,[23] Freundlich[24] and three-parameter (Redlich–Peterson,[25] Sips,[26] Dubinin–Radushkevich,[27] and Toth[28] adsorption isotherm models were selected. With the aid of Sigmaplot 10.0 software (Systat Software, San Jose, CA, USA), nonlinear dynamic fitting was done. Also, the level of fitness of each was adjudged by their corresponding estimations of error with the coefficient of determination (R^2) and sum of squared errors (SSE).

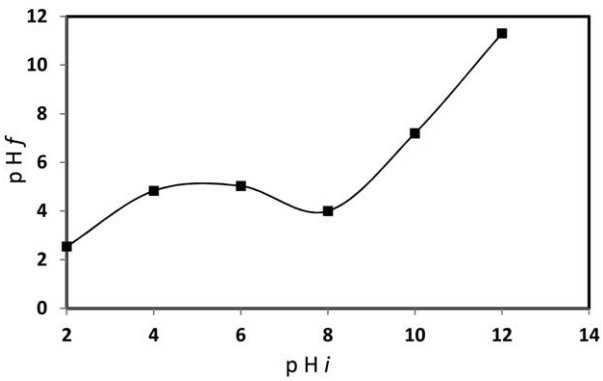

Figure 1. Plot showing the pH_{pzc} of the polysaccharide extract from cactus.

Desorption Studies

In order to determine the strength of the adsorption and investigate the feasibility of regeneration for reuse, desorption studies were carried out. This was performed at 25 °C by agitating the mixture of the metal ion–laden sorbent in 25 mL of 0.1 HNO_3. The mixture was agitated for 30 min at 180 rpm using a water bath shaker before it was left to settle for 2 h to equilibrate, followed by filtration. The concentration of the desorbed metal ions in the filtrate was determined using ICP-EOS. The desorption efficiency (in %) was calculated by eq. 3:

$$\%\text{Desorption efficiency (\% D.E)} = \frac{\text{Release metal conc}}{\text{Initially sorbed metal conc.}} \times 100 \quad (3)$$

Solubility Studies of the Polysaccharide Extract in Water

Approximately 0.02 g of the polysaccharide extract was added to 10 mL deionized water and conditioned at the pH values of 2, 5, 7, 9, and 12 according to a method described by Hovarth.[29] Thorough mixing was ensured with the use of a vortex, followed by equilibration for 24 h at ambient temperature. The resulting mixture settled down, and with careful suctioning the remaining solid material was obtained and then oven-dried at 40 °C to a constant mass. Solubility was determined as the difference between the initial mass of the extract (m_1) and that of the residue (m_2), as given by eq. 4:

$$\%S = \frac{m_1 - m_2}{m_1} \times 100 \quad (4)$$

where m_1 is the initial dry mass (g) of the polysaccharide extract, and m_2 is the dry mass (g) of the residue.

RESULTS AND DISCUSSION

pH_{pzc} Property of the Polysaccharide Extract

The surfaces of polysaccharide-rich materials are either positively or negatively charged depending on their interaction with the pH of the solution in contact. Hence, pH_{pzc} is used for such an investigation. From the pH_{pzc} curve of the sample depicted in Figure 1, the pH_{pzc} value was found to be around 4.4. This result reveals the possible presence of acidic oxygen-bearing surface functionalities, such as —COOH and —OH groups. Essentially, at pH_{pzc} values 4.6–7, these groups would become negative via deprotonation, creating vacant sites for the binding of positively charged metal ions. Considering that the sample has not been functionalized with any mineral acid yet, exhibiting such groups in significant quantities could be more economical. It is therefore expected that the adsorbent would bind to the metal ions through electrostatic interaction or by cation exchange. Hence, a high removal capacity (for the metal ions) from the solution is expected at pH values higher than pH_{pzc}. Our results are in agreement with the reported point of zero charge of cactus juice at 4.3.[30] Hence, a high removal capacity (for the metal ions) from the solution is expected at pH values greater than pH_{pzc}.

Textural Analysis

The polysaccharide extract was characterized in terms of its physical properties, such as the surface area, pore volume, and pore sizes, that may influence the sorption capacity of powdered materials. For instance, pore size and pore volume are associated with the adsorption, desorption, and porosity of the adsorbent. The surface area of our extract was found to be 2.3733 m^2/g. This surface area is small compared to the commercial adsorbents such as activated carbon, which has a surface area of 500–800 m^2/g.[31] In general, a large specific surface area is preferable since it gives a large sorption capacity. However, these results are in close agreement with the values reported for most biosorbents.[32] Despite the relatively low surface area, it is still of benefit to use the polysaccharide as green science for domestic water-treatment processes because biosorbents possess multiple functional groups.

The total average pore diameter and pore volume from the BJH equation were 19.0624 nm and 0.011077 cm^3/g. A larger pore diameter and a smaller volume would increase the mass transfer of metal ions in adsorbents through changes in active diffusivity.[33] This will, therefore, improve the adsorption of the metal ions within the structure and consequently lead to faster uptake of the pollutants from the solution.

FTIR Spectral Analysis

The FTIR spectra of the polysaccharide extract is illustrated in Figure 2. Bands similar to those of carboxylic, alcoholic, and carboxylate functional groups were observed in the polysaccharide spectra. The absorption bands at 2926 and 2854 cm^{-1} are due to the C—H stretching of methyl groups. The peaks around

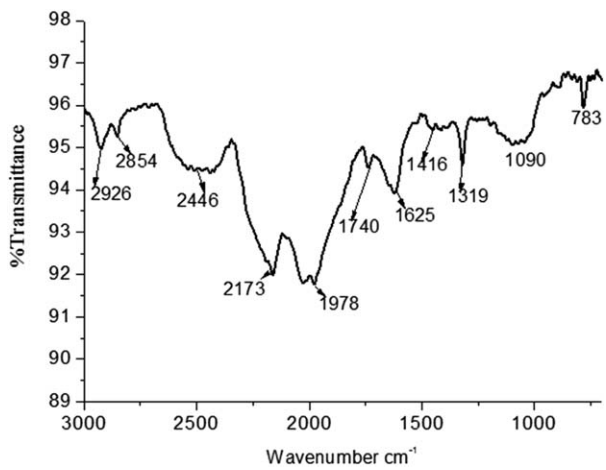

Figure 2. FTIR spectrum of the isolated polysaccharide extract.

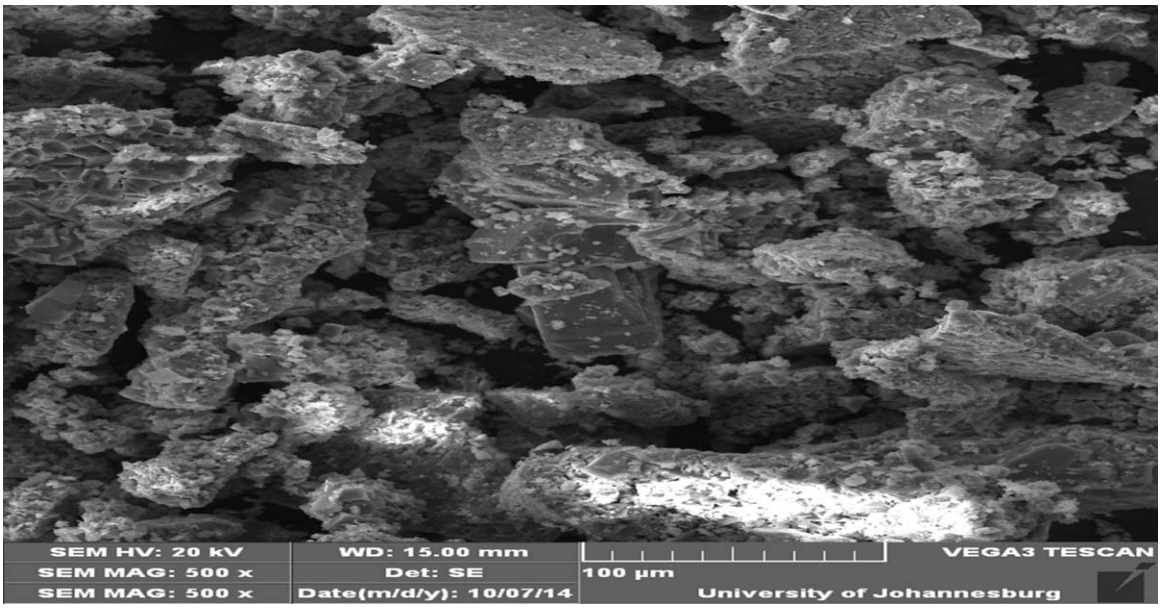

Figure 3. SEM micrograph showing the surface morphology of the isolated polysaccharide.

1416 cm^{-1} and 1319 cm^{-1} are indicative of CH_2 scissors vibration and CH symmetric bending vibrations on xylose rings of the polysaccharide extract. Furthermore, the occurrence of two peaks in the carbonyl region shows the presence of carboxylic acids. The bands at 1740 and 1625 cm^{-1} represent the C═O and COO— stretch from acetyl or COOH groups in the polysaccharide components.

A characteristic band at 1090 cm^{-1} corresponds to the C—OH, C—H, and C—C of ring and side-group vibrations, characteristic of pentopyranoses.[34] In addition, the peaks appearing at 2446, 1978, and 2173 cm^{-1} are attributed to the O—H stretch and C—C stretch of carboxylic acids and alkynes, respectively. Finally, a band observed at 783 cm^{-1} is attributed to O—H out-of-plane bending of polysaccharide molecules.[35] All spectra are typical of hemicellulose, characterized by absorption peaks at 2926, 1416, 1319, 1625, 1740, and 1090 cm^{-1}. These observations indicate the heterogeneous distribution of surface oxygen groups that is often characteristic of carbohydrate polymers.

The morphology of the extract was investigated by SEM and is presented in Figure 3. Generally, the images showed a rough surface with large voids evincing an estimated average particle size of 255 nm (using ImageJ software). The rough surfaces are advantageous, as they could provide more sites (i.e., higher surface area) for the transfer (via diffusion) of the metal ions from the solution matrix onto the sorbent, thereby enhancing its adsorption efficiency.

pH Variation

The pH of a solution is an important factor during metal adsorption since it influences the adsorbents' surface charge and metal ion speciation. For instance, it has been reported that, at pH < 7, Pb and Cd exist in the divalent ion form. In this study, the effect of the solution pH on the adsorption of Pb^{2+} and Cd^{2+} was investigated. The pH range of 5.0 ± 0.1 to 8.0 ± 0.1 was selected. The results obtained showed that the removal of Pb^{2+} and Cd^{2+} increased with an increase in the pH (Figure 4). A possible explanation for this observation could be that as the pH increases, the H^+ are desorbed from the functional groups. Hence, the adsorbent's surface becomes more negative, thereby increasing the attraction of metal ions to the free sites of the polysaccharides, resulting in high adsorption capacities. In particular, it is worth noting that the sorbent's removal efficiencies toward Pb^{2+} and Cd^{2+} were optimized by 31% and 33%, respectively. Similar observations on the sorption of Pb^{2+} on wheat fibers was recently reported.[36] Therefore, our findings are in agreement with those of Tang and coauthors, who observed maximum adsorption of Pb^{2+} on wheat fibers at pH 6.

However, as the pH was increased beyond 7, a sharp reduction in metal ion adsorption for both cations was observed. This trend is attributed the fact that, at pH > 7, hydroxide ions (OH^- ions) in solution begin to complex the metal ions, reducing the available metal ions in solution for adsorption. In our preliminary experiments, we conducted control experiments to investigate the dependence of the cations' solubility on pH as

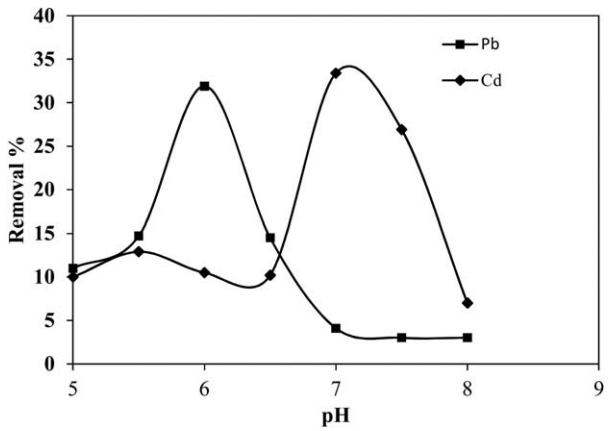

Figure 4. Effect of pH on the sorption process.

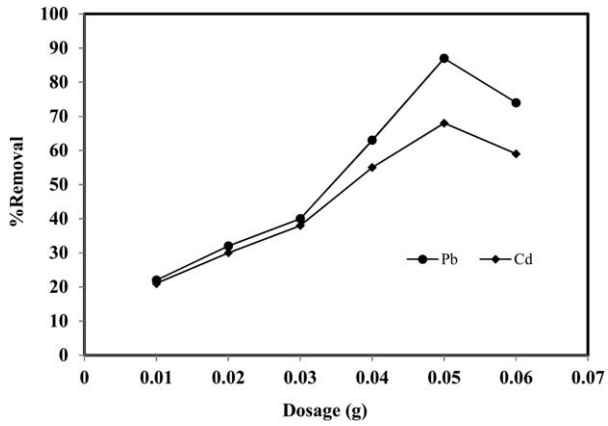

Figure 5. Effect of sorbent dose on metal ion removal.

well. This was necessary to account for or eliminate the effect of precipitation (as hydroxides) at neutral pH (6.5–7.5). Subsequently, all experiments were conducted at pH 6 and 7 for Pb^{2+} and Cd^{2+}, respectively.

Effect of Dosage

Investigation on the effect of sorbent dose is very important because it affects the removal capacity of the sorbent of a given concentration of the metal ions. The removal efficiency of the target metal ions as a function of dosage in a standard solution of 100 mg/L was calculated and reported in Figure 5. The results showed an exponential increase in the removal of both Pb^{2+} and Cd^{2+} as the dosage was increased at constant metal concentration. This is because increasing the amount of the sorbent provides a larger surface area (more sorption sites) for binding metal ions. Furthermore, the low dosage of the adsorbent favors the metal/biosorbent ratio, hence increasing the metal uptake per gram of the biosorbent. However, the polysaccharide extract showed a different level of affinity for the metal ions. Generally, more preference for Pb^{2+} than for Cd^{2+} was exhibited. The optimum adsorption of Pb^{2+} was reached at a dosage of 0.05 g, while Pb^{2+} and Cd^{2+} removal efficiencies of 87% and 68%, respectively, were achieved. However, a further increase in the adsorbent dosage led to a decrease in the adsorption capacity. This drop could lead to a shortage of metal ions in solution or the aggregation of sorbent sites, resulting in a low adsorptive surface area.[37] Our results also show that the electrostatic interaction between the adsorbent and metal ions may not be significant in the adsorption process. The data obtained will be useful in the scale-up process to optimize the purification process.

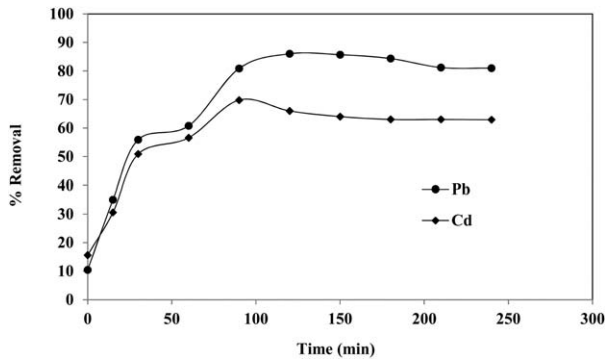

Figure 6. Effect of contact time on adsorption of metal ions.

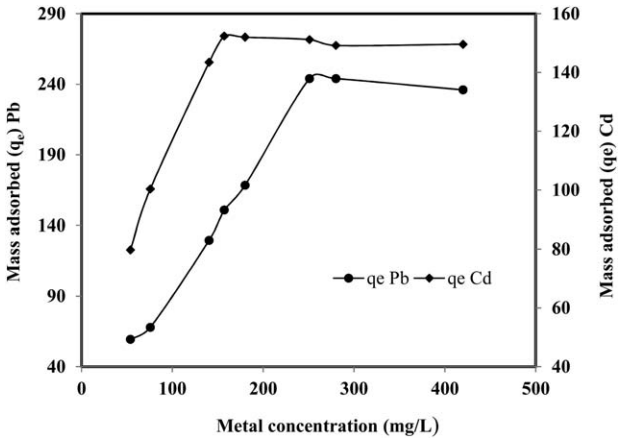

Figure 7. Impact of initial concentration on the removal efficiency.

Effect of Contact Time on Adsorption

The results on the adsorption capacity as a function of contact time examined between 10 and 240 min are presented in Figure 6. An increased removal rate was observed during the initial contact period (10–40 min and 10–70 min for Cd^{2+} and Pb^{2+}, respectively). As observed in the previous section, the removal of Pb^{2+} was favorable in both magnitude and rate compared to that of Cd^{2+}. However, after these aforementioned contact times, a rapid adsorption rate removal was observed for both

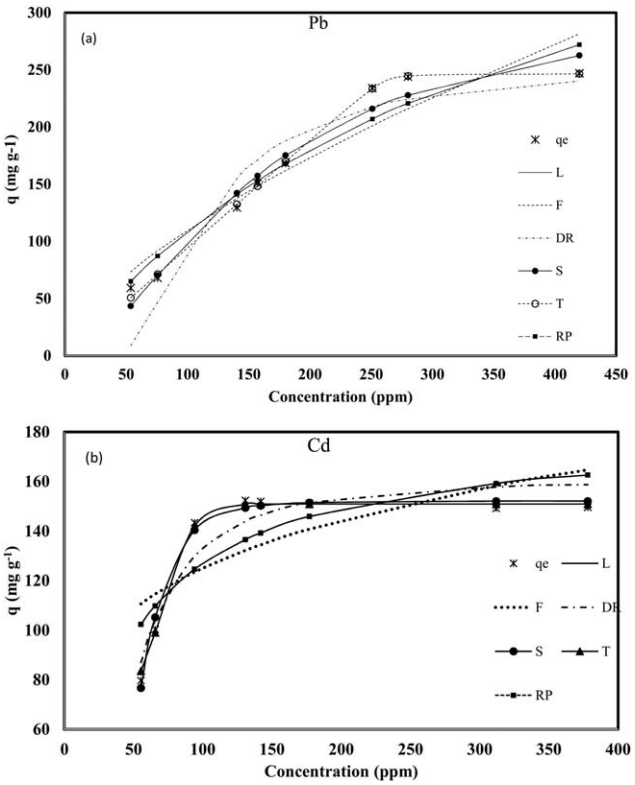

Figure 8. Nonlinearized fitting of selected isotherm of (a) Pb^{2+} and (b) Cd^{2+}.

Table I. Adsorption Parameters of Pb^{2+} and Cd^{2+} on Polysaccharide Extract

Isotherm model	Nonlinear equation	Parameters	Pb^{2+}	Cd^{2+}
Langmuir	$qe=\frac{q_0 bCe}{1+bCe}$	Q_{max}	509.8	180.9
		K_L	0.00273	0.0236
		R^2	0.9386	0.7012
		SEE	20.1583	16.675
Freundlich	$qe=K_F Ce^{1/n}$	K_F	54.46	48.14
		$1/n$	0.6532	0.2072
		R^2	0.90078	0.5188
		SEE	25.6258	21.187
Dubinin–Radushkevich	$q=(qs)\exp(-Kad\epsilon^2)$	qs	254	160.8
		K_{ad}	1654.92	323.1
		R^2	0.870623	0.9091
		SEE	29.2619	3.7014
Sips	$qe=\frac{K_S C_e^{\beta s}}{1+\alpha_S C_e^{\beta s}}$	K_S	309.5	152.12
		α_S	0.00648	0.01813
		β_S	1.7182	4.642
		R^2	0.966202	0.9877
		SEE	16.3835	1
Toth	$qe=\frac{K_T C_e}{(\alpha_T+C_e)^{1/T}}$	K_T	246.6	150.88
		α_T	0.00383	0.01
		T	23.293	321.1
		R^2	0.99733	0.9953
		SEE	4.6052	2.2891
Redlich–Peterson	$qe=\frac{K_R C_e}{1+\alpha_R C_e^g}$	K_R	509.8	180.9
		α_R	0.00273	0.00223
		g	1	1
		R^2	0.93867	0.70195
		SEE	22.0823	18.267

qe, amount of metal ions adsorbed; C_e, equilibrium concentration of the metal ions; Q_{max}, maximum adsorption capacity; K_F, freundlich constant (mg g^{-1})(L $mg^{-1})^{1/n}$,Freundlich constant; n, empirical parameter that is related to the biosorption intensity; K_T, equilibrium binding constant (L/mmol) corresponding to the maximum binding energy; constant B is related to the heat of adsorption; R, gas constant; T, absolute temperature; β, mean free energy, E of sorption per molecule of sorbate; K_S, Sips constant; $1/n$, Sips model exponent; K_R (L g^{-1}) and α_R (L $mmol^{-1}$), Redlich–Peterson constants; g, exponent that lies between 0 and 1.

metal ions. This is attributed to the availability of sufficient active sites on the polysaccharide sample as the system became more homogenized and the sorption equilibrium state was reached. When the active sites were occupied, the removal decelerated, and an equilibrium state was reached (at approximately 150 min for Cd^{2+} and 120 min for Pb^{2+}). A further increase in contact time did not change the adsorption of the metal, possibly due to saturation of the adsorbent. Based on these results, subsequent experiments were employed at an optimal contact time of 150 min.

Effect of Initial Metal Ion Concentration on Adsorption

The subsequent removal of metal ions using a constant amount of polysaccharide extract was examined at various concentrations in the range 100–450 mg/L. As presented in Figure 7, there was a general increase in the adsorbed mass of Pb^{2+} and Cd^{2+} with the increase in initial metal ion concentration. The maximum adsorbed masses of 244 and 152 mg/L were recorded for Pb^{2+} and Cd^{2+}, respectively. The increase in the adsorbed mass as a function of the initial metal ion concentration could be attributed to the enhanced mass transfer of ions from the aqueous to the solid interphase. Beyond the maximum mass adsorbed, an increased concentration of these cations did not significantly influence their removal, due to the possible saturation of the active sites of the adsorbent. A similar observation and explanation have been reported for Pb^{2+} removal using activated carbon, in which the removal efficiency was found to increase with increasing metal ion concentration.[38]

Adsorption Isotherm Study

In order to propose the underlying scavenging phenomenon of the metal ions by the polysaccharide extract, selected isotherm models were used to fit the experimental adsorption data. The adsorption isotherms were obtained by plotting the amount of the metal ions adsorbed per unit weight of the sorbent (qe) against the equilibrium concentration of the metal ions in the solution (C_e) at a constant temperature of 25 °C. The values of the model parameters were evaluated by nonlinear curve fitting

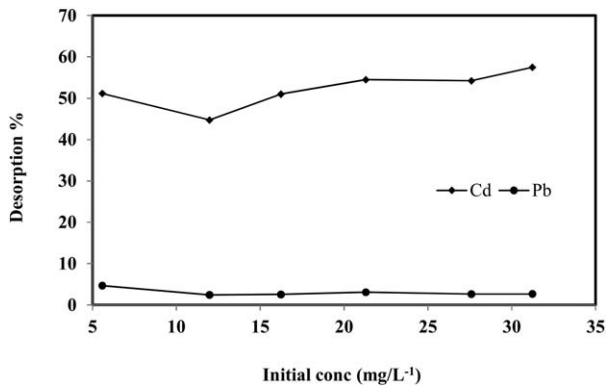

Figure 9. Investigation into the reliability of the desorption test.

methods. The applicability of the isotherm equations was evaluated through the correlation coefficient R^2 and sum of squared errors (SSE). The estimated adsorption parameters were plotted as shown in Figure 8(b), and the values of the error estimates are compiled in Table I. As can be seen in Figure 8(a), the Toth isotherm gave the best fit with the lowest error values and the highest R^2 (0.9973 and 0.9953 for Pb^{2+} and Cd^{2+}, respectively). The Q_{max} for Pb^{2+} (247 mg/g) was found to be higher than that of Cd^{2+} (151 mg/g), which implies that the cactus polysaccharide extract has a higher affinity toward Pb^{2+}. Regardless, neither the Langmuir nor the Freundlich model adequately fits the experimental data. However, the three-parameter models Dubinin–Radushkevich and Sips gave relatively better fits, especially with Cd^{2+}, as shown in Table I. The Sips isotherm model is a combination of Langmuir and Freundlich models used to describe adsorption onto heterogeneous surfaces. It suggests that, at high adsorbate concentration, a monolayer coverage that follows the Langmuir pattern is observed, while it approaches the Freundlich model at low concentration. The Toth model, in contrast, favors adsorption at both low and high boundaries of the concentration. Of all the models, the Toth is the best to describe the biosorption process as the R^2 from the Sips model (0.9662 and 0.9877) was found to be slightly lower than that obtained from the Toth model ($R^2 = 0.9973$ and 0.9953) for Pb^{2+} and Cd^{2+}, respectively. Of the more robust three-parameter models, Redlich–Peterson gave the worst fit for both Pb^{2+} and Cd^{2+} adsorption processes. Overall, these results show that the adsorption of heavy metals by cactus polysaccharide extract could be a complex (chemical reaction) process, capable of exhibiting both physical and chemical phenomena. Also, the desorption results obtained in the next section (Figure 8) also prove that the interaction at the interface is strong and could be of chemical nature (covalent or coordination bonding) and not a mere physisorption. Hence, it would be difficult to elute the metal ions after they are scavenged by the sorbent. In other words, despite showing high removal efficiency for the target metals, the regeneration and subsequent reuse of the material could be a challenge. Therefore, this should be considered through investigation at different pH values.

Desorption Test

A reliable desorption test could positively impact the overall cost of production and subsequent utilization of sorbents, by providing adequate information on the chances of its reusability. In the current work, the concentration of target cations was measured after equilibrium has been reached. The desorption efficiency (% DE) was derived as the amount of sorbed metal ions stripped from the sorbent's surface relative to the amount of that left adsorbed on the polysaccharide material (Figure 9). The % DE for Cd^{2+} was found to be higher than that for Pb^{2+}, which could imply that the active binding sites have higher affinity toward metal ions with higher electron affinity and electron radii forming a more stable structure with the coordination of oxygen atoms. This observation could also indicate that the attraction between the Cd^{2+} and the polysaccharide is a weak physisorption (a typical van der Waals force) and not of a true covalent or complexation interaction. In furtherance, an investigation into sorption bond strength (thermodynamic study) along with a removal kinetics study will be carried out in detail in our future work.

Solubility Studies of the Polysaccharide Extract in Water

The effect of pH on solubility of the extracts at pH values of 2, 5, 7, 9, and 12 was found to be 0.4%, 0.6%, 0.2%, 0.3%, and 0.5%, respectively. This is attributed to the amorphous nature of the polysaccharides, which allow them to be partially soluble in water; however, this would not affect the safety of the water, because of their nontoxicity.

CONCLUSIONS

In this work, the use of polysaccharide extracted from cactus for the removal of Pb^{2+} and Cd^{2+} from simulated drinking water showed a high removal capacity. The maximum adsorption capacities of the Pb^{2+} and Cd^{2+} were found to be 256 and 151 mg/L, respectively. These values are relatively high compared to the literature values observed for natural biosorbents. The various factors investigated showed distinct changes in the adsorption capacities. The equilibrium data obtained showed the best fit for the Toth isotherm, suggesting that the interaction at the adsorption and removal interface was due to the presence of some heterogeneously dispersed chemical processes. Generally, these results show that the adsorption of trace metals by cactus polysaccharide extract could be a complex chemical process, capable of exhibiting both physical and chemical phenomena.

Since the quantitative removal of Cd^{2+} and Pb^{2+} present in low levels in drinking water by the isolated polysaccharide has been established in this work, the next phase of our research involves its application to real-life wastewaters from different sources where the adsorbates (among other trace metal ions such as Cr and Zn) are expected to be present in elevated levels. An adsorption breakthrough study, with modeling of isotherm, kinetics, and thermodynamic parameters, will also be carried out after process optimization. The results obtained from future work will determine the plausibility of large-scale production and eventual commercialization of the sorbent.

ACKNOWLEDGMENTS

We wish to thank the Organization for Women in Science for the Developing World (OWSD) (fund reservation number

3240274097) and the Swedish International Development Agency (SIDA) for generously supporting this project. The authors acknowledge the contribution of the Centre for Nanomaterials Science Research (CNSR) in the department of Applied Chemistry, University of Johannesburg.

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