ADSORPTIVE REMOVAL OF LEAD IONS FROM WASTEWATER USING SORBENTS DERIVED FROM *Cedrusdeodara* PLANT AND IT'S COMPOSITE WITH Ca-ALGINATE BEADS

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ABSTRACT

Three adsorbents based on *Cedrusdeodara* plant materials are developed for the removal of Pb^{2+} from water. *Cedrusdeodara* Stem Powder (CDSP), its H_2SO_4 -generated active carbon (CDAC) and CDAC-doped Ca-alginate beads (CDAC-Ca-beads), are synthesized and investigated for their sorption abilities for Pb^{2+} ions. Various extraction conditions are investigated and optimized for the maximum adsorptivities. The sorption capacities are: 10.4 mg/g for CDSP; 16.8 mg/g for CDAC; and 25.6 mg/g for CDAC-Ca-beads. The cumulative sorption of active carbon assisted by Ca-alginate beads, result in higher adsorptivity for CDAC-Ca-beads. Beads show good Pb^{2+} -adsorptivity in a wide range of pHs: 3.0 to 9.0. This is a marked property as the beads can be used in the treatment of wastewaters having varied pHs. Four-fold excess of co-ions has a marginal effect on the % removal of Pb^{2+} ions from water. Thermodynamics parameters indicate that the sorption is endothermic, spontaneous and the nature of adsorption is more chemical than physical or electrostatic. ΔH values are in the order: CDSP < CDAC < CDAC-Ca-BEADS and so is the increasing order of complexing tendency of Pb^{2+} . Positive ΔS values for the sorbents indicate disorder at the solid-liquid interface and it is an ideal condition for Pb^{2+} ions to cross the solid/liquid surface barrier and hence more adsorptivity. Negative ΔG values reflect the spontaneity of the sorption process. Spent CDAC and CDAC-Ca-beads can be regenerated with marginal loss of sorption capacity. Adsorbents developed in this work are successfully applied to treat industrial effluent samples.

Keywords: Pb^{2+} removal, Adsorbents, *Cedrusdeodara* stems, Ca-alginate beads, Applications.

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INTRODUCTION

Removal of Pb^{2+} from industrial effluents is one of the interesting areas of pollution control research.^{1,2} The toxicity of lead ions is well known and it is a 'human carcinogen' as per USEPA.^{3,4} Inadequately treated effluents from Pb-based industries is an important pollution source of lead.¹⁻⁵ Even traces of Pb^{2+} , if enters into the water bodies due to ill-treated sewage disposal, gets amplified due to bio-accumulation processes. Lead-free water or a maximum limit of 0.01 ppm are recommended by WHO for human consumption because of its deleterious effects caused to the human beings.^{3,4}

Of the various methods of lead removal from water, adsorption methods based on bio-materials especially plants, are proving to be effective, simple, eco-friendly and economical. Further, they are based on materials that are renewable and abundantly available plant sources.

Adsorbents derived from Tamarind wood⁶, pine cone⁷, pumpkin-seed-shell⁸, coconut shell⁹, MaizeTassesl¹⁰, Prosopis mimosaceasawdust¹¹, apple juice residue¹², exhausted coffee grounds¹³, Banana Pseudo stem¹⁴, Annona squamosa shell¹⁵ and acid activated clay¹⁶ are investigated for their efficiency towards the removal of Pb^{2+} from waste water.

Almondshell¹⁷, treated rice bran¹⁸, treated-Jackfruit leaves¹⁹, walnut shell powder²⁰, and diceriocaryumeriocarpum plant leaves²¹ are also investigated. Calcium-alginate beads doped with active carbon of Caryotaurens seeds²² and hydrazine sulphate treated red mud, are investigated for the removal of Pb^{2+} from industrial.²³

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This investigation is in this aspect. Our research group is intensively investigating these aspects and found some plant materials or their derivatives having adsorptivities towards metal ions²⁴⁻³⁰. India is endowed with different plants. If plant materials or their derivate are identified for their specific activity towards heavy metal ions, such investigations will turn to be a 'blessing-in-disguise'. These phyto-remediation methods are highly economical, eco-friendly and they are based on abundantly available plant materials. Our trail work reveals that stem powders of *Cedrusdeodara plant* have adsorptivity for Pb^{2+} ions. Further, when these stem powders are carbonized with H_2SO_4 -digestion process, the obtained activated bi-char has enhanced Pb^{2+} adsorptivity. The inherent disadvantage with these powdered adsorbents is that the filtration of water is slow. The size of the voids between the powdered particles are small and are not helpful for filtration and to make the process quick, pressure-heads are essential. To overcome this disadvantage, investigations are being made with open columns or with beads embedded with the adsorbents. In the present work, the activated bio-char of stems of *Cedrusdeodara plant* immobilized in Ca-alginate beads, is synthesized. Thus, stem powders of *Cedrusdeodara plant* (CDSP), their H_2SO_4 -generated activated carbon (CDAC) and Ca-alginate beads doped with the activated carbon (CDAC-Ca-alginate) are investigated for their adsorptivities for Pb^{2+} .

EXPERIMENTAL

Plant Description

Cedrusdeodara plant belongs to *Plantae* family of the plant kingdom and it grows to an average height of 45 meters. It is grown well in western regions of the Himalayas. It is a sacred tree for Hindus and it is known to have medicinal values.

Fig.-1: *Cedrusdeodara* Plant having Affinity for Pb^{2+} Ions

Preparation of Adsorbents

Raw Stem Powder

The cut Stem pieces of *Cedrusdeodara plant* were washed with distilled water and hot-oven dried at $102^{\circ}C$ for two hours. The dried material was crusted to the powder of sieve size less <75 microns and preserved in air-tight brown bottles. This material of *Cedrusdeodara stem powder* is termed as CDSP.

Active Carbon

Requisite amount of CDSP was taken into a suitable size round bottom flask and to it, the needed quantity of Conc H_2SO_4 was added until the material was fully immersed. Then a reflux condenser was set-up. The material in the flask was digested for 3 hours until all the material was completely carbonized. Then the material was taken out from the flask, diluted with water, filtered, washed the activated carbon for neutrality with water, dried at $102^{\circ}C$ and preserved in an air-tight brown bottle. It is termed as CDAC.

Synthesis of Beads

Beads doped with CDAC were synthesized by cross-linking Sodium alginate with Ca^{2+} ion in the same lines of our previous reports for Ca-alginate³¹ and Zn-alginate³² beads but with a change in optimum conditions of synthesis.

Method

2.5 g of sodium alginate in 100 ml distilled water was constantly stirred and the temperature of the solution was gradually raised to $70^{\circ}C$. Then 2.5 g of CDAC was added while stirring was continued and

the temperature was maintained at 70°C for about 1 hour. The resulting solution was cooled. This solution was added in drop-wise into a previously cooled (10°C) 2.5% w/v CaCl₂ solution with the aid of a pipette. As the drop oozed out from the tip of the pipette was touched to Ca²⁺ solution, it got solidified due to cross linking by Ca²⁺ ions to form beads. Thus obtained beads containing CDAC were allowed to be digested with its mother-liquor for over-night. Then beads were filtered, washed and dried at 102°C. The beads were termed as CDAC-Ca²⁺-beads.

Chemicals and Reagents

Analytical Graded pure Chemicals were used in this work. Using double-distilled water, reagents and simulated solutions were prepared. Pb²⁺ stock solution of concentration: 50.0 mg/l was prepared and diluted as per the requirement.

Adsorption Studies

Batch methods^{33,34} were adopted using simulated Pb²⁺ solutions. Extraction conditions were optimized for the maximum Pb²⁺ adsorptivity of the three sorbents: CDSP, CDAC and CDAC-Ca²⁺-beads.

Procedure

Pb²⁺ ion (20 ppm) solutions of volume: 100 ml, were taken into 250 mL Iodine flasks. Known quantities of CDSP, CDAC and CDAC-Ca²⁺-beads, were added to the solutions. Initial pHs of solutions were adjusted with dil HCl/ dil NaOH. Then solutions were shaken at 350 rpm in an orbital shaker for the desired time at room temperature. Then the solutions were filtered. The residual content of Pb²⁺ in the filtrate was estimated using the Atomic adsorption spectroscopic method as described in literature³. The instrument used was: AA 500 model and it has features: flame absorption; fuel flow rate: 1200 (mL/min); slit: 0.4; Lamp current: 5.0 amp; wavelength: 217.00 nm and High voltage: 416.25 V.

By using the following equations, the adsorbed amounts of Pb²⁺ ions at equilibrium (q_e) and % removal of Pb²⁺ were evaluated:

$$q_e = \frac{(C_i - C_e)}{m} V \quad (1)$$

$$\% \text{ removal} = \frac{(C_i - C_e)}{C_i} 100\% \quad (2)$$

Where C_i = initial Pb²⁺ concentration; C_e = equilibrium Pb²⁺ concentration; and V = volume of solution (in liters); m = mass of sorbent (g).³⁴

The influence of solution pH, the dosage of adsorbent, time of contact between the sorbent and Pb²⁺ solution, initial concentration of Pb²⁺ solution, co-ions and temperature on the adsorptivities of CDSP, CDAC and CDAC-Ca²⁺-beads were assessed by adopting the above-described method. In assessing the Pb²⁺ adsorptivities of CDSP, CDAC and CDAC-Ca²⁺-beads, the targeted parameter was progressively changed while all other parameters were kept at optimum and constant levels.^{35,36} The obtained results are presented in Fig.-2 to 12 and Tables-1 and 2.

The inference caused by three-fold excess of co-ions was investigated by using simulated solutions having four-fold excess of the concentration of co-ions than Pb²⁺ ions concentration. The results are presented in Fig.-8 and 9. Regeneration of Spent adsorbents was also investigated and results are depicted in Fig.-12. The adoptability CDSP, CDAC and CDAC-Ca²⁺- beads as adsorbents were investigated by applying them to treat real Industrial effluents samples from battery and electroplating industries. The findings are noted in Table-2.

RESULTS AND DISCUSSION

The extraction conditions were optimized for the maximum adsorptivities of CDSP, CDAC and CDAC-beads for Pb²⁺. Findings and their justifications are presented hereunder.^{35,36}

Solution pH (Initial)

It has a marked influence on the adsorptivities of the sorbents. By varying pH from 1.0 to 12.0 but keeping at constant levels the other extraction conditions, % removal of Pb²⁺ was assessed for each adsorbent. Fig 2 signifies the role of pH.

It is interesting to note that in a wide range of pH: 3.0 to 9.0, CDAC-CA-beads have shown good adsorptivity with a maximum of 85.0% at pH:7 (Fig.-2). In the case of CDSP and CDAC, the optimum pHs are found to be 5.0 and 6.0 respectively.

Fig.-2: pH Vs % removal of Pb^{2+} Conc. of Pb^{2+} : 20 ppm

The adsorptivities of sorbents are of the order: CDAC-Ca-beads > CDAC > CDSP. Highest removal of Pb^{2+} observed are: 60.0% for CDSP, 65.0% for CDAC and 85.0% for CDAC-Ca-beads. CDAC-Ca-beads have good adsorptivity in neutral and also in slight basic as well as in acidic solutions. Percentage removal with CDAC-CA-beads as sorbents is: 70.0% at pH: 3.0; 76.0.0% at pH: 4.0; 83.0 at pH: 5.0; 85.0% at pH: 6.0; 82.0% at pH: 7.0; 80.0% at pH:8; and 70.0% at pH: 9.0. Above pH: 9.0, adsorptivity of CDAC-Ca-beads falls sharply. With CDSP, removal is : 35.0% at pH: 2.0; 51.0% at pH:3.0; 54.0% at pH: 4.0; 60.0% at pH:5.0; 59.0% at pH:6; 58.0% at pH:7.0; 45.0 % at pH:8.0; 35.0% at pH:9.0; 25.0% at pH:10.0; 21.0% at pH:11 and 9.0% at pH:12. With CDAC as sorbent, Pb^{2+} removal is: 24.0% at pH: 2.0; 34.0% at pH: 3.0; 45.0% at pH: 4.0; 56% at pH: 5.0; 65.0% at pH:6.0; 60.0% at pH: 7.0; 55.0% at pH: 8.0; 49.0% at pH:9.0; 30.0% at pH:10.0; 21.0% at pH:11.0 and 9.0% at pH:12.0.

Sorbents pHzpc values and Pb-speciation will account for these observations. pHzpc values for CDSP, CDAC and CDAC-Ca-beads were found as per procedures available in literature^{23,24}. They are 5.1 for CDSP, 6.3 for CDAC and 7.2 for CDAC-Ca-beads, vide Fig.-3. At pHzpc, the sorbent surface has an equal number of positive and negative charges and hence, the surface is neutral. Above pHzpc, the surface is negatively charged when in contact with the solution due to ionization of functional groups viz., -OH, -COOH etc. Below pHzpc, ionization is less favored; at very low solution pHs, surfaces may acquire a 'positive' charge due to protonation. The nature of Pb (II) ions in the solution depends on pH of solution: < pH 4: Pb^{2+} ; pH: 4 to 6: $Pb^{2+}/Pb(OH)_2(s)/PbOH^+$ and pH: 7 to 12: $Pb(OH)_3^-$ and $Pb(OH)_4^{2-}$.²⁻³⁷ It is interesting to note the nature of curves in Fig.-3 depicted between pH and % removal. With CDAC-Ca-beads, a symmetrical hump is noted in a wide range of pH: 3 to 9 with good adsorptivity. This symmetrical hump indicates a kind of surface complex formation between Pb^{2+} and the functional groups of CDAC-Ca-beads. Though to a less extent, such curves are observed for CDSP as well as for CDAC. At high pHs (basic conditions), the adsorptivities for the three sorbents are low. In basic conditions, the surface of the adsorbents, as well as the Pb(II) species [$Pb(OH)_3^-$ and $Pb(OH)_4^{2-}$], are negatively charged and hence, they experience repulsion; so less adsorptivity. At very low pHs, H^+ will compete with Pb^{2+} for sorption sites and hence low adsorptivities. Adsorption is found in the pH range: 3.0 to 9.0 for CDAC-Ca-beads; 3.0 to 9.0 for CDSP and 5.0 to 9.0 for CDAC.

Sorbents Dosages

The minimum concentration of sorbent required for maximum Pb^{2+} removal is to be investigated. While changing the concentration from 0.25/l to 2.5 g/l but keeping all other extraction conditions at constant optimum levels as furnished in Fig.-4, the adsorptivities of CDSP, CDAC and CDAC-Ca-beads were investigated. Fig.-4 depicts the results.

Fig.-3: Evaluation of pH_{zpc} for CDSP, CDAC & CDAC-Ca-BEADS Fig.-4: Effect of Dosage of Adsorbents, Initial Concentration of Pb²⁺: 20 ppm

With the increase in the concentration of CDSP, CDAC and CDAC-Ca-beads, % removal is progressively increased initially but slows down later; after a certain concentration, % removal has come to a study state. With CDAC-beads, the % removal is varied from 30.0% to 85.9% as the concentration of CDAC-Ca-beads is changed from 0.25 g/l to 0.25 g/l to 1.0 g/l; and above 1.0 g/l, % removal is marginally varied. A similar tendency is shown in the case of CDAC and CDSP. With CDAC, % removal is increased from 25.0% to 65.0% with the increase in concentration of CDAC from at 0.25 g/l to 1.25 mg/l; above 1.25 g/l, % removal is marginally varied. With CDSP as adsorbent, as the concentration of CDSP is varied from 0.25 g/l to 1.5 g/l, % removal is changed from 21.0% to 60.0%; with more than 1.5 g/l, there is a little effect on the % removal. Plateau regions in curves reflects the steady states: > 1.5 g/l for CDSP; >1.25 g/l for CDAC; and >1.0 g/l for CDAC-Ca-beads. An increase in adsorbent concentration naturally increases the active sites and so, progressive increase in the % removal is noted initially. But later, the proportional increase in % removal is not observed. Overlapping of active sites and blocking of some path-ways for the migration of adsorbate (Pb²⁺) in sorbent to reach and interact with the active sites, are the causes for the decrease in the rate of % removal.^{35,36} At the study state, the rate of desorption and the rate of sorption are equal for the adsorbate. These study-states are reached because as the adsorbate (Pb²⁺) concentration is fixed, after a certain dosage, all the Pb²⁺ ions are engaged with the available sites of adsorbents. This results in no further adsorption and so, the plateau regions in the curves are resulted.²²

Contact Time

Another important extraction condition to be optimized is the contact time. It is the time for the sorbent and solution to be in contact with each other at constant agitation conditions at the desired rpm. By varying the time of contact from 10 minutes to 100 minutes but keeping other extraction conditions at

constant levels as had been noted in Fig.-5, % removal of Pb^{2+} from water using the sorbents, CDSP, CDAC and CDAC-Ca-beads, were investigated. The findings are noted in Fig.-5.

Fig.-5: Effect of Equilibration Time on % Removal of Pb^{2+} Initial Concentration of Pb^{2+} : 20 ppm

The nature of curves indicates that the removal of Pb^{2+} from water is almost linearly related to agitation time initially but with lapse of time, the % removal is slow-down and after a certain time, a steady-state is reached. With CDAC-Ca-beads as adsorbent, % of Pb^{2+} is found to be 76.0% at 30 minutes and reached 85.0% only after 50 minutes and then onwards, % removal is marginally varied from 85.0%. With CDAC, 52.0% of Pb^{2+} is removed within 20 minutes of equilibration but 65% only after 60 minutes. With CDSP, 48.0% removal of Pb^{2+} is observed within 30 minutes and 60.0% only after 90 minutes.

These findings are as per expectations. Plenty of active sites are available initially and hence, % removal is more but with the progress of time, active sites are used up and so, adsorption is mellowed. As the added adsorbent is fixed (i.e. 1.5 g/l for CDSP, 1.25 g/l for CDAC and 1.0 g/l for CDAC-Ca-beads), the available active sites are also limited. Hence, after a certain duration, when all the sites are engaged in the adsorption process, further adsorption is not possible and so, a steady state is reached. The time needed to reach this steady state is 90 minutes for CDSP, 60 minutes for CDAC and 50 minutes for CDAC-Ca-beads.²⁴

Initial Concentration of Pb^{2+} (Adsorbate)

Initial concentration of Pb^{2+} has profound influence on the adsorptivities of the sorbents. The optimization of this parameter is one of the important features. Maintaining all other conditions at constant levels, initial Pb^{2+} concentration was varied from 5.0 ppm to 50.0 ppm for finding the adsorptivities of CDSP, CDAC and CDAC-Ca-beads for Pb^{2+} . Figure-6 and 7 depict the observations. Figure-6 is: % removal Vs initial concentration and Fig.-7 is: adsorption capacity, q_e Vs initial concentration. With the increase in initial concentration of Pb^{2+} , % removal decreases while adsorption capacity increases. With CDAC-Ca-beads as adsorbent, % removal is observed to be 89.0% with 5.0 mg/l; 88.0% with 10.0 mg/l; 85.0% with 15.0 mg/l, 84.0% with 20.0 mg/l; 76.0% with 25.0 mg/l; 72.0% with 30.0 mg/l; 70.0% with 35.0 mg/l; 64.0% with 40.0 mg/l; 56.0% with 45.0 mg/l; and 47.0% with 50.0 mg/l.

Similarly, as initial Pb^{2+} concentration is varied from 5.0 mg/l to 50.0 mg/l, % removal is decreased from 70.0% to 32.0% with CDAC and 65.0% to 30.0% with CDSP as adsorbents. But, q_e is increased.

The adsorption capacity q_e is increased linearly (nearly) from 2.16 mg/g to 10.40 mg/g as the initial concentration is varied from 5.0 mg/l to 30.0 mg/l and remains almost constant around 10 mg/l for CDSP as adsorbent. With CDAC, q_e is varied from 2.8 mg/g to 11.8 mg/g with raise in Pb^{2+} concentration from 5.0 mg/l to 25.0 mg/l and latter remains constant around 12.0 mg/g. With CDAC-Ca-beads, q_e is varied almost linearly from 4.45 mg/g to 24.5 mg/g as the Pb^{2+} concentrations is varied from 5.0 mg/l to 35.0 mg/l and after that, q_e almost remains around 25.0 mg/g even when the initial concentration is increased upto 50.0 mg/l. These findings are as per expectations. With the increase in Pb^{2+} concentration, Pb^{2+} ions are forced to migrate towards the surface of adsorbents due to the concentration gradient between the surface layers of sorbent and bulk of the solution. So adsorptivity is progressively increased with an

increase in Pb^{2+} concentration. But with a fixed amount of adsorbent (1.5 g/l for CDSP; 1.25 g/l for CDAC and 1.0 g/l for CDAC-Ca-beads), there are only a limited number of active sites. When all the sites are exhausted, further sorption is not possible. So, saturation conditions have resulted and hence, plateaus are observed in the curves after 30.0 mg/l for CDSP, 25.0 mg/l for CDAC and 35.0 mg/l for CDAC-Ca-beads.²⁵

The decrease of % removal with an increase in the initial concentration of Pb^{2+} ion can be explained. At low Pb^{2+} concentrations, plenty of active sites are available for the adsorbate, Pb^{2+} and so good adsorption. As the concentrations of sorbents are fixed, only a limited number of active sites are available. So, a proportional number of sites needed in-tune with the raise in Pb^{2+} concentration, are not available. The result is a fall in % removal with raise in Pb^{2+} concentration.²⁵

Fig.-6: Initial Conc. Pb^{2+} Vs Pb^{2+} Removal

Interference of Co-ions

Interference caused by Co-ions on the extraction of Pb^{2+} from the water was investigated. For this simulated solutions containing four-fold excess of co-ions to the Pb^{2+} concentration, were prepared. From these solutions, Pb^{2+} was extracted using CDSP, CDAC and CDAC-Ca-beads as adsorbents as per the procedures established in this investigation. Figures-8 and 9 depict the results. From the Figures, it may be inferred that anions namely: F^- , NO_3^- , Cl^- , phosphate, carbonate and bicarbonate as well as the cations: Ca^{2+} , Mg^{2+} , Zn^{2+} , Al^{3+} and Fe^{2+} , are marginally interfered with the extraction of Pb^{2+} . This indicates the successful adoptability of procedures for real waters where in multiple co-ions exist along with Pb^{2+} ions.

Effect of Temperature

The temperature has a profound effect on the adsorptivities of CDSP, CDAC and CDAC-Ca-beads for Pb^{2+} . The % removal at 303 K, 313 K and 323 K were investigated at the optimum extraction conditions as depicted in Fig.-10. It may be inferred from Fig.-10 that as the temperature increases, % removal of Pb^{2+} also increases. This indicates the endothermic nature of adsorption. The raise in solution temperature enhances the vibrational motions of surface functional groups pertaining to the adsorbents. The consequence is that more channels are opened for an adsorbate to penetrate deep into the adsorbent's surface layers. Moreover, the kinetic energy of diffusing Pb^{2+} ions is also increased. These two factors result in enhanced adsorption.³¹

Thermodynamic Studies

Thermodynamic parameters, change in free energy: ΔG^0 (kJ/mole), enthalpy : ΔH^0 (kJ/mole) and entropy : ΔS^0 (J/K.mole) were found^{34,35} adopting equations:

$$\Delta G^0 = -RT \ln K_d \quad (3)$$

$$\ln K_d = \Delta S^0/R - \Delta H^0/RT \quad (4)$$

$$K_d = q_e/C_e \quad (5)$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (6)$$

Where K_d = distribution coefficient; q_e = amount of Pb^{2+} sorbed; C_e = equilibrium Pb^{2+} concentration ; T = temperature (Kelvin) , R = gas constant. The results are presented in Fig.-11 and Table-1.

Fig.-7: Initial Concentration Vs Sorption Capacity, qe

Fig.-8: Interference of Co-cations on the % removal of Pb^{2+}

Fig.-9: Effect of Co-anions on the % Removal of Pb^{2+}

Fig.-10: Effect of Temperature on the Adsorptivities of Sorbents
(Initial Concentration of Pb^{2+} : 20 ppm)

Fig.-11: 1/T Vs lnKd

The salient features of the thermodynamic investigations are:

- As the ΔH values are positive, the nature of adsorption is endothermic for CDSP, CDAC and CDAC-Ca-beads. Further, as the values are more than 24.0 KJ/mole, the nature of the binding of Pb^{2+} to the surface of the adsorbent is chemical. The ΔH value for CDAC-CA-beads is 2.5 folds more than the other two adsorbents. It emphasized that the adsorption is more oriented towards chemical nature in the beads. It is presumed that a kind of surface complexation between the functional groups of adsorbents surface and Pb^{2+} ions. Further, ΔH values increase in the order: CDSP < CDAC < CDAC-Ca-BEADS. The chemical nature of binding also increases in the same order.
- Positive ΔS values for CDSP, CDAC and CDAC-Ca-beads, reflect disorder at the solid-liquid interface^{33,34} and the values fall in the order CDAC-Ca-beads > CDAC > CDSP. ΔS for CDAC-Ca-beads is 213.770 J/mole and it is nearly 2.5 times higher than the values of CDAC (79.726 J/mole) and CDSP(83.336 J/mole). More is the disorder, higher is the penetration of adsorbate into the adsorbent and hence, more adsorptivity. So, beads having higher ΔS values are good adsorbent of Pb^{2+} among the three sorbents investigated.
- ΔG values are negative for CDSP, CDAC and CDAC-Ca-beads. This emphasizes the spontaneity of the sorption process and it is more in beads than the other two adsorbents from the viewpoint of the

magnitude of the values. The values indicate attracting forces are good enough to cross the potential barrier at the solid/ liquid interface.^{22,23}

Spent CDSP, CDAC and CDAC-Ca-beads Regeneration

Reuse of the spent sorbents after regeneration assumes importance from the viewpoint of cost-effectiveness. As CDSP is a mere raw plant stems powder and is abundantly available, we have not investigated the regeneration of CDSP. But the regeneration of CDAC and CDAC-Ca-beads were investigated by employing various eluting agents such as acids, bases and salts at different dilutions and various experimental conditions.

We observed that 0.1N HCl was effective. 5.0 g of spent CDAC or CDAC-Ca-beads were taken in a beaker and was treated with 50.0 ml of 0.1N HCl at room temperature. The adsorbents were filtered, washed with distilled water until the washings were neutral and oven-dried at 102°C. Thus regenerated CDAC and CDAC-Ca-beads were reused for extracting Pb²⁺ ions from water. The cycles of regeneration-cum-reuse were repeated. Figure-12 depicts the findings. It can be inferred from the Fig.-12 that CDAC can be regenerated and reused upto four cycles while CDAC-Ca-beads upto three cycles.

Fig.-12: Spent CDAC and CDAC-Ca-beads: Regeneration and Reuse

Table-1: Thermodynamic Parameters: for Pb²⁺ Adsorptivity of Adsorbents

Sorbent	ΔH (KJ/mole)	ΔS (J/mole)	ΔG (KJ/mole)			R^2
			303K	313K	323K	
CDSP	24.149	83.336	-1.1010	-1.9350	-2.7680	0.9960
CDAC	24.038	79.726	-0.11898	-0.9162	-1.7135	0.9994
CDAC-Ca-BEADS	60.749	213.770	-4.0224	-6.1601	-8.2978	0.9638

Applications

The new adsorbents developed in this investigation: CDSP, CDAC and CDAC-Ca-beads, were applied to treat real battery and lead plating industry sewage samples. The samples were treated with CDSP (pH: 5.0; sorbent dosage: 1.5g/l; Eq. time: 90 minutes), CDAC (pH: 6.0; sorbent dosage: 1.25 g/l; Eq. time: 60 minutes) and CDAC-Ca-beads (pH: 7.0; sorbent dosage: 1.0 g/l; Eq. time: 50 minutes) at room temperature, 303 K. In Table-2, the results are depicted.

The data in Table-2 indicates adsorptivities of the adsorbents for the removal of Pb²⁺ from samples is in the increasing order: CDSP (58.4 to 60.9%) < CDAC (62.7 to 65.7%) < CDAC-Ca-BEADS (81.9 to 85.3%). Hence, CDAC-Ca-beads is a highly effective adsorbent among the three sorbents developed in this work for the removal of Pb²⁺ from water.

Comparison

The sorbents developed in this work namely, CDSP, CDAC and CDAC-Ca-beads are compared with some of the important sorbents reported in the literature. Comparison concerning pH and Sorption capacity are presented in Table-3.

Table 2: Applications

Samples	Ci*	Adsorbent					
		CDSP		CDAC		CDAC-Ca-BEADS	
		Ce*	% Removal	Ce*	% Removal	Ce*	% Removal
Battery Industry Sewages							
1	5.5	2.2	60.0	2.0	63.6	0.85	84.5
2	7.5	3.1	58.7	2.8	62.7	1.1	85.3
3	9.0	3.7	58.9	3.3	63.3	1.4	84.4
Lead- Plating Industry Sewages							
1	8.5	3.5	58.8	3.0	64.7	1.3	84.7
2	10.5	4.1	60.9	3.6	65.7	1.9	81.9
3	12.5	5.2	58.4	4.5	64.0	2.2	82.4

*Ci = initial Pb²⁺ concentration; Ce = Equilibrium conc. of Pb²⁺

* mean value of five determinations; SD: ± 0.39

Table-3: Comparison of Present Work with Previous Works

S. No.	Adsorbent	pH	Sorption Capacity, mg/g	Reference
1	Pine cone- activated carbon	6.7	27.53	7
2	Fluted pumpkin seed shell- active carbon	7	14.286	8
3	Coconut shell-carbon	6.0	30.0	9
4	Maize Tassel based -Activated carbon	5.4	37.31	10
5	Acid activated clay	6	9.08	16
6	Caryotaurens seeds active carbon	7	42.9	22
	Ca-alginate beads impregnated with Caryotaurens seeds-active carbon.	7	89.6	22
7	Hydrazine sulphate-Activated red mud impregnated in Ca-alginate beads	6.0	13.8	23
8	Waste tire rubber ash	6	22.35	38
9	CDSP	5	10.4	Present work
	CDAC	6	16.8	
	CDAC-Ca-beads	7(substantial removal in pH range : 4 to 9	25.6	

It may be informed from the Table that CDSP, CDAC and CDAC-Ca-alginate beads have comparable good sorption capacities than many reported in the literature. Especially, CDAC-Ca-beads have shown good sorption capacity than CDSP and CDAC. The beads have shown substantial sorption in a wide range of pH 3 to 9 with a maximum at pH: 7. This is an important finding as the said adsorbent is effective in slightly acidic, neutral and slightly basic solutions of Pb²⁺. This wide applicability is desirable in treating waste waters from industries.

CONCLUSION

- Three adsorbents are developed from the plant materials of *Cedrusdeodara* plant. Raw fine *Cedrusdeodara* Stem Powder (CDSP) and H₂SO₄-generated active carbon from *Cedrusdeodara* stem powders (CDAC) are prepared. Further, CDAC-doped Ca-alginate beads (CDAC-Ca-beads), are synthesized by cross-linking Na-alginate with Ca²⁺. These materials are investigated as adsorbents for their ability in removing Pb²⁺ from water.
- Various extraction conditions viz., initial pH of Pb²⁺ solutions, sorbent concentration, equilibration time, temperature, Pb²⁺-initial concentration and effect of co-ions have been investigated and optimized for the maximum adsorptivities.

- The sorption capacities are: 10.4 mg/g for CDSP; 16.8 mg/g for CDAC; and 25.6 mg/g for CDAC-Ca-beads. The cumulative sorption of active carbon assisted by Ca-alginate beads, result in higher adsorptivity for CDAC-Ca-beads.
- Optimum extraction conditions are: pH: 5.0, sorbent conc.: 1.50g/l, eq. time: 90 min. for CDSP; pH: 6.0, sorbent conc.: 1.25g/l; eq. time: 60 min for CDAC; and pH: 7.0, sorbent conc.: 1.0 g/l, and eq. time: 60 min for CDAC-Ca-beads.
- The beads show good Pb^{2+} - adsorptivity in a wide range of pHs: 3.0 to 9.0. This is a marked property as the beads can be used in the treatment of wastewaters having varied pHs. This feature paves its applicability to industrial effluents.
- Four-fold excess of co-ions has marginally affected the % removal of Pb^{2+} ions from water.
- Thermodynamics parameters indicate that the sorption is endothermic, spontaneous and the nature of adsorption is more chemical than physical or electrostatic. Positive ΔH values reflect the endothermic nature of the three sorbents. Values >24.0 KJ/mole for CDSP and CDAC and 60.75 KJ/mole for CDAC-Ca-beads, reflect the chemical nature of binding between functional groups -OH, -COOH of sorbents and Pb^{2+} ions. This chemical nature is clear especially in the case of beads as the relation curve between pH and % removal shows a huge hump in the pH range: 3 to 9. ΔH values are in the order: CDSP < CDAC < CDAC-Ca-BEADS and so is the increasing order of complexing tendency of Pb^{2+} .
- Positive ΔS values for all the sorbents show disorder at the solid-liquid interface.^{24,25} The high value of the order of 213.77 J/mole for CDAC-Ca-beads, indicate greater disorder and so, an ideal condition for Pb^{2+} ions to cross the solid/liquid surface barrier and hence more adsorptivities.
- Negative ΔG values reflects the spontaneity of the sorption process for all the investigating sorbents.
- Spent CDAC can be regenerated and reused upto four cycles while CDAC-Ca-beads upto three cycles with marginal loss of adsorptivities.
- Adsorbents developed in this work are successfully applied and the beads-based sorbent (CDAC-Ca-beads) is very effective in removing Pb^{2+} from industrial effluents.

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[RJC-5977/2020]