

Removal of heavy-metal ion by adsorption on chitosan gel beads

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The adsorption of heavy metal ions Co^{2+} , Pb^{2+} , and Cd^{2+} into the Cross-linking chitosan gel beads has been investigated. Batch experiments were carried out as a function of pH, agitation period, and concentration of heavy metal ions. It was shown that the adsorption of Co^{2+} , Pb^{2+} and Cd^{2+} ions occurred only at the optimum pH. Kinetic studies showed that the optimum agitation periods for adsorption of Pb^{2+} , Cd^{2+} and Co^{2+} ions were about 20 min, 30 min and 40 min, respectively. Langmuir and Freundlich equations were used for analysing the experimental data, which showed a better fit to the Langmuir model. Equilibrium parameters of adsorption were determined for both models. Maximum adsorption capacities for Cobalt, Cadmium and Lead were 73.98, 68.52 and 78.67 ($\text{mg}\cdot\text{g}^{-1}$), respectively. The high amounts of adsorbed heavy metal ions demonstrates the great efficiency of cross-linked chitosan gel beads which can be considered as an alternative material for the removal of metal ions from polluted water.

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1. Introduction

Most heavy metals are well-known toxic and carcinogenic agents and, when discharged in wastewater, represent a serious threat to human populations and the fauna and flora of receiving water bodies. Currently, many industries use heavy metals in the processing of raw materials, and consequently, the discharge of these metals into aquatic bodies and sources of drinking water has begun to be strictly controlled.

The wastes of the textile, electroplating industries and accumulator electrocute are heavy metals-rich in Cobalt, Cadmium, Lead forms of the metal. However, the reduction of chromium (VI) to chromium (III) within cells and the binding of the metal to proteins and nucleic acids increases the toxic potential of both forms. Sorption technology, including physical and chemical and ion-exchange process technologies have the potential to treat waters and industrial residues. In the adsorption process, atoms or ions (adsorbent's) contained in a fluid phase diffuse to the surface of a solid (adsorbent), where they are chemically bound to the surface or held there by intermolecular forces. The search for cheap and efficient unconventional adsorbents to remove heavy metal ions has been the subject of many investigations [1-6].

The adsorbent used in the present experimental procedure is chitosan. It was obtained by the desacetylation of chitin, a natural carbohydrate biopolymer extracted from the shells of arthropods such as shrimps,

lobsters, and crabs. Chitosan can be obtained from them very cheaply and with the advantage of being harmless to human beings. Chitosan has many useful characteristics such as hydrophilicity, biocompatibility, biodegradability, and anti-bacterial properties. It is also a known sorbent for heavy metal ions because the amino ($-\text{NH}_2$) and/or hydroxyl ($-\text{OH}$) groups on chitosan chains serve as coordination sites. The isotherms were usually force-fitted to the common two-parameter Langmuir and Freundlich equation although such equation was generally valid only over a very restricted concentration range [7-20].

The objectives of this study are to develop a procedure for adsorbing the gel beads onto chitosan and to evaluate the adsorption of Cobalt, Cadmium, and Lead using batch experiments. Desorption studies have also been carried out.

2. Materiel and methods

The heavy metal concentration in the aqueous samples was analyzed by flame atomic absorption spectroscopy (AAS), using a Varian Spectre AA-475 spectrometer in an air-acetylene flame. Where required, the pH was adjusted by 1N HCl or 1N NaOH and analysed by ELTECH (5000) pH-meter.

For determining the adsorbent (BGC), the degree of desacetylation chitosan used is $85\% \pm 5$. Chitosan flakes in an amount of 3.5 g were dissolved in 200 cm^3 of 1vol% acetic acid. The solution was agitated at 25°C, for 2h. The

solution was allowed to stand for one week, until the viscosity was within 300-450 Cp. The resulting solution was then sprayed through a thin nozzle into 1 dm³ of glutaraldehyde solution 25%. The spherical chitosan gel beads formed were allowed to stand in solution for 2h at 24°C. After filtration, the beads were washed with deionised water [9].

Such chemical modification of linear chitosan chains can render the beads insoluble in acidic media and improve mechanical strength and resistance to chemical degradation. This will decrease chitosan crystalline, increase porosity, and improve superficial area of the beads. It also improves diffusion properties and accessibility to internal sites [10]. The beads diameter was about 2 mm. The porosity and pore volume of the beads were measured to be 0.6-0.7 and 0.06 cm³.g⁻¹, respectively, using a mercury porosimeter (Micrometric Autopore II 9200).

3. Heavy metal synthetic solution

Cobalt, Cadmium, and Lead solutions were prepared in distilled water with the salts CoSO₄.5H₂O, CdSO₄.H₂O and PbSO₄.H₂O. The solution concentrations and pH were adjusted according to each experiment. Standard solutions were prepared in distilled water using cobalt sulfate (1000 mg.L⁻¹), cadmium sulfate (1000 mg.L⁻¹), and Lead Sulfate (1000 mg.L⁻¹).

4. Batch sorption uptake experiment

Adsorption isotherms relate the concentration of metal retained in the sorbent phase (q_e , mg.g⁻¹) to the adsorbate concentration in the fluid phase at equilibrium (C_e , mg.l⁻¹). They were obtained by adding variable amounts of sorbent to 25 mL of 1 g.L⁻¹ Cobalt, Cadmium, or Lead synthetic solution (pH= 5) in 250 mL Erlenmeyer flasks. Experiments showed that equilibrium was reached after a contact time of 1h. The solutions were mixed by a thermostatic shaker at constant temperature (25°C), and the samples were withdrawn and filtered through a membrane filter (0.45 μm, Millipore). The quantity of adsorbed Cobalt, Cadmium, and Lead on BGC was calculated as the difference between the initial and final equilibrium concentrations (eq.1), where C_i and C_e are the initial and final (equilibrium) concentrations, respectively, of the metal ion in solution (mg.L⁻¹); q_e is the metal concentration retained in the adsorbent phase (mg.g⁻¹); V is the solution volume (mL); and W is the mass of adsorbent (g).

$$q_e = V(C_i - C_e) / W. \quad (1)$$

An analysis of the relationship between BGC adsorption capacity and metal ion concentration was performed using the equations of Freundlich and Langmuir.

The tests were performed to obtain information about the effects of concentration, pH, and the presence of other metal ions in the Cobalt, Cadmium, and Lead synthetic solutions [21, 22].

5. Batch desorption experiments

A study of metal loading was carried out in a series of 50 mL flasks, each one containing 2g of BGC and 30 mL of Cobalt, Cadmium, and Lead synthetic solution (1 g.L⁻¹). The mixture, whose pH was adjusted to 5, was allowed to remain in contact with the adsorbent for 24 h. The mixture was then filtered, and the filtrate was analysed to determine the Cobalt, Cadmium, and Lead concentration. The loaded cross-linked Gel beads chitosan was transferred to another flask and treated for 48 h with 10 mL of different types of eluants : NaCl (10%), EDTA (0.25 M), NaOH (1N), H₂SO₄ (1N), HNO₃ (1N) and HCl (5M).

6. Results and discussion

6.1. Treatment efficiency

To evaluate the capacity of BGC in removing Cobalt, Cadmium, and Lead from synthetic aqueous solution, batch experiments were performed with untreated and cross-linking treated adsorbents. From the results shown in table 1, it can be seen that the cross-linking changes the solid surface and enhances by at least 10 % compared with that of the samples without treatment. Then, the beads treated were insoluble in acidic media and improve mechanical strength and resistance to chemical degradation.

Table 1. Equilibrium concentration of heavy metal ions on untreated and glutaraldehyde - treated - adsorbents ($C_i=125$ mg.L⁻¹; pH=5; T=25 °C).

Metal	M ⁽²⁺⁾ _{eq} (mg.L ⁻¹)		[M ⁽²⁺⁾ _{eq}]/[M ⁽²⁺⁾ _{added}] (%)	
	Untreated	treated	untreated	treated
Co ²⁺	40.93	36.29	67.26	70.97
Cd ²⁺	31.8	27.72	74.56	77.82
Pb ²⁺	47.08	40.18	62.34	67.86

Then, the mixture was filtered, and the filtrate was analysed to obtain the Cobalt, Cadmium, and Lead concentration (1g.L⁻¹). The loaded cross-linked Gel beads chitosan was transferred to another flask and treated for 48h with 10 mL of different types of eluents.

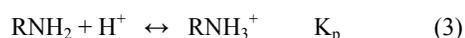
6.2. Effect of pH on Cobalt removal

The pH of the aqueous solution is an important controlling parameter in the heavy metal adsorption process, so the role of the hydrogen ion concentration was examined in batch experiments (Figure 1). The pH was varied over a range of 2-6, (2; 3; 5 and 6). The synthetic solution volume (200mL) and initial concentration (125mg.L⁻¹) were maintained constant. As it can be seen, the best results of adsorption capacity were obtained at pH

5. Cobalt begins to precipitate when the solution enters into contact with the adsorbent at pH values higher than 6. The present result indicates that the gel beads chitosan used are very suitable for this purpose. It is known that the uptake of transition metals is mainly occurred via coordination with the amine groups (NH_3) [11, 12]. Two OH groups and one NH_2 groups are fixed by $[\text{Co}^{2+}, \text{Cd}^{2+}, \text{Pb}^{2+}]$, and the fourth site is probably occupied by a water molecule or the OH group is on the third carbon atom. Hence, we have:



It is known that the amino groups of chitosan may react with H^+ according to



Because the protonation ($\log K_p$) equals 6.3 [13], on the average, more than 20% and 90% of the amino groups of chitosan are protonated even at pH 6 and 5, respectively. The two reactions of equations 2 and 3 compete during adsorption, which is supported from experiments that the solution pH more or less increases after adsorption.

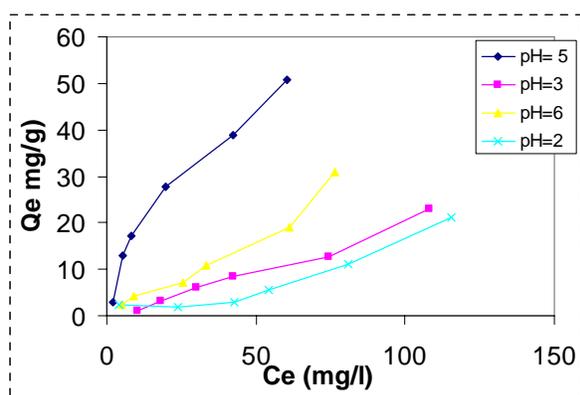


Fig.1. Effect of equilibrium pH on amount of single Co^{2+} adsorption at different initial concentrations.

6.3. Effect of agitation period

Fig. 2 shows the effect of agitation period on the adsorption of Co^{2+} , Cd^{2+} , and Pb^{2+} by chitosan beads. The percentage adsorption increases with agitation period and attains equilibrium at about 20 min for Pb^{2+} , 30 min for Cd^{2+} , and 40 min for Co^{2+} for an initial Pb^{2+} , Cd^{2+} , Co^{2+} concentrations singulars of 125 mg.L^{-1} . It shows that the adsorption of Co^{2+} , Pb^{2+} , and Cd^{2+} remained constant, implying equilibrium has been reached. Therefore, the optimum agitation periods for adsorption of Pb^{2+} , Cd^{2+} , and Co^{2+} were about 20 min, 30 min, and 40 min, respectively.

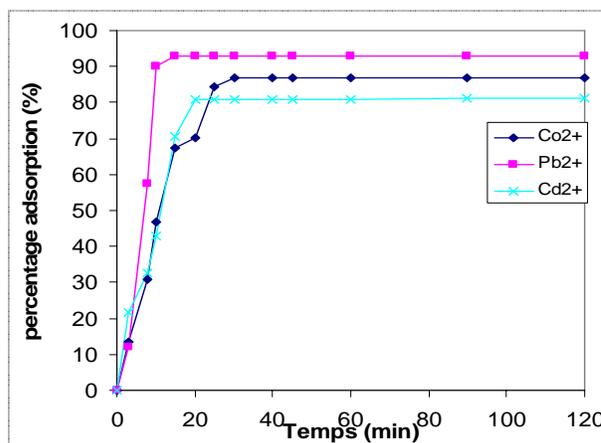


Fig. 2. Effect of agitation period on the adsorption of Co^{2+} , Cd^{2+} , and Pb^{2+} on chitosan beads.

6.4. Isotherms studies

The adsorptive capacity of BGC cross-linking bed for Cobalt, Cadmium, and Lead removal was determined through adsorption isotherm studies. Figure 3, shows the relationship between the quantities of heavy metal adsorbed per unit mass of BGC and the equilibrium concentration at 25°C . All of the isotherms showed similar behaviour, and the BGC adsorptive capacity increased as the metal concentration in the solution increased. This result shows that the BGC bed has a good adsorption capacity and that its efficiency increases as the synthetic solution concentration increases.

The BET equation is unsuitable to describe such isotherms due to chemical nature of adsorption on chitosan. The stepped rise of q_e at high C_e was also found in Cd^{2+} adsorption on glutaraldehyde cross-linked chitosan beads, which is explained by the pore-blockage mechanism. SEM-EDS photographs revealed that the sites of Cd^{2+} adsorption inwardly penetrate within the chemically modified chitosan beads to a large extent with increasing Cd^{2+} concentration [14].

The Langmuir and Freundlich models were used to determine the adsorption capacity of Cobalt, Cadmium, and Lead on BGC. From the correlation coefficients values (R^2) obtained for the two models, it can be seen that the Cobalt, Cadmium, and Lead adsorptive behaviour on BGC is better described by the Langmuir models (Fig. 3).

The Langmuir value of q_s was calculated from the slope of each isotherm, and K_L was calculated from the ordinate at the origin of each isotherm straight line. The results are show in Table 2.

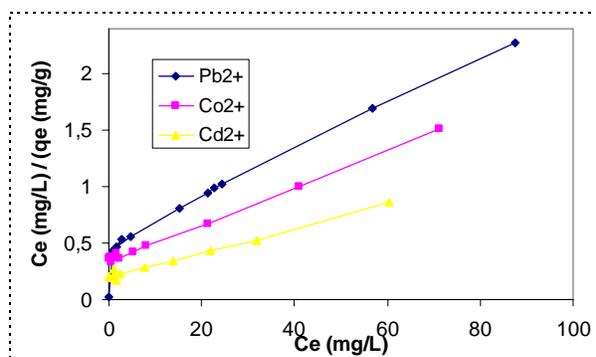


Fig. 3. Langmuir isotherms for the Co^{2+} , Cd^{2+} , and Pb^{2+} synthetic solution/BGC system at 25°C , $\text{pH}=5$.

Table 2. Adsorption parameters and correlation coefficients values for the Freundlich and Langmuir models.

	Freundlich			Langmuir		
	1/n	K_F	R^2	$q_s(\text{mg}\cdot\text{g}^{-1})$	K_L	R^2
Co^{2+}	0.81	9.15	0.89	73.98	0.36	0.98
Cd^{2+}	0.42	35.5	0.77	68.52	0.24	0.99
Pb^{2+}	0.89	5.57	0.89	78.67	0.42	0.99

6.5. Desorption studies

With the purpose of reusing the Cobalt, Cadmium, and Lead and/or the adsorbent, desorption tests were performed. The heavy metal ions adsorbed in batch experiments were eluted using several solutions in a solid-liquid ratio of $0.1\text{g}\cdot\text{mL}^{-1}$ (Table 3). The mineral acids proved to be effective eluents. This result was expected because adsorption process present electrostatic interactions between the surfactant molecule (RCOO^-) and the heavy metal and, when the acidic solution makes contact with the loaded adsorbent during the elution process, the H^+ ion has more affinity with the surfactant molecule so the Cobalt, Cadmium, and Lead molecules is released. Because the mineral acids dissolve the adsorbent almost completely, however, its reutilisation becomes difficult.

Table 3. Desorption of heavy metal using several eluents.

Aqueous eluents	% Cd^{2+} eluted	% Co^{2+} eluted	% Pb^{2+} eluted
NaCl (10%)	0.29	7.15	0.9
EDTA (0.25M)	10.22	5.24	2.32
NaOH (1N)	22.42	13.02	27.28
H_2SO_4 (1N)	97.47	85.10	98.65
HNO_3 (1N)	70.04	92.77	90.13
HCl (5M)	71.54	87.75	79.98

6.6. Retention of heavy metal ions in mixture by BGC

The BGC cross-linking bed capacity for retaining heavy metals was evidenced though batch experiments

using 1L of a synthetic solution of Cobalt, Cadmium, and Lead, chromium, nickel and zinc ($C=125\text{mg}\cdot\text{L}^{-1}$) for each ionic species, $\text{pH}=5$). Through an analysis of the breakthrough curves obtained for each metal, it can be seen that the largest capacity ($85\text{mg}\cdot\text{g}^{-1}$) was obtained in the case of zinc (Table 4). These results will make possible a study of the selective separation of these metals.

Table 4. Retention of heavy Metal ions in mixture by BGC.

Elements	Pb^{2+}	Cr^{3+}	Cd^{2+}	Ni^{2+}	Co^{2+}	Zn^{2+}
$Q_e(\text{mg}/\text{g})$	79	43	68	41	73	85

7. Conclusion

This work allowed us to conclude that cross-linked chitosan beads (BGC) is an efficient for the removal of heavy metals ions and its adsorption capacities increases as the metal concentration in the solution increases. It was observed in the batch experiments that the largest metal ions adsorption capacities were obtained with $\text{pH}=5$. The Cobalt, Cadmium, and Lead adsorptive behaviour on BGC is better described by the Langmuir model ($R^2 > 0.99$) than the Freundlich model. The maximum capacities determined through batch experiments in the case of Cobalt, Cadmium, and Lead are 73.98 ; 68.52 and $78.67\text{mg}\cdot\text{g}^{-1}$ respectively. Tests accomplished with a solution containing a mixture of heavy metals allowed us to conclude that BGC adsorbs zinc best, followed by chromium, Cobalt, Cadmium, Lead and Nickel.

The aqueous mineral acids proved to be effective eluents.

Nomenclature

- b = Adsorption equilibrium constant or constant related to the energy of adsorption ($\text{mL}\cdot\text{g}^{-1}$)
- C_o = Initial concentration of M^{2+} ($\text{mg}\cdot\text{L}^{-1}$)
- C_e = Equilibrium of final concentration of M^{2+} ($\text{mg}\cdot\text{L}^{-1}$)
- Q_e = Amount of M^{2+} adsorbed per unit weight at equilibrium ($\text{mg}\cdot\text{L}^{-1}$)
- R = Correlation coefficient
- t = Time taken for adsorption (min)
- v = Volume of M^{2+} solution (g)
- W = Weight of chitosan (g)
- (*) BGC: Beads Gel of Chitosan

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