

Regeneration of Calcium Alginate and Chitosan Coated Calcium Alginate Sorbents to be Reused for Lead (II) Removal from Aqueous Solutions

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The application of biopolymer-based sorbents in solving some environmental problems such as the removal and recovery of heavy metals from natural polluted water and wastewater has received lately a lot of attention due to their unique characteristics. The fundamental properties that recommend the usage of biopolymers-based sorbents for environmental remediation are: high selectivity and sorption capacity, renewability, safe manipulation, sorption capacity increase through simple physical and chemical methods, easy separation from treated water, and easy regeneration and reuse for repetitive sorption-desorption cycles. Accordingly, this research study has as purpose to present the results related to the usage of two types of alginate sorbents (calcium alginate and chitosan coated calcium alginate) in four repetitive lead(II) ions sorption-desorption cycles and to examine the influence of desorption agents on structural sorbent's characteristics. The results obtained showed that both calcium alginate and chitosan coated calcium alginate are good stable sorbents to be used in lead(II) ions sorption-desorption cycles.

Keywords: lead removal, desorption, regeneration, reusability, alginate-based sorbents

Lead is known as one of the most dangerous heavy metals for environment and human life. The main effluents loaded with lead ions come from electroplating baths, acid mine drainage, metal processing industry, organic and inorganic chemical industry, energy industry, battery manufacturing [1-3]. Due to the high volume of wastewaters that result from industry and municipal activities, corroborated with their negative impact upon the environment and human health, the authorities imposed strict limitations regarding wastewater that can be discharged safely into environment. Thus, there is a growing interest related to lead removal from wastewaters. Many traditional methods such as chemical precipitation [4], ion exchange [5], coagulation-flocculation [6], solvent extraction [7], electrocoagulation [8], electrodialysis [9], adsorption [10] have been studied for lead removal from natural polluted water and wastewaters. Results of these studies showed that each of these methods has both advantages and disadvantages. Therefore, unconventional heavy metals removal methods have been developed to overcome the drawbacks of traditional methods. From these, sorption on natural polymers has been extensively studied recently [11-14], due to its numerous advantages, like: high efficiency, low cost, removal of heavy metals even at low concentration in wastewater, ease of regeneration, environmental friendliness, and possibility of heavy metals recovery [11, 12].

In a previous paper, we reported on the capacity of calcium alginate (CA) and chitosan coated calcium alginate (CCCA) to remove lead ions from wastewater [10]. We extended our previous research to investigate the desorption process and, thus, the reusability of CA and CCCA in several adsorption-desorption cycles. The present paper reports on the experimental conditions for regeneration of CA and CCCA, their structural modifications

during the process and the performance decay as the number of cycles increases, because of these changes.

Experimental part

Materials and testing equipments

The CA and CCCA used in the regeneration tests have been previously characterized [10]. Lead nitrate (Merck, Germany) has been used to prepare a 1000 mg Pb(II)/L stock solution. This stock solution was diluted to 107 mg Pb(II)/L solution. Hydrochloric acid (HCl) (0.01-0.5%), and nitric acid (HNO₃) (0.01-3%) have been prepared from HCl 30% Suprapur[®] and HNO₃ 65% Suprapur[®] Sigma-Aldrich and they were used without further purification.

Lead(II) ions concentration in the initial solutions and in solutions after the sorption/desorption experiments has been determined by atomic absorption spectrometry, using an AAS 1N Carl Zeiss Jena Atomic Adsorption Spectrophotometer. The two phases (solid - CA and CCCA, and liquid - lead(II) ions synthetic solutions/desorbing agent solution) were put in contact in a GFL Shaker 3015 at 150 rpm.

The FT-IR spectra of both fresh and regenerated CA, CCCA were recorded on a FT-IR 620 Spectrometer (Jasco, Japan) in the 400-4000 cm⁻¹ range using potassium bromide pellets.

Sorption/desorption experiment

Sorption/desorption batch experiments were carried out at room temperature in duplicate to determine the possibility of reusability of sorbents tested. Experiments were performed using 107 mg Pb(II)/L solution. 0.05 g of CA and CCCA loaded with lead(II) ions were contacted with 50 mL of two types of desorbing agents for 24 h.

The effect of the types and concentration of desorbing agent on the desorption amount was determined using

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HCl solutions of 0.01; 0.05; 0.1; 0.2; 0.3% (weight) concentration and HNO₃ solutions of 0.01; 0.05; 0.1; 0.2; 0.3; 1; 2; 3% (weight) concentration. A higher number of concentrations of HNO₃ has been used, since the published data advocate that HNO₃ is a more suitable desorbing agent than HCl. Sulfuric acid was disregarded due to the formation of insoluble lead(II) sulfate, which precipitates onto the surface of the sorbent thus blocking its active sites.

The amount of lead(II) ions adsorbed by CA and CCCA particles (mg/g) was calculated using eq. (1):

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

where Q represents lead(II) ions uptake (mg/g), C_i is the concentration of lead ions in the initial solution (mg/L), C_e is the concentration of lead ions in the solution at equilibrium (mg/L), V - volume of the solution (L) and m - mass of CA/CCCA used (g).

Regeneration efficiency has been assessed using eq. (2):

$$\text{Efficiency (\%)} = \frac{m_{\text{des}}}{m_{\text{ads}}} \times 100 \quad (2)$$

where m_{des} represents the amount of Pb(II) desorbed (mg), while m_{ads} is the amount of Pb(II) adsorbed (mg) [15].

Results and discussions

Effect of types and concentration of desorbing agent on regeneration efficiency

The type and concentration of desorbing agent could influence both the regeneration efficiency and the physico-chemical characteristics of the adsorbent. According to literature, some of the reported desorbing agents are: proton exchangers such as acids, heavy metal chelator solutions as ethylenediamine-tetraacetic acid together with its sodium salt, and competing counter ions such as salt solutions [15]. The suitable desorbing agent choice depends on both the adsorbed heavy metal and the nature of adsorbent. In case of lead(II) ions adsorbed on CA or CCCA, the proper recommended desorbing agents are acid solutions. In the presence of Ca(II) complexants [16] or monovalent ions (excluding protons) [17], the alginate matrix is readily destabilized, and consequently, its reuse

will no more be possible. Therefore, HCl and HNO₃ solutions were chosen as lead(II) desorbing agents. Beside this, other issues recommended HCl and HNO₃ solutions as desorbing agents: the potential of these acids to dissolve lead, relatively low cost, ability to desorb heavy metals, well established properties.

The results of the regeneration experiments are presented in table 1 and table 2.

The results presented in tables 1 and 2 revealed that the most appropriate desorbing agent for lead(II) ions from CA and CCCA is the HNO₃ 0.5% solution. Therefore, this solution has been chosen for the determination of the kinetics of regeneration and for repetitive adsorption/desorption cycles.

Desorption kinetics

Desorption of lead(II) ions from CA and CCCA loaded with lead by HNO₃ 0.5% solution was studied in function of time in the range 0-420 min. The quantity of adsorbent loaded with lead used for desorption experiments is 0.025 g, and the desorbing agent volume used is 25 mL. The experiments were performed at room temperature in duplicate, and the results obtained are presented in figure 1.

It can be seen from figure 1 that the regeneration process can be divided in two phases. The first phase is faster, in the first 50-60 minute more than 75% from lead(II) ions being desorbed. The second phase is much slower due to the decrease of the mass transfer driving force. In fact, there are two dichotomic processes during regeneration: a) the replacement of lead(II) ions from the active sites by protons - desorption; b) adsorption of lead(II) ions to the free active sites, since the interactions between the protons and the active sites are reversible - back-adsorption. As the concentration of the lead(II) ions into the solution increases, the latter process becomes more important, thus diminishing the overall driving force. As the sorbent is stronger (CCCA has a higher capacity than CA), its regeneration becomes more problematic, the efficiency, for the same operating conditions, being lowered by the stronger back-adsorption. Therefore, the regeneration efficiency is higher for CA than CCCA, as seen in figure 1.

Table 1

THE EFFECT OF TYPE AND CONCENTRATION OF DESORBING AGENT ON REGENERATION EFFICIENCY OF CALCIUM ALGINATE

Desorbing agent	Pb(II) sorption capacity, mg/g	mg Pb(II) in 0.025 g CA	Pb(II) desorbed, mg/L	Pb(II) desorbed, mg	Efficiency, %
HNO ₃ 0.01%	100.4	2.51	4.68	0.12	4.66
HNO ₃ 0.05%			23.51	0.59	23.42
HNO ₃ 0.1%			43.01	1.08	42.84
HNO ₃ 0.2%			61.61	1.54	61.37
HNO ₃ 0.5%			99.40	2.49	99
HNO ₃ 1%			67.68	1.69	67.41
HNO ₃ 2%			59.81	1.50	59.97
HNO ₃ 3%			63.89	1.60	63.64
HCl 0.01%			2.17	0.05	2.16
HCl 0.05%			32.37	0.81	32.24
HCl 0.1%			47.41	1.19	47.22
HCl 0.2%			57.34	1.43	57.11
HCl 0.5%			60.71	1.52	60.47

Table 2
THE EFFECT OF TYPE AND CONCENTRATION OF DESORBING AGENT ON REGENERATION EFFICIENCY OF CHITOSAN COATED CALCIUM ALGinate

Desorbing agent	Pb(II) sorption capacity, mg/g	mg Pb(II) in 0.025 g CCCA	Pb(II) desorbed, mg/L	Pb(II) desorbed, mg	Desorption, %
HNO ₃ 0.01%	106.9	2.6725	1.90	0.05	1.78
HNO ₃ 0.05%			6.55	0.16	6.13
HNO ₃ 0.1%			19.16	0.48	17.92
HNO ₃ 0.2%			27.20	0.68	25.44
HNO ₃ 0.5%			100.10	2.50	93.64
HNO ₃ 1%			56.96	1.42	53.28
HNO ₃ 2%			56.50	1.41	52.85
HNO ₃ 3%			61.30	1.53	57.34
HCl 0.01%			0.36	0.01	0.34
HCl 0.05%			11.59	0.29	10.84
HCl 0.1%			20.47	0.51	19.15
HCl 0.2%			29.87	0.75	27.94
HCl 0.5%			33.93	0.85	31.74

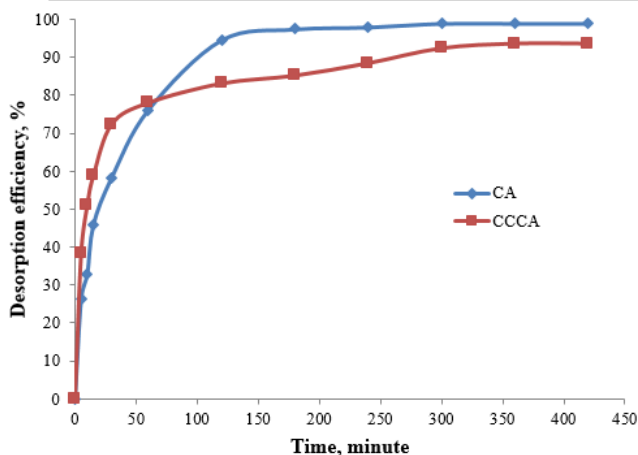


Fig. 1. Time profiles of the efficiency of regeneration of CA and CCCA sorbents loaded with Pb(II) using HNO₃ 0.5%

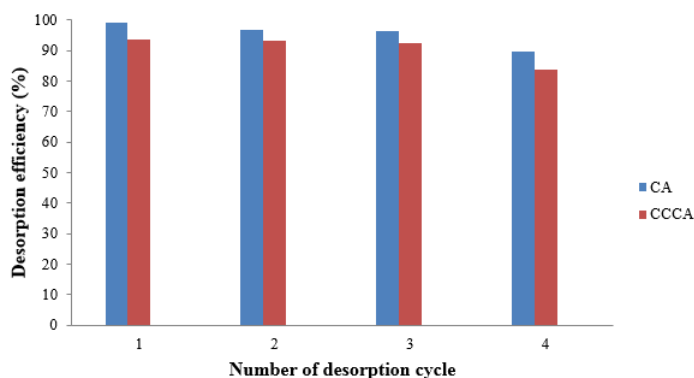


Fig. 3. Variation of regeneration efficiency of CA and CCCA with the number cycles (HNO₃ 0.5% as regeneration agent) solution

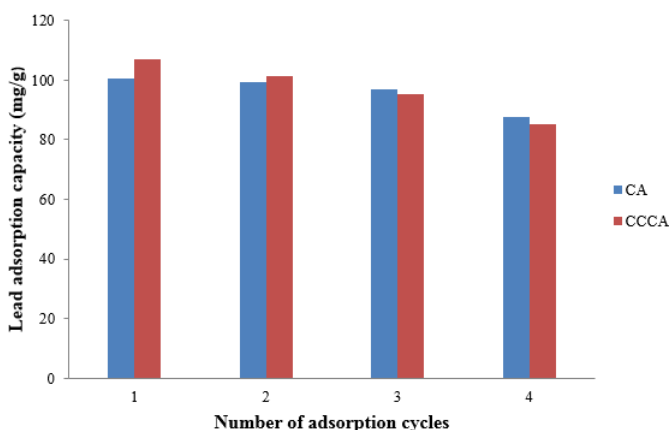


Fig. 2. Variation of adsorption capacity of CA and CCCA with the number of cycles (HNO₃ 0.5% as regeneration agent)

The process of regeneration lasts around 300 min, irrespective of sorbent, which is the same with the time needed for lead(II) ions removal from synthetic wastewaters [10].

Our findings are backed-up by Chiew et al. [15] (they observed that the desorption process is not faster than the

adsorption process) and Katsou et al. [18] (they reported that desorption is not slower than adsorption process).

Reusability studies

The ability of both adsorbents to participate in multiple sorption-desorption cycles was examined in four identical cycles. The results obtained are summarized in the figures 2 and 3.

Throughout four cycle, the adsorption capacity of CA decreased by 12.70%, while the adsorption capacity of CCCA decreased by 20.33% (as it can be seen from figure 2). At the same time, the regeneration efficiency of CA decreased by 9.60% compared to the regeneration efficiency of CCCA, that decreased by 10.70% (fig. 3). The highest decrease of both regeneration efficiency and adsorption capacity was observed after the second cycle. Quite remarkably, starting with the third cycle, the CCCA adsorption capacity drops under the CA capacity, probably due to some inherently structural changes in the former.

The experiments showed that, after four sorption-desorption cycles, the regeneration efficiency and the adsorption capacity became rather stable, indicating the structural stability of alginate and chitosan-based adsorbents, thus their potential to be used for many sorption-desorption cycles.

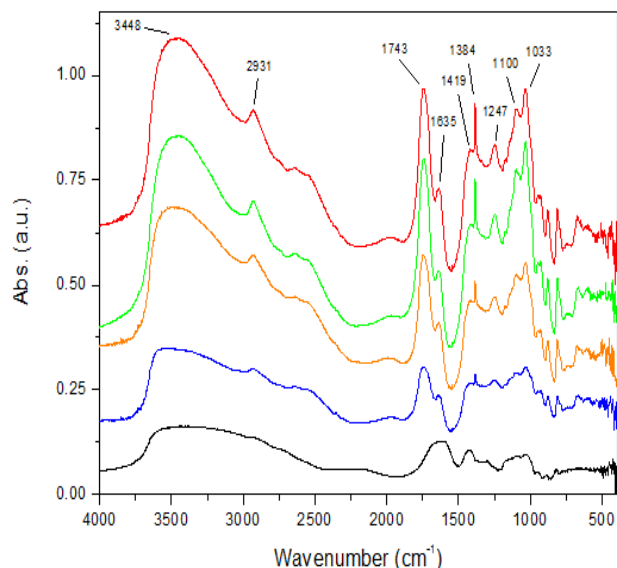


Fig. 4. FT-IR spectra of: CA (black line); CA after first regeneration (red line); CA after second regeneration (red line); CA after third regeneration (orange line); CA after fourth regeneration (green line); HNO₃ 0.5% as regeneration agent

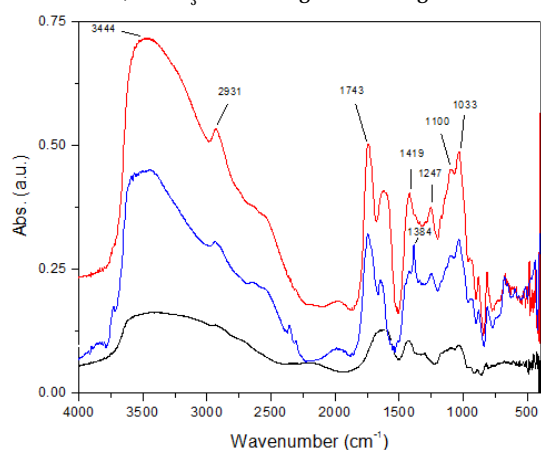


Fig. 5. FT-IR spectra of: CA (black line); CA after first regeneration using HNO₃ 0.5% (blue line); CA after first regeneration using HNO₃ 0.05% (red line)

Influence of regeneration agent concentration on the structure of adsorbent after several cycles

FT-IR spectra of adsorbents after several regeneration cycles were registered and presented in the figures 4 to 7.

Figures 4 to 7 show that the calcium-alginate matrix was changed to alginate acid after acid desorption. This observation has been demonstrated by the splitting of the absorption band at 1635 cm⁻¹ in two bands at 1635 and 1743 cm⁻¹ after lead desorption (fig. 4). This band is characteristic of the free carbonyl double bond (C=O) [15]. Another observation is the presence of a new band at 1384 cm⁻¹, characteristic to the NO₃⁻ group. Furthermore, the intensities of these two bands increased with the concentration of the acid used, which means that more ionic bonds were replaced by hydrogen bonds (fig. 5). In the case of CCCA, the band of free carbonyl double bond appears at 1616 cm⁻¹ and splits into two absorption bands at 1637 and 1647 cm⁻¹ (figs. 6 and 7).

The split of bands at 1635/1616 cm⁻¹ in two bands at 1635/1637 and 1743/1747 cm⁻¹ reflects the successful displacement of lead ions with protons from HNO₃. After regeneration with HNO₃, CA is partially converted into alginate acid which will further participate at the next sorption/regeneration cycles. There are no other changes in the FT-IR spectra of both adsorbents after the second cycle,

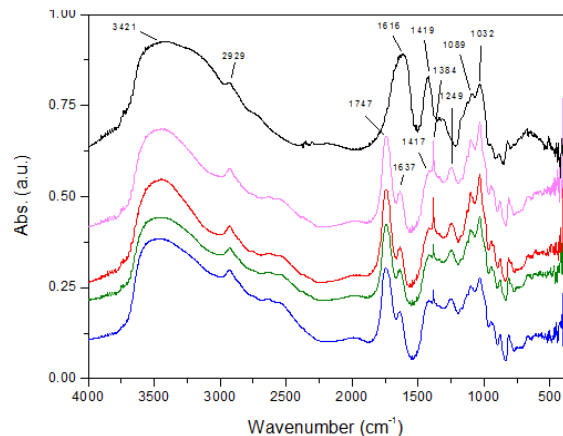


Fig. 6. FT-IR spectra of: CCCA (black line); CCCA after first regeneration (pink line); CCCA after second regeneration (blue line); CCCA after third regeneration (green line); CCCA after fourth regeneration (red line); HNO₃ 0.5% as regeneration agent

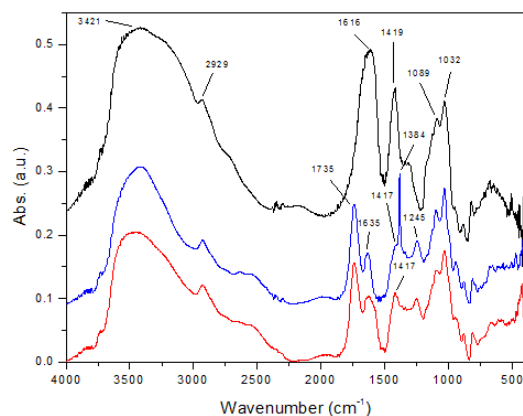


Fig. 7. FT-IR spectra of: CCCA (black line); CCCA after first regeneration using HNO₃ 0.5% (blue line); CCCA after first regeneration using HNO₃ 0.05% (red line)

witnessing that the structural properties of both adsorbents do not modify further.

Conclusions

The present research investigates the regeneration efficiency of CA and CCCA adsorbents to be used in multiple Pb(II) ions sorption from aqueous solutions cycles. Batch experiments were performed to determine both regeneration efficiency and the post-regeneration sorption capacity of both sorbents. HCl and HNO₃ at different concentrations were tested as regeneration agents. From the comparative study, HNO₃ 0.5% proved to be the most suitable regeneration agent. The regeneration kinetics studies revealed that both sorption and regeneration processes have almost the same rates. The asymptotic decrease of both adsorption capacity and regeneration efficiency, after four sorption-regeneration cycles proved that both adsorbents loose only about 10 to 14% of the original capacities. Therefore, they can be reused many cycles more without severe losses in adsorption capacity/regeneration efficiency. These is the result of preservation of the alginate/chitosan coated alginate beads structural integrity; nonetheless, care should be taken in considering the possible dissolution of alginate acid in the solution, marginal in the present study.

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