THE ADSORPTION OF HEAVY METAL IONS ON POROUS CALCIUM ALGINATE MICROPARTICLES

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abstract: Microparticles from nontoxic biopolymer were prepared in order to investigate the adsorption process of heavy metals in polymeric porous beads. The aim of the study is a new method to remove bivalent ions (Pb^{2+}; Cd^{2+}) from synthetic wastewater using calcium alginate microparticles. The alginate (a natural polymer obtained from marine algae) was tested as adsorbent material, due to its good affinity for the bivalent metal ions. The adsorption of the heavy metals was studied as a function of contact time between the alginate and the synthetic wastewater samples and the morphology of polymeric beads. The calcium alginate microparticles were prepared using a laboratory procedure, dropping aqueous solution of sodium alginate in a calcium chloride solution. The polymeric microparticles with controlled porosity appear to be a suitable alternative to develop a method for heavy metal removal from industrial wastewater.

Introduction

Environmental pollution by toxic metals arises from industrial, agricultural effluents and waste disposal from various sources. Many industries such as metal plating facilities, mining operations and tanneries discharge waste containing heavy metal ions [1].

As pollutants, heavy metals were intensively studied due to their significance from the point of view of persistence and toxicity. These toxic metals can cause accumulative poisoning, cancer and brain damage when found above the tolerance levels [2]. The agencies for the environmental monitoring have set permissible limits for heavy metals levels in drinking water because of their harmful effects. The removal and rapid decontamination of heavy metals (Cd, Pb, Cu, Hg) become very important for the environmental remediation. Many processes have been used for the removal of heavy metals from waste waters, such as chemical precipitation, coagulation, solvent extraction, membrane separation, ion exchange and adsorption [3].

For dilute metal concentrations, ion exchange, reverse osmosis and adsorption can be applied [4]. However, the common use of ion exchange and reverse osmosis is restricted by

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the high operating cost. As an alternative to chemical precipitation, membrane filtration, or ion exchange, adsorption processes with a wide variety adsorbents have been tested.

The adsorbents used should have some specific properties, such as a high ability to reduce the concentration of heavy metals below the acceptable limits, high adsorption capacity and long lifetime [5]. Thus, it is a continuing need to identify and develop low-cost and efficient adsorbents for facile and efficient removal process. Heavy metal adsorption was studied on various adsorbents such as activated carbon [6], fly ash [7], and bioadsorbents (adsorbents from plant- and animal-origin materials, for example bark/tannin-rich materials, humus, peat moss, modified cotton and wool, chitin, chitosan, seaweed, and biopolymers [8-10].

Alginate is a biopolymer with many applications in drug delivery systems, cell encapsulation, food industry, cosmetics. In wastewater treatment could play an important role in removal heavy metal ions due its advantages, such as facile obtaining procedure, biodegradability, biocompatibility, economical, environmental friendly.

Alginate is water-soluble linear polysaccharide extracted from brown seaweed and it's composed of alternating blocks of 1-4linked α-L-guluronic and β-D-mannuronic acid fragments.

The aim of this study was to investigate the influence of the preparation procedure on the performances of the Ca-alginate microparticles in the removal process of the heavy metal ions from the wastewater. A facile preparation of alginate beads is proposed, resulting in porous microparticles with increased efficiency in the up-take of Cd ions from very diluted water samples.

Experimental

Materials. Sodium alginate was supplied from Sigma, as well as calcium chloride and sodium bicarbonate. All other reagents were of analytical grade (Merck). The stock solutions of reactants were used and the diluted solutions were freshly prepared daily. The synthetic waste water were prepared by dissolving $Cd(NO)_3x4H_2O$ and $Pb(CH_3COOH)_2x3H_2O$ in deionized water.

Preparation of Ca-alginate beads by dripping technique. The homogeneous sodium alginate solution (2%) was dropped into calcium chloride solution (4%) to form hydrogel beads. Then, gas-forming agent such as sodium bicarbonate was added to the alginate solution in ratio: 0:1, 1:1; 1:4 (gas-forming agent/alginate, w/w). For the beads containing gas-forming agent, the solution for the crosslinking of the polymeric beads was a calcium chloride (1%)- acetic acid (10%) aqueous solution. The acetic acid is required to ensure the decomposition of sodium bicarbonate salt and to produce carbon dioxide. With this procedure particles with various structures and porosity were obtain, according to the content of gas-forming agent and other parameters of preparation. The dimension of the microparticles was checked by optical microscopy. The surface morphology of beads and the porosity was examined with an Environmental Scanning Electron Microscope (ESEM)-Quanta 200 FEI.

Adsorption of heavy metal. For the absorption studies, the alginate beads were immersed in 5 mL of heavy metal (Pb^{2+}; Cd^{2+}) solution of various concentrations, under moderate stirring conditions, at room temperature. The synthetic waste water samples used were aqueous solutions of $Pb(CH_3COO)_2x3H_2O$, $Cd(NO_3)_2x4H_2O$. For the kinetics experiments the alginate microparticles were filtered from samples after 10;20;40;60, 180 and 360 minutes. The samples were centrifuged for 15 min. at 12 000 r.p.m to remove any polymeric traces. Before the measurements of the metal concentrations from samples, the extraction procedure for the heavy metal ions was applied, using chloroform and dithisone as complexation reagent. In the presence of Pb(II) and Cd(II) a red, respective orange complex combination were formed. The pH of the sample was adjusted to 8-9 with ammonia aqueous solution, in order to ensure the selectivity of the reaction. The measurements were carried out with an UV-VIS spectrometer (Jasco) at suitable wavelength (λ=520 nm for lead, respectively λ=518 nm for cadmium). After the adsorption process, the lead and cadmium concentrations from solutions were read out from the standard curve. The profiles of the curves give the straight-line equation generated by linear regression: $y = 0.1242x + 0.0125$ for lead and $y = 0.1518x + 0.2461$ for cadmium with correlation coefficient $r^2 = 0.9869$, respective $r^2 = 0.9896$.

Results and discussion

Most heavy metal ions are toxic or carcinogenic and exhibit a threat to human health and the environment, even at very low concentrations.

The adsorption on biomaterials, as alginate, is considered a reliable, efficient and low-cost technique for metal removal from wastewater. The anionic biopolymer has the ability to bind multivalent cations, leading to the formation of insoluble hydrogels. Any multivalent cation can cause crosslinking of alginate, but the calcium ions react preferentially with the polyguluronic acid segments. The structure of the formed calcium alginate gel is known as "egg box model", in which the polyguluronic acid segments associate into aggregates with interstices (electronegative cavities) where the calcium ions fit.

Even if many data are reported on the removal of heavy metal ions (Cd2+, Hg2+, Pb2+) on alginate, a model of the adsorption of metal from the aqueous solutions on various polymeric matrix is not fully developed. It is presumed that the adsorption process is controlled by various steps, such as:

– metal ion transfer from the bulk solution to the boundary film covering the adsorbent surface (i),

– metal ion transport from the boundary film to the surface of the adsorbent, (external diffusion) (ii),

– transfer of the metal ion from the surface to the intraparticular active sites, (internal diffusion) (iii)

– metal ion uptake on the active sites of adsorbent (iv).

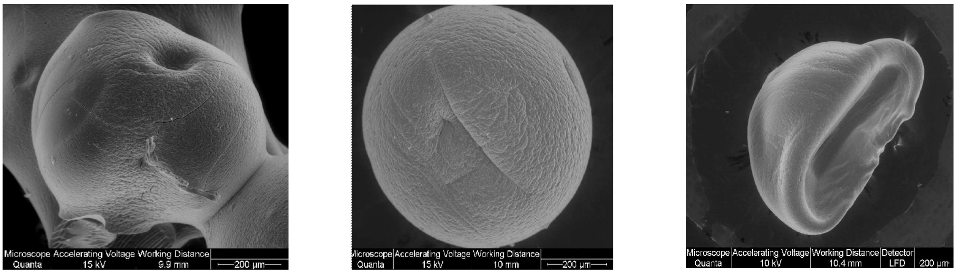
The last two processes are closely related to the composition and morphology of the polymeric matrix used in the removal procedure.

In the present study were prepared alginate beads with different morphologies by variation of the preparation conditions. The concentration of the crosslinking media and the alginate-sodium bicarbonate ratio were modified, in order to obtain beads with controllable porosity. The influence of the morphology of the alginate beads was investigated, related to efficiency of lead and cadmium adsorption on microparticles.

The variation of the concentration of $CaCl_2$ solution and time of the reaction leads to the formation of alginate microbeads with various degree of crosslinking. In this study, the most common procedure to prepare Ca-alginate beads was chosen, by using 2% CaCl2 aqueous solution and 12 hour as reaction time. The mentioned conditions leads to the formation of beads with moderate resistance, a rather compact structure, with random small pores and medium degree of crosslinking. A smaller $CaCl_2$ concentration and a shorter reaction time results in polymeric microparticles with nonhomegeneous structure: the inner part remain semifluid, consists in Na-alginate with a solid Ca-alginate shell at the surface.

Adding the gas-forming agent (Na bicarbonate) during the preparation of the polymeric beads, the dimension and the number of pores in the ca-alginate matrix are modified according to the content of the Na bicarbonate.

The ESEM images from Fig. 1 show the surface morphologies of the calcium alginate beads obtained at various polymer-gas forming agent ratio. Thus, the particles that contain only alginate (b) and alginate-gas forming 4:1 ratio present a compact morphology (a), while the beads with 1:1 ratio have tend to contract at high vacuum, due to the high porosity (c). These observations confirm the results of the porosity measurements performed by using BET technique, which indicate that the beads prepared with 1:1 polymer-gas forming agent ratio are much more porous than the ones obtained with low content of Na bicarbonate.

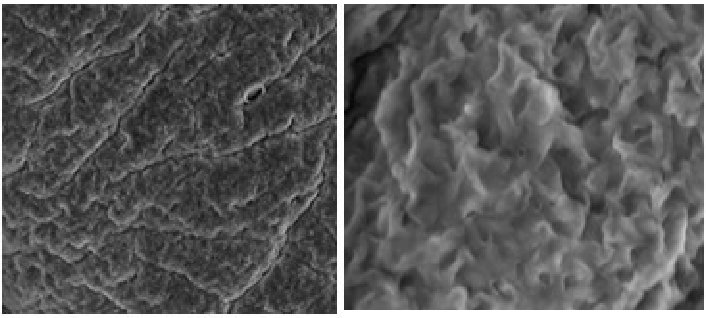


(a) (b) (c)

Fig. 1 *ESEM images of the alginate particles (the alginate-gas forming agent ratio:* a) 1:0, b) 4:1, c) 1:1).

Images in Fig. 2 show details on the surfaces of alginate microparticles, where it is possible to that beads without gas forming agent are rather smooth, while increase in alginate – sodium bicarbonate ratio leads to the formation of more roughness surfaces, even crevases.

The kinetics studies were performed both in dilute and concentrate samples of synthetic wastewater. The variation of the kinetic profile of the heavy metal adsorption on alginate beads, presented in Fig. 3, shows the kinetics of cadmium adsorption onto the algae. The plots represent the amount of metal adsorbed, q_t, versus time for an initial cadmium concentration of 250 mg/L.



(a) (b)

Fig. 2 *Surface details of the calcium alginate beads* (a) 1:0, (b) 1:1 *alginate –sodium bicarbonate ratio.*

The quantities of metal ions adsorbed per 1-mg polymer, on particles with different morphologies, presenting in previous ESEM images were compared.

For the concentration less than 3 mg/L Pb^{2+}, the maximum was reached into short period of time and the lead was adsorbed approximately 100% from metal quantity (Fig. 3). Similar results were obtained for Cd^{2+} adsorption efficiency at low concentration.

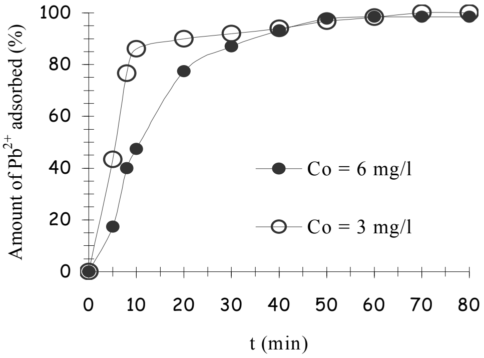
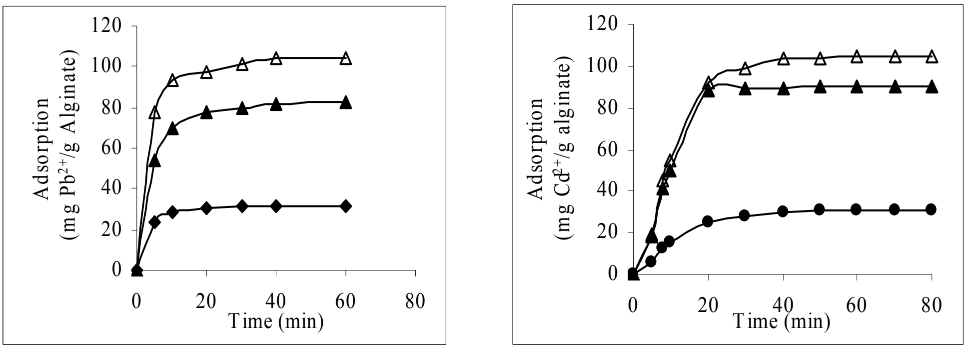


Fig. 3 *The influence of the heavy metal initial concentration on adsorption kinetics on polymeric particles.*

From the kinetic adsorption study a significantly increase of adsorption after 10 minutes for cadmium, respective 20 minutes for lead is observed, for both types of alginate beads.

The results of the kinetics of the adsorption process show that the microparticles with different content of a gas-forming agent (sodium bicarbonate) present a higher adsorption capacity of metal ions, which is explained by the increase in the contact surface between wastewater and polymeric material.

Increasing the ratio between the gas-forming agent and polymer particles with a much more porous aspect were obtained and the efficiency to up-take the heavy metal ions increase (Fig. 4).



(a) (b)

Fig. 4 *The influence of polymeric particle types on adsorption kinetics of lead* (a) *and cadmium ions* (b) *Alginate –sodium bicarbonate ratio* 1:0 (♦) 4:1 (▲) and 1:1 (Δ).

The kinetic of the up-take is related to the specificity of the interaction of heavy metal ions with the polymeric matrix. As it is shown in Fig. 4., adsorption maximum is reached much faster for cadmium ions, after 10 minutes and 30 minutes for lead ions.

In both cases, for lead and cadmium, the microspheres ensure a removal of 100% from initial quantities of metals for low initial concentrations, up to 10 mg/L. For higher initial concentration, the maximum removal capacity is 70% for lead and 82% for cadmium in the range of 200-300 mg/L (data not shown).

To investigate the adsorption capacity as a function of aqueous concentration of the heavy metals adsorption isotherms are widely employed for fitting the data, using the representation of the adsorption (expressed as mg metal adsorbed per g of solid adsorbent) versus concentration of the heavy metals at equilibrium c_{eq}. Adsorption isotherms for Cd^{2+} ions on different alginate beads are shown in Fig. 5.

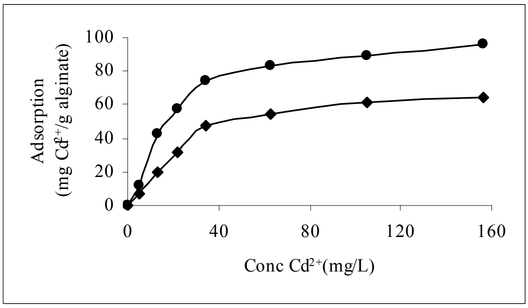


Fig. 5 *Adsorption isotherms for Cd^{2+} ions on different alginate beads: alginate-gas forming agent ratio 1:0 (•) and 1:1 (♦)*

The Langmuir and Freundlich equations are most widely used. The Langmuir model assumes that the adsorption of metal ions is a process occurring on a homogenous surface, without any interaction between adsorbed ions. The adsorption proceeds until a complete monolayer is formed. To get the equilibrium data, sample with different initial cadmium concentration and constant adsorbent mass in each sample were studied. The equilibrium concentration is measured at the final period for sorption experiments.

The Langmuir model equation is:

$$q = q_{\max} (K_L c_{eq} / (1+ K_L c_{eq}) \quad (1)$$

where q (mg/g) is the amount of heavy metal ions adsorbed onto the unit mass of the polymeric beads, KL is the Langmuir equilibrium constant which is related to the affinity of binding sites; Ceq the equilibrium metal ion concentration, and q_{max} is the maximum adsorption capacity (theoretical monolayer saturation capacity) [11]. The main characteristics of the Langmuir equation, constants KL and q_{max} can be determined from a linerized form of the Langmuir equation, as follows:

$$c_e/q_e = 1/q_{\max}K + c_e/q_{\max} \quad (2)$$

Therefore, a plot of c_e / q versus c_e, gives a straight line of slope $1 / q_{\max}$ and intercept $1/KL\ q_{\max}$.

The Freundlich model based on adsorption on a heterogeneous surface develop an empirical equation:

$$q_e = k\ c_e^{1/n} \quad (3)$$

where q_e is the adsorption (mg/g); c_e is the concentration of adsorbate in solution (mg/l); k and n – empirical constants, characteristics of the system, indicating the adsorption capacity and the adsorption intensity, respectively. The above equation can be linearized as the following form, also used to confirm the applicability of the model:

$$\ln q_e = \ln k + 1/n \ln c_e \quad (4)$$

The Langmuir and Freundlich equations were used to describe the isotherm data obtained for the adsorption of Cd^{2+} and Pb^{2+} ions by each type of alginate beads over the entire concentration range studied. The characteristics of Langmuir and Freundlich equations are shown in Tables 1 and 2.

The regression coefficients in Table 1 show that the experimental data reasonably well fitted the linearized equation of the Langmuir isotherm over the whole Cd^{2+} and Pb^{2+} concentration range studied.

Table 1. Parameters for the Langmuir adsorption isotherms for Cd^{2+} and Pb^{2+} on the alginate beads with various composition.

Heavy metal	Alginate-gas forming agent ratio in polymeric beads	q_{max} (mg/g)	K (l/mg)	Correlation coefficient r^2
Cd^{2+}	1:0	156	0.069	0.9966
Cd^{2+}	1:1	182	0.063	0.8977
Pb^{2+}	1:0	145	0.061	0.9917
Pb^{2+}	1:1	167	0.069	0.9103

Data in Table 2 show that the Freundlich isotherm was also representative for the both heavy metal adsorption by all types of tested adsorbent. However, Langmuir isotherm could be considered as a better fitting model than Freundlich for Ca-alginate beads without gas forming agent, indicating the applicability of a monolayer coverage of the metal ions on the surface of polymeric beads. The maximum adsorption capacity is higher for the alginate beads with gas-forming agent for both metal ions.

Table 2. Parameters for the Freundlich adsorption isotherms for Cd^{2+} and Pb^{2+} on the alginate beads with various composition.

Heavy metal	Alginate-gas forming agent ratio in polymeric beads	*k* (l/g)	*n*	Correlation coefficient r^2
Cd^{2+}	1:0	3.69	1,55	0.9896
Cd^{2+}	1:1	8.07	2.97	0.9921
Pb^{2+}	1:0	2.84	1.77	0.9887
Pb^{2+}	1:1	6.55	3.65	0.9935

In the case of the alginate beads prepared with high content of gas forming agent (with high porosity) Freundlich model seems to fit better the experimental data. It has been stated that magnitude of the exponent $1/n$ gives an indication of the favourability or adsorption capacity of the solid adsorbent for the studied adsorbate. Values $n > 1$ represent favourable adsorption conditions [12]. For the porous alginate beads prepared with gas forming agent a higher value for n indicate more favourable adsorption of both metal ions.

Conclusions

The conventional methods for removal of heavy metal ions in the rivers, underground water or wastewater have been performed by using the chemical precipitation, ion exchange resin, and separation membrane, respectively, but these are expensive methods, result in secondary contaminants, and are not efficient for low concentrations.

In this study polymeric microparticles with different morphologies, from a natural polymer and nontoxic material, were prepared. The study of adsorption capacity showed that the most efficiently beads are microparticles which contain gas-forming agent in 1:1 ratio and we can consider this a possible new improved method for the removal of metals ions at low concentrations.

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