BULETINUL Universităţii Petrol – Gaze din Ploieşti	Vol. LXII No. 3A/2010	47 - 50	Seria Tehnică

Lead Ions Removal with Cellulose Acetate/Hydroxyapatite Composite Membranes

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Abstract

This work describes the characteristics of cellulose acetate/hydroxyapatite composite membranes. The capacity of cellulose acetate/hydroxyapatite composite membranes for removal of lead ions from aqueous solution was investigated. Cellulose acetate/hydroxyapatite composite membrane has shown an ability to retain Pb^{2+} ions from aqueous solutions. Cellulose acetate/hydroxyapatite composite membrane was effective in removing Pb^{2+} ions from solutions with 81 % Pb removed. The effective removal of Pb^{2+} ions from aqueous solution suggests that porous cellulose acetate/hydroxyapatite composite membranes have the potential to immobilize Pb^{2+} ions in lead-contaminated wastewaters.

Key words: *cellulose acetate, hydroxyapatite, composite, lead ions removal*

Introduction

Lead can be toxic for humans and animals at some concentrations and it is a serious public health issue worldwide. Extensive reports and reviews are available on the immunological, neurological and carcinogenic effects of acute to chronic lead exposure by the inhalation, oral and dermal routes of administration. Consequently, extensive effort has been made to treat Pb-containing wastes. Various methods have been proposed for the removal of lead from wastewaters. Chemical precipitation, solvent extraction, electrochemical technique, ion exchange, biosorption, and adsorption are several of the frequently used processes [1-3].

Hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] is the most important bioceramics materials for its unique bioactivity and stability. Also, hydroxyapatite is a good inorganic ions fixators and it can admit a series of cationic and anionic substitutions in its structure. Several studies have recognized the capacity of hydroxyapatite to bind divalent heavy metal ions (Pb, Cd, Zn, Sb and V) from aqueous solutions [4-6]. At the same time, ion exchange reaction between Ca^{2+} ions that exists in the hydroxyapatite structure and positive ions in the solution is possible. Therefore, it shows superior removal rate for divalent positive metal ion through ion exchange between heavy metal existing in water and Ca^{2+} ion of hydroxyapatite.

Cellulose acetate is one of the most important synthetic organic esters because of its broad applications, such as in fibers, films, and membranes, and because it is made from cellulose, the

most abundant biopolymer on earth. In recent years, natural cellulose materials have gained attention as phases for polymer composites [7-10].

In this study, the hydroxyapatite was deposited on cellulose acetate surface to utilize its ion-exchangeability. The capacity of cellulose acetate/hydroxyapatite composite membranes for removal of lead ions from aqueous solution was investigated.

Experimental

The cellulose acetate membranes were prepared by phase - inversion method using cellulose acetate polymer, acetone as solvent, formamide or water as non-solvents, whereas water was used as coagulation medium. A simple Supersaturated Calcification Solution (SCS) with high calcium and phosphate ion concentrations was used for biomimetic coating study. The morphology and properties of the hydroxyapatite/cellulose acetate composite films were characterized by field emission scanning electron microscopy (Fe-SEM, with Fe-SEM MIRA II LMU CS 01 TESCAN microscope) and pore sizes measurement. Further details on the materials processing and respective properties of membranes and composites used in this study can be found elsewhere [11,12].

The removal of Pb^{2+} ions was studied on pure cellulose acetate membranes and hydroxyapatite/cellulose acetate composite membranes. Kinetic reaction of Pb removal by membranes was examined by a batch experiment. A sample of each membrane was immersed to 100 ml of solution containing a Pb concentration of 1000 mg/L prepared by $Pb(NO_3)_2$. The solution was stirred for a certain period of time at room temperature (25 ^{0}C). During experiments, solutions samples were taken and the lead concentration of the solution was determined by photocolorimetric method with dithizone, using a FEK-M photocolorimeter.

Results and discussion

Cellulose acetate porous membranes prepared in our laboratory consist of three-dimensional polymeric structure, with pore sizes of molecular dimensions [11].

Biomimetic treatment in SCS used in our study consisted in formation and deposition of hydroxyapatite layer on the active surface of cellulose acetate membranes. The hydroxyapatite formed on cellulose acetate membranes soaked in SCS was examined by field emission scanning electron microscopy (Fe-SEM). In SEM picture of the cross-section of cellulose acetate membrane immersed in SCS, the hydroxyapatite deposits were observed (Fig. 1).

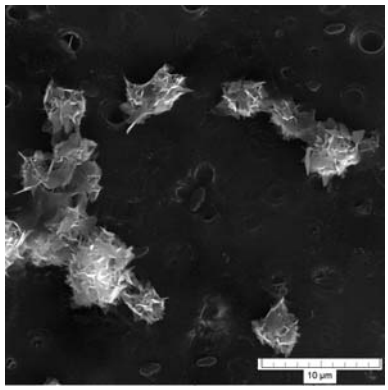

Fig. 1. SEM image of the membrane sample after soaking in SCS for 120 h

In this study, the capacity of cellulose acetate/hydroxyapatite composite membranes for removal of lead ions from aqueous solution was investigated. Removal of Pb^{2+} ions was performed using 1 - 2 g of membrane sample and the time for treatment varied ranging from 1 to 3 h.

First, we studied the influence of pH on the process of retention of lead from aqueous solution. Under the experimental conditions, the variation of lead removal percentage with solution pH is shown in Fig. 2a. It can be observed that removal percentage decreases as solution pH increasing. The best removal percentage occurs under acid condition (pH=3); it is about 81 %.

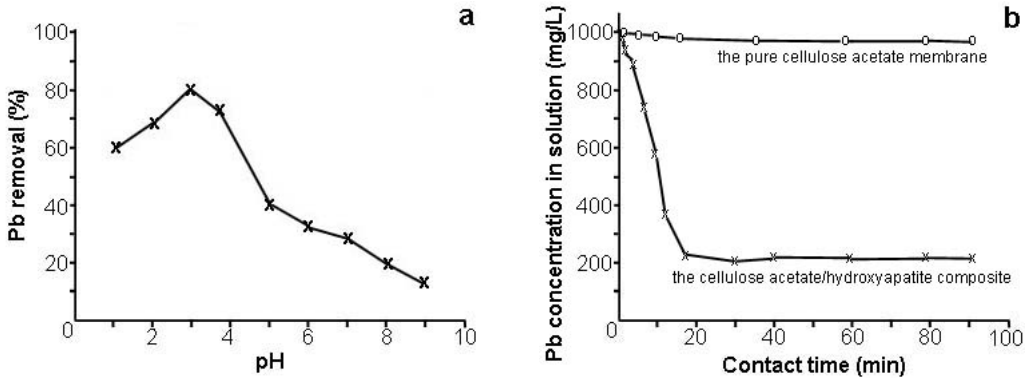

Fig. 2. Lead removal by cellulose acetate/hydroxyapatite composite membrane. The influence of: pH (a) and contact time (b)

Also, the influence of contact time on lead removal is investigated. As shown on the Fig. 2b, a rapid kinetic reaction of Pb removal occurred within the first 10 - 30 min, at pH=3. The aqueous Pb concentration at 30 min decreased from 1000 mg/L to 965 mg/L by pure cellulose acetate membrane and from 1000 mg/L to 229 mg/L by cellulose acetate/hydroxyapatite composite membrane. In contrast to the pure cellulose acetate membrane, cellulose acetate/hydroxyapatite composite membrane had a superior rate of aqueous Pb removal and removed 81 % aqueous Pb within 100 min. The result on the rapid kinetic reaction of Pb and hydroxyapatite agreed with those described elsewhere [14,15].

The crystallinity of the hydroxyapatite phase is expected to affect the manner by which heavy metal ions are removed from solution phase. Highly crystalline phases, such as hydroxyapatite, have a relatively low solubility. A low solubility hydroxyapatite phase may favor surface-mediated metals removal mechanisms, e.g., sorption or ion-exchange, or perhaps heterogeneous nucleation and precipitation at the crystal surface. Mechanisms for Pb ions retention by hydroxyapatite is the adsorption of Pb^{2+} ions on the hydroxyapatite surfaces followed by the ion-exchange reaction between Pb^{2+} ions adsorbed and Ca^{2+} ions of hydroxyapatite [4,13,14].

These results showed that the cellulose acetate/hydroxyapatite composite membrane can be used as an effective adsorbent for removing Pb ions from aqueous solution.

Conclusions

The asymmetric porous cellulose acetate membranes were fabricated by wet phase inversion method. The SEM images of the cellulose acetate membranes evidence the asymmetry / heterogeneity of these systems. The Supersaturated Calcification Solution (SCS) was used to investigate hydroxyapatite formation on cellulose acetate matrix. Also, the capacity of cellulose acetate/hydroxyapatite composite membranes for removal of lead ions from aqueous solution was investigated. Cellulose acetate/hydroxyapatite composite membrane has shown a certain ability to retain Pb^{2+} ions from aqueous solutions. These composite membranes were effective in removing Pb^{2+} ions from solutions with 81 % Pb removed. The removal of Pb^{2+} ions from

aqueous solution suggests that porous cellulose acetate/hydroxyapatite composite membranes have the potential to immobilize Pb^{2+} ions in lead-contaminated wastes.

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Îndepărtarea ionilor de plumb cu ajutorul membranelor compozite pe bază de acetat de celuloză şi hidroxiapatită

Rezumat

Această lucrare descrie o serie de caracteristici ale unor membrane compozite pe bază de acetat de celuloză şi hidroxiapatită. A fost investigată capacitatea acestor compozite în îndepărtare a ionilor de plumb din soluţii apoase. Compozitele de tip acetat de celuloză/hidroxiapatită demonstrează o abilitate bună în a reţine ionii Pb^{2+} din soluţii apoase, respectiv pot elimina un minim de 81 % Pb. Eliminarea efectivă a ionilor Pb^{2+} din soluţie apoasă sugerează că aceste membrane compozite au o bună capacitate de a imobiliza ionii Pb^{2+} din apele contaminate.