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Combined nano-membrane technology for removal of lead ions

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ABSTRACT

The removal of toxic lead ions from aqueous solution by a combined nano-membrane separation technique was investigated. Biodegradable poly-gamma-glutamic acid (γ-PGA), a linear biopolymer, and its cross-linked nanoparticles were used to capture the metal ions by forming nanosized particles. The polymer-metal ion particles, with sizes in the range of 80–350 nm, were then removed by membrane separation. Two ultrafiltration techniques were studied with the aim of developing a nanoparticle-enhanced separation process for the efficient removal of lead ions from aqueous solution. The influence of parameters such as the feed lead ion and γ-PGA concentrations and their proportions, the γ-PGA cross-linking ratio and the pH of the solution on the lead-removal efficiency and permeate flux was studied. It was found that γ-PGA could bind and remove more than 99.8% of the lead ions from water through a convenient, low-pressure ultrafiltration technique, resulting in a permeate that satisfied the standard for drinking water recommended by the WHO.

1. Introduction

Water pollution comprises all of those compounds that change the quality of groundwater and surface water, therefore reducing the suitability of natural water for human use and other vital processes. These compounds result from human activities, especially those that are industrial, agricultural and domestic.

As a consequence of the rapid development of industry, hazardous waste materials containing heavy metals have accumulated in the environment in appreciable quantities, a process that (though perhaps to a reduced extent) is continuing today. Contamination of water by toxic heavy metals has become an increasingly serious environmental and health problem, even at low concentrations [1]. At least 20 metals are considered toxic, and one of the most toxic is lead. It is not biodegradable, and it can accumulate in the environment and in the body, promoting diseases including hypertension, kidney failure and nervous diseases through its nephro- and neurotoxicity [2,3].

Various methods have been developed to remove toxic heavy metals from water. Treatment processes such as adsorption, complexation, ion exchange, chemical precipitation and membrane filtration have been devised for water treatment and remediation. Some of the processes, such as electrolysis and the destruction of sludge by ignition, require high energy input and are expensive. These techniques have several disadvantages, including high energy and chemical requirements, inappropriate efficiency at metal concentrations in the range 1–100 mg/L, which are the most frequent in the case of environmental pollution, and the hazardous materials requiring safe and expensive storage after removal. As can be clearly seen, effective technologies are needed, and many investigations have described methods to improve water treatment, including hybrid processes [4–6], the use of specific adsorbents [7–9], advanced chelating materials [10] and enhanced membrane filtration [11,12].

Membrane filtration is increasingly used as a water and wastewater treatment process for the removal of heavy metals [13,14]. Ultra- and nanofiltration are widely utilized because of their high separation selectivity and low-energy, low-pressure and room-temperature operational parameters. As such, significant effort has recently been made to study heavy metal removal through surfactant- [15,16], micellar- [17–19] or complexation-assisted [20] filtration, polyelectrolyte-enhanced [21,22] and polymer-enhanced [23–26] membrane filtration. Biopolymers are widely available that are biocompatible or biodegradable and, therefore, environmentally safe, and because of the presence of functional groups, they are capable of binding metal ions even at low

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concentrations. These advantages of biopolymers have led to increasing interest in biosorption [27,28].

Biopolymers as adsorbents are known to bind metal ions strongly, so they have been widely investigated for the removal of heavy metals in water treatment. For example, studies have been made of the adsorption affinity of biopolymers, including chitosan [29–32], cellulose [33–35], alginic acid [36,37], poly-γ-glutamic acid [38] and many other biomaterials [39–42].

Ion exchange or reverse osmosis is suitable for removal of lead ions from water. However both technologies are expensive, thus their application is limited. Lead ions can form stable complexes with certain biomolecules with size of about 80–350 nm in diameter. These nanoparticles are than easily removed with Ultra Filtration technology, which needs less energy, is cost effective, and is faster then previous ones.

Polymer regeneration stage is a key step after the complexation and filtration processes during the water- or wastewater treatment. Several practices can be found for polymer regeneration, including traditional chemical regeneration and electrochemical regeneration, as new clear alternative [12,43,44].

Use of biopolymers has several advantages in the field of water treatment, including heavy metal removal. The biopolymers are biodegradable macromolecules. They can be filtered using ultrafiltration, and after that biodegradation of polymers can be performed if it is necessary. After filtration, biopolymer–heavy metal complex particles are concentrated in the retentate. The regeneration of biopolymers can be executed with simplicity, low energetic cost and sufficient recovery percentage. Besides regeneration, other possibility is the biodegradation of biopolymer, but no recovery could be observed in this case.

Poly-γ-glutamic acid (γ-PGA) is a water-soluble, biodegradable, edible and nontoxic biopolymer [45–47] that consists of repetitive glutamic acid units connected by amide linkages between α-amino and γ-carboxylic acid functional groups. Naturally produced γ-PGA is an anionic polypeptide usually containing nearly equal amounts of D- and L-units, and the molecular weight of the polymer is generally high [48,49]. γ-PGA and its derivatives have been utilized in a wide range of industrial fields, including cosmetics, food, medicine and water treatment [50–53]. One problem that arises with aqueous solutions of macromolecules is the high viscosity of the solutions even at low polymer concentrations; the viscosity is usually sensitive to changes in pH and salt concentration. These effects can subsequently hamper their controlled use.

We studied the formation of complexes of γ-PGA with Pb^{2+} [54], and the size and solubility of these nanoparticles in the dried and swollen states were discussed. In aqueous solution, the average size of the particles varied strongly depending on the pH and the concentrations of γ-PGA and Pb^{2+}. The γ-PGA–Pb^{2+} complexes also formed stable particles in aqueous media, depending on the reaction conditions. As γ-PGA is a polyacid with good flocculating activity and high affinity and tightly binds toxic heavy metal ions such as Pb^{2+}, it may therefore be useful for treating wastewater. This study thus focuses on the removal of Pb^{2+} from aqueous solution by the biodegradable biopolymer γ-PGA and its cross-linked nanoparticles. Previously, nano-sized cross-linked γ-PGA particles were prepared and characterized under various conditions to facilitate the planning of different applications for these particles [55].

The present investigation is related to the removal of Pb^{2+} from an aqueous environment by combined nano-membrane technology. Biodegradable linear γ-PGA and its cross-linked nanoparticles were used to complex and remove Pb^{2+}, and different ultrafiltration techniques with biodegradable systems requiring low energy input were compared in their Pb^{2+} removal efficiencies. The permeate flux and efficiency of Pb^{2+} removal were studied as a function of the Pb^{2+} and γ-PGA concentrations and their proportions, the cross-linking ratio of γ-PGA and the pH of the aqueous environment.

Table 1
Reaction conditions for the formation of γ-PGA nanoparticles by lead ion complexation. The solutions were prepared at pH 3.0 and 6.0 for γ-PGA and pH 3.0 and 4.5 for Pb^{2+} to study the effect of pH.

Sample	γ-PGA solution (mL)	$Pb(NO_3)_2$ solution (mL)
PGA + Pb1	10	1
PGA + Pb2	10	2
PGA + Pb4	10	4
PGA + Pb8	10	8
PGA + Pb12	10	12
PGA + Pb16	10	16

For the measurement of permeate flux, 10-fold volumes of solutions were used.

2. Materials and methods

2.1. Reagents

γ-PGA (Mw = 400 kDa) was purchased from the Vedan Group, Taiwan. Lead nitrate was purchased from Sigma–Aldrich Co., Hungary. 2,2′-(Ethylenedioxy)bis(ethylamine) was obtained from Sigma–Aldrich Co., Hungary and was used as the cross-linking agent. 1-(3-(Dimethylamino)propyl)-3-ethylcarbodiimide methiodide was purchased from Sigma–Aldrich Co., Hungary and was used as the coupling agent in the cross-linking process to produce γ-PGA nanoparticles. All of the solutions were prepared with deionized water from a Milli-Q Gradient system (conductivity <0.05 μS/cm).

2.2. Modification

Cross-linked γ-PGA nanoparticles were prepared by a previously described process [55]. Briefly, γ-PGA was dissolved in water to produce a solution with a concentration of 1 mg/mL. The diamine cross-linker was also dissolved in water, and the solution was adjusted to pH 5.5 with 0.1 M hydrochloric acid solution. The diamine solution was then added to the γ-PGA solution and mixed for 30 min at room temperature. After the dropwise addition of water-soluble carbodiimide solution, the reaction mixture was stirred at 4 °C for 4 h and then at room temperature for 20 h. The solution containing cross-linked γ-PGA nanoparticles was purified by dialysis for 7 days against distilled water and freeze-dried. Cross-linked γ-PGA nanoparticles were synthesized in this way at various stoichiometric cross-linking ratios.

2.3. Binding measurements

γ-PGA linear biopolymer and cross-linked γ-PGA nanoparticle solutions at different pH were used for the removal of Pb^{2+} from aqueous solution. γ-PGA or cross-linked γ-PGA nanoparticle (c = 1 mg/mL or 5 mg/mL) and $Pb(NO_3)_2$ (c = 1 mg/mL or 5 mg/mL) solutions were prepared to study binding affinity. For the experiments, the $Pb(NO_3)_2$ solution (V = 1, 2, 4, 8, 12, or 16 mL, pH = 3.0 or 4.5) was added dropwise to the γ-PGA solution (V = 10 mL, pH = 3.0 or 6.0). The mixture was then diluted to 30 mL and stirred for 30 min at room temperature. Table 1 summarizes the various reaction conditions.

2.4. Characterization of the samples

2.4.1. Transmittance

The transmittances of γ-PGA–Pb^{2+} complex mixtures of different compositions and pH were measured with a Hitachi U-1900 Spectrophotometer at a wavelength of λ = 500 nm in optically homogeneous quartz cuvettes. These results support the