

Lead and Gold Removal Using Sugar-Beet Pectin Gels With and Without Immobilized *Fucus vesiculosus*

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Abstract. Sugar-beet pectin gels are a novel material with applications in heavy and precious metal removal and biomass immobilization which are similar to those of alginate. This paper presents the experimental results of the kinetics of Pb(II) and Au(III) batch removal with these gels, with and without immobilized biomass of the brown algae *Fucus vesiculosus*. The evolution of the metal concentration, solution pH and Ca²⁺ liberation was determined. The biomass was characterized before and after the metal removal using SEM-EDX, FESEM, FETEM, XRD and FTIR techniques. The Pb(II) removal followed a typical biosorption kinetics with a final equilibrium metal concentration. The immobilized algae had different biosorptive behaviour than both the original sugar-beet pectin gels and the free biomass. There was no Au(III) removal with the pectin gels without algae. In the case of the immobilized biomass, the Au(III) recovery occurred in two stages, where the biosorption was followed by the reduction of the Au(III) to Au(0) due to the presence of the own algae. The Au(0) precipitated preferably on the surface of the algal biomass and in the form of colloidal gold in the solution and entrapped within the pectin gel matrix.

Introduction

Lead is a toxic metal that can be concentrated in living tissues and accumulated along the food chain. On the other hand, gold is a precious metal that has a low toxicity, but its recovery is interesting due to its market prices. Biosorption is a cost-effective alternative to purify solutions that is useful at very low concentrations [1]. Compared to other heavy metals, there are few studies that describe the biosorption of gold. The most effective biosorbents seem to be those that use algae or microorganisms that have a high polysaccharide content whose functional groups (carboxyl, sulfate, phosphate and amino) are responsible of the gold recovery [2].

One of the advantages of biosorption is the possibility to use low-cost biomass that are residues from other processes or that are readily available, such as sugar-beet pulp or brown algae [3, 4]. Usually, biomass in its native state cannot be used directly for industrial applications due to its small particle size, low density, and lack of mechanical resistance. Therefore, an immobilization process is often necessary. Without immobilization, the separation stage can represent up to 60% of the cost of the process. The characteristics of an adequate immobilization method include: mechanical stability, permeability and high metal uptake in several cycles of sorption-desorption.

Pectins can be obtained from pulp residues of the food industry. Low-methoxyl pectins gel in the presence of different inorganic and organic substances, such as calcium ions, and are an interesting alternative to alginate gels, that are widely used as immobilization agents. Sugar-beet pectins can be obtained from the sugar-beet pulp that is a residue of the sugar industry, that generates more than 200,000 tons per year in Spain (Grupo Ebro-Puleva). Sugar-beet pectins have the advantage over other types of pectin, like apple and citric, that the raw material is already dry and is independent of

seasonality [5]. These type of pectins have been used alone for the biosorption of heavy metals, but constitute a novel support for biomass immobilization [6].

In this paper, the chemical stability and the gold and lead uptake of sugar-beet pectin gels as a support for biomass are determined for future applications in continuous systems.

Materials and Methods

The brown algae *Fucus vesiculosus* was prepared with the same procedure for *F. spiralis* in [7]. The sugar-beet pectin was extracted with H_2SO_4 , demethylated with NH_3 , gelled with $CaCl_2$ and dried as described in [8]. The algae was immobilized in a proportion of 1:1 algae:pectin. The pectin beads had a diameter of approximately 1.3mm without biomass and 2mm with biomass. Batch biosorption experiments were conducted according to [7]. The algal biomass and the pectin xerogels, with and without immobilized biomass and adsorbed metal, were analyzed with Fourier Transform Infrared Spectroscopy (FITR) scanning electron microscope (SEM-EDX), X-Ray diffraction (XRD), and field emission scanning and transmission electron microscopes (FESEM and FETEM).

Results and discussion

Brown algae are abundant and well known as biomasses for biosorption due to their high metal uptakes when compared to other biosorbents [3]. The pectin gels with and without biomass and the free algae presented similar lead uptakes (approximately 0.5 mmol/g). The free biomass reached the equilibrium values before the gels due to differences in particle size, diffusion and porosity (figure 1a). Part of the lead in solution was exchanged with the calcium in the algae and the pectin gels (table 1) [9, 10]. The pH value did not have a significant change, but ion exchange with protons still contributed to the biosorption [11].

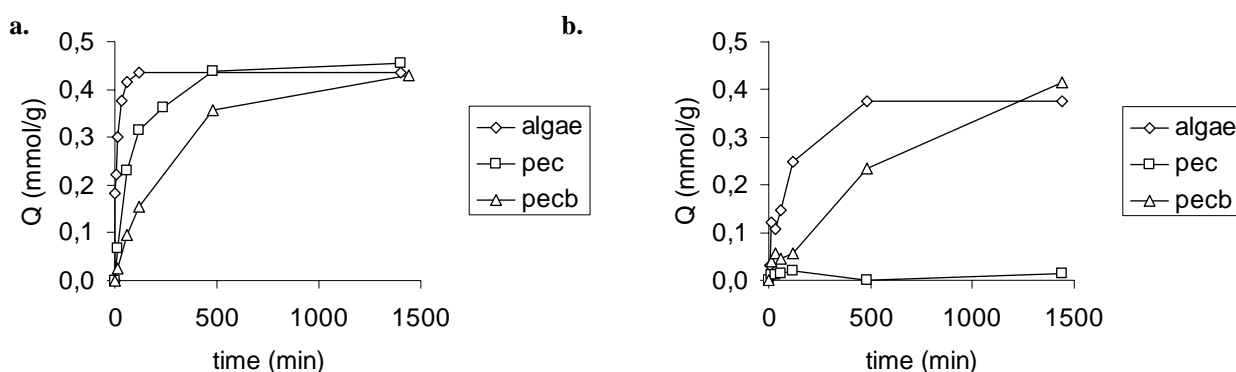


Figure 1. Metal uptake of lead (pH 5) (a) and gold (pH 7) (b) with the algae *Fucus vesiculosus* and the pectin gels with (pecb) and without (pec) immobilized algae (100 mg/l metal, 1 g/l biomass).

Table 1. Amount of calcium released by different biomasses during the biosorption of lead compared to the amount that was released in a solution without metal.

Biomass	Ca [mmol] after lead biosorption	Ca [mmol] after gold biosorption	Ca [mmol] without metal
<i>Fucus vesiculosus</i>	0.11	0.24	0.025
Pectin xerogels	3.62	-	0.29
Immobilized algae	3.19	4.29	0.25

The pectin gels did not significantly recover gold (figure 1). Gold biosorption with the algae, free and immobilized, has a different behavior than the biosorption of other heavy metals. After the biosorption, a reduction process occurs with a sharp decrease of the gold concentration and a change of color of the solutions [2, 12]. There are different biomasses that are capable of reducing ionic gold to its elemental state, such microorganisms and polysaccharides [13, 14]. Another interest of these studies is not only the recovery of gold, but the synthesis of gold nanoparticles of different size and shape, that occur during this second stage of reduction (figures 2 and 3) [15].

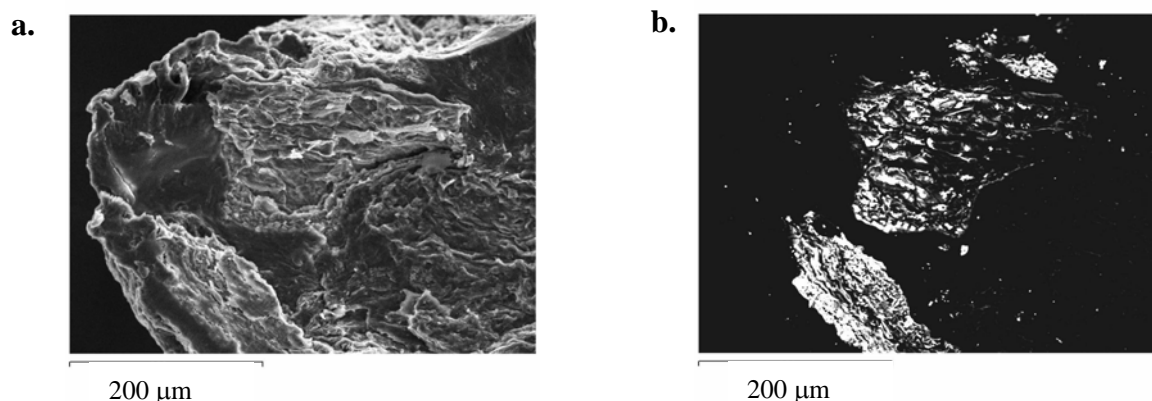


Figure 2. Secondary electron SEM micrographs (a) of immobilized algae after the gold recovery and backscattered electron images (b) showing metallic gold precipitated selectively on the biomass surface.

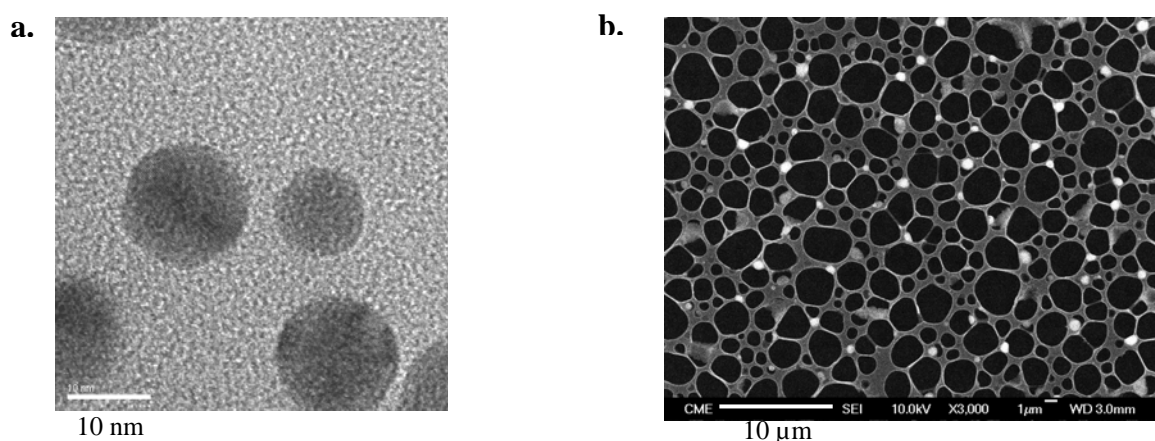


Figure 3. FETEM (a) and FESEM (b) micrographs of colloidal gold nanoparticles in the solution after the biosorption with the brown algae *Fucus vesiculosus*.

The first stage followed a typical biosorption curve and lasted 1 h with the free algae and 2 h with the immobilized algae. In the case of the free algae there was a deprotonation that did not occur during the lead biosorption (figure 4a). There was also more decalcification of the biomass (table 1). During the reduction stage there was a decrease of the solution Eh when the gold was recovered with the free algae that was not present in the lead recovery (figure 4b). The gold recovery with the immobilized algae did not present these decreases of the pH and Eh of the gold solutions, probably due to the calcium ions from the gel that stabilized the pH of the solution [16]. In this case, the gold recovery was higher, although it was also slower than the one obtained with the free algae. The pectin gel matrix, along with the larger bead size, relented the process. Although it did not reduce gold it could have favored the concentration and nucleation of the gold atoms around the immobilized algae causing the reduction of more gold. The presence of reduced gold on the algal surface was confirmed with EDX and XRD [8, 17]. The FITR studies confirmed the participation of the carboxyl groups in the gold and lead biosorption with all the biomass and of the sulfonate groups in case of the gold recovery with the algae, with a shift in the corresponding bands [8].

In conclusion, sugar-beet pectins with and without immobilized biomass constitute a stable support for the recovery of lead and gold with high metal uptakes, and for reducing this last metal.

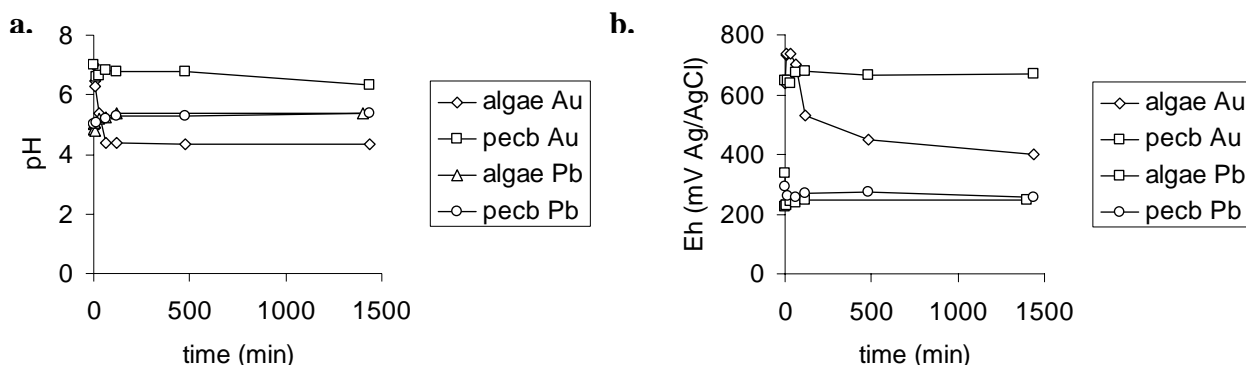


Figure 4. Evolution of the pH (a) and Eh (b) of the metal solutions during the recovery of gold and lead with different biomasses.

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