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Research paper

Gold(III) biosorption and bioreduction with the brown alga *Fucus vesiculosus*

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ABSTRACT

In this paper, the bioreduction of Au(III) to Au(0) using biomass of the brown alga *Fucus vesiculosus* was investigated. The recovery and reduction process took place in two stages with an optimum pH range of 4–9 with a maximum uptake obtained at pH 7. In the first stage, an induction period previous to gold reduction, the variation of pH, redox potential and gold concentration in solution was practically negligible and no color change was observed. In the second stage, the gold reduction was followed by a sharp decrease of gold concentration, pH and redox potential of solution and a color change from yellow to reddish purple. Hydroxyl groups present in the algal polysaccharides were involved in the gold bioreduction. Metallic gold was detected as microprecipitates on the biomass surface and in colloidal form as nanoparticles in the solution. Bioreduction with *F. vesiculosus* could be an alternative and environmentally friendly process that can be used for recovering gold from dilute hydrometallurgical solutions and leachates of electronic scraps, and for the synthesis of gold nanoparticles of different size and shape.

1. Introduction

Gold is a heavy metal that has a low toxicity, but its recovery is interesting due to its high market prices. Its recovery from exhausted or dilute effluents from mines or industries can be expensive, inefficient and/or polluting using conventional technologies, such as cyanide leaching, precipitation and filtration, electrochemical treatments, reverse osmosis, ion exchange resins, and evaporation. Biosorption is an alternative, clean and simple method for metal recovery at low concentrations. It is based on the passive retention of metals or other compounds on chemically active sites or functional groups present in certain types of biomass [1]. Dead biomass increase metal uptakes making the process nutrient independent. Additionally, residual or very low cost materials can be used, such as the brown alga *Fucus vesiculosus*, abundant in Northern Atlantic coasts.

Brown algae are well known biomass for biosorption due to their high metal uptakes compared to other microorganisms, such as fungi and other algae [2,3]. Their more complex cell wall, rich in mucilaginous polysaccharides (alginate and sulfatated fucoidans), can explain the higher metal uptakes. It contains the majority of the main functional groups, especially carboxyl groups, involved in metal recovery and accounts for 60–80% of the dry weight of the biomass [1]. Other functional groups present in the algal cell wall are: amino, sulfhydryl and sulfonates [4].

Cui and Zhang [5] have considered biosorption as an alternative and promising method for the recovery of precious metals from electronic waste leachates. These authors offer a comprehensive review of different biomass and their derivates that have been used for gold biosorption: bacteria, fungi, algae, plants, and chitosan. Some of those biomass, such as alginate, *Verticillium* fungi, and alfalfa, are also capable of reducing ionic gold to its elemental state, facilitating its recovery [6–8]. Binding mechanisms involving the same metal and different biomass can bear little or no similarity, especially in the case of precious metals [9]. The interest of such studies is not only gold recovery and reduction, but also the possibility of synthesizing nanoparticles in an environmentally friendly way. Nanoparticles have interesting applications based on their chemical, optical and electrical properties [7,10].

There are few works published in the literature on gold uptake and biosorption compared to the great number of articles on biosorption for other metals [9] and none using the alga *F. vesiculosus*. The few studies published use living bacteria, algae or plants, so the control of the process is more difficult and complex since it is necessary to keep optimum growth conditions.

In the present work, Au(III) was successfully recovered as metallic gold nanoparticles using dead biomass of the brown alga *F. vesiculosus*. The process is described and the influence of initial pH is investigated. Different analytical techniques were used, including Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy dispersive elemental analysis (EDS), transmission electron microscopy (TEM) and X-ray diffraction analysis (XRD), and a possible mechanism is proposed.

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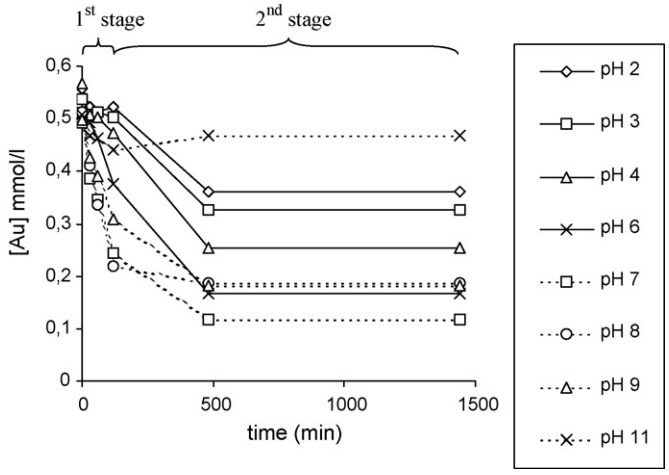

Fig. 1. Influence of the initial solution pH during gold recovery with *Fucus vesiculosus*.

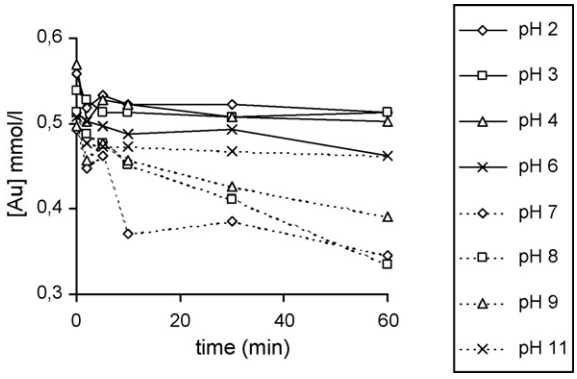

Fig. 2. Influence of the initial solution pH during the first stage of gold recovery with *F. vesiculosus*.

2. Materials and methods

2.1. Biomass

The brown alga *F. vesiculosus* was collected by Algamar in the Northern Atlantic coasts of Spain. The alga was washed, dried in an oven at 60 °C, ground with an agate mortar, and sieved to a mesh size of <0.5 mm.

2.2. Metal solutions

Gold biosorption studies were carried out with fresh solutions that were prepared from a 1000 mg/l stock solution of hydrochloroauric acid ($HAuCl_4$). The initial pH values were adjusted with NaOH flakes and HCl as needed.

2.3. Biosorption and bioreduction tests

Biosorption experiments were performed using the same procedure as in previous studies with the brown alga and other metals [3]. Algal biomass (1 g/l) was placed in contact with Au(III) solutions (75 ml, at 100 mg/l) at room temperature (±23 °C) and stirred magnetically. The influence of pH on gold sorption and reduction was investigated at different initial solution pH (2, 3, 4, 6, 7, 8, 9 and 11). Liquid samples removed at different times (0, 2, 5, 10, 30, 60, 120, 480 and 1440 min) were centrifuged (at 3000 rpm for 10 min) to determine pH, redox potential vs. Ag/AgCl (E) and metal concentrations, including calcium. Metal uptake was calculated using the following equation:

$$Q = \frac{C_0 - C_t}{B} \quad (1)$$

where q_t is the metal uptake at time t (mmol/g of biomass); C_0 the initial metal concentration (mmol/l); C_t the metal concentration at time t (mmol/l); B is the biomass concentration (g/l).

2.4. Analytical and characterization methods

Metal concentrations were determined by flame atomic absorption spectroscopy (FAAS) using a Perkin Elmer spectrophotometer model 1100B. After gold recovery, biomass and solution samples were dried and finely ground for X-ray diffraction analysis (XRD). X-ray patterns were obtained using a Phillips XPERT diffractometer using the Cu Kα radiation. Algal biomass, with and without retained metal, was coated with a thin layer of graphite and examined in a scanning electron microscope (SEM) (JEOL JSM-6400) with an energy dispersive elemental (EDS) analyzer. The remaining metal solutions after gold recovery were evaporated and examined in a field emission transmission electron microscope (FE-TEM) (JEOL JEM-3000F). TEM images of nanoparticles were obtained by dropping the colloidal solution after gold recovery onto a carbon-coated copper TEM grid. For FTIR analysis, KBr discs with 2% finely ground sample were analyzed in a MIDAC Prospect-IR spectrophotometer and processed with Nicolet OMNIC E.S.P software. Infrared spectra were recorded in the region of 500–4000 cm^{-1} at a resolution of 4 cm^{-1}.

3. Results and discussion

3.1. Influence of pH

pH is one of the most important variables that affects the speciation of metals in solution through hydrolysis, complexation and redox reactions during metal recovery [11]. This variable also influences the charge of the biomass functional groups, which can cause repulsion or attraction of metals in solution, and affects the conformation of the cell structure, which determines more or less the accessibility of binding sites to metals [12].

Table 1
Variation of pH, E and Q (mmol/g) after 1 and 8 h of gold recovery with *Fucus vesiculosus* at different initial pH values.

Initial pH	2	3	4	6	7	8	9	11
Initial E	730	726	722	699	676	661	625	444
1 h								
Q	0.046	0.025	0.066	0.051	0.147	0.178	0.107	0.046
pH	2.11	3.09	3.31	4.42	4.36	7.7	8.1	10.32
E	740	731	707	687	510	311	244	167
8 h								
Q	0.198	0.213	0.315	0.345	0.376	0.325	0.315	0.041
pH	2.15	2.71	2.67	3.13	3.85	5.22	6.96	9.59
E	353	304	292	286	215	233	210	208

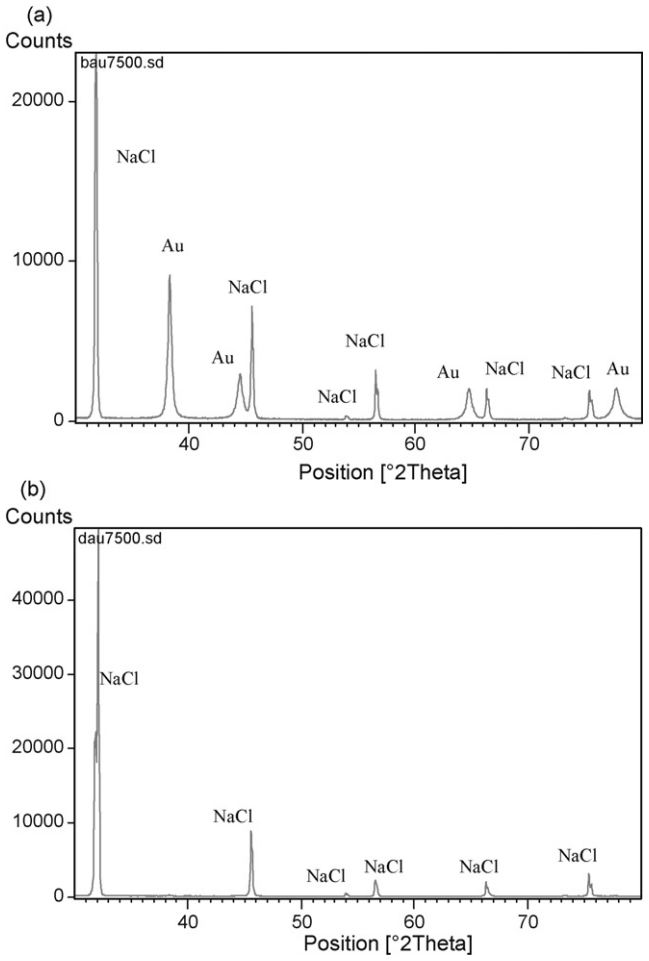

Fig. 3. XRD pattern of *F. vesiculosus* with gold (a) and of an evaporated solution after gold recovery (b) with this alga.

The effect of pH on the gold uptake with *F. vesiculosus* from $AuCl_4^-$ solutions was studied in the pH range of 2–11. Fig. 1 shows the evolution of gold concentration in solution at different initial pH values. The kinetics of gold recovery varied according to the initial solution pH. The evolution of gold concentration did not follow the typical sorption curve in which metal concentration decreases until equilibrium is reached. In this case, two separate stages were observed with an initial delay (first stage) before gold reduction and recovery took place (second stage).

During the first stage that lasted about 1 h, the variation of pH, redox potential and gold concentration in solution was small and no color change was observed. Fig. 2 depicts the evolution of gold recovery during the first 60 min, while Table 1 shows the numerical values of different parameters at that time. This stage, which was more pronounced at the initial pH values of 2, 3, 4 and 11, could be related to an induction period, before gold reduction, in which tetrachloroaurate anions are attracted to positively charged functional groups, e.g., amino (NH_2), on the algal surface [13]. The electrostatic interaction would favor any approximation of the anion to other functional groups responsible for its reduction.

During the second stage, the final equilibrium metal concentration was reached after 8 h and was characterized by a decrease of gold concentration and a color change of solution from bright yellow to reddish purple (Fig. 1). According to Turkevich [14], that color change of the solution is associated to gold reduction and the presence of gold nanoparticles. Metallic gold was detected by XRD analysis of the alga after gold uptake using the spectral patterns from the studies of Shankar et al. [15] (Fig. 3a). Lin et al. [16] also used that technique to detect metallic gold peaks after gold reduction with *Saccharomyces cerevisae*.

The XRD spectra of solutions previously colored only showed NaCl crystals (Fig. 3b). The dissociation of tetrachloroaurate complex ($HAuCl_4$) produced an excess of chloride ions in solution that crystallized with the sodium of the algal biomass after they were evaporated for analysis. NaCl crystals nucleated and grew around the gold nanoparticles that were masked and undetected during analysis. Fig. 4 shows SEM images and EDS microanalysis of colloidal gold nanoparticles within a NaCl crystal.

Colloidal solutions from gold recovery with *F. vesiculosus* were also observed by TEM, and nanoparticles of different size and shape were found at different initial pH values. For instance, pH 7 produced uniform and spherical nanoparticles smaller than those obtained at pH 4, which showed a greater variety of sizes and shapes (Fig. 5). An advantage of this method of synthesis of gold nanoparticles is that they can be obtained at extracellular level and in large quantities making easier its purification as compared to other methods where they are entrapped inside a polymer or living biomass [6,8,17,18].

3.2. Bioreduction process

During the second stage, there was also a sharp decrease of the solution pH and *E* values, which is another evidence of gold reduction (Table 1) [19]. Only the initial solution pH values were adjusted before metal recovery. Fig. 6 compares the final values of

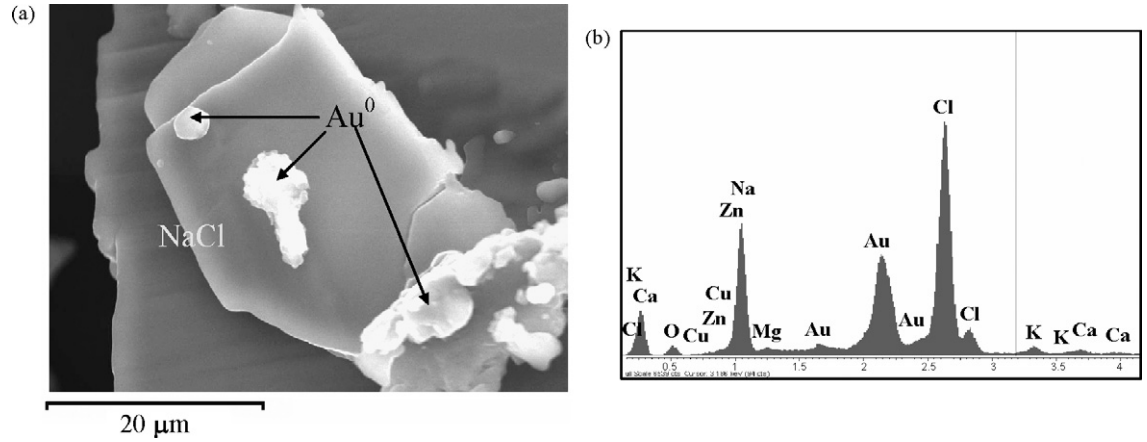

Fig. 4. (a) SEM micrograph of a NaCl crystal surrounding gold nanoparticles in an evaporated solution after gold recovery with *F. vesiculosus*. (b) EDS spectral analysis of gold clusters marked with arrows.

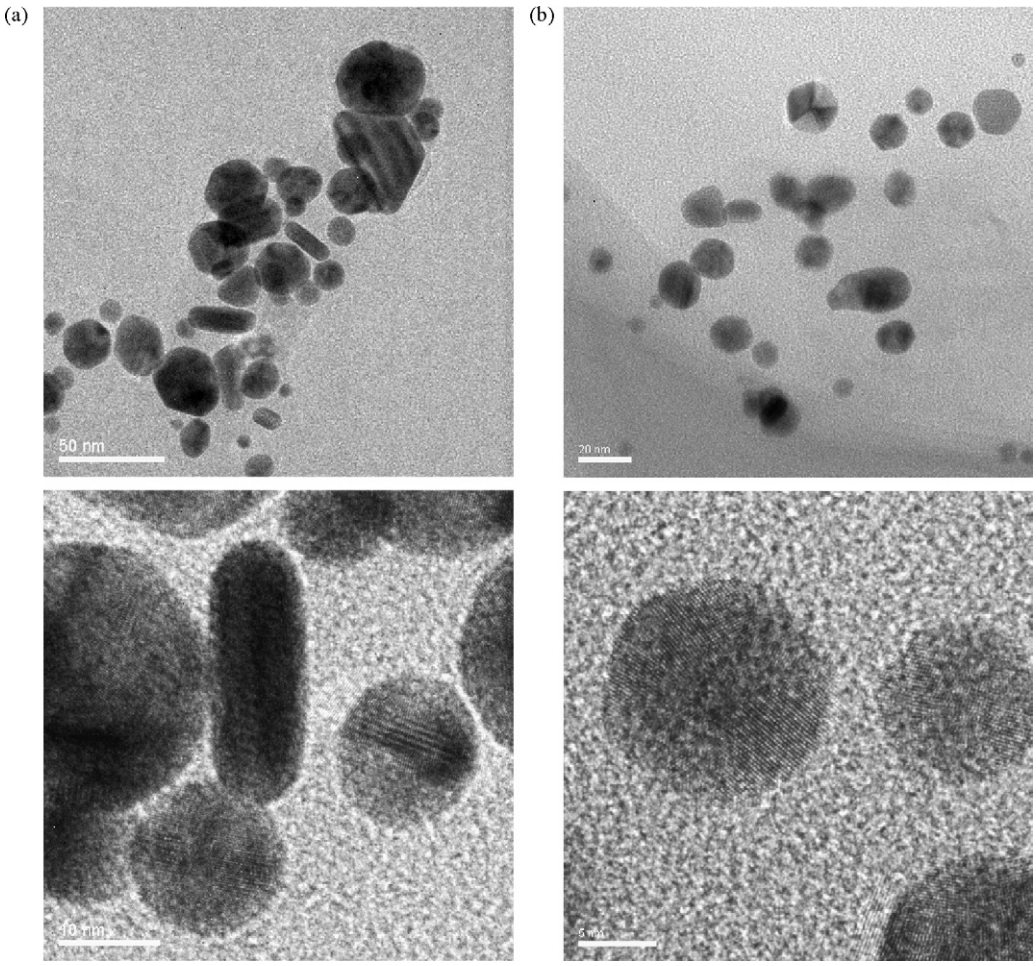

Fig. 5. TEM micrographs of gold nanoparticles obtained with *F. vesiculosus* in solutions at pH 4 (a) and 7 (b).

solutions, after gold recovery, with the initial ones. The variation of this parameter was greater within the range of initial pH values between 6 and 8.

Fig. 7 shows the final gold uptakes with *F. vesiculosus* at different initial pH values. The greatest gold uptakes were obtained at initial pH values between 4 and 9. Within this range of initial pH values, the induction period observed before gold reduction was shorter than with the other pH values, and the pH and *E* decrease and color change were faster. The maximum uptake was obtained at pH 7. The evolution of pH and redox potential shown in Fig. 8 confirms that reduction started after a short induction period (less than 1 h) and that both stages practically overlapped.

Interestingly, optimum gold recovery and reduction was achieved at neutral pH. Unlike that, in many gold biosorption studies efforts have been made to raise the optimum pH range from acid values [9]. Neutral pH is usually found in seawater (7.5–8), the natural environment for *F. vesiculosus* and other aquatic environments like river waters (6.5–8.5). For living alga, that pH condition would be related with the adsorption and deposition of different components from seawater that are needed for its survival and, in the case of waters in which gold is present, with its natural deposition.

According to SEM analysis, gold particles, besides being present in colloidal form in solution, were also microprecipitated on the surface of the biomass particles of *F. vesiculosus* (Fig. 9). The brighter areas of the backscattered electron image correspond to metallic

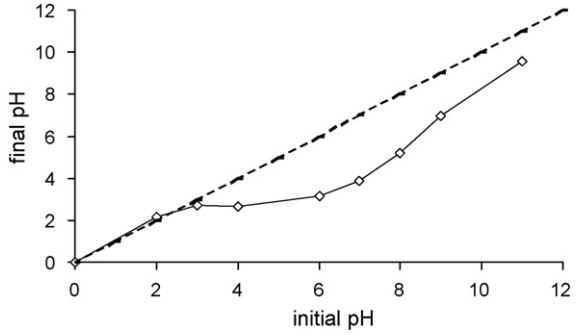

Fig. 6. Final pH values after gold recovery with *F. vesiculosus* at different initial pH values. The straight dotted line represents initial pH values and the continuous line final pH values.

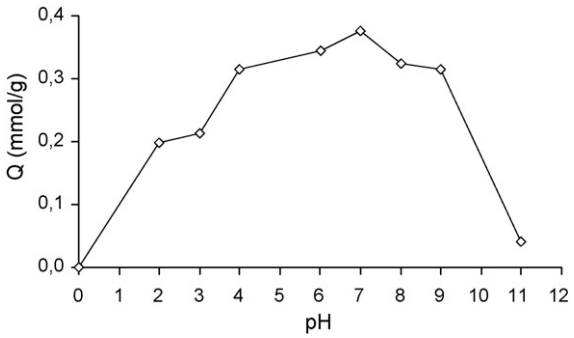

Fig. 7. Gold uptake with *F. vesiculosus* at different initial pH values.

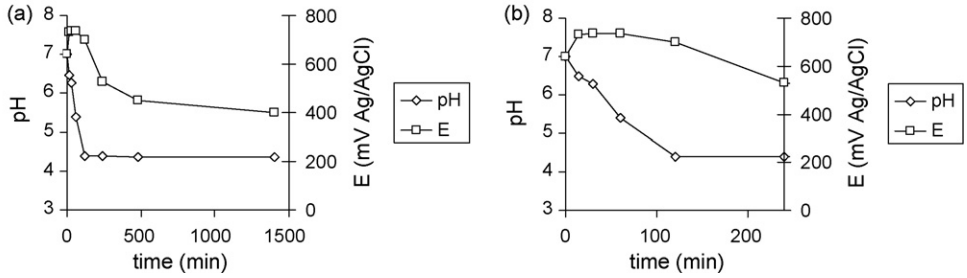

Fig. 8. (a) Evolution of the pH during gold recovery with *F. vesiculosus* at pH 7. (b) Detail of the first 240 min.

gold, as identified by EDS analysis. The analysis of the evaporated solutions also confirmed the presence of NaCl crystals with gold nanoparticles inside (Fig. 4). Kuyucak and Volesky [19] and Ting et al. [20] have also reported elemental gold precipitation on the algal biomass of *Sargassum* and *Chlorella*, respectively.

The sharp decrease of pH would be an indication that protons are released during gold reduction, in agreement with the reaction proposed by Kuyucak and Volesky [19]:

$$AuCl_4^- + 3R\text{–}OH \rightarrow Au^0 + 3R{=}O + 3H^+ + 4Cl^- \quad (2)$$

Reaction (2) indicates that reduction of Au(III) to Au(0) occurs through oxidation of hydroxyl to carbonyl groups. Hydroxyl groups (OH) are very abundant in polysaccharides of the algal cell wall [21] and its participation in the reduction process was confirmed by FTIR analysis of the biomass before and after gold recovery. There was a significant displacement of the (CO) stretching of (COH), from 1075 to 1113 cm^{-1} (Fig. 10). Although no significant displacement was observed in the FTIR spectrum, since it overlaps with other bands, the (OH) stretching band became sharper.

The displacement of the infrared bands corresponding to the carboxyl groups was expected. Previous studies have shown that the interaction between gold and these groups is more than simple electrostatic attraction and ion exchange. For instance, Lin et al. [16] observed modifications of these bands after gold recovery with *S. cerevisae*. Furthermore, Kuyucak and Volesky [19] determined by FTIR and XPS that carboxyl groups were involved in the gold recovery with the brown alga *Sargassum* and proposed the formation of oxygen bridges between gold and these groups. Those authors also reported that the hydrolysis of such groups caused a decrease in the amount of gold recovered. Gamez et al. [8] observed a decrease of the gold recovery when the carboxyl groups were esterified. Nevertheless, the displacement of these bands was not apparent in our study. The displacement of the asymmetric vibrations of the carboxyl groups (1625–1618 cm^{-1}) was only slightly above the resolution of the spectrophotometer (4 cm^{-1}).

Other functional groups have also been associated to gold recovery, but no reduction has been reported. Figueira et al. [12], using FTIR and XPS, mention that acetyl groups could also be involved in metal sorption of trivalent metals with brown algae. More recently, Fujiwara et al. [22] modified chitosan with lysine, rich in amino groups, as a chelating ligand for the recovery of gold and other precious metals. As mentioned earlier, these groups could be involved in the initial attraction of the tetracholoroaurate anion but not its reduction. These authors observed a typical biosorption behavior that fitted kinetic and isotherm models.

Since the reduction rate was faster at neutral pH, the second stage reduction of Au(III) to Au(0) took place almost simultaneously to the sorption of the tetrachloroaurate anion (Fig. 8). For that reason, the stages are less marked and overlap in the kinetic curve at initial pH values of 6, 7 and 8 (Fig. 1). Reduction of Au(III) to Au(0) was greater and faster at initial pH of 7, probably because of the higher stability of the algal cellular components at neutral pH. Reducing groups (OH) present in biomolecules of alga, such as polyols or even polysaccharides and proteins, are more reactive at neutral pH than at more acidic or alkaline pH. In fact, those algae grow in seawaters with an average pH of 7.5. Based on the O–H bond polarity, hydroxyl groups have a certain acid character and react with strong bases. That would explain the lack of its reducing ability at pH 11.

In acid medium, conversely, hydroxyl groups behave as weak bases, due to the existence of unshared pairs of electrons in the oxygen atom, and then become protonated. Protonated hydroxyl groups can be transformed into carbocations, provoking the loss of their reducing ability. On the other hand, the formation of carbocation involves a strong electrostatic attraction to the tetrachloroaurate ion which justifies the sorption of gold by the alga at acid pH. Thus, a decrease of pH favors the sorption of gold instead of its reduction.

Other highly reactive functional groups, with a similar chemical behavior to hydroxyl groups, such as sulfhydryl (–SH), could also be involved in the reduction process. Those groups are present

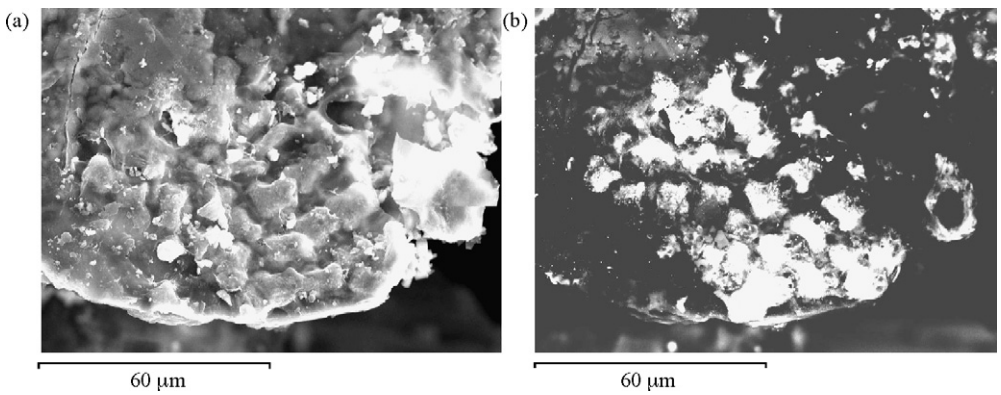

Fig. 9. Secondary (a) and backscattered (b) electron SEM micrographs of *F. vesiculosus* in contact with gold.

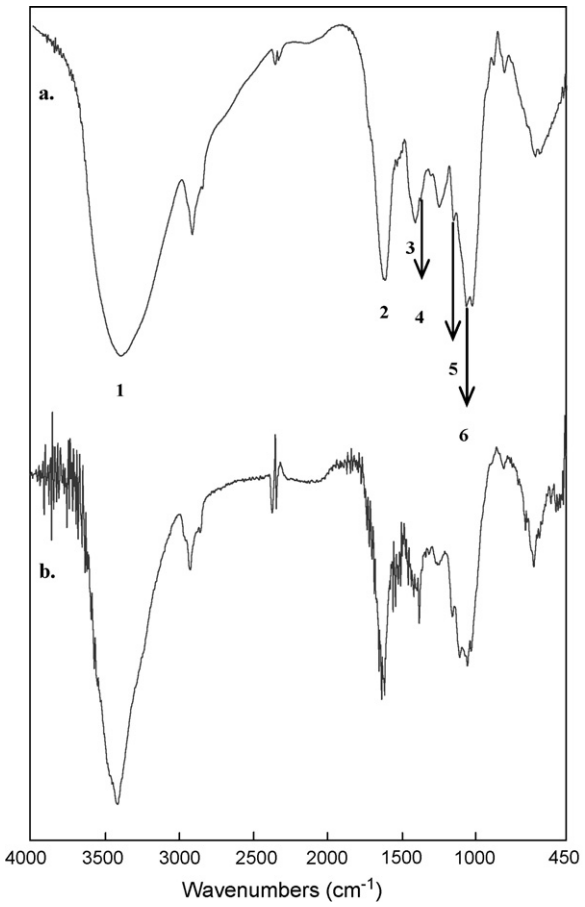

Fig. 10. FTIR spectra of the brown alga *F. vesiculosus* without metal (a) and with gold (b). The main bands are numbered: (OH) stretching (1); asymmetric (C=O) (2) and symmetric (C–OH) (3) stretching of (COOH); asymmetric (S=O) (4) and symmetric (S–OH) (5) stretching of (SO_3); and (CO) stretching of (COH) (6).

in polyssacharides of the algal cell wall and are responsible for its brown color (fucoidans) [21]. Greene et al. [23] determined the participation of these groups in experiments with the green alga *Chlorella vulgaris* after checking that their chemical modification reduced gold uptake.

An intermediate step of Au(III) into Au(I), before forming Au(0), has been detected by several authors using different biomass and spectroscopic methods: Gamez et al. [8] on alfalfa, Romero-Gonzalez et al. [13] on dealginated brown alga, and Greene et al. [23] on *Chlorella*. These authors have proposed a fast reduction from Au(III) to Au(I) while reduction to Au(0) is slow.

In our case, once the reduction started, gold nanoparticles could catalyse the oxidation of hydroxyl groups and Au(III) reduction improving the gold recovery rate during the second stage. It is well known that gold is an excellent catalyst for many organic oxidation reactions. In fact, current research is focused on the development of gold nanocatalysers for the chemical industry [24].

Algal pigments, such as fucoxanthins, a kind of carotenoids rich in hydroxyl groups, could also have participated in the gold reduction. These pigments have reductive properties and are released to solution by diffusion [19]. In fact, the solutions remained colored after centrifuging the biomass in a blank experiment only with deionized water and alga. Nevertheless, these pigments would only explain part of the reduction since it still occurs, to a lesser extent, within alginate beads that have no pigments [6]. With *F. vesiculosus*, these soluble elements could have acted as capping agents preventing the aggregation of nanoparticles in solution, playing a relevant role in their extracellular synthesis and shaping [25]. For instance, Vigneshwaran et al. [26] found a protein shell surrounding silver nanoparticles synthesized with spent mushroom substrate.

Reduction of tetrachloroaurate with brown algae *F. vesiculosus* is an effective method for the synthesis of gold nanoparticles from dilute solutions: cheap (alga is a very abundant biomass in nature), easy performance at neutral pH and room temperature using dead biomass (easier to handle than living biomass) and environmental friendly compared to other chemical methods that use toxic chemicals. Additionally gold can be obtained as a high value added product based on both the great number of potential applications and their interesting properties, such as the development of pollution sensors from gold colloids.

4. Conclusions

The brown alga *F. vesiculosus* successfully recovered and reduced Au(III) to Au(0). In the process, gold nanoparticles were formed. The greatest gold uptakes were obtained at initial pH values between 4 and 9, with an optimum at pH 7, unusual for a gold recovery. Uptake occurred in two stages with an induction period observed before gold reduction. Hydroxyl groups from algal components were involved in gold reduction and nanoparticle formation.

Gold recovery and reduction with *F. vesiculosus* is effective, nutrient independent, does not use toxic chemicals and occurs at neutral pH values. This could be an alternative process for gold recovering from dilute hydrometallurgical solutions and for the synthesis of reduced gold nanoparticles. Additionally, the study can provide further insights to understand the biogenic mechanisms of gold deposition involved in the formation of natural deposits.

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