Gold reduction in batch and column experiments using silica gel derivates and seaweed biomass

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Abstract

Gold recovery from aqueous solution was studied in the present work. Two synthetic materials composed of immobilized chelating agent on silica gel, and the brown seaweed *Sargassum muticum* were used as reducing agents inducing gold colloid nanoparticles formation. The results showed that there is no pH effect and no interference on gold recovery by the presence of other metals in solution, such as Co, Ni, and Cr(VI). A strong complexing reagent for gold leaching, such as thiourea, was able to recover a significant amount of the gold previously reduced over the surface of the materials. The investigated synthetic materials presented much faster rate than the algae for gold recovery. A first order model with respect to the oxidizable groups and gold concentrations accuracy described the entire kinetic process. The rate constant of the reaction and the concentration of oxidizable groups per gram of material were obtained from kinetic data fit. Column studies were conducted varying the flow rate and the quantity of material used. Under favourable conditions of flow rate (1 mL/min) and quantity of material in the column (≥ 0.2 g), more than 95% of the gold was recovery from the inlet solution. A mechanism based on the experimental evidences was proposed. FTIR and SEM analysis supported the suggested mechanism. Based on the results showed it can be concluded that the gold removal from aqueous solution is mainly based on a reduction mechanism where gold colloid nanoparticles are produced.

Keywords: Gold; *Sargassum muticum*; EDTA; DTPA; silica gel; nanoparticle.

1. INTRODUCTION

The gold recovery from aqueous solution is a process that has been reviewed extensively [1-3]. The interest of these studies not only comes from the high economic impact of this precious metal, but also from its multiple applications in nanoscience [4, 5].

Nowadays, gold colloid nanoparticles can be routinely manufactured. In the literature an enormous amount of work related to gold nanoparticle synthesis can be found. On the one hand, there are extensive studies where the fundamentals of the gold reduction process are described. This includes the synthesis of gold nanoparticles with tailored shape, size and stability [6]. On the other hand, the applications of these nanoparticles to several areas, such as medicine, electronic, catalysis, etc., constitute another important source of specialized manuscripts [7, 8]. Finally, there are basic studies devoted to find natural materials or chemical compounds with reducing properties [9-11]. They should be able to reduce the gold present in aqueous solution to metallic gold in the form of colloid nanoparticles. Moreover, it is important to embed these nanoparticles into a polymer matrix for practical applications.

In this manuscript three different materials with capacity to reduce gold ions were selected. Two of them are synthetic compounds obtained after mixing silica gel with a strong chelating agent: ethylene diamine tetraacetic acid (EDTA) or diethylene triamine pentaacetic acid (DTPA), a widely used sequestering compounds with multiple applications [12-15]. These functionalized materials, namely EDSG and DTSG, were previously prepared, characterized and successfully tested for the elimination of Ni and Co from aqueous solution [16-19]. The other material used in this work was the brown macroalga *Sargassum muticum*, an invasive species in European waters with a great potential as adsorbent for different contaminants [20-22].

The organic groups present in these materials (e.g. hydroxyl, amino, carboxyl, etc.) are able to induce the gold recovery from aqueous solution via chemical. This technique, called one-pot method, is based on a non-seeded mediated mechanism, where the synthesized gold colloid nanoparticles evolve to form different structures [6]. Operating in this way there is no control over the morphology of the gold colloid nanoparticles, obtaining a wide variety of shapes and sizes. Then, the objective of this work is not to obtain defined nanoparticles with a high yield, but to study the range of optimal conditions to recovery the gold initially presented in aqueous solution through its reduction. This includes the study of multiple factors that influence the metal reduction in batch and continuous experiments, such as: the dose of material, solution pH, kinetic of the process, regeneration agents and presence of other metals in solution.

Recently, Lodeiro et al. [23] studied the application of these materials for the recovery of gold from artificial seawater, but this is the first time that EDSG, DTSG and *S. muticum* are used to recover gold from aqueous solution.

2. EXPERIMENTAL SECTION

2.1 Materials

The chelating agents, EDTA and DTPA, were used to functionalize silica gel (LiChroPrep® Merck in powder form: diameter: 63–200 μm, surface area: 540 m^2/g) and to prepare the synthetic materials used in this work: EDSG and DTSG. The procedure to obtain these materials was described by Repo *et al*. [16, 17].

The brown marine alga *Sargassum muticum* was collected from the coast of A Coruña (NW Spain). After washing with tap and deionized water the samples were dried in an oven at 60 ºC overnight. The dried samples were crushed with an analytical mill (IKA A 10) and sieved to a size range of 0.5-1 mm. In order to improve its physical and

chemical properties, the biomass was protonated following the procedure from Figueira *et al*. [24]. The resulted material was storaged in polyethylene bottles until use.

2.2 Metal analysis

The samples were analyzed by an inductively coupled plasma optical atomic emission spectrometer (ICP-OES), model iCAP 6300 (Thermo Electron Corporation, USA). After filtering (0.45 μm acetate filter) and diluting with 2% HNO_3, the metal concentration in solution was measured at the following wavelengths: 242.7-267.5 nm for Au, 267.7 for Cr, 228.6 nm for Co, and 231.6 nm for Ni. The minimum detectable concentrations for Au, Cr, Co, and Ni ions by this equipment were 1.0, 1.1, 0.4, and 0.8 μg/L, respectively. The measurements of the samples were performed at least by triplicate.

The metal removal percentages were calculated from the expression:

where C_i is the initial metal concentration and C_f is the final metal concentration.

$$\text{Removal } \% = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

2.3 Effect of dosage

$HAuCl_4 \cdot 3H_2O$ salt was used to prepare 0.25 mM gold solutions. Ten mL of these solutions were added to essay tubes containing different quantities of EDSG and DTSG in order to obtain material dosages of 0.1, 0.5, 1, 2 and 4 g/L. The materials were put into contact with the metal solutions by magnetic agitation (each batch experiments). Gold concentration was measured following the procedure showed above after 24 and 216 hours (EDSG) or 72, 96 and 144 hours (DTSG) of contact time.

2.4 Effect of pH

The effect of pH, measured using a combined glass electrode (WTW SenTix 81meter), was studied at a fixed dosage (4 g/L). The studied gold concentrations in aqueous solution were 0.05 and 0.5 mM ($HAuCl_4 \cdot 3H_2O$). The solution pH was adjusted to

equilibrium values between 1 and 8 using HNO_3 or NaOH (Merck) for EDSG and DTSG. Equilibrium pH values in solution were between 1 and 3.5 when the protonated *Sargassum muticum* was used. Gold concentration in solution was measured as stated above after 24 hours of contact time.

2.5 Kinetic studies

The effect of contact time on gold recovery was studied at room temperature mixing 0.4 g each of EDSG, DTSG and *S. muticum* into sealed glass cells containing 100 mL of gold solutions ($HAuCl_4 \cdot 3H_2O$) with different initial concentrations (0.05, 0.25 or 0.5 mM). pH values were recorded during the entire kinetics.

2.6 Regeneration studies

The gold deposited in EDSG and DTSG during the experiments conducted at fixed pH (3.0) and gold initial concentration (0.5 mM) was recovered using thiourea 0.5 M in HCl 1 M. The gold-saturated materials were dried overnight in an oven at 60 ºC. After, they were put into contact with the regeneration agent during 24 and 120 hours (dosage of 4 g/L). The quantity of gold returned back to solution was measured as mentioned above.

2.7 Effect of metal competition

CrO_3, $Co(NO_3)_2 \cdot 6H_2O$, and $Ni(NO_3)_2 \cdot 6H_2O$ salts (Sigma-Aldrich) were used to prepare solutions of different initial metal concentration (0.05, 0.5 and 5 mM). These solutions containing also gold (0.5 mM), were put into contact with DTSG (dosage of 4 g/L) during 96 hours. Equilibrium pH values of the solutions were recorded. Au, Cr, Ni and Co, were measured by ICP-OES as described above.

2.8 Column studies

EDSG was selected for column studies. Plastic columns with an internal diameter of 0.5 cm were filled with 0.05, 0.1, 0.2 or 1 g of EDSG. Gold standard (1000 mg/L Au in

HNO_3, Sigma-Aldrich) was used to prepare 0.05 mM Au solutions that were fed through the columns in down-flow mode using a Watson Marlow peristaltic pump (1, 5 and 10 mL/min). The pH value was measured in the effluent solution. The operation of the column was stopped when the gold concentration in the effluent remained constant.

2.9 Characterization of the materials

2.9.1 FTIR analysis

EDSG, DTSG and protonated *S. muticum* materials were analyzed using FTIR spectroscopy before and after their use in gold recovery experiments. The samples were examined within the range 350–4000 cm^{-1} using a Bruker Vertex 70 spectrophotometer equipped with a Speac Golden Gate ATR (Attenuated Total Reflection) device.

2.9.2 SEM analysis

The surface morphology of the adsorbents was characterized by scanning electron microscope (SEM) analysis, recorded on a JEOL JSM 6400 SEM equipped with an Oxford Inca Energy 200 system for Energy Dispersive X-ray Spectroscopy (EDS). The examinations were carried out at different magnifications (from 45 to 8000×) at a 20 kV acceleration voltage.

3. RESULTS AND DISCUSSION

Gold recovery from aqueous solutions under different experimental conditions (not fixed ionic strength) was studied in this work. Two materials derived from silica gel (EDSG and DTSG) and a brown macroalga (*S. muticum*) were used. In a previous manuscript it was demonstrated the potential of these materials for gold recovery from artificial seawater [23]. In order to compare both studies and denote the different mechanisms involved, a similar experimental arrangement was proposed.

First, the effect of material's dosage on gold elimination from aqueous solution was studied. As in the case when artificial seawater was used, no significant differences were found between the doses tested when contact time was enough. Only with the minimum dose tested (0.1 g/L) the gold initially present in solution (0.5 mM) was not totally removed after 24 or 72 hours of contact time using EDSG or DTSG, respectively. Dosage experiments showed that as the dose is decreased, the equilibrium time for gold recovery is significantly increased. Then, to ensure a reliable equilibrium time and not to use an excessive quantity of material, a dose of 4 g/L was selected.

Another important parameter that must be carefully examined is the solution pH. It controls metal speciation and the ionization state of the chemical groups present in the materials. Moreover, protons can actively participate in the redox reactions involving gold and the organic groups of the materials. At acidic pH, high gold concentration (>0.01 M) and chloride excess, it was demonstrated that $AuCl_4^-$ complex is the predominant species in aqueous solution [25]. In this work, speciation diagrams at several initial gold concentrations (from 0.05 to 0.5 mM) were obtained using the software program Hydra-Medusa [26]. The formation of the solid species $Au(OH)_3(s)$ was not considered since evidence of its appearance was not found during the experiments. From the results (Figure S1) it was observed that at pH values equal or higher than 3 the presence of the neutral species $Au(OH)_3$ is predominant. For pH values between 1 and 3 the speciation diagrams showed the presence of different charged gold compounds, highlighting the species $AuCl_4^-$. Electron-transfer reactions should be included in the speciation diagrams in order to considerer the coupled redox reactions between gold and some organic groups in the materials. Nevertheless, their structural complexity makes very difficult to know unequivocally which specific groups are involved and the values for the corresponding redox potentials. However,

experimental evidences using Raman spectroscopy technique demonstrated that no neutral gold species are formed under these conditions [25]. Moreover, at pH values between 1-4 and in absence of chloride excess, the complex $AuCl_4^-$ is less stable and might be hydrolyzed to $AuCl_3OH^-$. This reaction appears at lower pH values in solutions with decreasing gold concentrations.

The gold recovery from aqueous solution using EDSG and DTSG is not pH dependent (values between 1 and 5). After 24 hours of contact time gold was totally removed from solution independently of the equilibrium pH value. Considering the macroalga *S. muticum*, it was observed that final equilibrium pH was always lower than 3.5. Initial pH values were adjusted from 1 to 8, but the great buffer effect of the protonated algae makes final pH values to be between 1 and 3.5. Other authors using a different brown macroalga previously observed this behavior [27]. In this range of pH no significant differences were found in the gold recovery by the alga.

The ionization state of the chemical groups present in the material's surface is very important in adsorption processes [28]. The chemistry of these functionalities is also essential when reduction reactions are involved. The determination of the quantity and type of titratable chemical groups present in protonated *S. muticum*, EDSG and DTSG materials were previously studied by potentiometric studies [29]. The titration of the algae *S. muticum* revealed the presence of two main acid functionalities: carboxyl and hydroxyl groups. Regarding EDSG and DTSG it was quantified the presence of different amino groups, but the existence of hydroxyl and carboxyl functionalities was also suggested. These groups are probably involved in the retention of gold by a complex mechanism. It can include electrostatic interactions of the charged chloro-gold species with the protonated amine and hydroxyl groups at low pH; and redox reactions, where the oxidation of several groups, such as amine and hydroxyl functionalities,

makes Au(III) ions to be reduced to Au(0). Other authors also proposed the implication of hydroxyl radical groups as well as free hydrogen radicals [30]. Gold agglomerates and nanoparticles, which remain attached to the material's surface, can be formed as a consequence of these redox reactions. A continuous color change in the surface of the materials was observed during the gold recovery experiments carried out in this study. The color change from yellow-white (EDSG and DTSG) or brown (*S. muticum*) to purple-gray-black, more and more intense as the redox reaction proceeded (gold surface plasmon resonance effects), confirmed the formation of gold colloid nanoparticles.

Different regeneration agents were used to recover the gold previously deposited on the surface of the materials. Moreover, these studies allowed to better understanding the gold recovery process. First, HNO_3 and NaOH were tested at different concentrations without success. This demonstrated that ionic exchange is not the predominant mechanism during the gold recovery process. Only a strong complexing reagent for gold leaching, such as thiourea, was able to recovery a significant amount of the gold previously reduced using EDSG (97% in 120 hours under acidic conditions). Therefore, Au(0) is supposed to be initially presented on the surface of the materials studied. The following reaction describes this process:

$$Au^0 + 2CS(NH_2)_2 \leftrightarrow Au[CS(NH_2)_2]_2^+ + e^- \quad (2)$$

3.1 Kinetic studies

The kinetic study of the gold recovery from aqueous solution was not easy to carry out due to the high speed of the processes that take place. Around 53 and 80% of the gold initially present (0.5 mM) was removed from solution during the first minute of contact time, using EDSG and DTSG, respectively. To recover all the gold dissolved in aqueous solution (99%) it was necessary only 20 (EDSG) or 10 (DTSG) minutes. When the initial gold concentration was diminished, to 0.05 mM (EDSG) or to 0.25 mM (DTSG)

a small decrease in the retention percentages was observed after the first minute of contact time (44 or 69%), while total gold recovery was attained after 35 (EDSG) or 12 (DTSG) minutes. The pH was measured and presented a value between 2.8 and 3.2 during the entire kinetic experiments. When the protonated seaweed was used, the gold recovery kinetic was significantly slower. During the first minute of contact time it was retained a 3.4% of the gold initially present in the aqueous solution. After 220 minutes this percentage was raised to 95%, while only after 16 hours no significant gold was measured in the solution. In this case, pH was between 2.5 and 2.9.

As stated before, the fast processes involved in gold recovery avoided the attainment of true kinetic data (not equilibrium). Only with EDSG and *S. muticum* enough representative data was obtained to apply a kinetic model (Figures 1 and 2). Moreover, as other studies demonstrated, the presence of reduced gold on the material surface produces a rapid increase in the reaction rate as a result of the autocatalytic redox reaction that take place [31].

In this study and others related, it is easy to demonstrate that Au(III) is reduced to Au(0) in presence of materials containing oxidizable groups [9, 10, 32]. There are many examples in the literature where the description of a metal reduction, such as Cr(VI), follows a first-order kinetics with respect to metal concentration and the amount of oxidizable groups in the materials used [33, 34]. When the algae *S. muticum* and other biomass of biological origin are used, the implication of hydroxyl and carboxyl groups is normally stated [21, 27, 35, 36]. On the other hand, synthetic materials such as EDSG and DTSG present amino groups that can also undergo oxidation [16]. In this paper, the number of oxidizable groups capable to reduce Au(III) from aqueous solution was calculated following the procedure of Park *et al.* [37]. The number of these groups was 6 (EDSG and *S. muticum*) and 7 (DTSG) mmol/g. Nevertheless, only a small part of

them actively participate in gold reduction, since the initial gold concentration in solution is low and the oxidizable groups are always present in great excess.

The reduction kinetic model presented here involves the complete and irreversible gold reduction. The following equation is proposed to represent gold reduction in aqueous solution:

$$OG + Au(III) \rightarrow OG(oxidized) + Au(0) \quad (3)$$

where *OG* represents the groups in the material with potential to reduce Au(III).

Considering a first order reaction with respect to *OG* groups and Au(III) concentration and also that the *OG* groups have a similar kinetic equation, reacting in parallel, the following equation can be deduced [34]:

$$\frac{d[Au(III)]}{dt} = k[OGt][Au(III)] \quad (4)$$

k, being the kinetic constant of the reaction, depends on the total fraction of oxidizable compounds, and [*OGt*] the concentration of the total oxidizable compounds.

If it is considered the reduction in the *OG* group's reactivity as they undergo oxidation, then it can be obtained:

$$[OGt] = [OGt]_0(1 - X_{ox}) \quad (5)$$

$$X_{ox} = \frac{\Delta[Au(III)]}{[OGt]_0} = \frac{[Au(III)]_0 - [Au(III)]}{[OGt]_0} \quad (6)$$

$$[OGt]_0 = C_0[M] \quad (7)$$

where $[OGt]_0$ represents the concentration of compounds capable of reducing Au(III), X_{ox} the fraction of oxidized groups, C_0 the concentration of oxidizable groups per gram of biomass and [M] the material's dose. From equations 4-7 it can be obtained the following relation used to fit kinetic data:

$$[Au(III)] = \frac{[Au(III)]_0[M]C_0 - [Au(III)]_0^2}{[M]C_0 e^{k[M]C_0 t} - [Au(III)]_0 t - [Au(III)]_0} \quad (8)$$

Data fit was carried out minimizing the sum of the difference from the experimental and theoretical logarithms of the squared gold concentrations in aqueous solution (Figures 1 and 2). Solver tool from Excel software was used. Fitted parameters were k and C_0.

In Table 1 it is shown the parameters for EDSG and protonated *S. muticum*. Simultaneous fit of EDSG data at two different concentrations, 0.05 and 0.5 mM, was carried out. The kinetic constant, k, was considered in common for both data series (independent of initial gold concentration), while C_0 was considered to vary with the metal concentration.

As expected, the values of C_0 obtained from the fit were lower than the previously obtained via experiments (see above) which implies that not all the oxidizable groups participate in gold reduction. Furthermore, the kinetic constant obtained for EDSG was more than 35 times higher than the found for the protonated seaweed, accordingly to the kinetic rate observed.

This simple model was able to describe in an accurate way the kinetic data (regression coefficients shown in Table 1 were obtained using the knife model [38]) and also allowed to obtain important parameters such as k and C_0. This also supports the mechanism based on the reduction of the Au(III), initially present in aqueous solution, to Au(0) colloid nanoparticles.

3.2 Effect of metal competition

The effect on gold recovery of the presence of Ni, Co or Cr(VI) in aqueous solution was studied using DTSG. The results showed that after 96 hours of contact time the gold (0.5 mM) was completely removed from solution when the competitive metals were presented at 0.05, 0.5 and 5 mM initial concentrations. Then, it was evidenced that there is no competition effect of those metals on gold recovery from aqueous solution.

Speciation studies under these conditions demonstrated that cobalt and nickel appear in aqueous solution as divalent cations (Co^{+2} and Ni^{+2}) at pH values between 1-7. The speciation diagram for Au species in presence of cobalt, nickel or chromium is not changed due to these competitive metals. The negative species $AuCl_3OH^-$ is predominant at low gold concentration and no excess of chloride.

The pH values in solution varied between 1.7 and 3.2, depending on the metal concentrations. The mechanism of Ni and Co removal by DTSG is mainly based on an ion exchange process, and their recovery values are similar to the ones obtained in a previous work in the absence of gold (not identical conditions) [16, 17]. In this case, when the initial concentration was 0.05 mM, the recoveries were 100 and 96 %, for Ni and Co, respectively. Increasing the initial concentration to 0.5 mM the Ni was also completely removed from the aqueous solution, while the recovery of Co was reduced to 61%. At the highest concentration tested, 5 mM, the recovery of both metals were near 30%. The groups responsible for the adsorption of Ni^{+2} and Co^{+2} ions are probably not participating in the reduction of gold (or at least not interfering) and then, its recovery is not affected by their presence in solution. Nevertheless, Cr(VI) is expected to be reduced in presence of materials containing chemical groups with tendency to oxidation [39, 40], in a similar way than the proposed for gold recovery. Speciation diagrams for Cr(VI) (0.05 and 0.5 mM) showed that at pH between 1 and 5 more than 95% of chromium is presented as $HCrO_4^-$ and around 4% as $Cr_2O_7^{-2}$. When the initial Cr(VI) concentration was increased to 5 mM $HCrO_4^-$ and $Cr_2O_7^{-2}$ represent around 78 and 22% of the total species in aqueous solution, respectively. In this case, chromium is presented as negative species, like gold. The obtained recovery percentages for Cr(VI) were 91, 81 and 64% for initial concentrations of 0.05, 0.5 and 5 mM, respectively. The fact that gold was preferentially eliminated by DTSG can be justified based on the

higher redox potential value for the gold reduction reaction, making this process more favorable [41]. In addition, it is probable that the negative chromium species does not adsorb in the DTSG surface before its reduction, as others authors suggest when it interacts with different materials [42, 43]. Then, the possible interaction of gold with DTSG is not affected by the presence of chromium in solution.

3.3 Column studies

Different quantities of EDSG (0.05, 0.1, 0.2 and 1 g) were used to fill plastic columns in order to carry out continuous experiments of gold recovery at three different flow rates (1, 5 and 10 mL/min). The pH measurements were done in the outlet of the columns. The obtained values were always between 2.8 and 3.0.

In Figure 3 it is shown the breakthrough curves obtained at fixed flow rate (5 mL/min) varying the bed depth of the column. As expected, the increase in the quantity of EDSG produced higher values for the breakthrough point of the curves. The breakthrough point was defined as the point when the relation between the gold concentrations in the inlet and outlet is equal to 0.1. It was exceeded after passing less than 25 and 330 mL of gold solution for columns containing 0.05 and 0.1 g, respectively. When the mass of EDSG inside the column was increased up to 0.2 g the breakthrough took place after more than 100 hours (27 L passed). After passing more than 46 L the column was stopped. The gold concentration in the effluent was only 0.0003 mM. On contrary, the saturation of the column occurred after passing 32 and 51 L of gold solution on a column filled with 0.05 and 0.1 g of EDSG, respectively.

Moreover, when the column was filled with 1 g of EDSG (flow rate of 1 mL/min) the maximum gold concentration found in the effluent was always lower than 2% of the inlet concentration (0.005 mM). This column was stopped after passing 20 L of gold solution with no evidence of saturation of the EDSG gold removal capacity.

Using a fixed mass of EDSG of 0.2 g and varying the flow rate (figure not shown), the breakthrough point was reached after more than 1 and 100 hours for 10 and 5 mL/min, respectively. When the flow rate was diminished to 1 mL/min the gold concentration in the effluent solution was always lower than 0.0002 mM (17 L of gold solution were passed).

In the column, the oxidizable groups present in the EDSG are in great excess with respect to the gold existing in the aqueous solution. Then, under favourable conditions of flow rate (1 mL/min) and quantity of material in the column (0.2 g or more), the gold presented in the influent solution can be removed in percentages greater than 95 %. Visual evidences of the continuous reduction of gold were obtained. The initial white-yellow colour of the material was continuously changed to a purple-black, showing the plasmon resonance effect occurring in the gold surface. As the influent was passed the change in colour was expanding through the column.

A regeneration study was carried out using the column filled with 0.1 g of EDSG. After passing 51 L of solution at a flow rate of 5 mL/min, the column was saturated with 25 mg of gold. Then, a 0.5 M thiourea solution in HCl 1M was recirculated through the column in up-flow mode at 1 mL/min. The column was stopped when 97% of the precious metal was returned back to solution. Following, a fresh gold solution (0.005 mM) was feed to the column, obtaining the breakthrough curve showed in Figure 3. This curve is sharper than the obtained in the first cycle. The saturation of the column was achieved after passing 26 and 51 L of gold solution for the second and first cycle, respectively. Nevertheless, the breakthrough point was achieved after more than 4 hours while in the first cycle only 1 hour was enough to exceed this point.

3.4 Characterization of the materials

The characterization of the materials was studied using several techniques. The quantification of the type and number of the protonable chemical groups present in the surface of the materials tested can be found in previous studies [23, 29]. Potentiometric acid-base titrations allowed identifying the main functionalities involved in metal sequestration. The presence of two main acid functionalities: carboxyl and hydroxyl groups, was determined for the alga *S. muticum*. Regarding the synthetic materials, EDSG and DTSG, amino groups were identified as the main functionalities, but the presence of hydroxyl entities was also suggested. In this case, the existence of carboxylic groups, present in the material's surface, could not be quantified by potentiometric titrations.

FTIR is a useful technique for qualitative determination of surface chemical groups. Spectra interpretation is sometimes a difficult task when natural or heterogeneous materials are analyzed. Nevertheless, it can be a valuable technique to provide confirmation about the presence or absence of certain chemical groups.

In a previous work FTIR analysis of EDSG, DTSG and *S. muticum* was carried out before and after gold recovery experiments in artificial seawater [23]. In this case, FTIR spectra of the materials after kinetic experiments at different initial gold concentrations were studied. The results were comparable to the obtained in artificial seawater, and the presence of gold in the surface of these materials did not produce significant changes in their FTIR spectra. Moreover, the FTIR analysis of the materials after metal competition and desorption experiments showed the appearance of new bands in the same way that occurred when gold was recovered from artificial seawater. In Figure 4 and Table 2 it is shown some of the FTIR spectra obtained and the band assignment, respectively. Details about band assignation and spectra interpretation can be found in a previous work [23].

SEM analysis was carried out to obtain information about the structure of the materials and to confirm the presence of nanoparticles and different chemical elements. Using this technique it was possible to check the presence of gold nanoparticles and aggregates of different shapes and sizes in the surface of the studied materials.

In Figure 5 it is shown two examples of the obtained back-scattered electron images after gold recovery from solution under different conditions using EDSG and *S. muticum*. The bright points in these pictures were identified as gold. The SEM image obtained for EDSG clearly shows gold particles of different shapes: triangles, spheres, hexagons and wires.

A detailed chemical analysis of the SEM image obtained after the kinetic experiment using DTSG (Au 0.05 mM) is shown in Figure S2. As expected, carbon, oxygen, silicon and gold are the main chemical elements found. Moreover, an example of the position and identification of the different elements present in the SEM images using a RX map is shown in Figure S3. In this way the presence of gold nanoparticles attached on the EDSG surface was highlighted.

No gold was detected in the SEM images obtained after the regeneration studies (Figure not shown). This confirms the success of thiourea as desorbent agent.

It is worth mentioning that using this SEM under the mentioned conditions it is difficult to detect particles whose diameter is less than 40 nm.

4. CONCLUSIONS

Based on the results showed above it can be concluded that the gold removal from aqueous solution is mainly based on a reduction mechanism.

The lack of pH dependence found in the experiments implies that the groups involved in gold complexation are protonated in the pH interval studied. Moreover, this could also

indicate an instant reduction reaction of the gold species not favored by previous electrostatic interactions with the charged groups of the materials.

The presence of different metals in solution did not affect the gold reduction reaction. Batch and continous experiments showed a high yield in gold recovery from aqueous solution.

The oxidation of the hydroxyl and/or amino groups produced a continuous formation of reduced gold on the surface of the materials. The following general reactions that could describe the process are proposed:

$$AuCl_3OH^- + 3e^- \leftrightarrow Au(s) + 3Cl^- + H_2O$$

$$R - OH \leftrightarrow R = O + H^+ + e^-$$

$$R_3N^- - H + H_2O \leftrightarrow R_3N^+ - OH + 2H^+ + 2e^-$$

The colour change observed during the experiments and the FTIR and SEM studies confirmed that the gold initially presented in solution was reduced to gold colloid nanoparticles.

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TABLES

Table 1. Parameters obtained from the fit of the kinetic data of gold recovery from aqueous solution using EDSG and *S. muticum*. pH= 3.0±0.2, dose of 4 g/L.

	[Au] 0.05 mM			[Au] 0.5 mM		
	k $L \cdot mmol^{-1} \cdot min^{-1}$	C_0 $mmol \cdot g^{-1}$	r^2	k $L \cdot mmol^{-1} \cdot min^{-1}$	C_0 $mmol \cdot g^{-1}$	r^2
EDSG	3.5±0.6	0.020±0.002	0.898	3.5±0.6	0.125±0.00005	0.983
Sargassum muticum				0.096±0.002	0.124±0.0004	0.881

Table 2. Band assignment for FTIR spectra obtained for: EDSG, EDSG after contact with Au 0.5 mM solution and EDSG after gold recovery from its surface using thiourea 0.5 M in HCl 1 M.

Wavenumber (cm^{-1})	**Band assignment**
2750-3500	Stretching of –OH / -NH groups
1400-1500	NH in plane bend and CN stretching vibrations (amide II) / stretching of C=O in carboxylic groups
1056-1065	Si-O-Si stretching / C-N stretching of aliphatic amines / C-O stretching of alcohols
795	Si-O bending
697	Si-H / N-H wagging
450	Si-O out of plane deformation

FIGURE CAPTIONS

Figure 1. Kinetic of Au recovery at different initial metal concentrations: 0.05 mM (a) and 0.5 mM (b) by EDSG. pH= 3.0±0.2, dose of 4 g/L. The lines represent the fit of kinetic data to equation 8.

Figure 2. Kinetic of Au 0.5 mM recovery by *S. muticum*. pH= 2.7±0.2, dose of 4 g/L. The line represents the fit of kinetic data to equation 8.

Figure 3. Breakthrough curves for gold recovery from solution at different EDSG quantities: 0.05 (circles), 0.1 (triangles), and 0.2 g (squares) and fixed flow rate of 5 mL/min. Filled triangles represent data from a second column cycle after desorption experiment (0.1 g of EDSG at 5 mL/min).

Figure 4. FTIR spectra for EDSG (black continuous line), EDSG + Au 0.5 mM after 31 hours of contact (gray dashed line) and EDSG containing gold + thiourea 0.5 M + HCl 1M after 48 hours of contact (gray pointed line).

Figure 5. RX maps of EDSG (2000x) after competition experiment with Au 0.5 mM and Co 5 mM, contact time of 96 hours (a); and *S. muticum* (8000x) after contact (54 hours) with Au 0.5 mM (b).

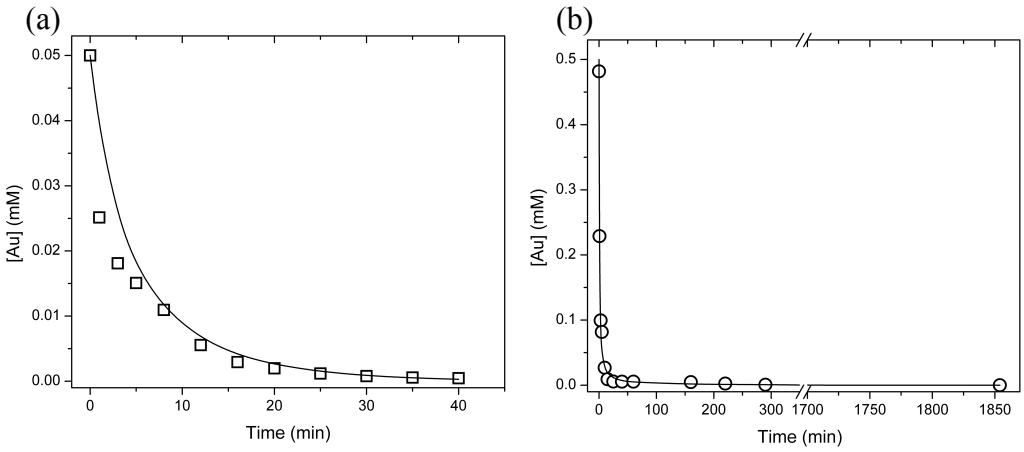

(a)
[Au] (mM)
0.05
0.04
0.03
0.02
0.01
0.00
0
10
20
30
40
Time (min)
(b)
[Au] (mM)
0.5
0.4
0.3
0.2
0.1
0.0
0
100
200
300
1700
1750
1800
1850
Time (min)

Figure 1

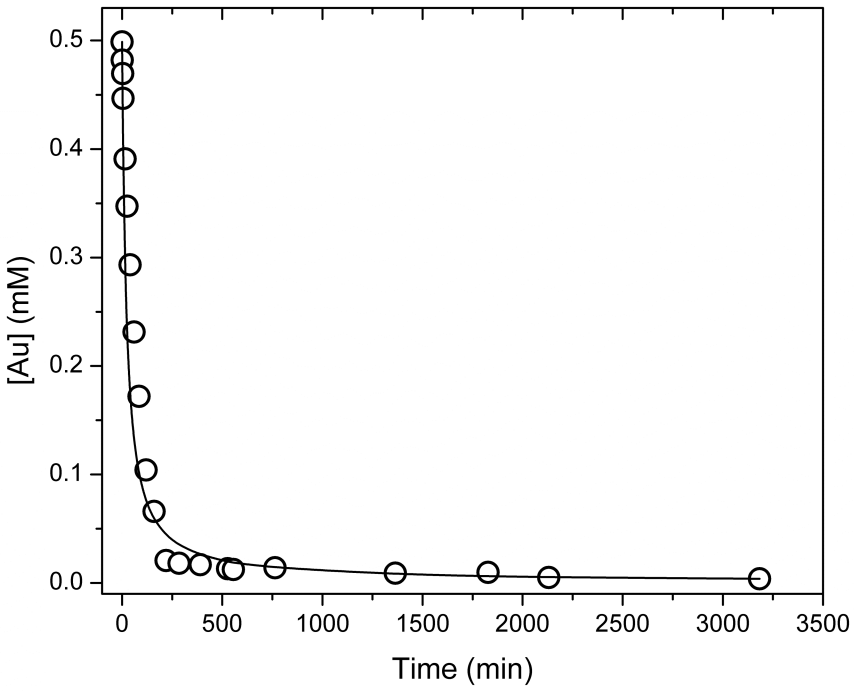

[Au] (mM)
0.0
0.1
0.2
0.3
0.4
0.5
0
500
1000
1500
2000
2500
3000
3500
Time (min)

Figure 2

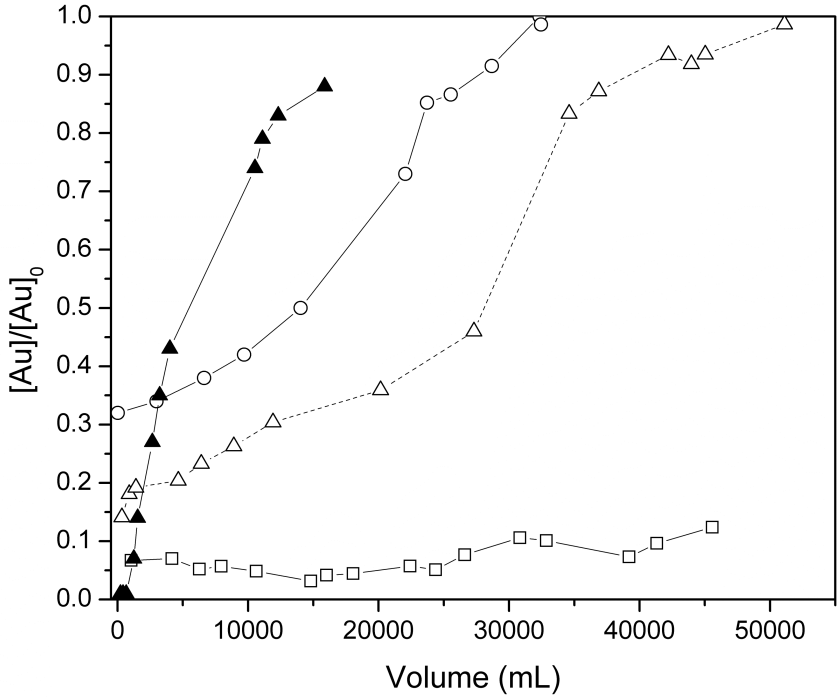

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
[Au]/[Au]0
0
10000
20000
30000
40000
50000
Volume (mL)

Figure 3

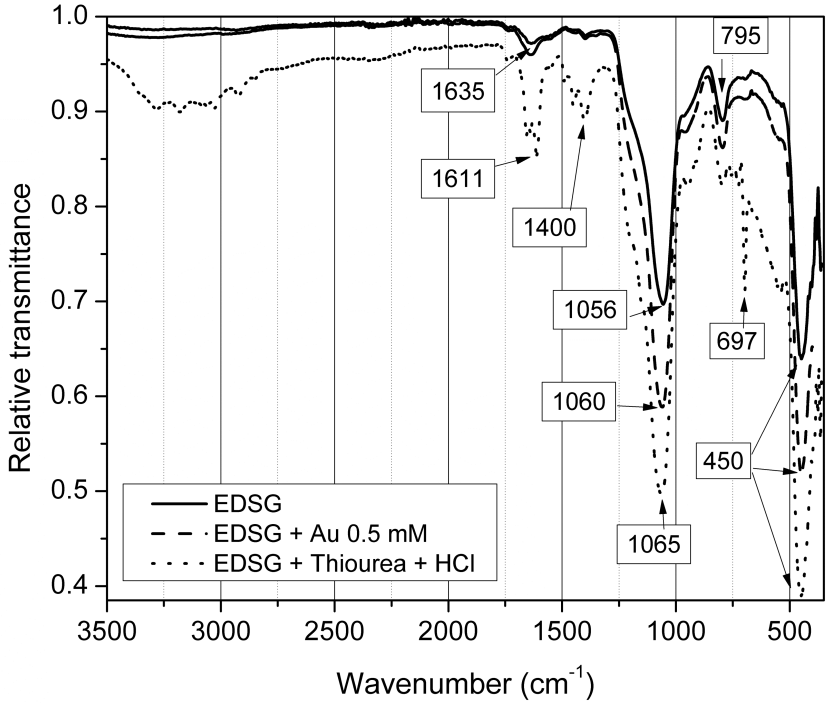
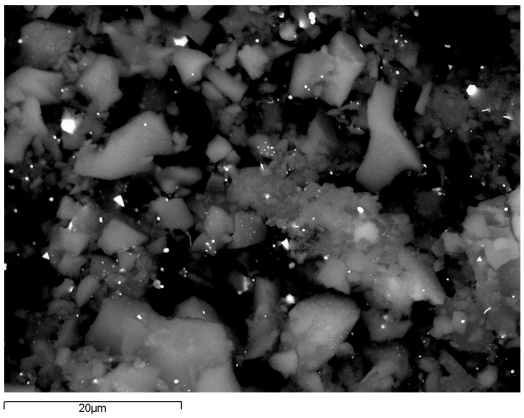

Relative transmittance
Wavenumber (cm-1)
EDSG
EDSG + Au 0.5 mM
EDSG + Thiourea + HCl
1635
1611
1400
1056
1060
1065
795
697
450

Figure 4

(a)



(b)

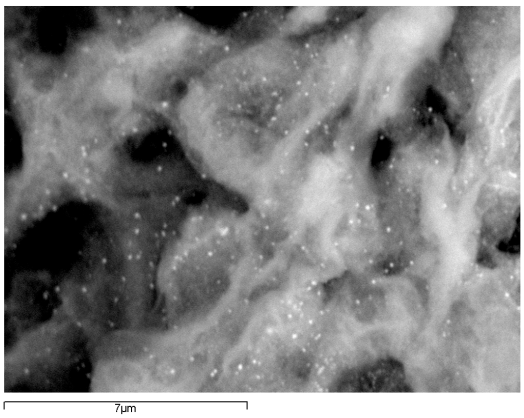


Figure 5

Electronic Supplementary Material available