

Article

# Uptake and Recovery of Gold from Simulated Hydrometallurgical Liquors by Adsorption on Pine Bark Tannin Resin

Maria Beatriz Q. L. F. Torrinha, Hugo A. M. Bacelo, Sílvia C. R. Santos \* , Rui A. R. Boaventura  and Cidália M. S. Botelho

Laboratory of Separation and Reaction Engineering—Laboratory of Catalysis and Materials (LSRE-LCM), Chemical Engineering Department, Faculdade de Engenharia da Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal; up201305818@fe.up.pt (M.B.Q.L.F.T.); up201204895@fe.up.pt (H.A.M.B.); bventura@fe.up.pt (R.A.R.B.); cbotelho@fe.up.pt (C.M.S.B.)

\* Correspondence: scrs@fe.up.pt

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**Abstract:** The recovery of critical and precious metals from waste electrical and electronic equipment (WEEE) is an environmental and economic imperative. Biosorption has been considered a key technology for the selective extraction of gold from hydrometallurgical liquors obtained in the chemical leaching of e-waste. In this work, the potential of tannin resins prepared from *Pinus pinaster* bark to sequester and recover gold(III) from hydrochloric acid and aqua regia solutions was assessed. Equilibrium isotherms were experimentally determined and maximum adsorption capacities of  $343 \pm 38$  and  $270 \pm 19$  mg g<sup>-1</sup> were found for Au uptake from HCl and HCl/HNO<sub>3</sub> (3:1 v/v) solutions containing 1.0 mol L<sup>-1</sup> H<sup>+</sup>. Higher levels of acidity (and chloride ligands) significantly impaired the adsorption of gold from both kinds of leaching solutions, especially in the aqua regia system, in which the adsorbent underperformed. Pseudo-first and pseudo-second order models successfully described the kinetic data. The adsorbent presented high selectivity towards gold. Actually, in simulated aqua regia WEEE liquors, Au(III) was extensively adsorbed, compared to Cu(II), Fe(III), Ni(II), Pd(II), and Zn(II). In three adsorption–desorption cycles, the adsorption capacity of the regenerated adsorbent moderately decreased (19%), although the gold elution in acidic thiourea solution had been quite limited. Future research is needed to examine more closely the elution of gold from the exhausted adsorbents. The results obtained in this work show good perspectives as regards the application of pine bark tannin resins for the selective extraction of Au from electronic waste leach liquors.

**Keywords:** precious metals; hydrometallurgical processing; biosorption; selectivity; pine bark

## 1. Introduction

Gold is a precious metal commonly used in jewellery and electronics [1], but also in medicine and as a catalyst in various chemical processes [2]. Waste electrical and electronic equipment (WEEE) is a fast-growing waste stream. In 2019, 53.6 Mt of e-waste were generated in the world, corresponding to an average of 7.3 kg per capita [3]. Globally, however, only 17.4% was documented to be formally collected and recycled [3]. In Europe, the management of WEEE is regulated by the Directive 2012/19/EU [4], which states that, from 2019, member states should achieve an annual collection rate of WEEE of 65% of the average weight of EEE placed on the market in the three preceding years. Although Europe was the continent presenting the highest rate (42.5%), collection and recycling must increase even further to meet the target [3]. WEEE contains bulky metals, along with plastics and toxic elements, but also technology metals which, in the frame of a circular economy, should be recovered. The content of

precious/critical metals in WEEE vary considerably, but in certain types of WEEE can even exceed those found in primary sources [5–7]. For instance, levels of 250–2050 ppm of gold have been reported in waste printed circuit boards [8]. However, greener and more economically competitive routes are necessary to extract metals from WEEE and achieve sustainable processes.

The recovery of precious metals from e-waste usually involves dismantling, comminution, and separation [8–10], chemical pre-treatments to dissolve base metals [10,11], followed by pyrometallurgical and/or hydrometallurgical processes. Despite the challenges related to the use of strong acids in leaching processes, and the need to minimise the loss of chemicals, hydrometallurgical processes have been considered a cleaner option to be integrated at the back-end of a recycling scheme for the recovery and production of high purity metals [6,7,12]. They also have lower capital costs and benefit from easier implementation at the small scale. Cyanide has been the dominating leaching reagent of Au from primary resources [13] and possibly the most reliable and economic for WEEE [10]. However, the toxicity of cyanide makes its use prohibitive in modern processes. Alternative leaching reagents have been proposed to dissolve Au from WEEE, including chloride, aqua regia, thiourea and thiosulfate [13]. The subsequent stage of a typical flowsheet is the extraction of gold from leaching liquors. Among the various techniques that can be implemented, adsorption has been the dominant one, especially in cyanide liquors, and due to a favourable cost-effectiveness [14], in which activated carbon has been for decades the adsorbent of choice [15,16]. The current interest in moving forward a more benign recovery has been motivating the search for alternative adsorbents, at more competitive prices and able to sequester gold from non-cyanide leach liquors. The use of bio-derived adsorbents has been regarded as a key technology [17], offering advantages related to the ready availability of the biomass, to the simple synthesis and chemical functionality, which usually make them good sequestrants of metals. Important criteria to be met by biosorbents for gold recovery include: (i) high uptake capacity of the metal from actual matrices; (ii) selectivity, i.e., adsorbents should be able to uptake gold to the detriment of other base metals and noble metals coexisting in solution; (iii) fast adsorption kinetics; and (iv) feasible subsequent recovery of the adsorbed metal. In addition, the adsorbents should have particle sizes suitable for use in fixed bed systems, avoiding pressure drop and column clogging, and should have also good chemical stability in strong acidic solutions, considering this is the condition of typical gold-bearing liquors [18]. Various adsorbents have been investigated for gold recovery, including commercial resins [19,20], crosslinked polyethyleneimine resin [19], and a wide range of natural-derived adsorbents such as polyethylenimine modified  $\text{Ca}^{2+}$ -alginate fibres [18], polyethylenimine modified *Lagerstroemia speciosa* leaves [21], banana peel derivatives [22], raw date pits [23], and tannin-derived materials [6,24–26]. The successful uptake of gold has been explained by electrostatic interaction between the gold complexes in solution and the adsorbent surface, followed by a reduction mechanism, involving amine, hydroxyl, and aldehyde groups of the adsorbents [18,21,27,28].

Tannins are natural polyphenolic macromolecules present in leaves, wood, bark, seeds and fruits of various plants. Their abundance in nature, easy extraction with water, richness in hydroxyl groups and easy tailoring have made tannin materials interesting biosorbents for the removal of contaminants from water and for the uptake and recovery of precious metals [26]. Tannin resins may be prepared through a crosslinking reaction (gelification) with aldehydes [24,25]. Further chemical modifications, such as anchoring of amine groups [24,29] are possible to improve the adsorptive performance of the materials. Immobilization in support materials [28,30] and magnetization [24] have been also investigated to enhance solid-liquid separation. Outstanding uptake capacities of gold have been reported for different tannin-derived biosorbents [24,27,29], explained by the oxidation of polyhydroxyl groups and the reduction of the metal to its elemental form [24,28]. Literature on the recovery of gold by tannin adsorbents has been however limited to few sources of the precursor, namely tannin acid, commercial tannins, valonea, and persimmon tannins [26,28–30]. Despite the fact that pine bark tannin resins have been investigated to remove pollutants from water, in a remediation perspective [31–33], no studies were found in the literature evaluating the uptake of precious metals by this material and

subsequent recovery. More research is also needed to obtain results in aqua regia solutions and stronger chloride and acidic media.

This work comes in response to the need of economical and environmentally competitive processes for the recovery of precious metals from WEEE. The adsorption of gold(III) by a tannin resin prepared from bark of maritime pine (*Pinus pinaster*) is studied. The bark of this native Mediterranean tree is a forest residue and a by-product of wood conversion industry, which can give a contribute to bioeconomy. Chloride and aqua regia solutions were used, and the uptake of gold was investigated from single and multi-metal systems, simulating actual hydrometallurgical liquors. The final recovery of the metal was achieved by elution.

## 2. Materials and Methods

### 2.1. Adsorbent

A tannin resin, prepared from maritime pine (*P. pinaster*) bark, was used in this work as adsorbent. *P. pinaster* bark was collected (direct sampling) from the coastal North region of Portugal, milled using a regular coffee grinder resulting a final particle size distribution of (percentages by mass, % *w/w*): 40% in the fraction <0.15 mm, 24% in the range 0.15–0.50 mm, 29% of 0.50–1.0 mm, and 7% of 1.0–2.0 mm. Tannins were extracted from the pine bark in batch mode, using an alkaline aqueous solution of 7.5 % NaOH (% *w/w*, in respect to the bark), and a bark-to-liquid ratio of 1:6 (*w/w*). The extraction was carried out under magnetic stirring at a temperature of 90 °C and for a contact time of 60 min. These extraction conditions were the best found in a previous work [33]. After solid-liquid separation (suction filtration, using a vacuum pump), the resulting solution was neutralized with HCl 2.0 mol L<sup>-1</sup> and subjected to freeze-drying (FreeZone 2.5 Plus, Labconco, Kansas City, MO, USA). NaOH and HCl solutions were prepared from analytical grade salt and acid, respectively. The obtained solid extract was converted into an insoluble material by a cross-linking reaction (gelification). For this purpose, 3.0 g of tannin extract were solubilized in 12.0 mL of a 0.25 mol L<sup>-1</sup> NaOH solution and mixed with 0.6 mL of formaldehyde (36% *w/w*, analytical grade). The reaction was carried out at 80 °C in digestion vessels for 8 h. The precipitate was dried, milled, washed with HCl 0.05 mol L<sup>-1</sup> (prepared from analytical grade 37% *w/w* acid) and distilled water, and dried at 65 °C. These operating conditions were also selected according to the optimization studies previously conducted [33]. Particle size analysis was performed by laser diffraction (Coulter LS230, Beckman Coulter, Pasadena, CA, USA): 32%, 43%, 14%, and 11%, respectively found for particles sizes < 0.15 mm, 0.15–0.50 mm, 0.50–1.0 mm, and 1.0–2.0 mm. The fraction 0.15–0.50 mm was selected and used as adsorbent in the present work. The point of zero charge of the pine bark tannin resin was 6.2 ± 0.1 [33]. The high chemical stability of the adsorbent at acidic conditions was demonstrated by low values of dissolved organic carbon concentration at pH 2.0 (4.98 ± 0.07 mg-C L<sup>-1</sup>), for a tannin resin dosage of 2.0 g L<sup>-1</sup> and a contact time of 24 h [33].

Scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS) were used to observe the morphology and detect the chemical elemental composition in the tannin adsorbent surface, before and after adsorption of gold. The SEM/EDS exam was performed at CEMUP-LMEV (Materials Centre of the University of Porto—Laboratory for Scanning Electron Microscopy and X-ray Microanalysis) using a high resolution (Schottky) environmental scanning electron microscope with X-ray microanalysis and electron backscattered diffraction analysis (Quanta 400 FEG ESEM/EDAX Genesis X4M). Samples were coated with a gold/palladium thin film by sputtering, using the SPI Module Sputter Coater equipment.

### 2.2. Gold Solutions

In this work, gold(III) was used as adsorbate. Aqueous solutions of the metal, with concentrations ranging from 10 to 550 mg-Au L<sup>-1</sup>, were prepared by dilution of a commercial standard 1000 mg-Au L<sup>-1</sup>, containing 2 mol L<sup>-1</sup> HCl. Considering the aim of the study, to evaluate the uptake of Au(III) from

chloride and aqua regia liquors, two types of strong acidic solutions containing different levels of  $H^+$  were used as aqueous matrices: hydrochloric acid (HCl) and a mixture of hydrochloric acid and nitric acid (HCl/HNO<sub>3</sub> in a ratio of 3:1 (*v/v*), molar ratio of 2.6:1.0). The desired HCl and HNO<sub>3</sub> concentrations were obtained by the addition of analytical grade commercial acid solutions (HCl 37% *w/w*, density 1.19 g mL<sup>-1</sup>; HNO<sub>3</sub> 65% *w/w*, density 1.39 g mL<sup>-1</sup>) and taking into account the pre-existing HCl concentration in the gold standard solution.

### 2.3. Analytic Methods

The analysis of dissolved metals (Au and Cu, Fe, Ni, Pd, Zn—multi-metal experiments) in aqueous solutions was performed by AAS (Atomic Absorption Spectroscopy), with flame atomization (GBC Scientific 932 Plus, Australia). The calibration plots were taken daily and accepted for coefficients of determination ( $R^2$ ) higher than 0.995. In particular, the dissolved gold was measured by air-acetylene flame, using a hollow-cathode lamp operating at 242.8 nm, intensity of 4.0 mA. Potassium nitrate (analytical grade) was added to the standards and samples at final concentrations of 2000 mg-K L<sup>-1</sup>, in order to suppress ionization.

### 2.4. Adsorption Studies

Adsorption studies were conducted in batch mode. Accurately measured volumes of Au solutions (15.0 mL) were put in contact with the required amount of adsorbent (depending on the adsorbent dosages defined in the Sections 2.4.1–2.4.4) in Erlenmeyer closed flasks. Suspensions were stirred in an orbital shaker, operating at 280 rpm. Samples taken from the suspensions were filtered using cellulose acetate membranes (0.45 μm porosity), the liquid phase was diluted when necessary and analysed for metal concentration. All the experiments were made in duplicate and results presented as the average values with corresponding uncertainties (absolute deviations or propagated errors).

#### 2.4.1. Effect of the Leaching Reagent

Aqueous solutions of 100 mg-Au L<sup>-1</sup> were prepared in HCl, using acid concentrations varying from 0.2 to 3.7 mol L<sup>-1</sup>, and in aqua regia (HCl/HNO<sub>3</sub>) dilutions with total  $H^+$  varying from 0.3 to 4.2 mol L<sup>-1</sup>. These solutions were mixed with the tannin resin (adsorbent dosage of 2.0 g L<sup>-1</sup>) and stirred for two days. The uptake percentages of gold from the initial solution was calculated by Equation (1), where  $C_0$  and  $C_e$  denote gold concentrations (mg L<sup>-1</sup>) in the initial and the final solutions, respectively.

$$\text{Uptake (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

#### 2.4.2. Adsorption Equilibrium Isotherms

Adsorption equilibrium data allow for the design and optimization of the adsorption systems and provide information on the capacity of an adsorbent to accumulate the adsorbate on its surface. Equilibrium isotherms were obtained for the adsorption of Au(III) by the tannin resin at 20 °C and for different aqueous matrices: HCl 1.0 mol L<sup>-1</sup> and 2.0 mol L<sup>-1</sup>, and aqua regia (3:1 *v/v* HCl/HNO<sub>3</sub>) dilutions corresponding to 1.0, 1.4 and 2.0 mol L<sup>-1</sup> total  $H^+$  levels. The experimental data was obtained using solutions with initial concentrations of Au in the range 10–550 mg L<sup>-1</sup> and a constant solid-to-liquid ratio ( $S/L = 1.0$  g L<sup>-1</sup>). Adsorbent dosages in the range 0.3–3.0 g L<sup>-1</sup> have been reported in literature [34–36] for gold uptake. Usually, a higher adsorbent dosage provides a higher uptake efficiency, but a lower usage capacity of the solid [31]. Considering the results obtained with 2.0 g L<sup>-1</sup> (effect of leaching reagent, previous subsection), it was decided to use a lower solid-to-liquid ratio (1.0 g L<sup>-1</sup>) to ensure that final measurable gold concentrations (significantly different from zero) would be obtained to plot the isotherm. Suspensions were stirred for 72 h (enough to attain the steady state). The amount of metal adsorbed per gram of adsorbent in the equilibrium ( $q_e$ , in mg

Au per g of tannin resin) was calculated as a function of the final Au concentration in equilibrium ( $C_e$ , mg L<sup>-1</sup>) by the mass balance expressed by Equation (2).

$$q_e = \frac{C_0 - C_e}{S/L} \quad (2)$$

Langmuir [37] and Freundlich [38] models, expressed by Equations (3) and (4), respectively, were fitted to experimental data by non-linear regression. In Equation (3),  $Q_m$  (mg g<sup>-1</sup>) symbolizes the maximum uptake capacity, corresponding to the monolayer coverage assumed by the Langmuir model, and  $K_L$  denotes a constant related to the energy of adsorption. In Equation (4),  $K_F$  and  $n$  are constants related to the adsorption capacity and adsorption intensity, respectively.

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

$$q_e = K_F C_e^{1/n} \quad (4)$$

#### 2.4.3. Kinetic Study

The contact time effect on the amount of adsorbed Au was studied using 1.0 mol L<sup>-1</sup> HCl solution and aqua regia at the same HCl level (total H<sup>+</sup> concentration of 1.4 mol L<sup>-1</sup>), adsorbent dosages of 0.5, 1.0 and 2.0 g L<sup>-1</sup>, and different initial Au concentrations (100 mg L<sup>-1</sup> and 300 mg L<sup>-1</sup>). The liquid solutions were stirred with the tannin resin for different periods of time, at room temperature (20 ± 2 °C). Control assays (with no adsorbent) were conducted in parallel. After designated times, suspensions were immediately filtered, and the liquid phase analysed for Au concentration ( $C$ ). The amount of Au adsorbed per gram of tannin resin ( $q$ , mg g<sup>-1</sup>) at each contact time ( $t$ ) was calculated by Equation (5).

$$q = \frac{C_0 - C}{S/L} \quad (5)$$

Lagergren's pseudo-first order and pseudo-second order reaction-based models have been widely applied in numerous adsorption systems, due to their simplicity and the commonly good fittings generated. Despite their questionable significance and fairly empirical nature [39], these models were also employed in the present work. Lagergren's pseudo-first order [40] and pseudo-second order models [41,42] are represented by Equations (6) and (7). In these expressions,  $q$  and  $q_e$  (mg g<sup>-1</sup>) symbolize the amount of gold adsorbed per mass unit of adsorbent, at time  $t$  (h) and at equilibrium, respectively, and  $k_1$  (h<sup>-1</sup>) and  $k_2$  (g mg<sup>-1</sup> h<sup>-1</sup>) are the kinetic constants.

$$q = q_e [1 - \exp(-k_1 t)] \quad (6)$$

$$q = q_e \frac{q_e k_2 t}{1 + q_e k_2 t} \quad (7)$$

In addition, an intraparticle diffusion model was also used. Linear Driving Force (LDF) approximation (Equation (8)) [43] assumes that the uptake rate of an adsorbate is proportional to the difference between the adsorbed phase concentration at the solid/fluid interface ( $q^*$ , given by Langmuir model) and the average adsorbed phase concentration in the particle ( $q$ ). The calculation of the LDF constant ( $k_{LDF}$ ) was done using the explicit equation (Equation (12)) that results from Equation (8), combined with the use of the variables expressed in Equations (9)–(11) [44]. The solver tool in Excel was used to obtain  $k_{LDF}$  constants, by minimizing the sum of squared residuals. The calculation of  $D_p$ , based on Equation (13) [45], assumes spherical adsorbent particles ( $r_p$  denotes the average particle radius) and a parabolic profile of metal concentration inside the particle.

$$\frac{\partial q}{\partial t} = k_{LDF} \times (q^* - q) \quad (8)$$

$$\xi = \frac{Q_m}{C_0} \times S/L \quad (9)$$

$$y = \frac{C}{C_0} \quad (10)$$

$$a = \xi - 1 + \frac{1}{K_L \cdot C_0}; b = \frac{1}{K_L \cdot C_0}; \alpha = \frac{-a + \sqrt{a^2 + 4b}}{2}; \beta = \frac{-a - \sqrt{a^2 + 4b}}{2} \quad (11)$$

$$t = -\frac{1}{k_{LDF}} \left\{ \frac{1}{2b} \times \ln \left[ \frac{y^2 + ay - b}{a - b + 1} \right] + \left( 1 - \frac{a}{2b} \right) \left( \frac{1}{\alpha - \beta} \right) \times \ln \left[ \frac{(1 - \beta)(y - \alpha)}{(1 - \alpha)(y - \beta)} \right] \right\} \quad (12)$$

$$k_{LDF} = \frac{15D_h}{r_p^2} \quad (13)$$

#### 2.4.4. Competitive Adsorption and Selectivity

The dissolution of precious metals from WEEE is usually preceded by chemical pre-treatments to dissolve base metals (e.g., copper, lead) [10]. However, certain amounts of these metals remain in the residue, together with the precious metals, and are leached out with gold in the subsequent steps. The presence of these metals in solution may affect the adsorption capacity of the adsorbent, due to possible competition. In addition, if an adsorbent sequesters significant amounts of other metals, besides gold, the generation of a final high purity recovered product may be compromised. Assessing the performance of an adsorbent in a multi-metal solution simulating an actual hydrometallurgical liquor is therefore important. Multi-metal solutions containing Au(III) (200 mg L<sup>-1</sup>), Cu(II) (200 mg L<sup>-1</sup>), Fe(III) (150 mg L<sup>-1</sup>), Ni(II) (80 mg L<sup>-1</sup>), Zn(II) (10 mg L<sup>-1</sup>) and Pd(II) (40 mg L<sup>-1</sup>) were prepared in aqua regia (0.75, 1.3 and 2.0 mol L<sup>-1</sup> H<sup>+</sup> solutions). The desired concentration of each metal was obtained by the dilution of commercial metal standards (1000 mg L<sup>-1</sup>) or, in the case of Cu(II), by the dissolution of CuCl<sub>2</sub>·2H<sub>2</sub>O salt. The metal composition of the simulated solutions was based on the levels reported in literature for aqua regia liquors of WEEE [25,29]. Simulated leaching solutions were then mixed with the tannin resin at an adsorbent dosage of 1.0 g L<sup>-1</sup>. After 72 h of stirring, the concentration of each metal was analysed in the liquid and uptake percentages and adsorbed amounts calculated (Equations (1) and (2)). Control assays were conducted in parallel, in similar conditions, but using single-metal solutions (200 mg-Au L<sup>-1</sup>).

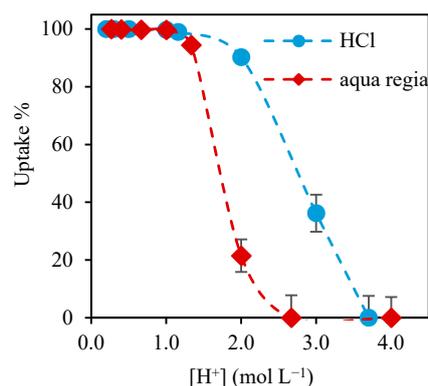
#### 2.5. Desorption and Regeneration

Desorption and regeneration studies were conducted in order to evaluate the recovery of gold by elution from exhausted adsorbents and the possibility to reuse the regenerated material. A sample of Au-loaded adsorbent was prepared by stirring the tannin resin (1.0 g L<sup>-1</sup>) with 500 mg L<sup>-1</sup> Au solution, prepared in HCl 1.0 mol L<sup>-1</sup> H<sup>+</sup>. After the saturation with gold, the adsorbent was separated from the remaining liquid by vacuum filtration, washed with distilled water and dried at 50 °C overnight. The first desorption stage was conducted using a solid-to-liquid ratio of 2.5 g L<sup>-1</sup> and two different eluents: acid thiourea solution (0.5 mol L<sup>-1</sup> thiourea and 0.5 mol L<sup>-1</sup> HCl) and HCl 50% (v/v). After 3 days stirring, the liquid phase was analysed for Au and the desorbed percentage calculated. Adsorption and desorption steps were repeated for 3 cycles, using the thiourea solution as eluent.

### 3. Results and Discussion

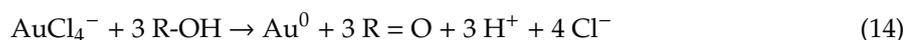
#### 3.1. Effect of the Leaching Solution

Figure 1 presents the results on gold(III) uptake from aqueous matrices containing different levels of HCl and HCl/HNO<sub>3</sub>. In both aqueous systems, the acidity of the medium affects the amount of gold adsorbed by tannin resin.



**Figure 1.** Effect of hydrogen ion concentration ( $[H^+]$ ) on the uptake of gold by the pine bark tannin resin from HCl and HCl/HNO<sub>3</sub> (aqua regia) aqueous solutions.

Total removal of gold from HCl solutions is achieved up to 1.2 mol L<sup>-1</sup> H<sup>+</sup>. Above 2.0 mol L<sup>-1</sup> HCl, the uptake of the metal is seriously affected, and for 3.7 mol L<sup>-1</sup> HCl is practically suppressed. Results can be explained considering the effect of H<sup>+</sup>, but also the presence of Cl<sup>-</sup> ligands, and their effect on the adsorbate species (gold complexes) and on the adsorbent surface. The adsorption mechanism that has been proposed for the uptake of gold by tannin materials is based on an electrostatic attraction followed by the reduction of Au(III) and the oxidation of hydroxyl groups [19,24]. The redox reaction is expressed by Equation (14), where the reduction of the chlorogold complex is accompanied by the oxidation of hydroxyl to carbonyl groups [46].



Under the HCl concentrations used in this study, Au should be present in solution as tetrachloroaurate(III) complex ( $\text{AuCl}_4^-$ ) (speciation diagram presented in [47]), and the resin surface should present a high positive charge. These conditions favour the uptake of Au complexes by electrostatic attraction, which explains the good results observed up to 1.2 mol L<sup>-1</sup> HCl. However, an excessive increase in HCl concentration (and consequently, in H<sup>+</sup> and Cl<sup>-</sup> levels) impairs the reduction of gold (Equation (14)), and chloride ions, abundantly present in solution, may also compete with  $\text{AuCl}_4^-$  to the active sites of the adsorbent [19,24]. This explains the marked reduction in the gold uptake observed for HCl levels above 2.0 mol L<sup>-1</sup>.

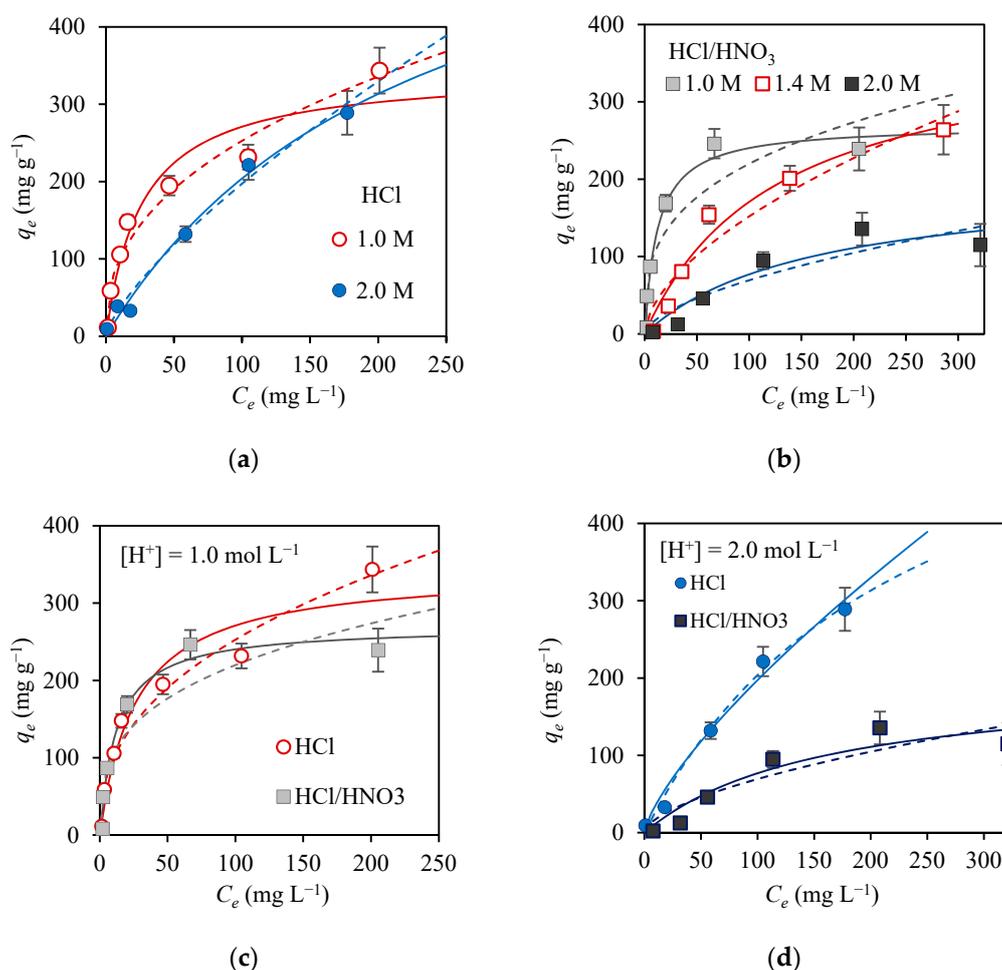
With regards to the aqua regia, Figure 1 shows that 100% of gold in HCl/HNO<sub>3</sub> solutions is sequestered by the tannin resin for acidic levels below 1.0 mol-H<sup>+</sup> L<sup>-1</sup>. The adsorptive ability sharply decreased for higher acid concentrations and ceases at 2.7 mol L<sup>-1</sup> H<sup>+</sup> (corresponding to 2.0 and 0.7 mol L<sup>-1</sup> of HCl and HNO<sub>3</sub>, respectively), results that can be explained in the same way as for the HCl solutions. As it can be seen, for acidity levels higher than 1.2 mol-H<sup>+</sup> L<sup>-1</sup>, the tannin resin exhibits a higher performance for the uptake of Au(III) from HCl solutions than from aqua regia, and it is much more affected by the acid concentration in the latter system than in the former. This means that the presence of nitric acid in solution impairs the uptake of Au by the adsorbent, being a result of the strong oxidizing capacity of aqua regia which hinders the reduction of Au(III) [25].

The results here obtained are generally in line with those reported in literature. Fan et al. [25] studied the adsorption of Au(III) by a persimmon tannin in HCl and HNO<sub>3</sub> media. Under the studied conditions, the adsorbent performance was only significantly reduced for HCl and HNO<sub>3</sub> concentrations higher than 3.74 and 3 mol L<sup>-1</sup>, respectively. The adsorbent performed better in HCl than in HNO<sub>3</sub> aqueous medium. Yi et al. [29] studied the effect of HCl concentration on the adsorption of gold(III) by ethylenediamine modified persimmon tannin adsorbent and reported a gradual decrease in the Au uptake when the H<sup>+</sup> concentration rose from 0.1 to 5.82 mol L<sup>-1</sup>. Al-Saidi [23] reported an increase in Au(III) removal by raw date pits for HCl concentrations up to 0.5 mol L<sup>-1</sup>, but a decrease in the uptake efficiency above this level. Most of literature studies were conducted using HCl aqueous

matrices. In the present study we have investigated also the use of aqua regia because it is also employed as leaching solution for WEEE, superior to chloride leaching in some criteria [10,13]. Several works have also evaluated the uptake of gold under HCl levels equal and lower than  $0.1 \text{ mol L}^{-1}$ , corresponding to pH values between 1 and 5–6 [18,21,22], which are weaker acidic conditions than those used in the present work. In fact, our experiments were carried out by using  $1.0\text{--}2.0 \text{ mol L}^{-1}$  (HCl and HCl/HNO<sub>3</sub> solutions), closer to the H<sup>+</sup> concentration in actual leach liquors of WEEE, even though that acid levels below  $1.0 \text{ mol L}^{-1}$  would assure a greater adsorbent performance.

### 3.2. Adsorption Equilibrium Isotherms

Figure 2 shows adsorption isotherms obtained for the uptake of gold by the tannin resin, in different acidic systems (HCl and aqua regia).



**Figure 2.** Equilibrium isotherms for the adsorption of gold by the pine bark tannin resin from different acidic matrices ( $20 \text{ }^\circ\text{C}$ ,  $S/L = 1.0 \text{ g L}^{-1}$ ): effect of H<sup>+</sup> concentration in (a) HCl and (b) aqua regia solutions; effect of the leaching solution for a total H<sup>+</sup> concentration of (c) 1.0 and (d) 2.0 mol L<sup>-1</sup>.  $C_e$  denotes the gold concentration in the liquid phase, in equilibrium with the metal adsorbed amount,  $q_e$ . Langmuir and Freundlich models are represented by solid and dashed lines, respectively.

In line with the previous results, Figure 2a,b shows a negative effect of increasing the solution acidity. The slope of the isotherms for low equilibrium concentrations gives indication about the affinity adsorbent/adsorbate, and in both charts (Figure 2a,b), the decrease of adsorption is evident for higher H<sup>+</sup> concentrations. However, the results show that the negative influence of acid concentrations tends to cease as the Au concentration increases. The adsorbed amounts of Au from  $1.0 \text{ mol L}^{-1}$  HCl solution

are significantly higher than the ones recorded at 2.0 mol L<sup>-1</sup> only for equilibrium gold concentrations below 100 mg L<sup>-1</sup>, but are practically the same for higher adsorbate levels (Figure 2a). The same happens when it comes to aqua regia (Figure 2b), as the isotherms measured at 1.0 and 1.4 mol L<sup>-1</sup> H<sup>+</sup> get closer for Au concentrations of ca. 200 mg L<sup>-1</sup>. This is reflected by the similarity of the maximum adsorbed amounts obtained experimentally ( $q_{e,m}$ , Table 1) for 1.0 and 2.0 mol L<sup>-1</sup> HCl, and for 1.0 and 1.4 mol L<sup>-1</sup> H<sup>+</sup> aqua regia. The use of 2.0 mol L<sup>-1</sup> of H<sup>+</sup>, however, impaired more dramatically the uptake ability, as even for higher Au levels the adsorbed amounts remained significantly below the values obtained at 1.0 and 1.4 mol L<sup>-1</sup>.

**Table 1.** Parameters of Langmuir and Freundlich isotherms for the adsorption of gold from HCl and aqua regia solutions using pine bark tannin resin, at 20 °C, and comparison between the maximum adsorbed amounts obtained experimentally ( $q_{e,m}$ ) and from Langmuir modelling ( $Q_m$ ).

	exp.		Langmuir			Freundlich			
	$q_{e,m}$ (mg g <sup>-1</sup> )	$Q_m$ (mg g <sup>-1</sup> )	$K_L \times 10^3$ (L mg <sup>-1</sup> )	R	SE (mg g <sup>-1</sup> )	$K_F$ (mg <sup>1-1/n</sup> g <sup>-1</sup> L <sup>1/n</sup> )	n	R	SE (mg g <sup>-1</sup> )
HCl Solution									
1.0 mol L <sup>-1</sup> H <sup>+</sup>	344 ± 30	343 ± 38	38 ± 13	0.97	31.0	38 ± 7	2.4 ± 0.3	0.98	23.7
2.0 mol L <sup>-1</sup> H <sup>+</sup>	289 ± 28	675 ± 152	4 ± 2	1.00	12.6	7 ± 2	1.4 ± 0.1	0.99	15.7
Aqua Regia Solution									
1.0 mol L <sup>-1</sup> H <sup>+</sup>	246 ± 19	270 ± 19	81 ± 21	0.99	19.3	51 ± 21	3 ± 2	0.91	47.2
1.4 mol L <sup>-1</sup> H <sup>+</sup>	264 ± 32	386 ± 62	8 ± 3	0.98	20.9	10 ± 6	1.7 ± 0.3	0.96	31.5
2.0 mol L <sup>-1</sup> H <sup>+</sup>	136 ± 21	200 ± 65	6 ± 4	0.95	19.3	5 ± 4	1.7 ± 0.5	0.92	24.8

Figure 2d compares isotherms measured from HCl and aqua regia matrices, under the same total H<sup>+</sup> concentrations. For 1.0 mol L<sup>-1</sup> H<sup>+</sup>, the two isotherms are quite similar, mainly for low gold concentrations. For 2.0 mol L<sup>-1</sup> H<sup>+</sup>, the performance of the tannin resin is unquestionably worst under aqua regia solutions (Figure 2d). In this case, the maximum adsorbed amounts, recorded within the experimental conditions were 289 mg g<sup>-1</sup> in HCl solution and 136 mg g<sup>-1</sup> in aqua regia solution (Table 1). Such behaviour should be related to the strong oxidizing power of aqua regia that inhibits the reduction of Au and limits the sequestering ability of the adsorbent. Therefore, the use of HCl as a leaching agent for gold in hydrometallurgical processes has proven to create more favourable conditions than aqua regia, considering its subsequent uptake and recovery.

The parameters of Langmuir and Freundlich models are shown in Table 1. The coefficients of correlation (R) and the standard error of the regressions (SE) are also presented, as measures of the quality of the fittings. Modelled curves are illustrated in Figure 2. As it can be seen, both equilibrium models described quite well the experimental data. Considering the higher correlation coefficients and the lower standard errors, the Langmuir model provided better fittings (exception is the isotherm measured at 1.0 mol L<sup>-1</sup> HCl). Despite this, in the experimental range of concentrations studied and in certain conditions (e.g., 2.0 mol L<sup>-1</sup> HCl; 1.4 and 2.0 mol L<sup>-1</sup> HNO<sub>3</sub>/HCl), the maximum experimental adsorbed amounts (denoted as  $q_{e,m}$ , in Table 1) are lower than the  $Q_m$  values predicted by Langmuir model. This is an indication that the monolayer capacity was not attained, which means that the adsorbent still has capacity to sequester more gold ions from solution. Indeed, other studies present similar observations. A continuous rise of the isotherm curve, even for Au equilibrium concentrations of 1500–2000 mg L<sup>-1</sup>, has been reported for the adsorption of gold by crosslinked polyethylenimine/calcium-alginate fibres, and attributed to a continuous reduction process of Au(III) [18].

In a general way, and despite the negative effect of H<sup>+</sup> and aqua regia, pine bark tannin resin showed an excellent ability to sequester and accumulate gold on its surface in all the conditions tested. Table 2 presents maximum adsorption capacities of gold(III) reported in the literature for different adsorbents. In order to allow a suitable comparison, maximum adsorbed amounts obtained experimentally ( $q_{e,m}$ ) and from Langmuir modelling ( $Q_m$ ) are presented, together with the most relevant operating conditions. The pine bark tannin resin presents adsorbed amounts in the range of the reported values for other biosorbents. Looking only at the uptake capacities of gold, its performance

seems to be comparable to the banana peel derived adsorbent and PEI-modified *L. speciosa* leaves, superior to some other biosorbents or synthetic polymers (e.g., commercial resin Lewatit TP214, raw date pits, activated rice husk), but worse than other tannin adsorbents. However, it is worth noting that the adsorption capacity of the pine bark tannin resin was evaluated here under more harsh acidic conditions ( $1.0 \text{ mol L}^{-1}$  acid solutions) than most of the data collected from literature and referred in Table 2. Although strong acidic conditions are more representative of the actual conditions found industrially, it is known that they impair the uptake of gold (Figure 1; [25,29]). On this basis, it can be said that pine bark tannin resin proved to be a promising material for gold uptake.

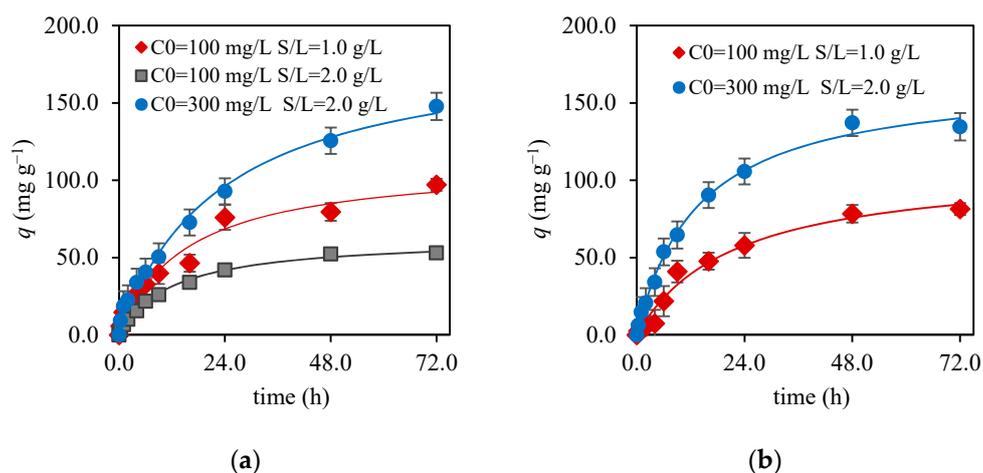
**Table 2.** Maximum adsorption capacities reported in literature for the adsorption of gold from chloride media by different adsorbents: maximum adsorbed amounts, obtained experimentally ( $q_{e,m}$ ) and calculated monolayer capacities ( $Q_m$ ) by Langmuir modelling.

Adsorbent	T (K)	pH or $[\text{H}^+]$	$C_e$ ( $\text{mg L}^{-1}$ )	$q_{e,m}$ ( $\text{mg g}^{-1}$ )	$Q_m$ ( $\text{mg g}^{-1}$ )	Ref.
Commercial resin IRA400		pH 2	0–215		902.3	[19]
Commercial resin Lewatit TP214	298	pH 6.1	35–225		108.7	[20]
Polyaniline modified by TMP	298	pH 4	0–300	881	883	[48]
Crosslinked PEI resins		pH 2	0–210		943.5	[19]
NIPA gel	323	$1 \text{ mol L}^{-1}$	0–790		125.5	[49]
Activated rice husk	298	pH 6.1	50–260		93.46	[20]
PEI-alginate fibers	298	$0.1 \text{ mol L}^{-1}$	0–2000	1240	1404	[18]
GA-PEI-alginate fibers	298	$0.1 \text{ mol/L}$	0–1500	2325	2182	[18]
Cellulose acetate fibers	298	$2 \text{ mol L}^{-1}$	0–800	110		[50]
Raw date pits	298	$0.5 \text{ mol L}^{-1}$	0–35	78	61	[23]
Banana peel	298	pH 1	0–1200	370.18	377.2	[22]
Banana peel (lipid extraction)	298	pH 1	0–1000	475.48	448.4	[22]
Oil palm trunk (dewaxed)	303	pH 2	0–120	91.47	95.16	[35]
PEI-modified <i>L. speciosa</i> leaves	298	pH 1	0–200	282	286	[21]
Persimmon resin	303	pH 2	150–351	$\approx 965$	1905	[36]
Persimmon peel gel	303	$0.1 \text{ mol L}^{-1}$	$0-11 \times 10^3$	$1.8 \times 10^3$		[51]
Crosslinked persimmon tannin gel	303	$0.1 \text{ mol L}^{-1}$	$0-2.4 \times 10^3$	1517		[34]
TEPA-persimmon tannin gel	303	$0.1 \text{ mol L}^{-1}$	$0-1.2 \times 10^3$		1168	[6]
EDA-modified persimmon tannin	303	$0.1 \text{ mol L}^{-1}$	$0-1.5 \times 10^3$		1550.4	[29]
persimmon tannin onto						
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> microspheres	298	pH 5	$(0.2-1.8) \times 10^3$	860	917.4	[24]
persimmon tannin						
functionalized viscose fiber	298	pH 2	0–120	528	536	[28]
Sericin and alginate particles						
chemically crosslinked by	298	pH 2.5–3	0–140	196.1	188.4	[27]
proanthocyanidins						
Pine bark tannin resin	298	$1 \text{ mol L}^{-1}$	0–200	344	343	This work
Pine bark tannin resin	298	$1 \text{ mol L}^{-1}$ (HCl/HNO <sub>3</sub> )	0–200	246	270	This work

EDA—ethylenediamine; GA—glutaraldehyde; NIPA—N-isopropylacrylamide; PEI—polyethylenimine; TEPA—tetraethylenepentamine; TMP—trimethyl phosphate.

### 3.3. Kinetic Study

The effect of contact time on the uptake of gold was studied at  $20 \text{ }^\circ\text{C}$ , for different adsorbate concentrations, solid-to-liquid ratios and acidic aqueous matrices. The kinetic profiles are presented in Figure 3 and show a relatively slow adsorptive process, with equilibrium times of two or three days. Similar contact times were found by Gurung et al. [34], with persimmon tannin resins, although other authors report considerably lower values (8 h) [36]. The slow kinetics on the gold uptake appears to be a shortcoming of many biosorbents, but this has been explained by the reductive process of gold, which is essential for high uptake capacities.



**Figure 3.** Effect of contact time on the uptake of gold by the pine bark tannin resin at 20 °C, different initial gold concentrations, adsorbent dosages and using aqueous solutions of (a) 1.0 mol L<sup>-1</sup> HCl (a) and (b) aqua regia 1.0 mol L<sup>-1</sup> H<sup>+</sup>: experimental data and pseudo-second order modelling.

The adsorption dynamics is a result of a multi-step process involving [52,53]: (i) transport through the external film up to the surface of the adsorbent, (ii) intraparticle diffusion (in pores and/or over the surface), and (iii) final adsorption reaction on the active sites. The last step is usually very fast and do not determine the overall adsorption rate [52]. In well-stirred batch systems, the external resistance of mass transfer can be also considered negligible. Despite the fact that the adsorption reaction is also usually fast, Lagergren's pseudo-first order and pseudo-second order reaction-based models have been widely applied in numerous adsorption systems, due to their simplicity and the commonly good fittings generated. Table 3 presents kinetic parameters for Lagergren's pseudo-first and pseudo-second order models. As it can be seen, both models describe very well the experimental data, with all coefficients of correlation equal or higher than 0.98. Despite the fact that the pseudo-second order model (Figure 3) has mostly provided the lowest SE, the pseudo-first order predicted equilibrium adsorbed amounts ( $q_e$ ) closest to the experimental values.

**Table 3.** Kinetic parameters of reaction-based models ( $k$ , kinetic constants;  $q_e$ , equilibrium adsorbed amounts) for the adsorption of gold from HCl and aqua regia solutions by the pine bark tannin resin, at 20 °C and for different initial Au(III) concentrations ( $C_0$ ) and adsorbent dosages ( $S/L$ ).

$C_0$ (mg L <sup>-1</sup> )	$S/L$ (g L <sup>-1</sup> )	Pseudo-First Order Model				Pseudo-Second Order Model			
		$q_e$ (mg g <sup>-1</sup> )	$k_1 \times 10^2$ (h <sup>-1</sup> )	R	SE (mg g <sup>-1</sup> )	$q_e$ (mg g <sup>-1</sup> )	$k_2 \times 10^4$ (g mg <sup>-1</sup> h <sup>-1</sup> )	R	SE (mg g <sup>-1</sup> )
<b>1.0 mol L<sup>-1</sup> HCl</b>									
100	1.0	91 ± 6	6 ± 1	0.98	7.2	112 ± 9	6 ± 2	0.98	6.2
100	2.0	52 ± 2	7.7 ± 0.6	0.99	2.2	63 ± 2	1.3 ± 0.1	1.00	1.4
300	2.0	147 ± 8	4.7 ± 0.6	0.99	7.5	190 ± 12	2.3 ± 0.5	0.99	6.0
<b>1.4 mol L<sup>-1</sup> H<sup>+</sup> Aqua Regia Solution</b>									
100	1.0	84 ± 4	5.3 ± 0.7	0.99	4.5	109 ± 9	4 ± 1	0.99	4.8
300	2.0	136 ± 3	7.2 ± 0.5	1.0	4.2	167 ± 5	4.4 ± 0.5	1.0	3.8

The kinetics of gold uptake by the tannin resin was also analysed considering an intraparticle diffusion-controlled process. Assuming a negligible mass transfer resistance in the outer layer and considering that intraparticle resistance is governed by surface diffusion (as this adsorbent is essentially a non-porous material), homogeneous solid diffusion model (HSDM) combined with Linear Driving Force (LDF) approximation were used to model kinetic data and to calculate the average values of the homogeneous diffusion coefficients ( $D_h$ ) (equations in Section 2.4.3). Table 4 presents  $k_{LDF}$  and  $D_h$  estimated values. The good agreement between the LDF fitting and the experimental data

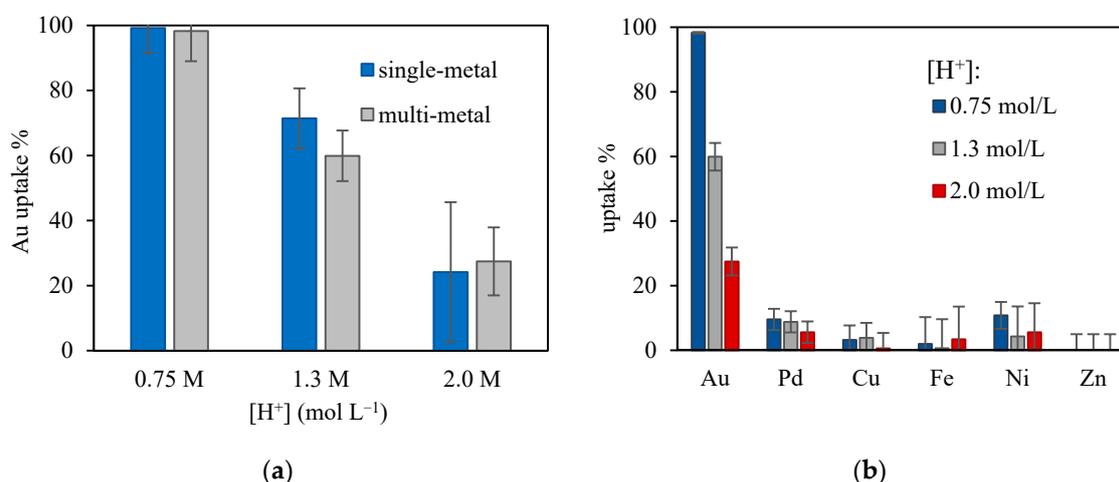
(coefficients of correlation equal or higher than 0.98) shows that this model can also successfully describe the adsorption of gold by the tannin resin. The homogeneous solid diffusivity coefficients calculated were in the range  $10^{-14}$ – $10^{-13}$   $\text{m}^2 \text{s}^{-1}$ . Saman et al. [35] reported values in the order of magnitude of  $10^{-13}$   $\text{m}^2 \text{s}^{-1}$  for the adsorption of Au(III) by oil palm trunk biosorbents. For the same adsorbent dosage, the results show an increase in  $D_h$  with the initial adsorbate concentration, which has been reported in various adsorptive systems [44,54], including on the uptake of gold cyanide by activated carbon [16]. For the same initial adsorbate concentrations and adsorbent dosages, lower  $k_{LDF}$  and  $D_h$  values were obtained for the aqua regia solutions, in comparison to HCl, which indicates slower adsorption kinetics.

**Table 4.** Kinetic constant ( $k_{LDF}$ ) of LDF approximation and solid diffusivity coefficients ( $D_h$ ) calculated by HSDM model for the adsorption of gold from HCl and aqua regia solutions by the pine bark tannin resin.

$C_0$ ( $\text{mg L}^{-1}$ )	$S/L$ ( $\text{g L}^{-1}$ )	R	$k_{LDF}$ ( $\text{h}^{-1}$ )	$D_h$ ( $\text{m}^2 \text{s}^{-1}$ )
<b>1.0 mol L<sup>-1</sup> HCl</b>				
100	1.0	0.98	0.076	$3.6 \times 10^{-14}$
100	2.0	0.98	0.051	$2.5 \times 10^{-14}$
300	2.0	0.99	0.215	$1.1 \times 10^{-13}$
<b>1.4 mol L<sup>-1</sup> H<sup>+</sup> Aqua Regia Solution</b>				
100	1.0	1.00	0.021	$1.0 \times 10^{-14}$
300	2.0	0.99	0.087	$4.3 \times 10^{-14}$

### 3.4. Competitive Adsorption and Selectivity

The tannin resin was tested in multi-metal solutions containing Cu(II), Fe(III), Ni(II), Zn(II), Pd(II), and Au(III). The results are depicted in Figure 4.



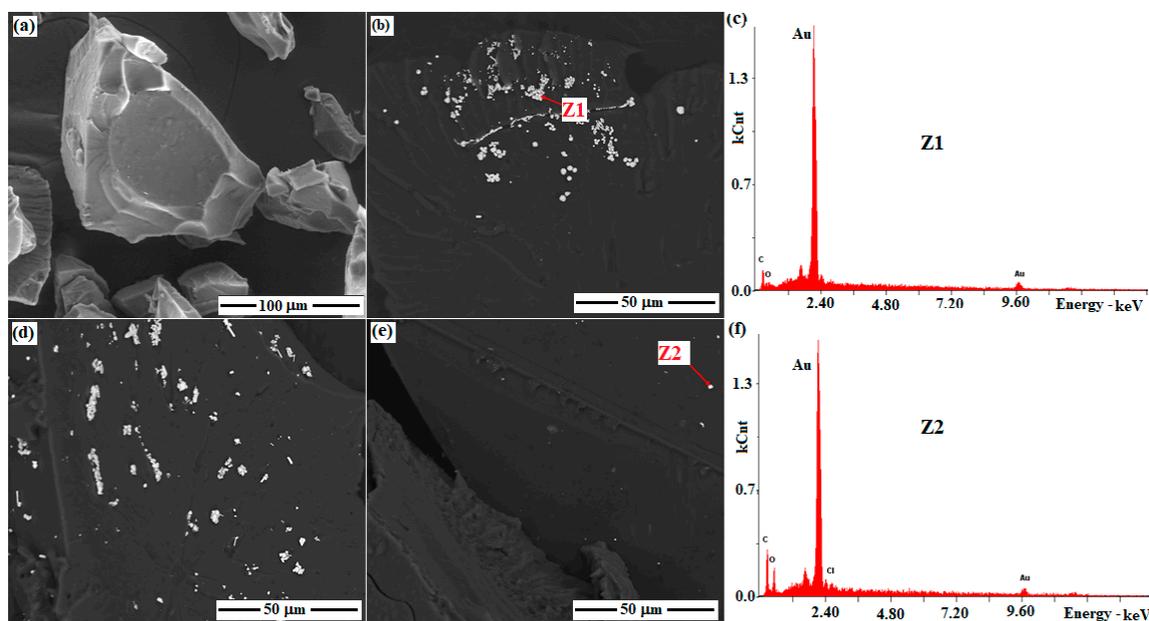
**Figure 4.** Percentages of metals extracted from simulated liquors containing aqua regia in different  $\text{H}^+$  concentrations by the pine bark tannin resin from ( $20^\circ\text{C}$ ,  $S/L$   $1.0 \text{ g L}^{-1}$ , initial Au concentration  $200 \text{ mg L}^{-1}$ ): (a) comparison of Au uptake from single and multi-metal solutions; (b) uptake of metals from the multi-metal solution.

As it can be seen (Figure 4a), the ability of the tannin resin to uptake gold from the simulated liquors is practically the same as that found in single-metal solutions. The uptake percentages of gold obtained in multi-metal systems (Figure 4b) were noticeably higher than those of the other metals (which has never surpassed 11%), particularly for total acidities of 1.0 and  $1.4 \text{ mol L}^{-1}$ . For instance, at acidic level of  $0.75 \text{ mol L}^{-1} \text{ H}^+$ , almost 100% of the gold in solution was adsorbed by the tannin resin, whereas Ni

and Pd were very weakly extracted ( $11 \pm 4\%$  and  $10 \pm 3\%$ , respectively), and other metals remained practically solubilized (uptake percentages  $< 3\%$ ). In the presence of high chloride concentrations and low pH, gold and platinum group metals are present as anionic chloro-complexes, which favour their uptake by the positively charged adsorbent surface. Palladium has similar properties and behaviour as Au, namely a low reduction potential. It has been reported that  $\text{PdCl}_4^-$  can be also adsorbed by tannin-adsorbents through the oxidation of the functional groups of tannins and reduction to Pd(0) [24], which justify its co-adsorption. Base metals, on the other hand, are present in solution as cationic species and are electrostatically repelled. Indeed, in biosorption processes, anions are typically adsorbed at low pH (1.0–3.0), whereas metal cations are typically adsorbed under optimum conditions of pH 5.0–5.5 [55]. This explains the reduced competition observed between gold and base metals. The present results are generally in line with results published in literature, which have shown very good selectivity for gold over other metals for different HCl and  $\text{HNO}_3$  media [25].

### 3.5. SEM and EDS Analysis

Figure 5 presents the SEM images of the tannin resin adsorbent, before and after gold uptake. As it can be observed, the adsorbent particles present an irregular shape and a faceted non-porous surface (Figure 5a). After adsorbing gold from HCl (Figure 5b) and aqua regia solutions (Figure 5d,e), the adsorbent surface presented an accumulation of metal particles, identified as gold through the EDS spectra performed in the micro areas denoted as Z1 and Z2 (Figure 5f). These images are in line with the quantitative adsorption results previously obtained, considering that Figure 5d (Au-loaded adsorbents in HCl and aqua regia solutions  $1.0 \text{ mol L}^{-1} \text{ H}^+$ , respectively) show high amounts of gold particles, whereas Figure 5e shows a much scarce distribution. The EDS spectra obtained in areas not covered by gold particles (not illustrated) showed an abundance of carbon and oxygen (also observed before adsorption), but the additional presence of chlorine. This confirms the competition between chloride and gold to the adsorbent surface.



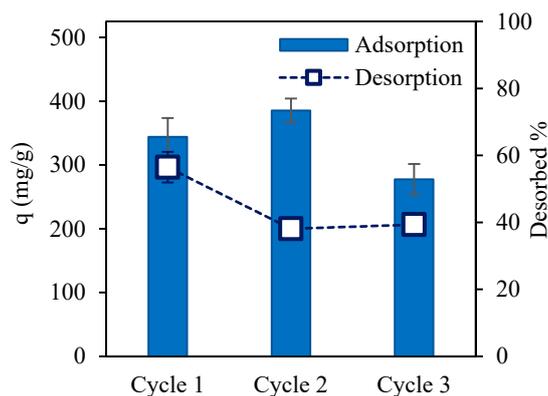
**Figure 5.** SEM images obtained for the pine bark tannin resin (a) before contact with gold, and after adsorption of gold (b) from  $1.0 \text{ mol L}^{-1} \text{ HCl}$ , and from aqua regia solutions (d)  $1.0 \text{ mol L}^{-1} \text{ H}^+$  and (e)  $2.0 \text{ mol L}^{-1} \text{ H}^+$ . EDS spectra obtained in the areas denoted as (c) Z1 and (f) Z2.

### 3.6. Desorption and Regeneration

The final recovery of gold from the loaded adsorbent and the regeneration of the adsorbent are important for industrial applications. A first desorption test of gold(III) was conducted using HCl 50%

( $v/v$ ) and  $0.5 \text{ mol L}^{-1}$  acidic thiourea as eluents. Negligible desorption percentage ( $<1\%$ ) was obtained in HCl eluent, whereas 57% was registered using the acidic thiourea solution. In fact, formulations of thiourea with HCl have been identified in literature as the most effective desorbing solutions for gold [18,22,27,56]. The desorption mechanism of the process is based on the displacement of the electrostatically adsorbed Au(III), that complexes with chloride in the HCl eluent, and on the oxidation of the elemental gold forming the gold(I)-thiourea  $\text{Au}(\text{CS}[\text{NH}_2]_2)_2^+$  [18,56]. Details about the reactions of gold dissolution through the use of acid thiourea solution can be found in literature [57,58].

Adsorption–desorption assays were then conducted for three cycles, using the acidic thiourea solution. The results are presented in Figure 6.



**Figure 6.** Results obtained in the adsorption ( $C_0 = 500 \text{ mg L}^{-1}$ ,  $S/L = 1.0 \text{ g L}^{-1}$ ,  $20 \text{ }^\circ\text{C}$ ) and desorption cycles (eluent:  $0.5 \text{ mol L}^{-1}$  thiourea and  $0.5 \text{ mol L}^{-1}$  HCl solution,  $S/L = 2.5 \text{ g L}^{-1}$ ,  $20 \text{ }^\circ\text{C}$ ).

As it can be seen, the desorption efficiency observed in the first cycle (57%) decreased to 38% and 39% in the two subsequent desorption steps. In spite of that, the regeneration ability of the tannin resin was quite good, as the adsorbed amount remained practically constant in two cycles and reduced moderately (19%) in the third one, indicating that the regenerated tannin resin still has capacity to accumulate gold in its surface. These results are promising, but the necessity of more research is evident to find an improved solution (e.g., increasing HCl concentration) to desorb gold more efficiently from the pine bark tannin resins. Although from environmental and cost-effectiveness points of view, the desorption and regeneration seem to be the most interesting options to recover gold, incineration could be considered in future as it is a direct way to obtain metallic gold.

#### 4. Conclusions

Tannin resins prepared from maritime pine (*Pinus pinaster*) bark were evaluated for the uptake and recovery of gold from simulated e-waste hydrometallurgical liquors. Higher extraction efficiencies of gold were obtained from HCl solutions, in comparison to aqua regia, but excessive levels of HCl caused a severe impact in the metal uptake from both aqueous systems. Even though, at strong acidic levels and in both acidic systems, the pine bark tannin resin presented a good performance, with maximum adsorption capacities ranging from 200 and  $343 \text{ mg g}^{-1}$  ( $2.0$  and  $1.0 \text{ mol L}^{-1} \text{ H}^+$ , respectively). The adsorption process was found to be a rather slow process (2–3 days to be completed) and successfully described by the homogeneous solid diffusion model and LDF approximation. The selectivity of the adsorbent towards gold was evaluated using simulated hydrometallurgical liquors. The amount of gold extracted by the tannin resin from multi-metal solutions was similar to the values registered in the single-metal solutions and the co-adsorption of Pd(II), Cu(II), Fe(II), Ni(II) and Zn(II) was in general low. Desorption and regeneration studies conducted through three adsorption–desorption cycles, using a solution of  $0.5 \text{ mol L}^{-1}$  thiourea and  $0.5 \text{ mol L}^{-1}$  HCl as eluent, indicate desorption percentages of 38–57%, although with only a mild loss of the adsorption capacity of the regenerated adsorbent.

Considering the harsher conditions at which the pine bark tannin resin was evaluated, it can be said that it presents analogous or even better performance when compared to other biosorbents or synthetic resins. A deeper analysis on the final recovery of gold from the exhausted adsorbents will be considered in forthcoming work. More research is needed in this field to improve the circularity in WEEE, particularly by the promotion of benign practices.

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