Integrated Master in Bioengineering

Adsorption of Gold from Leach Liquors using Tannin Adsorbents - Towards a Benign Au Recovery from E-waste

Master's Dissertation

of

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Abstract

Gold is a precious metal that is present in electronic devices in concentrations much higher than in natural ores. With the fast pace of today's consumption behaviour high volumes of electrical and electronic waste, e-waste, are generated and most of it is not properly recycled. However, e-waste is a source of a variety of base metals and precious metals, including gold, that can be recovered by leaching processes followed by adsorption mechanisms. Biosorption uses biomass as the adsorbent in order to concentrate metallic ions in solution, that can be posteriorly recovered. Tannins, by-products of the metabolism of plants, have been used as precursors of biosorbents. There are several studies available that use tannins for the recovery of precious metals, such gold, from e-waste leach liquors, but none using *Pinus pinaster* bark, a very common vegetal species in Portugal. Therefore, in the present dissertation, a tannin resin produced from a *Pinus pinaster* bark extract was used to uptake gold from simulated leach liquors by means of adsorption.

The uptake of gold from solution was studied in single-metal solutions containing two leaching agents, HCl and a mixture of HCl:HNO_3, 3:1 (v/v), known as aqua regia. The concentration in which the leaching agents are present in solution proved to influence the adsorption of Au; up to a concentration of 0.5 mol L^{-1} HCl it was recovered 100% of all Au in solution but as concentration gets higher the uptake rates get lower, until zero for 2.0 mol L^{-1} HCl:0.8 mol L^{-1} HNO_3 (aqua regia) and 3.7 mol L^{-1} HCl, showing that the acidity of the medium interferes with the capacity of the resin to uptake Au from solution. In the kinetic studies, it was analysed the influence of different parameters over the adsorption of Au from solution, namely, the initial concentration of the metal, the adsorbent dosage and the leaching agent. Pseudo-first-order and pseudo-second-order models were used to successfully describe the adsorption kinetics. In the equilibrium studies, the Langmuir isotherm was chosen to describe the adsorption of Au from an aqua regia solution and the Freundlich isotherm to describe in HCl medium. HCl was defined as the best leaching agent for the recovery of Au, presenting uptake rates of 100% and a maximum adsorptive capacity of 343 ± 9 mg g ^{1} vs. 264 ± 12 mg g ^{1} for aqua regia. Finally, a selectivity study was conducted and the uptake of Au was evaluated from an aqua regia solution also containing Cu, Fe, Ni, Pd and Zn. Au adsorption was not affected by the presence of the other metals in solution, presenting similar uptakes in the mono-metal and multi-metal solutions. Therefore, the results obtained in this dissertation present good perspectives for the application of tannin resins in the selective extraction of Au from electronic waste leach liquors.

Key words: Gold, Tannin Resin, Adsorption, Recovery, Leaching.

Resumo

O ouro é um metal precioso que está presente em certos equipamentos eletrónicos em concentrações muito maiores do que nos minérios naturais. Com o elevado ritmo de consumo atual, é gerado um grande volume de lixo elétrico e eletrónico, o chamado *e-waste*, que não é, na sua maioria, devidamente reciclado. Contudo, o *e-waste* é fonte de uma variedade de metais base e preciosos, incluindo o ouro, que podem ser recuperados por processos de lixiviação seguidos por mecanismos de adsorção. A biossorção usa biomassa como adsorvente para concentrar iões metálicos a partir de uma solução, que podem posteriormente ser recuperados. Os taninos, produtos secundários do metabolismo das plantas, têm sido utilizados como precursores de biossorventes. Existe uma série de estudos que usam taninos para recuperar metais preciosos, como o ouro, de soluções obtidas por lixiviação de resíduos elétricos e eletrónicos, mas nenhum usando casca de *Pinus pinaster*, uma espécie vegetal muito comum em Portugal. Assim, nesta dissertação, uma resina tanínica, produzida a partir de um extrato de casca de *Pinus pinaster,* foi usada para recuperar ouro de licores simulados de *e-waste*, por meio de adsorção.

A recuperação de ouro em solução foi estudada para soluções mono-metal contendo dois agentes lixiviantes distintos, HCl e uma mistura de $HCl:HNO_3$, 3:1 (v/v), conhecida por aqua regia. A concentração na qual os agentes lixiviantes estão presentes em solução mostrou influenciar a adsorção do Au; até 0.5 mol L^{-1} de HCl recuperou-se 100% de todo o Au em solução, mas com o aumento da concentração as percentagens de recuperação diminuíram até serem nulas para 2.0 mol L^{-1} HCl:0.8 mol L^{-1} HNO_3 (aqua regia) e 3.7 mol L^{-1} de HCl, provando que a acidificação do meio interfere na capacidade da resina em extrair Au da solução. Nos estudos cinéticos analisou-se a influência de diferentes parâmetros na adsorção de Au da solução, nomeadamente, a concentração inicial de Au, a dosagem de adsorvente e o lixiviante utilizado. Recorreu-se a modelos de pseudo-primeira-ordem e pseudo-segunda-ordem para descrever com sucesso a cinética de adsorção. Nos estudos de equilíbrio, a isotérmica de Langmuir foi escolhida para descrever a adsorção de Au em aqua regia e a isotérmica de Freundlich para descrever em HCl. O HCl foi definido como o melhor lixiviante para a recuperação de Au, apresentando recuperações de 100% e uma capacidade máxima adsortiva de 343 ± 9 mg g^{-1} vs. 264 ± 12 mg g^{-1} para a aqua regia. Finalmente, realizou-se um estudo da seletividade e avaliou-se a recuperação de Au de uma solução de aqua regia contendo também Cu, Fe, Ni, Pd e Zn. A adsorção de Au não foi afetada pela presença de outros metais em solução, com recuperações semelhantes nas soluções mono-metal e multi-metal. Assim, os resultados obtidos nesta dissertação apresentam boas perspetivas para a aplicação de resinas tanínicas na extração seletiva de Au de licores de lixiviação de resíduos electrónicos.

Palavras Chave: Ouro, Resina Tanínica, Adsorção, Recuperação, Lixiviação.

Declaration

I, Maria Beatriz de Queiroz e Lencastre de Fleming Torrinha, declare, under honour commitment, that this work is original and all the non-original contributions were properly referenced with the identification of the source.

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Notation and Glossary

Symbols

wt%	*Weight percentage (%)*
ppm	*Parts per million (ppm)*
SA	*Surface area* (m^2 g^{-1})
q	*Adsorbed amount per mass unit of adsorbent (mg Au* g^{-1} *resin)*
q_{max}	*Maximum adsorbed amount per mass unit of adsorbent (mg Au* g^{-1} *resin)*
ρ	*Density* (g mL^{-1})
Uptake (%)	*Uptake percentage (%)*
rpm	*Rotation per minute*

Nomenclature Subscripts

e	In equilibrium
max	Maximum

Acronyms List

CPT	Crosslinked Persimmon Tannin
DACS	Dialdehyde Corn Starch
DEAE	Diethylaminoethyl Cellulose
DMA – PW	Dimethylamine Persimmon Waste Gel
DVD	Digital Versatile Disc
EEE	Electrical and Electronic Equipment
EPPFR	Ethylenediamine Modified Persimmon Tannin Adsorbent
E-waste	Electronic and Electrical Waste
GAC	Granular Activated Carbon
LOD	Limit of Detection
LSSS	Lime Sulphur Synthetic Solutions
MAE	Microwave-Assisted Extraction

MAS	Methanesulfonic Acid
PAC	Powder-powered Activated Carbon
PC	Portable Computer
PCB	Printed Circuit Board
PGM	Platinum Group Metals
PGE	Platinum Group Elements
PLE	Pressurized Liquid Extraction
REEs	Rare-Earth Elements
REMs	Rare-earth Metals
TA	Tannin Acid
TV	Television
UAE	Ultrasound-Assisted Extraction
WEEE	Waste Electrical and Electronic Equipment
WPCBs	Waste Printed Circuit Boards
ZIF	Zeolitic Imidazolate Framework

1 Introduction

1.1 Background and Project Presentation

Precious metals, such as gold (Au), platinum (Pt) and palladium (Pd), are metals with high economic interest, being used in a variety of applications, due to their physical and chemical properties [1]. One of the most recent applications for these metals are in low-carbon energy technologies and electronic devices, e.g. computers, printed circuit boards, smart phones, batteries, due to its high chemical stability and high conductivity [2,3].

However, due to the over exploration of resources, precious metals are becoming more and more scarce, demonstrating a high supply-chain risk, which lead them to be considered in the “critical metals” list [4]. Furthermore, such materials used to be obtained mainly through mining of primary sources, the so-called mineral ores, which are also limited and rapidly decreasing due to urbanization, population growth and increasing standard of living [2].

Therefore, new ways to recover precious metals from their natural ores and from a variety of different sources should be considered, with recycling from secondary sources being one of the most viable options, including recovery from mine tailings and wastewaters [1,2].

On the other hand, the increasing amount of electronic and electrical waste, generally known as e-waste or WEEE, due to the technological revolution of the last decades, economic growth and market expansion, but also due to their short life span, is damaging the environment [5–7]. In fact, the disposal and incineration of e-waste generates gases such as dioxins, furans and other pollutants, but also the dissolution of heavy metals on the ground water at landfill sites, which represent serious environmental and human health problems [6].

Additionally, it is known, that e-waste contains large amounts of precious metals in its constitution and in much higher concentrations than when found on their natural ores, and therefore represents a possible, viable, secondary source for metals recovery [3,8].

For the recovery of metals from e-waste there are a variety of methods options based on conventional mechanical, physical, pyrometallurgical and hydrometallurgical processes [5]. However, precious metals have to be leached from solid wastes, such as in the case of e-waste, before they can be isolated [9].

Pyrometallurgical processes involve very high working temperatures (1200 ºC), which translates in high economical costs and high energy necessities, but also leads to the release of toxic components to the atmosphere like dioxins [10]. On the other hand, bio-metallurgical processes, such as biogical leaching, have the disadvantage of being slower and less efficient than chemical leaching [10].

Hydrometallurgical processes consist firstly on a chemical leaching process for metal extraction in an acid or alkaline medium, followed by solution purification by various methods, for example, precipitation, cementation, adsorption (typically using activated carbon), ion exchange and solvent extraction [10]. These processes offer a relatively low capital cost, a reduced environmental impact, since no hazardous gases are released, ease and flexibility of operations and high metal recoveries with their suitability for small scale applications [1,5]. However, precipitation, ion exchange and solvent extraction have the disadvantage of being energy and time consuming and, therefore, economically uninteresting; alternatively, adsorptive recovery of precious metals has emerged as a potentially attractive and environmentally benign option [7].

Leaching is an hydrometallurgical process of extracting a soluble constituent from a solid using a solvent [11]. The most common leaching agents used in recovery of precious metals include cyanide, halides (fluorine, chlorine, bromine, iodine and astatine), thiourea, and thiosulphate [11].

For a long time, cyanide has been the main leaching agent used for the extraction of precious metals, but it has been used less and less due to its toxicity [12]. Alternatively, chlorine/chloride has been the main halide leaching agent applied industrially on a significant scale [13]. The traditional medium for dissolving platinum group metals is aqua regia, a mixture of three parts concentrated hydrochloric to one part concentrated nitric acid [11].

Posteriorly, after leaching, its necessary to selectively separate the metals of interest from the liquor, and that is when adsorption takes place. Biosorption has been identified as a key technology for the recovery of elements from hydrometallurgy processes [4]. It uses the capacity of inactive, dead, microbial biomass materials to concentrate metal ions from aqueous solutions [14]. Biosorption has been gaining a growing interest in recent years, in part because biomass materials are relatively inexpensive and available in large quantities worldwide, but also because they have a high efficiency, produce minimal sludge and can be regenerated simultaneously with the recovery of metals by desorption [9,14].

Recently, researchers have tried to utilize biomass in order to uptake precious metals, in particular Au, Pt, Pd and ruthenium, Ru, and aiming at the subsequent recovery [9]. One of the biomaterials studied for such recovery are tannins [15]. Tannins have been proposed as adsorbents precursors since they contain multiple adjacent hydroxyl groups and exhibit extraordinary chelating ability with many metal ions [16,17].

Pine is one of the main vegetal species of the Portuguese territory [18]. Therefore, the bark from some species of pine, like *Pinus pinaster,* is a very common and abundant residue in Portugal that should and can be taken advantage of for its valorisation, for example, trough tannin extraction for use as adsorbents [19,20].

Therefore, this project was focused on the study of the adsorptive capacity and selectivity of a tannin resin towards a particular precious metal, gold (Au), as a mean to extract it from hydrometallurgical liquors and, posteriorly, convert it into a chemical form that could be recovered.

Gold was selected as the precious metal in study due to its importance in green technologies and also due to the fact that is a limited resource and that its availability is decreasing day by day worldwide. Additionally, gold is one of the precious metal components found in e-waste in great concentrations, allowing for an effective recovery from such source. Even more, *Chancerel et al.* (2015) [21], considered that gold was by far the most relevant metal to be recovered in e-waste from an economic perspective.

1.2 Work Contributions

Eng. Hugo Bacelo provided the tannin resin used in the present dissertation as the adsorbent for the removal and recovery of gold. The tannin resin was prepared from a Pinus bark extract using an optimized process by *Bacelo et al. (2019)* [22].

1.3 Organization of the Dissertation

The present dissertation starts with a brief introduction on the subject of discussion (*Chapter 1.*), presenting the reasons that lead to the choice and development of the project.

Posteriorly, the dissertation continues with a literature revision on the subject in the ***2. State of Art*** section.

Chapter ***3 (Technical Description)*** refers to an experimental section, where the materials and methods used to conduct the project and that permitted the gathering of numerical data are presented. Results and corresponding analysis and discussion are presented in section ***4***.

In the ***5. Conclusions*** section all the main conclusions that were able to be taken from the study are presented, as well as the limitations that were faced and suggestions of future work that would be of the highest interest to continue.

2 Context and State of Art

2.1 Precious and Critical Metals

Precious metals are rare and naturally existing metallic chemical elements of high economic value [1]. This definition includes members of the platinum group metals (PGMs), gold (Au) and silver (Ag) [1]. Besides their extensive use in jewellery and ornamental purposes, precious metals are also used in other applications, such as catalysts in a variety of chemical processes, in electrical and electronic industries and in medicine, mainly because of their chemical and physical properties such as lustrous/ductile, non-corrosive and highly stable [1,7,23]. However, these are limited resources and, therefore, their recovery from secondary metal-containing sources has become a necessity [23].

On other hand, critical metals are defined as a group of elements that have a high demand but a low availability, low substitutability and a high supply security risk [2]. The high demand is due to the role they play in electronic and green energy technologies which are a growing force in the present economic development [24]. As for the supply security risk, besides being related with its low availability and low substitutability it is also related with the fact that critical metals are often presented in only a few countries in the world, representing a geopolitical risk [2].

The definition of which elements are “critical” depends on national concerns but rare-earth elements (REEs), platinum group metals (PGMs) and gold (Au) are examples of some consensus critical metals [4].

In fact, gold is one of the 8 geologically scarcest metals in the world, along with antimony, bismuth, boron, copper, molybdenum, rhenium and zinc [25]. In 2010 the global extraction of gold was equal to 2.56 thousand tons and it is expected that by 2050 the yearly extraction value reaches the 8 thousand tons mark; this means that it is expected that by 2050 there will only be left around 49 thousand tons of gold worldwide for exploration and that, maintaining the current behaviour, by 2056 all of the available gold in the earth’s crust is going to be depleted [25].

2.2 Electric Waste and Composition

Due to the technological development, a new source of waste has appeared in the last decades, namely the electronic waste, commonly known as E-waste.

E-waste describes all electrical and electronic waste, such as computers, cell phones and televisions, that are a source of valuable and hazardous materials [26,27]. E-waste is mostly composed by a mixture of metals, such as Cu, Al and Fe, plastic and ceramics, and in smaller concentrations by some critical and precious metals [26]. *Cui et al.* (2008) [11] made a survey about the documented metal composition of different e-waste sources and the results are presented in Table 1.

Table 1. Metal composition of some electronic residue sources [11]; Al, Cu, Fe, Ni and Pb are expressed as wt % and Ag and Au as ppm .

E-waste	Al	Ag	Au	Cu	Fe	Ni	Pb
TV board scrap	10	280	20	10	28	0.3	1.0
PC board scrap	5	1000	250	20	7	1	1.5
Mobile phone scrap	1	1380	350	13	5	0.1	0.3
Portable audio scrap	1	150	10	21	23	0.03	0.14
DVD player scrap	2	115	15	5	62	0.05	0.3
Calculator scrap	5	260	50	3	4	0.5	0.1
PCB scrap	7	280	110	10	12	0.85	1.2
PCB	1.9	3300	80	26.8	5.3	0.47	-
PC scrap	14	189	16	7	20	0.85	6
PC mainboard scrap	2.8	639	566	14.3	4.5	1.1	2.2
Typical electronic scrap	2	2000	1000	20	8	2	2

The concentrations of Au and Ag presented in Table 1 are in accordance with data survey by *Pant et al.* (2012) [28]. For example, an after analysis of Table 1, a typical electronic scrap presents a metal composition of 8% Fe, 20% Cu, 2% Al, 2% Pb, 2% Ni, 2000 ppm Ag, 1000 ppm Au and 50 ppm of Pd. Therefore, it can be concluded that e-waste is a potential source of critical and precious metals trough recycling methods.

In fact, studies have shown that the concentration of precious metals in secondary sources such as the electronic waste, are much higher than their content in natural ores; the average concentration of precious metals in natural ores is of about 1 to 30 ppm, while in secondary sources it can go up to 2000 ppm, or even higher, like shown in Table 1 [1,11]. When it comes to gold specifically, e-waste has been recognised as an appealing source of this metal, since the Au content in the electronic waste has been estimated to be 80 times higher than what is found in global primary mining deposits [8].

Due to its nature, e-waste requires different handling and recycling methods than the other sources of waste [26]. Despite the European Union efforts, establishing directives and encouraging an efficient treatment of e-waste, and despite its potential economic value, only around 20% of all e-waste generated is properly recycled, with the rest ending up mainly on landfills or incinerators [27,29].

In 2016, the global production of e-waste was equivalent to 44.7 million-metric tonnes, with the total value of all raw materials present in e-waste being of an estimated 55 billion euros; by 2021 e-waste production is expected to be of 52.2 million-metric tonnes worldwide [27].

2.3 Recovery of Metals from Waste PCBs

It is possible to apply direct separation procedures to aqueous solutions of metals, with adsorption being an example of a frequent applied method, but when the metals of interested are in the solid form, such as they are presented in the case of e-waste, there are a few pre-treatment steps required before metals can be extracted [1]. Firstly, the e-waste sample, for example a PCB scrap, has to be disassembled and crushed, followed by calcination of the sample [4]. Lastly, to dissolute the metals in solution, a process known as leaching, an hydrometallurgic procedure, occurs, using suitable solvents [1]. Posteriorly, the dissolved metals can be separated, concentrated and recovered through adsorption methods [30].

There are several different leaching agents that can be used for the recovery of precious metals but, in the case of gold and in the past century, cyanide has been the main leaching agent applied, despite its toxicity [3]. However, and due to the increasing preoccupation over the environment, some other, non-cyanide leaching agents, can be considered for the dissolution of this precious metal, such as hydrochloric acid/chlorine mixtures and aqua regia, a mixture of concentrated nitric acid and hydrochloric acid in a proportion of 1:3 [31–33]. *Sheng et Etsell* (2007) [33] obtained the best results using 2 mL of aqua regia solution per gram of electronic substrate (2:1 mL g^{-1} ratio), at 90ºC, without the need for agitation. However, even though aqua regia presents a fast dissolution rate of electronic waste, allowing for a high recovery rate of gold, it is mostly applied at an experimental scale since in full scale operations aqua regia has a strong oxidation and high corrosion behaviour towards the equipment [34].

Other documented alternatives are ammonium thiosulfate, which is a low-price reagent, but it requires the use of an additive, copper sulphate, in order to be feasible [34,35]. Documented studies, such as the one led by *Tripathi et al.* (2012) [36], allowed for a total recovery of 56.7% of gold from waste mobile phone printed circuit boards (PCBs), under the optimum conditions of 0.1 mol L^{-1} ammonium thiosulfate, 40 mmol L^{-1} copper sulphate, pH 10-10.5, pulp density of 10 g L^{-1}, at room temperature and using a stirring speed of 250 rpm for 8 hours. However, thiosulfate requires large volumes in order to be used as a leaching agent, which is a disadvantage since it results in high economic costs [34].

Thiourea is another documented gold leaching agent which, once combined with sulphuric acid and ferric ions, offers a 4 times faster oxidation of the precious metals [35]. *Gurung et al.* (2013) [31] defined the optimum conditions for gold leaching from PCB, using acidothiourea, as 0.5 mol L^{-1} of thiourea in 0.05 mol L^{-1} of H_2SO_4 at 45ºC, in a solution of 0.00285 g mL^{-1} pulp density, with an agitation speed of 150 rpm. The complete leaching of gold occurred after 6 hours at room temperature when ferric ions were added, and after 2 hours in the presence of a 0.01 mol L^{-1} ferric sulphate concentration. *Birloaga et Vegliò* (2016) [37] obtained a yield of 90% of Au extraction with 20 g L^{-1} of thiourea, 6 g L^{-1} of ferric ion, 0.1 mol L^{-1} of sulphuric acid and with an agitation speed of 200 rpm for 1 hour at ambient temperature.

Additionally, electro-generated chlorine, halogens (besides chloride), sodium thiosulfate, and new reagents such as methanesulfonic acid (MSA) and lime sulphur synthetic solutions (LSSS), should also be considered as proper leaching agents for gold recovery [12,31,35].

There are several studies that reflect on the recovery of metals from PCB scrap, using aqua regia as the leaching agent; *Birloaga et al.* (2014) [10], determined the chemical composition of a waste computer printed circuit board (PCB) after preliminary treatment, where some electronic components were removed (e.g. capacitors, batteries, relays) and crushed, and then chemical attacked with aqua regia and hydrofluoric acid. The chemical composition obtained was the following, 305.7 g of Cu, 116.9 g of Al, 152.1 g of Fe, 73.6 g of Sn, 15.8 g Ni, 18.6 g of Zn, 67 g of Pb, 238 mg of Au and 688 mg of Ag, per kg of PCB scrap; On another hand, focusing exclusively on the leaching step, *Fan et al.* (2014) [38] determined that an original sample of PCBs leach solutions, after treatment with aqua regia, contained about 600, 5000, 800, 50, 150, 20 mg L^{-1} of Au(III), Cu(II), Ni(II), Pd(II), Fe(III) and Zn(II), respectively; Lastly, *Yi et at.* (2016) [39] determined that the metal concentrations presented in the leach liquor sample were of 158, 42, 1605, 80, 140, 8.5 mg L^{-1} of Au(III), Pd(II), Cu(II), Ni(II), Fe(III), Zn(II), respectively, after treatment, once again, with aqua regia.

2.4 Adsorption – Definition

Adsorption is considered the best and most universal water treatment method applied nowadays [40]. Its popularity is related with the fact that it is an effective, efficient, economic, convenient and environmentally friendly method for water treatment, being able to remove both inorganic and organic pollutants to a percentage up to 99.9%, contributing for the purification, decolorization, detoxification and deodorization of the treated effluent [40,41]. From an industrial point of view, adsorption is technologically simple and economically feasible, while simultaneously, being able to produce high-quality water, with pollutant concentrations under the legal limits [41].

Adsorption is the process of separation of substances, the adsorbate, from a fluid, liquid or gas phase, by binding to the exterior and interior surfaces of a solid material or a liquid condensed phase, the adsorbent, forming a superficial monomolecular layer [41,42]. In other words, adsorption is the exchange of materials at the interface between two immiscible phases in contact, a physical mass transfer process [42,43].

Adsorption can be divided in 3 steps: (I) external diffusion – transport of the contaminant molecule from the bulk to the exterior of the adsorbent and adsorption to the outer surface; (ii) gradual adsorption stage - migration of the adsorbate into the pores of the adsorbent; (iii) intraparticle diffusion – interaction of the contaminant with the available sites on the interior surfaces of the absorbent [43]. Figure 1 illustrates a schematic representation of the adsorption mechanism.

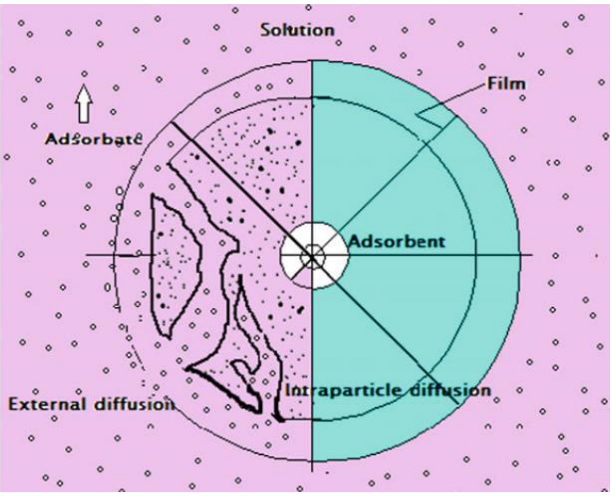


Figure 1. Adsorption mechanism [43].

The rate of adsorption is defined as the rate at which the adsorbate is transferred from the initial bulk to the solid phase (absorbent) [43].

In adsorption, the adsorbent is commonly characterized by being a porous material with a high surface area, that is able to adsorb organic and inorganic matter through the intermolecular forces [43]. In fact, a fundamentally important attribute for good adsorbents is a high porosity and consequent larger surface area with more specific adsorption sites. The porous structure increases the surface area and may increase the kinetics of the adsorption, taking less time to reach the equilibrium of adsorption [44].

On the other hand, the selectivity of the adsorbent towards the adsorbate is related with the specific interactions that are established between the surface of the adsorbent and the adsorbate [41]. The affinity between the adsorbent and the contaminants is the main interaction force controlling adsorption, even though the affinities between the adsorbate and the solution, the adsorbent and the solution, and between contaminant molecules can also play a major role in the process [41].

As for the nature of the bonding established between the adsorbate and the adsorbent, when the adsorbate bonds to the surface of the adsorbent by van der Waal forces the adsorption is known as physical adsorption; this type of adsorption is still reversible once the forces responsible are very weak [43]. On the other hand, when the adsorbed species bond to the surface by covalent bonding, making adsorption irreversible, adsorption is known as chemical adsorption, and the adsorbate is more tightly retained by the adsorbate than in the physical adsorption [43].

2.5 Conventional Adsorbents

Conventional adsorbents dominate the commercial use of adsorption. The list of conventional adsorbents includes activated carbons, ion-exchange resins and inorganic materials such as activated alumina, silica gel, zeolites and molecular sieves [40,44]. However, these adsorbents have the main disadvantages of being too expensive and can become exhausted and lose their capability for further adsorption of contaminants, therefore, limiting the capability of their employment [40,41]. Additionally, activated carbon has also the disadvantage of not being eco-friendly since its synthesis is very harsh [40].

Activated carbon is the most popular adsorbent worldwide for wastewater treatment, being able to adsorb a variety of contaminants such as metals, rare earth elements, phenolic and aromatic derivatives, dyes, pesticides, radionuclides, drugs and pharmaceuticals [41]. Activated carbon is produced from primary carbon following a 3 steps process: raw material dehydration, carbonization and activation [44]. In the activation phase the pores of the carbonized material are enlarged, resulting in a material with a large surface area, ranging from 600-2000 m^2 g^{-1} [44]. The activated carbon exists mainly in two forms, as a powder-powered activated carbon (PAC), and in a granular form – granular activated carbon (GAC) [44]. The GAC form is the most used one in wastewater treatment [44]. Besides removing pollutants from wastewater streams, activated carbon is also used for the adsorption of contaminants from drinking water sources and to extract metals from leaching liquors [41].

Soleimani et Kaghazchi (2008) [45] studied the adsorption of gold from an industrial wastewater using activated carbon derived from hard shell of apricot stones. Activated carbon proved to be a successful adsorbent of gold, allowing for a recovery percentage of more than 98%, under the optimum conditions, and after only 3 hours. *Altansukh et al.* (2016) [46] used activated carbon to recover gold from waste printed circuit boards (WPCBs) after treatment with an iodine-iodide leaching agent, recovering nearly 98% of gold under the optimum working conditions.

Alternatively, S*abermahani et al.* (2016) [47] used silica gel as the adsorbent for the recovery of gold in trace conditions from a water sample; rubeanic acid (dithiooxamide) was used as a chelating agent for preconcentration of Au and thiourea followed by HNO_3 were used as leaching agents, allowing to achieve a maximum recovery percentage of Au of over 99%.

On the other hand, activated alumina, which comprises partially hydroxylated alumina oxide (Al_2O_3), is a versatile adsorbent and has been successfully utilized for the removal of dyes and heavy metals from water, due to its amphoteric properties [40,44]. Its surface area ranges from 200 to 300 $m^2\ g^{-1}$ [44]. As an alternative to alumina, bauxite, composed mainly by aluminium hydroxide minerals, has a surface area that ranges from 25 to 250 $m^2\ g^{-1}$ [44]. However, there are no studies currently available for use of these two compounds as adsorbents for the recovery of precious metals.

Another conventional adsorbents are zeolites, which are porous crystalline aluminosilicates (Si/Al ratio > 1) with a surface area in the range of 1-20 $m^2\ g^{-1}$ [43,44,48]. *Wang et al.* (2018) [49] used a zeolitic imidazolate framework (ZIF) modified with thiourea for the recovery of Au from aqueous solutions, recovering more than 99% of Au from solution at the optimum conditions. On the other hand, *Mosai et al.* (2019) [50] used a hydrazine-functionalised zeolite for the recovery of platinum from an aqueous solution that resembles typical platinum group elements (PGE) processing solutions, with other metals (Fe, Ni, Zn, etc.) in solution. An HCl medium was used and under the optimised conditions, the recovery of Pt was 93%. Additionally, a cost-benefit analysis was done and for the ~120 g of Pt recovered per kg of adsorbent, a profit of $3355 can be generated, demonstrating the potential of such adsorbent for the recovery of Pt.

Ion-exchange resins, which are polymeric inorganic resins, have also been used for the removal of specific organic compounds [41,44]. *Mpinga et al.* (2018) [51] used a commercially available anion exchanger diethylaminoethyl cellulose (DEAE) for the recovery of two precious metals, Pd (II) and Pt (IV) from a HCl aqueous solution; results showed that the weak-base anion exchange resin was able to recover around 96% of Pt and 98% of Pd present in solution. Additionally, *Cyganowski et al.* (2017) [52] used two core-shell type anion exchange resins, 1EDA and 1AEP, to recover Au from a WEEE sample, with a mixture of other metals in solution (Fe, Ni, Ag, Cu, etc), after leaching with aqua regia; The 1EDA resin was able to recover a maximum of 86% of the Au in solution while 1AEP was able to recover up to 87% of all the Au in solution, with both resins presenting great selectivity towards gold.

2.6 Non-conventional Adsorbents and other Alternatives for Metal Recovery

In regard to non-conventional adsorbents the list is continuously growing. Among the more recent ones it should be considered the activated carbons obtained from agricultural solid waste and industrial by-products, natural materials (e.g. clays), industrial by-products (e.g. red mud), biosorbents (e.g. chitosan, bacterial biomass, algal, tannin), miscellaneous adsorbents (e.g. alginates), polymeric materials and magnetic materials [1,41].

Nanoparticles are an example of a good alternative for conventional adsorbents, mainly because of their special attributes such as their small size, large number of active sites with different contaminants, large surface area, ease of separation, catalytic potential and the reactive nature of the surface of the nanoparticles (given the high density of low coordinated atoms in the edges of the surface) [40]. Nanomaterials such a carbon nanotube, iron oxide, iron hydroxide, alumina and zinc sulphide nanoparticles have been recently used as adsorbents for water treatment purposes [40]. *Yen et al.* (2017) [53] used magnetic nanoparticles to recover precious metals, Pd(IV), Au(III), Pd(II) and Ag(I), in water. After 8 hours approximately 90% of Au in solution had been adsorbed by the nanoparticles. As for the rest of the precious metals, Pd(IV) presented an uptake of ~90% while Pd(II) and Ag(I) presented an uptake of ~65%. Thus, it was possible to prove the success of using nanomaterials for precious metals recovery from aqueous solution.

Additionally, non-living bio-derived materials, commonly referred to as biosorbents, have been intensively studied for the purpose of adsorption, originating the term “biosorption” [54]. Within the advantages of the use of biosorbents, being renewable materials, the ease of handling, the high metal uptake rates even in trace conditions, the minimal sludge production and their potential for regeneration and reusability are some of the reasons for such behaviour [4]. Furthermore, since biosorption often employs dead biomass, nutrient requirements are insignificant, lowering the costs of the procedure [55]. Plus, biosorption can be used in situ, may not need any industrial process operations and can be integrated in eco-friendly ways within systems [55]. Thus, biosorption has developed to be a low-cost and generally a low-tech option for the removal or recovery of metals [15].

There are several studies related with the recovery of precious and critical metals in literature using biosorbents, and more specifically of Au [4]. Some of the surveyed sorbents include chitosan [56,57], algae [58,59], bacteria [60] and protein-rich biomass [61]. Another example of biosorbents that have received a great attention in the last years are tannins. When it comes for the recovery of precious metals, tannins have demonstrated a special affinity towards gold because of their high content of multiple adjacent phenolic hydroxyls [38,62].

At last, and besides not being considered as an adsorptive mechanism so to speak, biomining uses microorganisms, mainly iron- and sulphur-oxidizing chemolithrophs, to extract minerals from sulphide and/or iron-containing ores and mineral concentrates [63]. Even though gold is inert to microbial action, when the ore is oxidized by these microorganisms, its structure is opened, allowing gold-solubilizing chemicals like cyanide to penetrate the mineral, in a process known as biooxidation [63]. However, the microorganism-based biosorbents have their disadvantages, such as low density, small particle size, poor mechanical strength and little rigidity [9].

2.7 Tannins – Definition and Classification

The term tannin is related with its initial application in the tanning of animal skin [64]. However, nowadays, tannins are used in different applications, such as in the medical/ pharmaceutical field, e.g. due to their anti-inflammatory, antidiarrheal, anti-viral, antibacterial properties, in food industrial fields, e.g. as antioxidants, to clarify beer and wine, in surface coatings and plastics, but also as biosorbent precursors [64,65].

Tannins are polyphenolic compounds with hydroxyl groups, soluble in water and with a molecular mass of 500 to 3000 Dalton [66,67]. Additionally, because of its phenolic groups, tannins present an anionic nature [20].

Chemically, tannins have very different structures and can be divided in hydrolysable, condensed and complex tannins, which have both units of hydrolysable and condensed tannins [66,68]. Figure 2 represents the possible classifications of different tannins according to their structures [69].

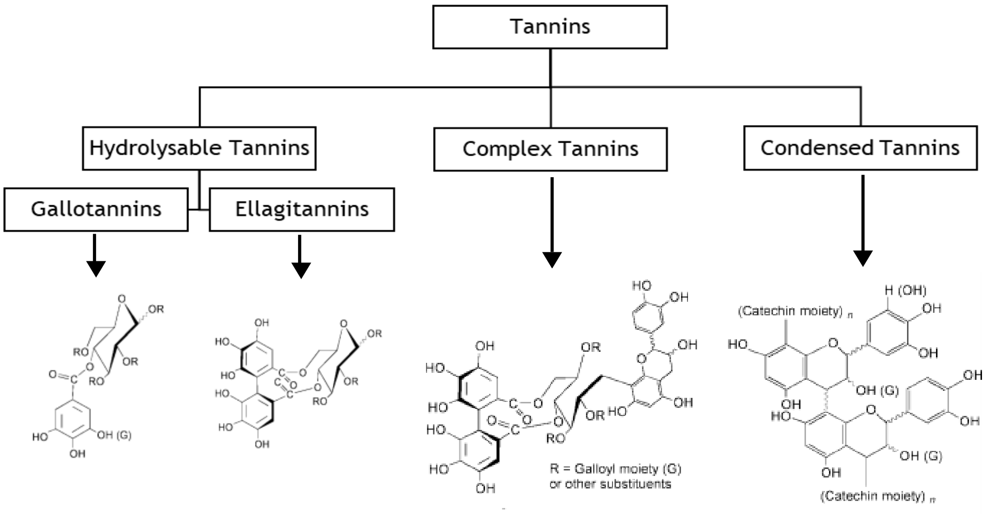


Figure 2. Tannins Classification (adapted from [69]).

Hydrolysable tannins, as the name indicates, can be fractionated hydrolytically into their components, originating gallic acid or ellagic acid, and therefore, can be subdivided in gallotannins and ellagitannins, respectively [69].

Both gallotannins and ellagitannins have a carbohydrate core, typically glucose, to which the gallic acid or a polygalloyl chain of variable length can bind by esterification with the hydroxyl groups [67]. Ellagic acid is formed from the gallic acid by C-C accopolation of two acid gallic units, followed by spontaneous lactonization [70]. Figure 3 represents the structure of the gallic acid (A) and of the ellagic acid (B).

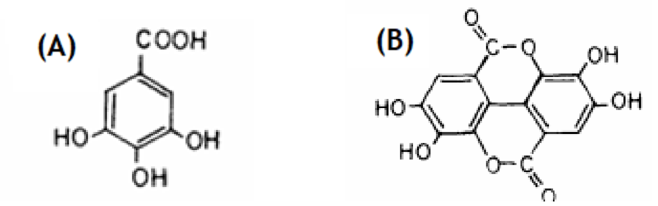


Figure 3. (A) Gallic Acid; **(B)** Ellagic Acid [67].

On the other hand, condensed tannins, also known as condensed proanthocyanidins, have phenolic cores and are not hydrolysable in the presence of acids, bases or enzymes [66]. Such polymers are formed by the condensation of two or more units of flavans [67]. Figure 4 illustrates an example of a proanthocyanidins precursor, flavan-3-ol [67]. As for complex tannins, they are formed by condensation of an ellagic tannin with a unit of flavan-3-ol [71].

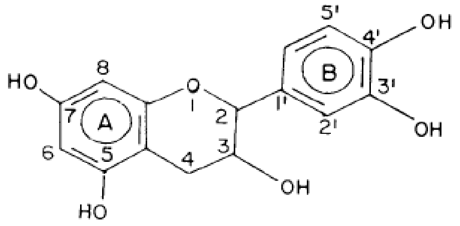


Figure 4. Flavan-3-ol, a precursor of condensed tannins [67].

Despite the existing information available about tannins, the reality is that their structure is still relatively unknown [67]. That is due to the fact that tannins are extracted from their matrix without a high level of purity and because of their high chemical complexity [67].

2.8 Tannin Extraction

Tannins are synthesized by plants as a by-product of their metabolism [72]. They can be found in the bark, fruits and leaves of leguminous species, such as *Acacia mearnsii de Wild,* and arboreal species, such as *Schinopsis balansae* and *Pinus pinaster* [68]. After the main compounds, like cellulose, hemicellulose and lignin, tannins are the most abundant compounds in biomass and are mainly found in the soft tissues of plants [71].

In literature, there is already information about tannins extracted from different arboreal and vegetable species and in different concentrations. Table 2 showcases some examples of plants from which the extraction of tannins was already documented and the percentage in which they were found [20].

Table 2. Documented species where tannins were already extracted and the percentage in which they were found [20].

Species	Percentage (%)
Accacia Bark	20 – 30
Black oak	8 – 12
Pinus pinaster (bark)	22.5
Eucalyptus (bark)	16 – 40
Chestnut (endodermics/bark)	2.50 / 0.94
Black and Grey Alder	12

Tannins can be extracted from their different sources using a variety of methods. One of the most common methods is based on the extraction with hot/boiling water, followed by concentration by evaporation in vacuum, in order to limit tannin oxidation [73]. To do so, at an industrial level, a certain temperature (around 50 to 110 ºC) and pressure (0.8 bar maximum) are fixed in an autoclave, working in counter-current through several hours (6 to 10 hours), using a wood/water ratio of 2:2.4 in mass [71]. After clearing by decantation, the tannin solution is concentrated until reaching the desirable concentration [71].

However, even though water can be used by itself for tannin extraction, the addition of alkaline solutions, such as NaOH, and of acid solvents, like hydrochloric acid and formic acid, can allow for an even higher extraction yield [71]. Furthermore, it is possible to also use organic solvents such as ethanol, methanol and acetone, which may allow for a higher extraction yields and extracts with different properties [71]. However, this type of extraction has the disadvantage of being too time consuming and of requiring the addition of high volumes of organic solvents which have a negative impact on the environment, are flammable (ethanol), toxic (methanol) and represent an extra cost [20,71].

Thus, in recent years, new, more environmentally friendly, extraction methods have been developed, like microwave-assisted extraction (MAE), ultrasound-assisted extraction (UAE) and pressurized liquid extraction (PLE) [20].

2.9 Preparation of Tannin Adsorbents

After extraction, tannins must be treated in order to be able to be used as adsorbents for metal uptake. Firstly, and because tannins are soluble in water, they must be modified into an insoluble solid; such treatment can be done either by gelification, with the reaction of the gallic acid units of gallotannins and a cross-linking agent such as formaldehyde, or by immobilization [14,74]. Immobilization gives the biosorbent the right size, rigidity, mechanical strength and good porosity, improving its sorption performance [9].

To induce insolubilization by a cross-liking agent, *Erdem et al.* (2013) [74] prepared a tannin resin from chemical activation of tannins from two different sources, mimosa and valonia, with formaldehyde [75]. For that, the tannin was added to an ammonium hydroxide solution and then mixed with a solution of formaldehyde. After filtration a yellow precipitate was obtained, distilled water was added and heated, and the solution was mixed to remove free formaldehyde. After filtration, HNO_3 was added to the obtained precipitate, stirred to make the precipitate insoluble and another filtration occurred. The precipitate was rinsed with distilled water and dried up, obtaining an insoluble tannin resin. With the same aim, *Bacelo* (2016) [76] extracted tannins from *Pinus pinaster* bark and proceeded gelification of the extracted tannins by dissolving them in a NaOH solution and adding formaldehyde into the same solution, to act as the crosslinking agent. After gelification occurred the product was dried and washed with HNO_3 and distilled water for removing unreacted substances and then dried again, allowing to obtain a final product in a gel formula. Additional studies include gelification of tannins from sources such as persimmon [3], *Quebracho* bark [77], *Acacia mearnsii de Wild*, *Schinopsis balansae* and *Cupressus sempervivens* [78].

As for immobilization procedures, there are several studies made over the best way to immobilize tannins onto water-insoluble matrices [74]; in one of the firsts, *Chibata et al.* (1986) [79] prepared immobilized tannins from several sources, such as Chinese gallotannin, nutsgalls-tannin and tannin of persimmon juice, by two different methods: in the first attempt a water insoluble matrix containing amino, carboxyl or hydroxyl groups was activated and then reacted with diaminoalkane to form a aminoalkyl matrix. Posteriorly, the tannin was activated by cyanogen bromide and finally the tannin and the matrix were coupled, producing an immobilized tannin; On the second attempt, the aminoalkyl matrix was further activated and then coupled with the tannin. On another hand, *Liao et al.* (2004) [80] prepared collagen-immobilized tannins from bayberry tannins, by dissolving the tannins in distilled water and mixing it with collagen fibre. The intermediate products were filtered and washed and then a crosslinking agent was added. The mixture was then stirred, washed and vacuum-dried originating the immobilized tannins. Other studies available in the same subject include immobilization of tannins from wattle [17,81], modified persimmon [82] and bark of *Myrica rubra* [20].

Once the tannin has become insoluble in water in can be used for the recovery of precious metals such as in the case of the recovery of gold, through adsorption mechanisms.

Future developments in the preparation of tannins for the use as adsorbents are related with the increase of the adsorption capacity and selectivity of tannin adsorbents and with the chemical stability of the native tannin, as well as to provide easier solid/liquid separations [83,84]. The adsorption capacity can be enhanced through chemical modifications such as cross-linking and functionalization which work by increasing the selectivity of raw tannins and therefore, increasing their capacity; such modifications can be made by anchoring nitrogen and sulphur containing ligating groups [83] as some authors have done, namely, *Yi et al.* (2016) [39], *Gurung et al.* (2013) [85] and *Choudhary et al.* (2018) [86]. Other chemical modifications include alkaline activation, which improves surface morphological features, such as porosity and stability, and iron loading, which improves adsorption capacity by generating specific sites for adsorption but also by shifting the pH to values that favour adsorption to occur [84].

2.10 Documented Studies of the Recovery of Precious Metals Using Tannin Adsorbents

In recent years bio-derivative materials have been the focus of studies for the recovery of metals from effluents, presenting high selectivity and high loading capacity for targeted metals like hazardous metals and valuable metals [4,87]. An example of those bio-derivate materials are tannins, which have proven themselves to be efficient adsorbents for selective binding and recovery of metal ions due to their specific affinity towards those metal ions [83].

Huang et al. (2010) [62] studied the adsorptive recovery of Au(III) from an aqueous solution using bayberry tannin-immobilized silica. The adsorptive recovery of Au was studied as well as the adsorptive capacity and the selectivity of the adsorbent towards Au when in the presence of other co-existing metals, Pb(II), Ni(II), Cu(II) and Zn(II). For the adsorption kinetics study, a solution with an initial concentration of Au of 50.0 mg L^{-1} and 0.1 g of adsorbent were used in 100 mL of solution (1.0 g L^{-1}). It was verified that the adsorption rate of Au by the bayberry tannin-immobilized silica adsorbent was extremely fast (30 min), showcasing the high affinity of the adsorbent towards Au. For the adsorption isotherms analysis, a ranging concentration of Au between 50.0-800.0 mg L^{-1} was used and the results obtained indicated a maximum adsorption capacity equal to 642.0 mg g^{-1} (pH 2, 323 K), when Au was presented by itself in solution. At last, for the selectivity study Au was present in a 1.0 mmol L^{-1} (~200 mg L^{-1}) concentration and the same amount of adsorbent as in the previous studies was used. The amount of Au adsorbed stayed practically unchanged, 196.7 mg g^{-1} vs. 196.6 mg g^{-1}, without and with the coexisting ions in solution, respectively, thus proving the high selectivity of the tannin-based adsorbent for Au.

Persimmon extract is rich in tannin and contains several polyphenols such as tannic acid and gallic acid. *Gurung et al.* (2011) [3] produced a tannin adsorbent (crosslinked gel) from persimmon extract and evaluated its adsorption capacity towards Au(III) in the presence of other metals in solution, Pd(II), Pt(IV), Zn(II), Ni(II), Fe(III) and Cu(II), in an acidic chloride media. For the adsorption tests, 10 mL of test solutions containing 0.2 mmol L^{-1} of precious and base metals were mixed with 10 mg of dry adsorbent (1.0 g L^{-1}) and HCl concentration varied between 0.1-6.0 mol L^{-1}. The results obtained showed that despite the concentration of HCl in the media, the adsorption of Au using the persimmon gel was of 100%. The uptake percentage verified for Pd(II) in HCl 0.1 mol L^{-1} was equal to 20%, with the other metals presenting lower removals. Therefore, it was possible to verify that Au was being selectively adsorbed from solution in detriment of the other metals. Simultaneously, a crude persimmon powder was studied as an adsorbent by the authors, presenting similar results to the gel adsorbent, but, reaching a given concentration of HCl in solution (~1.5 mol L^{-1}), the adsorption of Au decreases continuously until approximately 20%, for a HCl concentration of 6.0 mol L^{-1}. However, crude tannin powder was not recommended for use as adsorbent as it was found to be soluble in HCl solutions (detected by organic matter dissolution). As for the adsorption isotherms 10 mg of the dry adsorbent was used in 10 mL of test solutions containing 0.5–24 mmol L^{-1} of Au(III) in 0.1 mol L^{-1} HCl. In regard to the results obtained it was possible to verify the maximum gold uptake capacity was 7.7 mol kg^{-1} (1516.7 mg g^{-1}) for CPT gel and 5.8 mol kg^{-1} (1142.4 mg g^{-1}) for crude PT powder.

Yi et al. (2016) [39] studied the selective recovery of gold and palladium from e-waste using ethylenediamine modified persimmon tannin adsorbent (EPPFR). EPPFR was prepared by introducing amine groups into the persimmon tannin resin originating a bifunctional adsorbent. To study the effect of HCl concentration on the Au(III) adsorption, an Au(III) concentration of 200 mg L^{-1}, an adsorbent dosage of 1 g L^{-1} and different HCl concentrations were chosen, namely, 0.1-6.0 mol L^{-1} HCl. It was possible to verify that as concentration gets higher the uptake percentage gets lower, starting at 100% at 0.1 mol L^{-1} and reaching ~20% when HCl concentration is equal to 6.0 mol L^{-1}. As for the adsorption percentage as a function of time, it was possible to conclude that the maximum amount of gold recovered with the EPPFR was of approximately 100% within 6 hours from the beginning of the analysis, therefore proving that this tannin-based adsorbent is capable of successfully adsorbed Au. For the adsorption isotherm study, different initial concentration of Au(III) (200-3000 mg L^{-1}) were used with an adsorbent dosage of 1 g L^{-1} and 0.1 mol L^{-1} HCl. The maximum uptake of gold using EPPFR was 1550.4 mg-Au g^{-1}-EPPFR. The extremely high value is another evidence of the success of using ethylenediamine modified persimmon tannin as a gold adsorbent.

Furthermore, *Liu et al.* (2019) [88] produced a new biosorbent, DACS-TA, by crosslinking a tannin acid (TA) with dialdehyde corn starch (DACS) and studied its adsorption capacity towards Au(III) as well as its selectivity, adding a mixture of metals into solution such as Cr(III), Fe(III), Ni(II), Cu(II) and Zn(II). To do so, a solution containing 200 mg-Au L^{-1} and a DACS-TA dosage of 1 g L^{-1} was used in a HCl medium. The results obtained determine that the maximum adsorbed amount of gold when Au was present by itself was of 198.9 mg g^{-1} vs. 183.2 mg g^{-1} when the other metals were also present in solution, indicating that the presence of the co-existing metals had little effect over the adsorption of gold. In fact, the highest adsorbed amount after Au to be register was of Cr(III) and approximately equal to 20 mg g^{-1}, denoting that Au was being selectively adsorbed. For the adsorption isotherm study, 50 mg of DACS-TA was used in a solution with a varying concentration of Au, from 100 mg L^{-1} to 400 mg L^{-1}. The maximum Au uptake verified was equal to 298.5 mg g^{-1}; such value was then compared to other documented adsorbents, including chitosan, lignin and graphene oxide, and it was verified that DACS-TA exhibited the highest adsorption capacity among all the adsorbents considered, thus proving its outstanding ability to recover Au from solution.

At last, *Fan et al.* (2019) [89] developed a core-shell nanostructured magnetic bio-based composite from persimmon tannin and $Fe_3O_4@SiO_2$ microspheres for the adsorptive recovery of Au(III) and Pd(II). The adsorptive capacity and adsorptive percentage of the tannin-immobilized adsorbent was tested as well as its selectivity towards Au when other metals were present in solution, Pd(II), Cu(II), Zn(II) and Fe(III), from an initial solution with HCl and a concentration of Au equal to 200 mg L^{-1}. A maximum uptake of 100% of Au was registered after 24 hours and the maximum adsorptive capacity registered was equal to 917.43 mg g^{-1}, proving the success of the adsorbent in recovery Au from solution. As for the selectivity study, the adsorption recovery of Au was almost 100% while only small amounts of the other coexisting metals were recovered, thus proving the strong affinity between the adsorbent and Au.

Despite the small differences between studies, whether it is the type of tannin used as adsorbent or the existence or not of chemical modifications, the common point between all of them is that for the recovery of gold(III) adsorption occurs due to a redox reaction occurring between the tannin and the Au in solution, mostly present as a $AuCl_4^-$ complex [4], accordingly to the following process [15,87]: positively charged Au(III) ions interact with the oxygen atoms of hydroxyl groups in tannin compounds, enabling adsorption to occur; The adsorbed trivalent Au(III) ions are then reduced to Au(0) and, simultaneously, the hydroxyl groups are oxidized into carbonyl groups. Finally, the elemental gold particles suffer aggregation, originating bigger complexes.

The complete reaction is given by equation 1 [15],

$$AuCl_4^- + 3\,R - OH \rightarrow Au^0 + 3\,R = O + 3\,H^+ + 4\,Cl^- \qquad (eq.1)$$

The metal reduction, in HCl solution is described by the reaction (eq.2) [90],

$$AuCl_4^- + 3\,e^- \leftrightarrow Au^0 + 4\,Cl^- \qquad (eq.2)$$

if the gold(III) reduces directly to metallic gold, where e^- symbolizes the electrons; or described by [90],

$$AuCl_4^- + 2\,e^- \leftrightarrow AuCl_2^- + 2 \qquad (eq.3)$$

$$AuCl_4^- + e^- \leftrightarrow Au^0 + 2\,Cl^- \qquad (eq.4)$$

if the reduction occurs with the formation of an intermediate, $AuCl_2^-$.

3 Technical Description

3.1 Materials

3.1.1 Tannin Adsorbent

The tannin adsorbent used had already been prepared by Eng. Hugo Bacelo according to the following procedure [22]:

- *P. pinaster* bark was collected and milled. Tannins were then extracted in an alkaline solution (7.5% NaOH, w/w%), using a solid (bark)-to-liquid ratio of 1:6 (w/w), a temperature of 90ºC and a contact time of 90 min, according to the optimal set of conditions defined.
- The resulting freeze-dried solid material was converted in an insoluble material by gelification at 80 °C in basic medium, for 8 hours, using formaldehyde (0.2 mL of formaldehyde per g of extract). The precipitate was then dried, milled, washed and dried again so it could finally be used as the adsorbent.

3.1.2 Simulated Liquors Containing Gold

The leaching agents under study were the hydrochloric acid, HCl, and aqua regia, a mixture of hydrochloric acid and nitric acid under the ratio of 3:1 (v/v).

The hydrochloric acid solutions used were prepared from a commercial HCl solution at 37% m/m (ρ =1.19 g mL^{-1}, analytic grade, purchased from Chem-Lab NV, Zedelgem, Belgium).

Aqua regia was prepared using a combination of the HCl commercial solution and of HNO_3 65% m/m (ρ =1.39 g mL^{-1}, analytic grade, purchased from Chem-Lab NV, Zedelgem, Belgium).

In a first phase of the project the leaching liquors were simulated as mono-metal solution of Au. For that, gold solutions were prepared from a commercial standard with a gold concentration of 1000 mg L^{-1} ($H(AuCl_4)$ in HCl 2 mol L^{-1}; purchased from Merck KGaA, Darmstadt, Germany). The commercial standard was diluted until presenting the defined concentration of Au in the leaching liquors, using distilled water and the required amounts of

HCl or aqua regia, in order to find different concentrations of these leaching agents. Afterwards the commercial standard was kept in the fridge at 4ºC.

In a second phase of the project a synthetic solution was prepared containing Au and the typical coexisting metals of e-waste leaching liquors. The multi-metal solution was prepared after taking into consideration the concentration of metals reported in literature for liquors obtained from e-waste after treatment with aqua regia [38,39]. Therefore, the concentrations used for the synthetic liquor were the following: 2000 mg L^{-1} Cu (providing by the dissolution of $CuCl_2.2H_2O$, Merck), 150 mg L^{-1} Fe (obtained by dilution of a commercial standard of $Fe(NO_3)_3$ in HNO_3 0.5 mol L^{-1}, Merck), 80 mg L^{-1} Ni (dilution of a standard prepared in 4% HNO3, SCP Science), 10 mg L^{-1} Zn (obtained by dilution of a standard prepared in 0.5 mol L^{-1} HNO_3, Merck), 40 mg L^{-1} Pd (from a standard containing 10 to 20% of HCl, Chem-Lab) and 200 mg L^{-1} Au (obtained from a standard solution of $H(AuCl_4)$ in HCl 2 mol L^{-1}, Merck). Aqua regia was used as the leaching agent under three different levels, corresponding to final acid concentrations of 0.5 mol L^{-1} HCl:0.19 mol L^{-1} HNO_3, 1.0 mol L^{-1} HCl:0.38 mol L^{-1} HNO_3 and 1.5 mol L^{-1} HCl:0.58 mol L^{-1} HNO_3.

3.2 Analytic Methods

For metals analysis (Au, Cu, Fe, Ni, Pd and Zn) in the samples collected an atomic flame absorption spectrophotometer (*GBC Scientific Equipment Ltd. – 932 plus*) was used, with a hollow cathode lamp specific to the metal being measured (Cu, Fe, Ni, Pd and Zn lamps purchased from Photron PTY. Ltd., Australia, and Au lamp purchased from SCP Science, Canada). The instrumental and analytical conditions used in each analysis are presented in Table 3, as well as the detection limit, LOD (defined in ***Annex***). The flame was obtained using a combined gas current of air-acetylene, with a fuel flow of 2.00 l min^{-1} and an oxidant flow of 10.00 l min^{-1}.

Table 3. Instrumental and analytical conditions used for the spectrophotometric analysis of each metal studied.

Metal	**Wavelength** (nm)	**Intensity** (mA)	**Concentration range** (mg L^{-1})	**LOD** (mg L^{-1})
Copper	222.6	3.0	20 - 150	10.0
Iron	386.0	5.0	20 - 120	3.0
Gold	242.8	4.0	1 - 15	0.6
Nickel	232.0	4.0	1 - 10	1.0
Palladium	244.8	5.0	1 - 10	0.7
Zinc	213.9	5.0	0.1 - 1.0	0.1

For the calibration, standards were prepared by the dilution of commercial standards using distilled water (solvent and blank).

For Au measurements, potassium nitrate, KNO_3 (analytical grade), was added to the standards and samples to a final concentration of 2000 µg-K mL^{-1}. The addition of KNO_3 is necessary because Au tends to ionize once it contacts with the flame and therefore, the concentration read by the equipment tends to be lower than the real one. KNO_3 is added as an ionization suppressor, in in order to avoid such phenomenon [91].

Additionally, Lanthanum, La, was added to standards and samples where Pd was measured. In the air-acetylene flame and in the presence of elements like Ni, the atomic absorption signal is depressed, causing wrong measurements; such depression is eliminated in the presence of lanthanum [91].

Working ranges used were selected based on the recommended conditions provided by the supplier and the linear range (Lambert-Beer law). The samples were read 3 times and the mean determined. The spectrophotometer measured the absorbance, which was plotted as a function of the metal concentration (mg L^{-1}), and the calibration curve drawn through the Minimum Square Method. The calibration plot was taken daily and accepted for determination coefficients, R^2, over 0.995. In ***Annex*** it can be found an example of an obtained calibration curve for Au.

3.3 Adsorption Studies

3.3.1 Effect of the Leaching Agent

In a first phase of the experimental work the effect of the concentration of the leaching agents in solution in relation to the amount of Au adsorbed by the tannin resin was studied. To do so, an initial solution with an Au concentration of 100 mg L^{-1} was prepared and two leaching agents were used, HCl and aqua regia, and in different concentrations. HCl concentrations tested were 0.2 mol L^{-1}, 0.3 mol L^{-1}, 0.5 mol L^{-1}, 1.0 mol L^{-1}, 1.2 mol L^{-1}, 2.0 mol L^{-1}, 3.0 mol L^{-1} and 3.7 mol L^{-1}; aqua regia was used in order to find final HCl:HNO_3 concentrations of 0.20 mol L^{-1} : 0.08 mol L^{-1}, 0.30 mol L^{-1} : 0.12 mol L^{-1}, 0.50 mol L^{-1} : 0.19 mol L^{-1}, 1.00 mol L^{-1} : 0.38 mol L^{-1}, 1.50 mol L^{-1} : 0.58 mol L^{-1}, 2.00 mol L^{-1} : 0.77 mol L^{-1} and 3.0 mol L^{-1} : 1.2 mol L^{-1}, respectively. Samples with 15 mL volumes were prepared, in duplicate, and mixed with the tannin resin in a ratio of 2.0 g L^{-1}.

The samples were then stirred *(BioSan Orbital Shaker PSU-10i)* at a defined agitation (280 rpm) for a defined time interval (35 hours, supposed to be enough to reach adsorption equilibrium). Afterwards, the samples were filtered with a microfilter (cellulose acetate membranes, 0.45 µm porosity) and diluted when necessary.

After the spectrometric analysis, the results were translated as the uptake of Au (equation 5), in %, and the adsorbed amount, q_e, in mg of Au per g of resin (equation 6).

$$Uptake = \frac{C_o - C_e}{C_o} * 100\% \qquad (eq.5)$$

$$q_e = \frac{C_o - C_e}{V} * W \qquad (eq.6)$$

where, C_o is the concentration of Au, in mg L^{-1}, before adsorption; C_e is the concentration of metal adsorbed, in mg L^{-1}, after a given time interval; V is the volume of the solution considered, in L; and W is the weight of the dry tannin resin, in g.

3.3.2 Kinetic Study

The effect of contact time on the amount of Au adsorbed by the tannin resin was studied for different leaching agents, HCl and aqua regia, variable solid:liquid (S:L) ratios, 0.5, 1.0 and 2.0 g L^{-1}, and at different initial Au concentrations, 100 mg L^{-1} and 300 mg L^{-1}.

Firstly, to study the effect of the different leaching agents in the adsorption of Au, HCl and aqua regia, were employed at 1.0 mol L^{-1} and in 1.0 mol L^{-1} HCl:0.38 mol L^{-1} HNO_3 concentrations, respectively. The Au concentration was 100 mg L^{-1} and the tannin resin 2.0 g L^{-1}.

Secondly, to test the effect of the solid:liquid ratio, which translates the ratio in which the tannin resin was used in solution, three different levels were used, 0.5 g L^{-1}, 1.0 g L^{-1} and 2.0 g L^{-1}. The solutions prepared presented an Au concentration equal to 100 mg L^{-1} and 1.0 mol L^{-1} HCl was used as the leaching agent.

At last, to study the effect of dissolved Au concentration in the adsorption capacity of the resin, two different concentrations of Au were used, 100 mg L^{-1} and 300 mg L^{-1}, based on the typical concentrations of Au found in similar studies in literature [39,83], and prepared in 1.0 mol L^{-1} HCl. The tannin resin concentration was 2.0 g L^{-1}.

For every assay, the procedure followed was the same: Au solutions (15.0 mL) containing the leaching agent at test were combined with the required amount of the tannin resin. For every condition two replicates were made. The suspensions were then stirred in the orbital shaker, at 280 rpm, for different periods of time: 20, 60, 120, 240, 360, 540, 960, 1440 (1 day), 2880 (2 days) and 4320 (3 days) minutes. Two aliquots of the initial solution, containing only the Au and leaching agent in solution and without the resin, were collected to evaluate the initial conditions of the solution in study. After the designated time, samples were taken out of the orbital shaker and immediately filtrated, using a microfilter. The solutions were then diluted in order to be analysed in the atomic flame absorption spectrophotometer.

Once the spectrometric analysis ended, the results were translated as the adsorbed amount of Au, q, in mg Au per g of resin (equation 6), as a function of time.

3.3.3 Adsorption Equilibrium Isotherms

Equilibrium relationships, also known as Adsorption Isotherms, describe how the adsorbate interacts with the adsorbent material and, therefore, are critical data for the optimization of the adsorption process, for the expression of the surface properties and capacities of adsorbents, and also for the effective design of the adsorption systems [92].

For the equilibrium study, solutions with different concentrations of Au were prepared, namely, 10, 50, 100, 300 and 500 mg L^{-1}, in duplicate, and in two different leaching mediums, HCl (1.0 mol L^{-1}) and aqua regia (1.0 mol L^{-1} HCl:0.38 mol L^{-1} HNO_3). For every concentration of Au tested an initial aliquot was taken in duplicate. The tannin resin was used in solid:liquid ratio of 1.0 g L^{-1} and added to 15 mL solutions with Au and the leaching agent. The samples were then stirred at ambient temperature (20-22 °C), under an agitation speed of 280 rpm, for 72 hours.

After the defined time interval, the samples were filtered to be measured at the spectrophotometry equipment. Once the results of the spectrophotometer were obtained a plot of the amount of Au adsorbed (q_e, in mg Au per g of tannin resin) as a function of the dissolved Au concentration in equilibrium (C_e, in mg L^{-1}) was drawn.

3.3.4 Selectivity

To study the affinity of the tannin adsorbent towards Au from a multi metal matrix, a synthetic liquor containing other metals was prepared. The sample tried to simulate the typical constitution of an e-waste leach liquor and was prepared based on previous studies [38,39]. Therefore, the initial composition of the solution was 2000 mg L^{-1} Cu, 200 mg L^{-1} Au, 150 mg L^{-1} Fe, 80 mg L^{-1} Ni, 40 mg L^{-1} Pd and 10 mg L^{-1} Zn and aqua regia was used under different concentrations. A solid:liquid ratio, between the tannin resin and the solutions, of 1.0 g L^{-1} was used.

The suspensions were prepared in duplicate and posteriorly stirred at an agitation speed of 280 rpm for 72 hours. The samples were then filtered to be analysed in the spectrophotometer for the different metals.

Simultaneously, a solution containing only Au dissolved in a 200 mg L^{-1} concentration was prepared in order to allow direct comparison of the results of Au adsorption when a mono-metal solution was used vs. when Au was presented with other co-existing metals in solution. Aqua regia was also used as the leaching agent under the same concentrations in which it was used in the multi-metal solution.

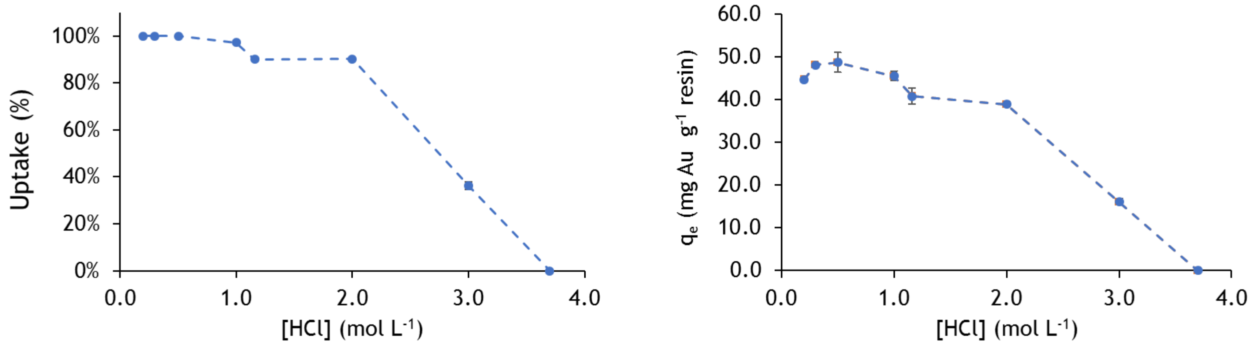
After the results of the spectrophotometer were obtained, plots for the uptake percentage of each metal were drawn, as well as a second plot were the uptake of Au was compared between the mono-metal solution and the multi-metal solution, using equation 5.

4 Results and Discussion

4.1 Effect of the Leaching Agent

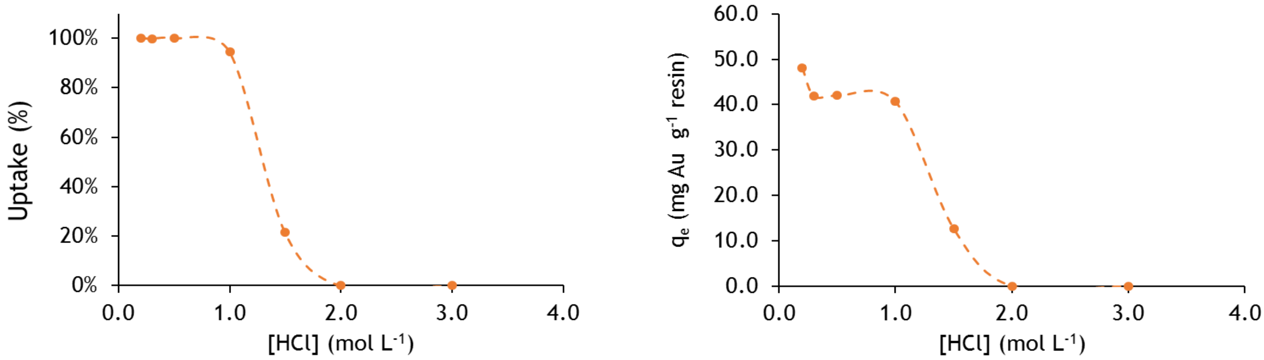
To test the effect of the leaching agents, different acids were tested in different concentrations for a defined Au concentration, 100 mg L^{-1}, like previously referred in the ***Adsorption Studies*** section.

The results obtained for the different leaching agents are present in Figure 5 and Figure 6. The figures represent the (A) uptake percentage of Au from solution as a function of the concentration of lixiviant used, in mg L^{-1}, and the (B) adsorbed amount of the tannin resin, mg of Au per g of resin, as a function of the concentration of lixiviant, mg L^{-1}, for HCl and aqua regia as leaching agents, respectively. The error bars for every measurement were considered and presented in the displayed plots.



(A) **(B)**

Figure 5. (A) Uptake of Au (%) and **(B)** Adsorbed Amount of the tannin resin (mg Au g^{-1} resin) as a function of the concentration of HCl, for 100 mg L^{-1} initial Au concentration (contact time: 35h).



(A) **(B)**

Figure 6. (A) Uptake of Au (%) and **(B)** Adsorbed Amount of the tannin resin (mg Au g^{-1} resin) as a function of HCl concentration included in aqua regia, for 100 mg L^{-1} initial Au concentration (contact time: 35h).

Starting from the HCl solutions (Figure 5) it can be seen that, up to a concentration of 1.0 mol L^{-1}, the total uptake of Au from the solution was of about 100%. For higher concentrations the recovery capacity tends do decrease, remaining at approximately 90% for 1.2-2.0 mol L^{-1} HCl but then decreasing until it is almost equal to zero (3.7 mol L^{-1} HCl). Looking into Figure 5 (B) it is possible to observe that the amount of Au adsorbed per gram of resin tends to decrease with the concentration of HCl (in coherence with the results on Fig. 5 (A)), meaning that the acidity of the medium interferes with the adsorption of gold by the resin. It is known that Au is present in solution under $AuCl_4^-$ complexes. In fact, for the very low pH values used here, the resin is probably positively charged and there may be a competitive adsorption between Cl^- and $AuCl_4^-$ ions to the active sites [88]. The maximum adsorbed amount was verified at 0.5 mol L^{-1} of HCl, 49 ± 3 mg Au g^{-1} resin, but the results were very similar for both 0.3 mol L^{-1} and 1.0 mol L^{-1}, 48.06 ± 0.01 mg g^{-1} and 46 ± 1 mg g^{-1}, respectively. Therefore, to make use of the best performance of the adsorbent, HCl concentrations in the leach liquors should not exceed 1.0 mol L^{-1} HCl. Furthermore, the results obtained showed that the tannin uptake capacity of Au is seriously affected for HCl levels above 2.0 mol L^{-1}.

As for aqua regia and starting by analysing Figure 6 (A), which presents the uptake percentage of gold as a function of the concentration of HCl in solution, and indirectly of the concentration of aqua regia, it can be seen that the uptake % tends to decrease with the acidification of the medium, exhibiting a total recovery of gold (100%) until the HCl concentration is 0.5 mol L^{-1}, slightly decreasing for 1.0 mol L^{-1} and decreasing even more, and more evidently, as the concentration gets higher than this level. As for Figure 6 (B), evidencing the adsorbed amount of Au as a function of HCl concentration, it can be seen that the adsorbed amount also decreases with the increase of HCl concentration, showcasing a maximum value of 48.1 ± 0.5 mg Au g^{-1} resin when HCl concentration is equal to 0.2 mol L^{-1}, and slightly decreasing until the concentration of HCl hits the 1.0 mol L^{-1} value, 40.7 ± 0.5 mg g^{-1}. Afterwards, as the HCl concentration increases, the adsorbed amount decreases faster and tends to zero around 2.0 mol L^{-1} HCl.

Yi et al. (2016) [39] also studied the effect of HCl concentration in the adsorption of gold(III) by ethylenediamine modified persimmon tannin adsorbent (EPPFR). HCl was used in a ranging concentration between 0.1 mol L^{-1} and 6.0 mol L^{-1}, with an Au concentration of 200 mg L^{-1} and a S:L ratio equal to 1 g L^{-1}. The same type of behaviour was observed between the authors study and the present one: Au recovery from solution decreases with the increase of

HCl concentration in solution. A recovery of 100% of Au from solution was recorded at the initial concentration of 0.1 mol L^{-1} HCl and progressively decreased until ~20% for a HCl concentration of 6.0 mol L^{-1}. At 1.0 mol L^{-1} of HCl in solution ~85% of Au was recovered and at 2.0 mol L^{-1} the value was equal to 65%. In these conditions, the tannin resin here used adsorbed 97 and 90% of the Au in solution, respectively, presenting a better performance than the EPPFR. Under more extreme acidic conditions, however, EPPFR performed best. Additionally, the influence of HCl was more prominent in this work.

At last, comparing the results for HCl and aqua regia, it can be seen that gold adsorption is more affected by the presence of aqua regia since the uptake percentage of Au from solution decreases faster than when in the presence of HCl by itself; at a concentration of 2.0 mol L^{-1} HCl the uptake % of Au was equal to 90% and ~0% for HCl and aqua regia, respectively. For the same total H^+ concentration, the uptake % and adsorbed amount generated in HCl solutions are in general higher than the ones obtained in aqua regia, especially for higher acidity. For instance, 39.0 ± 0.6 mg g^{-1} of Au were adsorbed from an HCl solution of 2.0 mol L^{-1}. In aqua regia, at the same H^+ concentration (corresponding to 1.4 mol L^{-1} HCl:0.6 mol L^{-1} HNO_3), the obtained results indicate a much lower adsorbed amount, close to 13 mg g^{-1}. It can also be observed that the ability of the tannin resin to remove gold has ceased for H^+ concentrations equal to 3.7 mol L^{-1} in HCl solutions; in aqua regia, negligible uptakes were found at lower acidity, for H^+ concentrations of 2.7 mol L^{-1}, corresponding to 2.0 mol L^{-1} HCl and 0.8 mol L^{-1} HNO_3. Therefore, these results show that the presence of nitric acid in solution impairs the uptake of Au by the adsorbent. In fact, *Fan et al.* (2014) [38] studied the influence of both acids in the aqua regia formula, HCl and HNO_3, in the recovery of gold. Different concentrations of both acids were used ranging between 0.5 to 8.0 mol L^{-1}. It was verified that the recovery % of Au was more affected by the concentration of HNO_3 than HCl; at a 5.0 mol L^{-1} of acid, ~95% of Au was being recovered from the HCl medium while only ~15% was being recovered from the HNO_3 medium.

Even though the optimum condition was defined when both leaching agents presented a HCl concentration equal or lower than 0.5 mol L^{-1}, the following studies were conducted with a HCl concentration of 1.0 mol L^{-1}, to enable closer comparison with reality.

4.2 Kinetic Study

To study the kinetics, different time intervals were tested in order to monitor the evolution of Au adsorption throughout time, for the different leaching agents used, for different concentrations of Au in solution and different solid:liquid ratios. Posteriorly, two kinetic models were adjust to all experimental data obtained and used to describe the adsorption kinetics, namely, the pseudo-first-order rate model (equation 7) and pseudo-second-order rate model (equation 8) [93].

$$q = q_e \ [1 - \exp(-k_1 * t)] \qquad (eq.7)$$

$$q = q_e * \frac{k_2 * q_e * t}{1 + k_2 * q_e * t} \qquad (eq.8)$$

where, q is the concentration of the adsorbate per adsorbent unit mass (mg g^{-1}) and q_e is the concentration of the adsorbate at equilibrium per adsorbent mass unit (mg g^{-1}); k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are two rate constants and t is a defined time (min).

Firstly, and to evaluate the effect of the two leaching agents on the adsorption kinetics, the Au concentration was defined at 100 mg L^{-1} and S:L ratio at 1.0 g L^{-1}. The concentration of HCl was 1.0 mol L^{-1} and aqua regia was used with 1.0 mol L^{-1} HCl:0.38 mol L^{-1} HNO_3. Pseudo-first-order rate and pseudo-second-order rate kinetic models were used to evaluate the results obtained, which are presented in Figure 7.

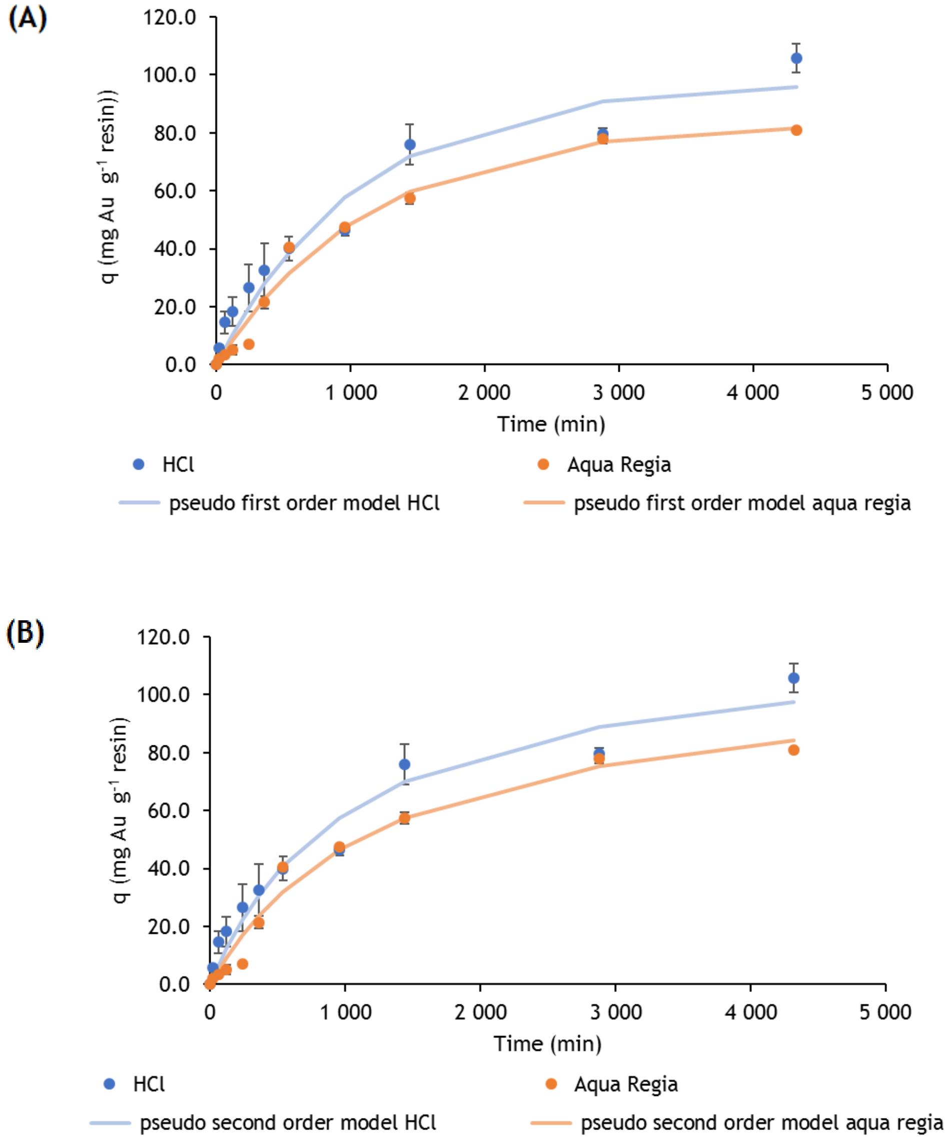


Figure 7. Resin adsorption capacity of Au, q (mg Au g^{-1} resin), as a function of time (min) for HCl (1.0 mol L^{-1}) and aqua regia (1.0 mol L^{-1} HCl and 0.8 mol L^{-1} HNO_3), and 100 mg L^{-1} initial Au concentration. Experimental values and comparison with **(A)** pseudo-first-order; **(B)** pseudo-second-order kinetic

Table 4 summarizes the values obtained for the kinetic parameters for the pseudo-first- and pseudo-second order kinetic models for the leaching agents, HCl and aqua regia, considering the standard error associated to the parameters, the determination coefficient (R^2) and the standard error (SE) of the fitting.

Table 4. Kinetic parameters for the pseudo-first and pseudo-second order kinetic models for the uptake of Au by tannin resin when HCl and aqua regia were present as the leaching agents.

Pseudo-first-order	**q_e** (mg g^{-1})	**k_1** (min^{-1})	**R^2**	**SE** (mg g^{-1})
HCl	97 ± 8	(9 ± 2) x 10^{-4}	0.95	8.22
Aqua regia	84 ± 5	(9 ± 2) x 10^{-4}	0.98	4.47
Pseudo-second-order	**q_e** (mg g^{-1})	**k_2** (g mg^{-1} min^{-1})	**R^2**	**SE** (mg g^{-1})
HCl	122 ± 12	(8 ± 2) x 10^{-6}	0.96	7.07
Aqua regia	110 ± 10	(7 ± 2) x 10^{-6}	0.98	4.86

By analysis of Figure 7, it is possible to verify that the final adsorbed amount of Au from the tannin resin is higher for HCl than for aqua regia, 106 ± 5 mg Au g^{-1} resin vs 81.1 ± 0.5 mg Au g^{-1} resin, respectively. Taking into consideration Table 4, it can also be seen that the predicted adsorption capacity at equilibrium, q_e, is slightly higher in HCl than in aqua regia solutions, although the difference between results is not statistically significant. Therefore, HCl seems to be the leaching agent that less impairs the uptake of Au from solution, in accordance with the conclusions taken in section ***4.1***, which already showed the advantages of using HCl. Such results can be explained by the fact that aqua regia is a strong oxidizing agent that will block the reduction and precipitation of metallic gold by the resin, which is the probable mechanism of Au uptake, interfering with the adsorbed amount of the precious metal and leading to lower adsorption results [94].

Considering the kinetic models, it can be seen that both models are capable to successfully describe the adsorption behaviour of the tannin resin, which can be validated by taking into account Table 4. In fact, it can be seen that R^2 values are within the acceptable limits for all cases. For HCl medium, the pseudo-first order model presents a lower R^2 value and a slightly higher SE than the pseudo-second-order model, which lead to conclude that the latter is a better fit for describing the adsorption. Additionally, it can be seen, by analysis of Figure 7, that the velocity of adsorption is relatively slow; for both leaching mediums, it needs 720 minutes (12 hours) of contact to adsorb half of the maximum amount of Au adsorbed at equilibrium. Based on the experimental data, it can be seen that the contact time to reach equilibrium for the aqua regia solution is of approximately 2 days. After that time no significant changes were seen for the adsorbed amount of Au. For the HCl solution, the experimental data for the 1440 min, 2880 min and 4320 min does not allow to define a certain time for when equilibrium is reached. However, taking into account the kinetic models applied, it is possible to conclude that after 2880 minutes (48 hours) there is no significant changes in the adsorbed amount of Au from solution (less than 5%); even so, only after 3 days the experimental value, q, equals q_e value predicted by the kinetic models.

Secondly, to test the influence of the solid-liquid ratio three conditions were tested, S:L = 0.5 g L^{-1}, S:L = 1.0 g L^{-1} and S:L = 2.0 g L^{-1}; A solution of 100 mg L^{-1} of Au was used and HCl was the acid applied since it was the one that offered the best results for the leaching of gold as seen previously.

Figure 8 represents the results obtained for the evolution of the adsorbed amount of Au by the tannin resin as a function of time, for every S:L ratio tested as well as the plots for the kinetic models considered.

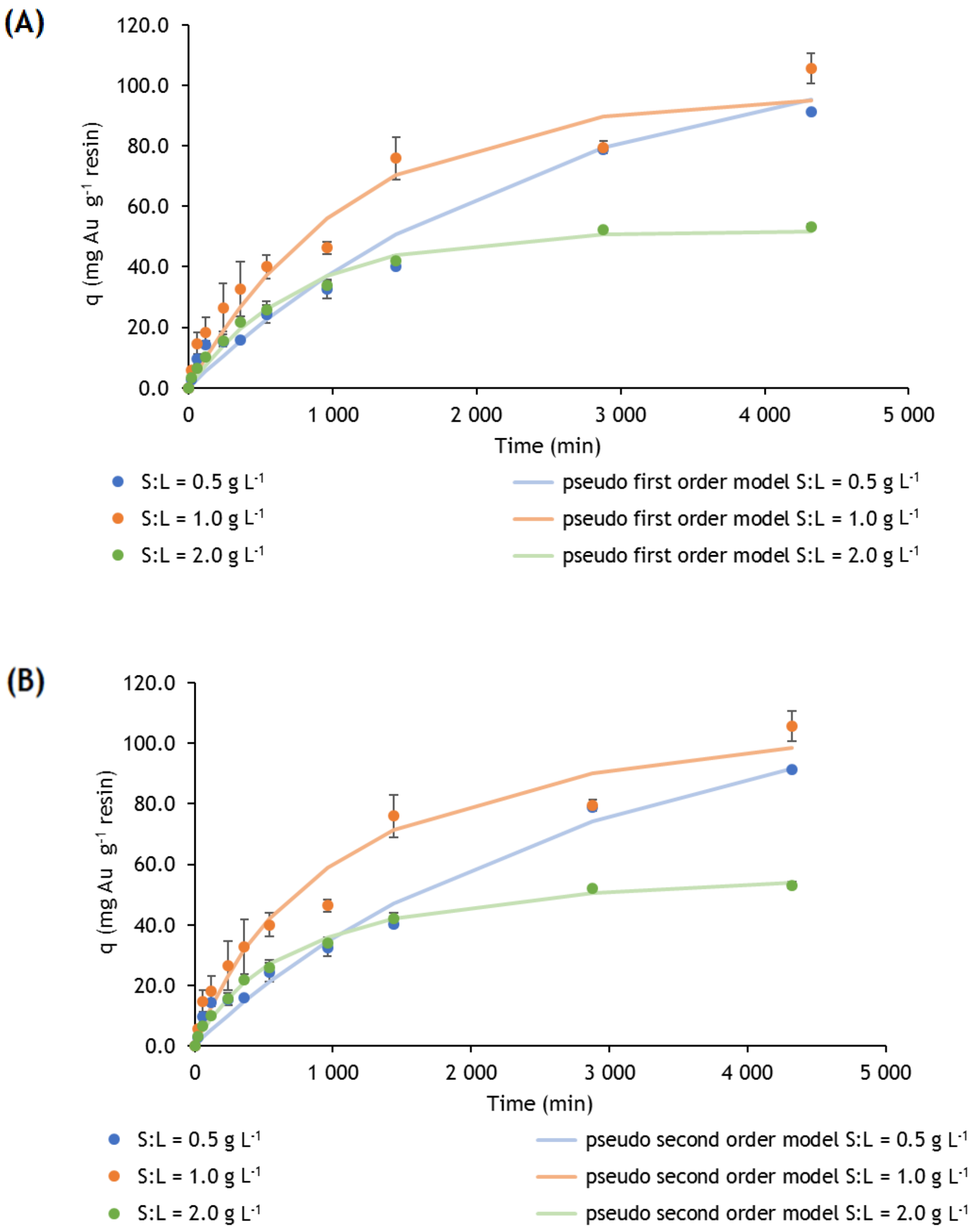


Figure 8. Resin adsorption capacity of Au, q (mg Au g^{-1} resin), as a function of time (min) for different S:L ratios, 0.5, 1.0 and 2.0 g L^{-1}, and 100 mg L^{-1} initial Au concentration. Experimental values and comparison between **(A)** pseudo-first-order; **(B)** pseudo-second-order kinetic models.

Table 5 summarizes the values obtained for the kinetic parameters for the pseudo-first and pseudo-second order kinetic models and different tannin resin dosages.

Table 5. Kinetic parameters for the pseudo-first and pseudo-second order kinetic models for the uptake of Au by tannin resin using different S:L ratios, 0.5 g L^{-1}, 1.0 g L^{-1} and 2.0 g L^{-1}.

Pseudo-first-order	q_e (mg g^{-1})	k_1 (min)	R^2	**SE** (mg g^{-1})
0.5 g L^{-1}	116 ± 17	(4 ± 1) x 10^{-4}	0.97	5.39
1.0 g L^{-1}	97 ± 8	(9 ± 2) x 10^{-4}	0.95	8.22
2.0 g L^{-1}	52 ± 2	(13 ± 2) x 10^{-4}	0.99	2.31
Pseudo-second-order	q_e (mg g^{-1})	k_2 (min)	R^2	**SE** (mg g^{-1})
0.5 g L^{-1}	175 ± 32	(1.5 ± 0.7) x 10^{-6}	0.97	5.29
1.0 g L^{-1}	122 ± 12	(8 ± 2) x 10^{-6}	0.96	7.07
2.0 g L^{-1}	63 ± 2	(22 ± 2) x 10^{-6}	0.99	1.46

Considering Figure 8, it can be seen that for all solid:liquid ratios tested, the adsorbed amount of Au by the tannin resin increases throughout time, proving adsorption is occurring.

It can also be seen from Figure 8, that at the highest S:L ratio the lowest adsorbed amount of Au per gram of resin was observed, namely, 53 ± 1 mg g^{-1} vs. 91.3 ± 0.7 mg g^{-1} and 106 ± 5 mg g^{-1} for S:L = 0.5 g L^{-1} and S:L = 1.0 g L^{-1}, respectively. Such observation can be explained by the fact that higher S:L ratios mean there is more resin in solution available to adsorb Au, and the adsorbent adsorption capacity was not fully utilized. However, and unlike what was expected, S:L =1.0 g L^{-1} presents a slightly higher q_e than S:L =0.5 g L^{-1}, but it should be pointed out that the difference was not very significant. Additionally, the q_e values predicted by modelling (Table 5) are practically the same for both S:L ratios. Therefore, these adsorbent dosages must correspond to the best use of the adsorptive capacity of the resin. In fact, in Table 5, it can be seen that the adsorptive capacity of the resin at equilibrium, foreseen by the kinetic models, decreases with the increase of the mass of resin in solution.

Furthermore, based on Figure 8, it can be concluded that the usage of low S:L ratios (0.5 g L^{-1}), results in slow adsorption kinetics, with adsorption taking place very gradually throughout time. In fact, for such ratio it can be seen that the equilibrium wasn't even reached after the final time interval of analysis (3 days). However, for higher S:L ratios, 1.0 g L^{-1} and 2.0 g L^{-1}, equilibrium was reached after approximately 2 days of analysis.

As for the kinetic models, and consulting Table 5, both models could be used to describe the systems behaviour since they present acceptable values of R^2. However, the pseudo-second-order model presents a higher R^2 for all the solid:liquid ratios and lower standard errors associated, and therefore it was chosen as the most appropriate to describe the adsorption kinetics.

At last, two different concentrations of Au, 100 mg L^{-1} and 300 mg L^{-1}, were tested to study its influence over the adsorbed amount of the resin using an S:L ratio previously defined, 2.0 g L^{-1}, and using HCl 1.0 mol L^{-1}.

Figure 9 illustrates the obtained plots for the evolution of the adsorbed amount of the tannin resin as a function of time and the representation of the kinetic models considered to describe the adsorption process, the pseudo-first-order and the pseudo-second-order models.

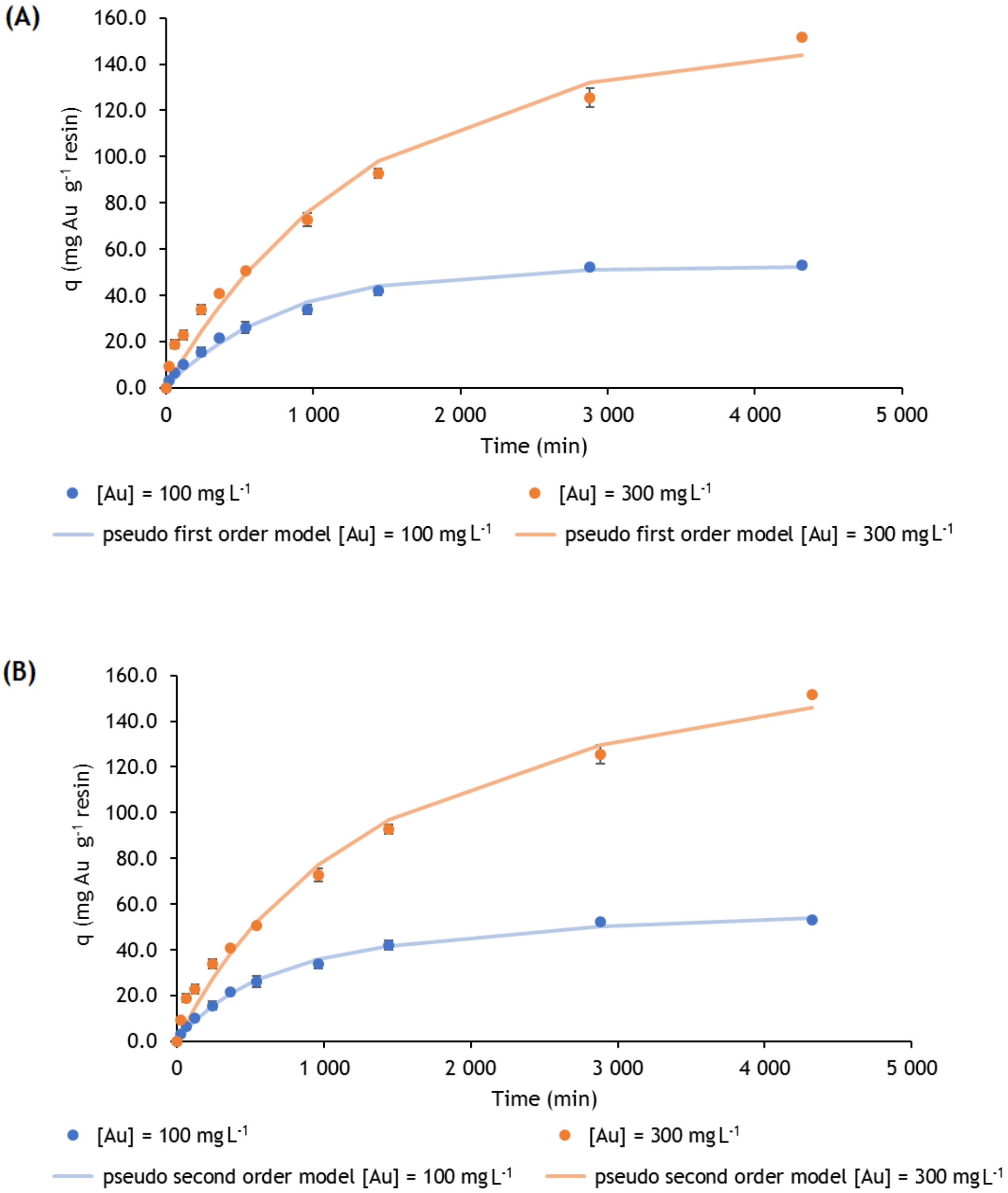


Figure 9. Resin adsorption capacity for Au, q (mg Au g^{-1} resin), as a function of time (min) for different Au concentration in the initial solution, 100 mg L^{-1} and 300 mg L^{-1}, and comparison **(A)** pseudo-first-order; **(B)** pseudo-second-order kinetic models.

Table 6 summarizes the values obtained for the kinetic parameters for two different initial Au concentrations tested, 100 mg L^{-1} and 300 mg L^{-1}, considering the standard error associated to the parameters, the determination coefficient (R^2) and the standard error (SE).

Pseudo-second-order presented the higher R^2 values and lower standard errors associated, for both concentrations of Au. However, the q_e values provided by the mathematical fittings (63 ± 2 and 196 ± 14 mg g^{-1}) significantly differ from the experimental values obtained (53 mg g^{-1} and 152 mg g^{-1}, respectively for Au initial concentrations of 100 mg L^{-1} and 300 mg L^{-1}). Even so, the quality of the fittings provided by both models are very acceptable.

Table 6. Kinetic parameters for the pseudo-first and pseudo-second order kinetic models for the uptake of Au by the tannin resin when different concentrations of Au were used in the initial solution, 100 mg L^{-1} and 300 mg L^{-1}.

Pseudo-first-order	**q_e** (mg g^{-1})	**k_1** (min)	**R^2**	**SE** (mg g^{-1})
100 mg L^{-1}	52 ± 2	(13 ± 2) x 10^{-4}	0.99	2.31
300 mg L^{-1}	150 ± 10	(7 ± 1) x 10^{-4}	0.98	7.92
Pseudo-second-order	**q_e** (mg g^{-1})	**k_2** (min)	**R^2**	**SE** (mg g^{-1})
100 mg L^{-1}	63 ± 2	(22 ± 2) x 10^{-6}	0.99	1.47
300 mg L^{-1}	196 ± 14	(3.5 ± 0.8) x 10^{-6}	0.99	6.34

By analysis of Figure 9, it can be seen that the adsorbed amounts by the resin at different contact times are higher for the highest Au concentration, 300 mg L^{-1}; such result would be expected since for the same amount of resin there is more Au species in solution, when the concentration is higher, and therefore the driving force for the adsorption is higher. Table 6 can support the previous statement since for both models the 300 mg L^{-1} Au solution presents higher values of q_e than the 100 mg L^{-1} one.

For the initial Au concentration of 100 mg L^{-1} it can be seen that after a contact time of 2 days (2880 min) equilibrium is reached. Such conclusion can be validated by the fact that at this time interval the adsorbed amount, q, is of approximately 52.2 ± 0.04 mg Au g^{-1} resin, corresponding to the adsorbed amount at equilibrium, q_e, foreseen by the pseudo-first-order kinetic model (and is also equal to the q value obtained after 3 days of contact time, 53 ± 1 mg g^{-1}). On the other hand, for an initial Au concentration of 300 mg L^{-1} the experimental data suggests that the equilibrium is reached only after a contact time of 3 days (4320 min) or more, since the adsorbed amount of Au after 2 days, 126 ± 4 mg g^{-1}, is still around 17% lower than the 3 days value, 151.7 ± 0.4 mg g^{-1}. Taking into consideration the pseudo-first-order model it can be indeed concluded that the contact time necessary to reach equilibrium is of 3 days once at that given time the experimental adsorbed amount equals the previewed by the kinetic model (150 ± 10 mg g^{-1}).

4.3 Adsorption Equilibrium Isotherms

Adsorption equilibrium data, also known as adsorption isotherms, allow for the design and optimization of the adsorption systems, providing information on the capacity of a biosorbent for removing an adsorbate (metal) from solution, under the system conditions [16].

Figure 10 shows the equilibrium adsorbed amounts of Au on the tannin resin as a function of the gold concentration in solution, for HCl and aqua regia aqueous media.

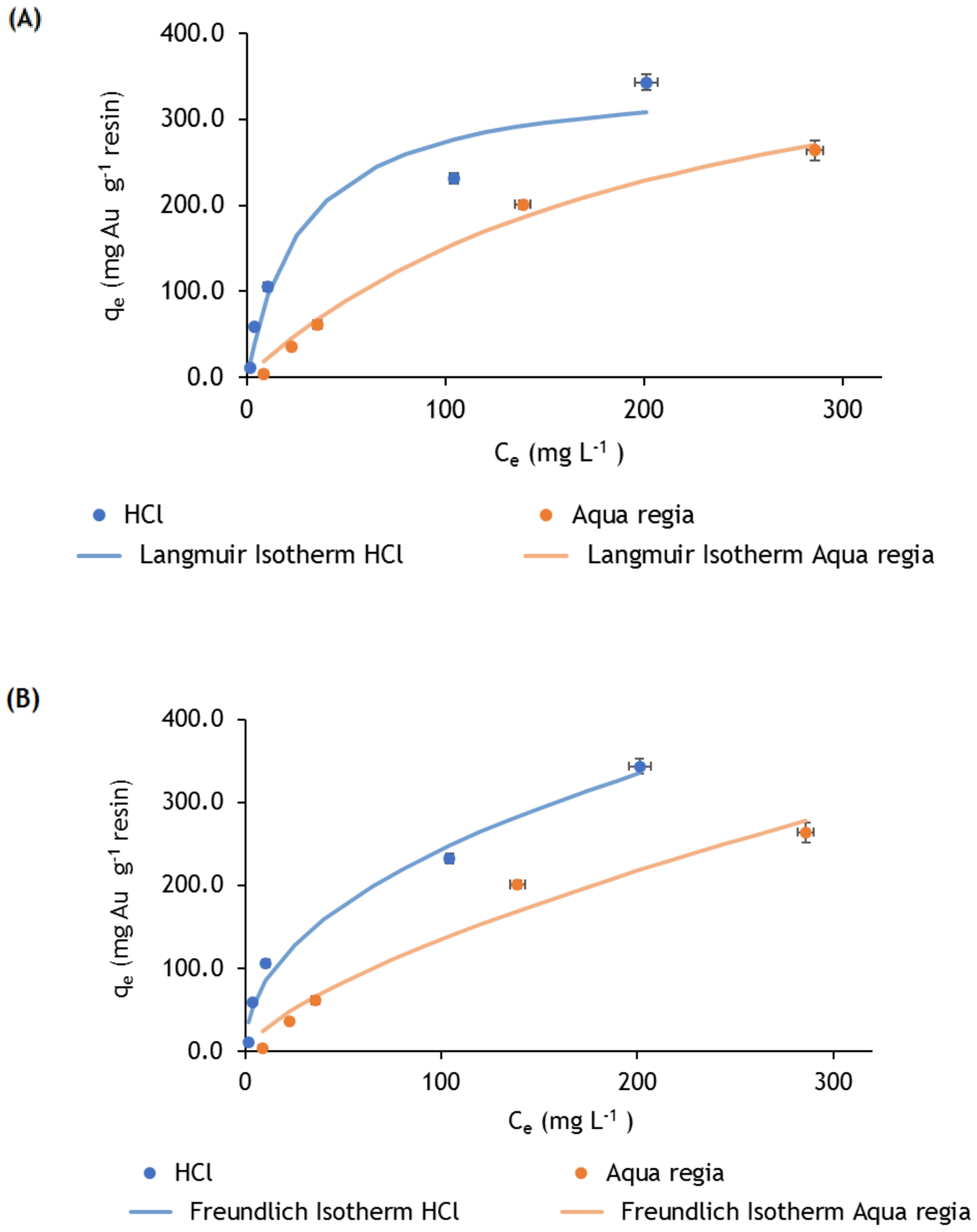


Figure 10. Adsorption capacity of the tannin resin for Au, q_e (mg Au g^{-1} resin), as a function of the equilibrium Au concentration in solution, C_e (mg L^{-1}), for HCl and aqua regia present as leaching agents. Experimental values and **(A)** Langmuir isotherms; **(B)** Freundlich isotherms associated.

To optimize the design of the adsorption systems, in order to recover the maximum amount of precious metals from electronic waste sources, it is required to define the most appropriate correlation for the equilibrium data [16]; the Langmuir and Freundlich isotherms were the chosen ones to do so.

The Langmuir adsorption isotherm is based on the assumption that all adsorption sites are equivalent and adsorption in an active site is independent of whether the adjacent sites is occupied or not [16]. The following equation defines the Langmuir isotherm,

$$q_e = \frac{Q * K_L * C_e}{1 + K_L * C_e} \qquad (eq. 9)$$

where q_e (mg g^{-1}) and C_e (mg L^{-1}) are the amount of adsorbed metal ion per unit weight of tannin resin and unabsorbed metal ion concentration in solution at equilibrium, respectively. The constant K_L is the Langmuir equilibrium constant (L mg^{-1}) and Q is the theoretical monolayer saturation capacity (mg g^{-1}).

As for the Freundlich isotherm, equation 10 should be used for the graphic representation,

$$q_e = K_F * C_e^{1/n} \qquad (eq. 10)$$

where, K_F is the Freundlich constant ($mg^{1-1/n}$ $L^{1/n}$ g^{-1}) and n the Freundlich exponent; if n<1 the isotherm is unfavourable and if n>1 the isotherm is favourable [76].

Table 7 summarizes the values obtained for the equilibrium models parameters, considering the standard error associated to the parameters, the determination coefficient (R^2) and the final standard error (SE).

Table 7. Equilibrium model parameters for Langmuir and Freundlich isotherms, for the adsorption of Au by the tannin resin and in the presence of HCl (1.0 mol L^{-1}) and aqua regia (1.0 mol L^{-1} and 0.38 mol L^{-1} HNO_3).

Langmuir Isotherm	**Q** (mg g^{-1})	K_L (L mg^{-1})	**R^2**	**SE** (mg g^{-1})
HCl	352 ± 50	(4 ± 2) x 10^{-2}	0.95	35.56
Aqua Regia	473 ± 85	(5 ± 2) x 10^{-3}	0.99	14.18
Freundlich Isotherm	**K_F** ($mg^{1-1/n}$ $L^{1/n}$ g^{-1})	**n**	**R^2**	**SE** (mg g^{-1})
HCl	29 ± 9	2.2 x 0.3	0.98	20.88
Aqua Regia	6 ± 4	1.4 x 0.3	0.96	24.87

Considering Figure 10, it can be seen that the adsorbed amount of Au on the resin increases with the increase of Au concentration in solution, without stabilizing, meaning that the resin has not become saturated and is able to adsorb more Au as its concentration increases in solution. Additionally, it can be seen that the adsorbed amount of Au by the resin in the HCl medium were significantly higher than the ones register in the aqua regia solution; in the experimental conditions the maximum amount of Au adsorbed in HCl was equal to 343 ± 9 mg g^{-1}, while for aqua regia was of 264 ± 12 mg g^{-1}. Such behaviour is un accordance with the results obtained in section ***4.1.*** and should be related with the strong oxidant power of aqua regia that inhibits the reduction of Au. Furthermore, it is also possible to conclude that the tannin resin has a higher affinity towards Au in HCl solutions than in aqua regia once the isotherm presents a higher slope for low Au concentrations; a higher slope means that even in small concentrations of Au the tannin resin is able to adsorb the metal from solutions. Therefore, HCl has proven once again to be a better leaching agent for the adsorption of Au than aqua regia.

Taking into consideration Table 7 and considering the isotherm models used, it is possible to conclude that the Freundlich isotherm is the better model to describe the equilibrium data obtained in HCl solution, since it presents higher values of R^2 and lower standard errors (SE) associated. As for aqua regia data, the Langmuir isotherm should be used since it has a higher R^2 and lower SE associated. It is important to denote that the Langmuir model provided values for Q with high uncertainties associated, which can be explained by the fact that saturation has not been reached yet in the experimental range tested. However, it was not understood the need to extend the concentration range because it would mean to use very high concentrations of Au that are not significant of what happens in reality. Since the value obtain for Q may not be representative, in the present work the maximum adsorbed amount of Au by the tannin resin was defined as the maximum experimental value registered, namely, 343 mg g^{-1} in 1.0 mol L^{-1} HCl and 264 mg g^{-1} in 1.0 mol L^{-1} HCl:0.38 mol L^{-1} HNO_3 (aqua regia).

Xiong et al. (2009) [95] studied the uptake of Au by a persimmon waste chemically modified with dimethylamine gel (DMA-PW) from a 0.1 mol L^{-1} HCl solution. The maximum adsorbed amount obtained experimentally was of 5.63 mol kg^{-1} (1108.9 mg g^{-1}) measured under an equilibrium Au concentration of ~395 mg L^{-1}. On the other hand, *Yi et al.* (2016) [39] studied the adsorption isotherms for the uptake of Au by an ethylenediamine modified persimmon tannin adsorbent. Au(III) was presented in a 0.1 mol L^{-1} HCl solution in a 200-300 mg L^{-1} concentration and a 1.0 g L^{-1} ratio of adsorbent was used. The Langmuir isotherm was chosen has the better fit to describe the equilibrium data, with a determined Q of 1550.4 mg g^{-1}. The reported values on the previous studies are much higher than the ones determined in the present work, but they can be partially explained by the fact that the authors used a 0.1 mol L^{-1} HCl medium against 1.0 mol L^{-1} used in this dissertation. Like previously referred, 1.0 mol L^{-1} is not the optimum HCl condition for the recovery of Au, but it is probably more realistic. Additionally, both authors used tannin resins with chemical modifications (anchoring of amine groups into the tannin matrix) that are expected to have better performances than the adsorbent used in the present study.

4.4 Selectivity

E-waste samples are composed by a mix of different metals; therefore, gold is present in the leaching solution with other metals that were also leached and must compete with them to access the surface of the resin [52]. Thus, it is important to test the effect of the presence of other metals in solution towards the adsorption of gold.

Figure 11 (A) represents the uptake percentage of the different metals in solution (Au, Cu, Fe, Ni, Pd and Zn) under three different concentrations of aqua regia: 0.50 mol L^{-1} HCl:0.19 mol L^{-1} HNO_3, 1.0 mol L^{-1} HCl:0.38 mol L^{-1} HNO_3 and 1.5 mol L^{-1} HCl:0.58 mol L^{-1} HNO_3. Figure 11 (B) compares the uptake percentage of gold when it was the only metal in solution (Au mono metal) and when it was present with all the other metals (Au multi metal), under the same conditions previously defined.

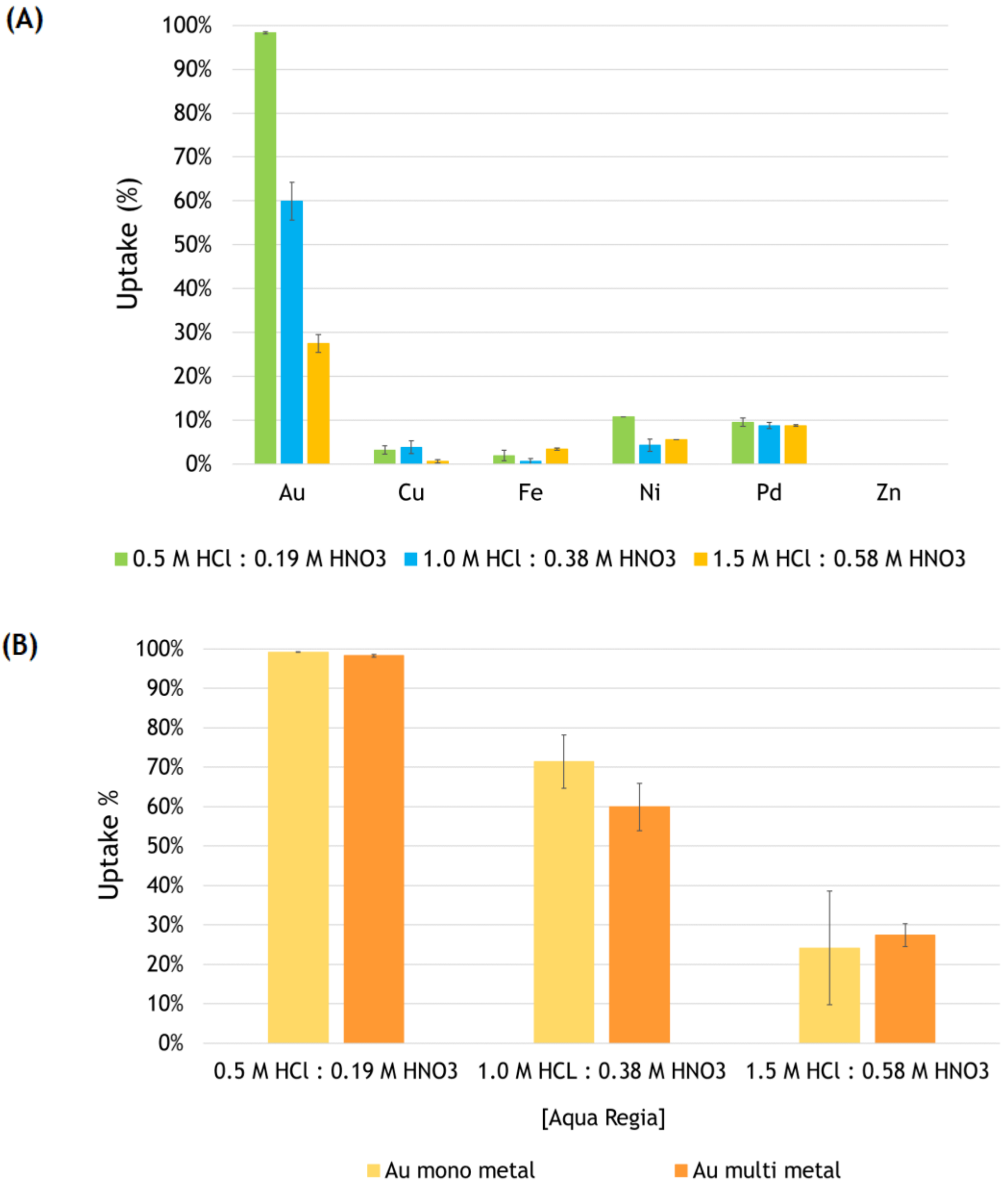


Figure 11. Uptake (%) of metals under three aqua regia levels. **(A)** uptake of typical e-waste metals in solution, Au, Cu, Fe, Ni, Pd and Zn, in the initial concentrations of 200, 2000, 150, 80, 40 and 10 mg L^{-1}, respectively; **(B)** uptake of Au in mono-metal and multi-metal solution, with an initial Au concentration of 200 mg L^{-1}.

By analysis of Figure 11 (A) it can be seen that Au is the main metal being adsorbed, with an uptake % of almost 100% when aqua regia is used at the concentration of 0.5 mol L^{-1} HCl:0.19 mol L^{-1} HNO_3, followed by Ni and Pd, but in much lower values, 10.8% and 9.6% , respectively, for the same condition. Since Pd is also a precious metal and presents similar properties and behaviour as Au, it was expected that, out of the metals in solution, it would be the one presenting a recovery percentage most similar to gold. Furthermore, Pd can be adsorbed by the resin through similar mechanisms as Au, based on the oxidation of the functional groups of the resin and reduction of Pd(II) into Pd(0) [84]. As for Ni, it was also assumed that it would present one of the highest recovery percentages because, as seen in the literature [52], in aqueous chloride solutions nickel can create different anionic forms that are suitable to react with the tannin resin.

Therefore, given that there is a big difference between the Au uptake percentage and the second and third highest uptake percentages, it can be concluded that Au is being selectively adsorbed from the multi metal solution and, consequently, that the tannin resin has a higher affinity towards Au than towards any other metal in solution. Such conclusions can be validated in the literature: *Inoue et al.* (2019) [87], verified that Au(III) was quantitatively adsorbed while other metal ions, such as Pd(II), Cu(II) and Zn(II), were not practically adsorbed. Into the same conclusion came *Fan et al.* (2019) [89]; for three different concentrations of HCl, the tannin adsorbent was able to recover 100% of Au from solution. Pd was registered the second highest recovery percentage, with a maximum of ~18%, followed by Zn, at a maximum of ~15%. Therefore, the authors were able to conclude that Au was being selectively adsorbed from solution.

Considering Figure 11 (B), it can be seen that no big changes happen when gold passes from being the only metal in solution to be present with other metals. When considering the most favourable aqua regia concentration, 0.50 mol L^{-1} HCl:0.19 mol L^{-1} HNO_3, the uptake rate ranges from 99.2% to 98.3% which is not that significant. For all the concentrations of aqua regia, and considering the uncertainties associated, it can be seen that there is not significant statistical variation between the results for the mono- and multi-metal solutions. Therefore, it can be concluded that the presence of other metals does not influence the recovery of Au from the aqua regia solution like it was expected to, since there are no significant differences between the uptake of Au from solution when it is present by itself or in a multi-metal solution. Such results present very good perspectives for future, practical application of the tannin resin under study.

5 Conclusions

5.1 Accomplished Objectives

In this work it was possible to study the adsorption of gold from e-waste simulated liquors using a tannin resin previously prepared from *Pinus pinaster* bark, a common biomass residue in Portugal which had not been studied for the effect of gold recovery yet.

The tannin resin proved to be efficient in the selective recovery of Au from the leaching mediums tested, HCl and aqua regia. However, it was also seen that as the lixiviant concentration gets higher, the recovery capacity of the resin gets lower which means that the adsorptive performance of the tannin resin is influenced by the acidity of the medium. Concentrations of HCl in hydrocloridric acid or in aqua regia solutions equal or lower than 0.5 mol L^{-1} allowed for Au uptake percentages of 100%. For the same total concentration of H^+ in solution, aqua regia proved to impair the performance of the tannin adsorbent.

In kinetic studies, the effect of contact time on Au adsorption by the tannin resin was tested, under the presence of two different leaching agents, using different adsorbent dosages and initial Au concentrations in solution. In general, the experimental data was well described by the pseudo-first-order and pseudo-second-order models, and it was possible to determine the kinetic constants. It was verified that Au adsorption is a relatively slow process, requiring around 2 to 3 days for the adsorption equilibrium to be reached.

The equilibrium study was conducted using initial Au concentrations between 10 mg L^{-1} and 500 mg L^{-1}, considered the range of practical interest. It was possible to verify that the resin had not become saturated in these conditions, as the maximum experimental adsorbed amounts are lower than the maximum adsorption capacities predicted by the Langmuir model. The Langmuir isotherm was found to be the best equilibrium model to describe the adsorptive behaviour in aqua regia, whereas the Freundlich isotherm was more suitable to describe the adsorption data obtained in the HCl solution. Furthermore, the tannin resin presented a higher affinity towards Au in HCl solutions than in aqua regia. The experimental maximum adsorbed amounts obtained were 343 mg g^{-1} and 264 mg g^{-1} for HCl and aqua regia mediums, respectively, which are very interesting values taking in account that the conditions used for the determination are quite close to the ones probably found in real systems.

Additionally, the tannin resin has also showed a higher affinity towards Au then towards any other metal in solution, with uptake percentages measured in the multi-metal solution containing aqua regia of 98% Au, 11% Ni, 10% Pd and <3% for Cu, Fe and Zn. The presence of other metals in solution showed no significant influence on the adsorption of Au by the tannin resin.

5.2 Limitations and Future Work

For future work it would be interesting to study the influence of temperature in the adsorption of gold since adsorption depends on the temperature. Additionally, it is known that e-waste leaching, in industrial processes, may be carried out using high temperatures (and higher than the ambient temperature) which further showcases the pertinence of such analysis. The effect of pH is frequently studied in metal adsorption, but since the leaching agents turn the Au solution extremely acidic, at least in the case of HCl and aqua regia, it would not make sense to analyse the influence of this parameter under the conditions tested. However, in a more theoretical perspective it might be interesting to study such influence. Also, it would be of the highest interest to study the desorption process after gold has been adsorbed in to the tannin resin, which leads to the final recovery of Au.

Furthermore, other leaching agents should be tested for the adsorption of Au such as thiourea and thiosulphate.

Lastly, for future work real e-waste samples should be used and leached, using different leaching agents and the tannin resin applied for Au uptake, since real samples can react differently than the simulated ones.

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Annex

I. Analytic Methods

i. Calibration Curves

Based on 7 standards of gold with different concentrations, calibration plots were drawn every time the spectrophotometer was used for the measure of the metal concentration.

Figure A1 is an example of a plot obtained after the calibration results were extrapolated.

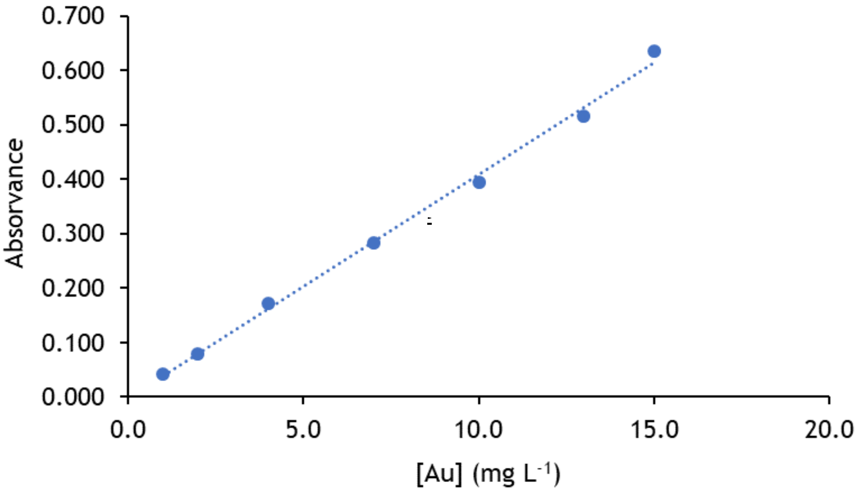

Figure A1. Calibration plot obtained from the measurement of 7 standards of gold with different concentrations. The plot was obtained as the Absorbance as a function of the Au concentration, in mg L^{-1}.

Posteriorly, the associated equation was obtained,

$$Abs = 0.041 * [Au]\ (mg\ L^{-1}) - 0.0016 \qquad (eq. A1)$$

and a correlation coefficient, R^2, equal to 0.997.

The same logic was followed for the calibration of the equipment when the other metals were read, namely, Cu, Fe, Ni, Pd and Zn.

The calibration curves were considered appropriate when the quantification parameters were observed.

Quantification Parameters for the Validation of the Calibration Curve

There are 5 parameters when it comes to validate the calibration curve of a given plot, namely:

- It must consider at least 5 points.
- The x values most differ at least by a factor of 10.
- The absolute deviation in relation to the slope should be lower than 5%,

  $s_a/a * 100\% < 5\%$
- The ordinate at the origin should contain the origin,

  $b - s_b < 0 < b + s_b$
- The correlation coefficient, R, must be greater than 0.995.

Thus, for the previous calibration curve, it can be seen that more than 5 points were considered, namely 7; The concentration axis ranges over a factor of 10 (from 1 mg L^{-1} to 15 mg L^{-1}) and, like previously announced, R > 0.995.

The values determined for s_a and s_b were 0.001 and 0.010, respectively. Therefore, the absolute deviation in relation to the slope, s_a/a *100 %, determined was lower than 5%, and equal to 3%, and the ordinate at the origin contains the origin. Consequently, the calibration curve can be accepted as a valid one.

ii. Limit of Detection (LOD)

The limit of detection, LOD, in spectrophotometry, is defined as the lowest concentration of metal that can be detected with a reasonable certainty. It is calculated by the following equation,

$$LOD\ (mg\ L^{-1}) = b + 3 * s_b$$

where b is the ordinate at the origin and s_b is the variance associated with b.