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TANNIN-BASED BIOMATERIALS: PRODUCTION, CHARACTERIZATION AND APPLICATION IN WATER AND WASTEWATER TREATMENT

Dissertação – Mestrado Integrado em Bioengenharia – Biotecnologia Molecular

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Porto, Julho de 2016

Para o Diogo.

Abstract

Water and wastewater treatments are of ever rising concern due to increasing pollution problems, where adsorption has proved its worth, providing high affinity and selectivity towards a wide array of chemical elements and compounds. Tannins have been showing to be excellent candidates to produce biosorbents. These ubiquitous and inexpensive natural biopolymers are of easy extraction and conversion into insoluble matrices. Tannin-based adsorbents (TBAs) have a natural affinity to uptake heavy metals, dyes, surfactants and pharmaceutical compounds from contaminated waters. Furthermore, it is somewhat easy to chemically modify a TBA, in order to enhance the adsorption ability of some substances. In this dissertation, a pine-tannin based adsorbent was modified with iron loading in order to assess its ability to uptake arsenic. Oxidation of the tannin gel prior iron treatment was proven to be essential for the iron uptake. Moreover, the iron content of the tannin gel was shown to improve its affinity towards arsenic. With a tannin gel containing 24 mg of iron per g of adsorbent, it was achieved a maximum adsorption capacity of 1.92 and 2.3 mg g^{-1} of As(III) and As(V), respectively, at 20 ⁰C and pH 3.5. Hence, the adsorbent here synthesized presents itself as a potential alternative for arsenic removal from aqueous solutions through adsorption.

Keywords: tannins, arsenic, biopolymer, adsorption, water and wastewater treatment.

Resumo

A importância do desenvolvimento de novos processos de tratamento de águas naturais e residuais é cada vez maior, devido ao aumento dos problemas de poluição. A adsorção tem demonstrado ser um processo eficiente devido à possibilidade de encontrar adsorventes com elevada afinidade e seletividade para um vasto espectro de elementos e compostos químicos. Os taninos revelaram ter excelentes condições para produzir biosorventes de baixo custo. Estes biopolímeros naturais são ubíquos e baratos assim como são de fácil extração e conversão em matrizes insolúveis. Adsorventes de base tanínica (TBAs) exibem uma afinidade natural para remover metais pesados, corantes, surfatantes e compostos farmacêuticos de águas contaminadas. Para além disso, é relativamente fácil modificar quimicamente um TBA, a fim de melhorar a sua capacidade de adsorção para algumas substâncias. Nesta dissertação, um adsorvente de base tanínica de pinheiro foi modificado com incorporação de ferro de modo a avaliar a sua capacidade para acumular arsénio. A oxidação do gel tanínico, previamente ao tratamento com o ferro, revelou-se essencial para a acumulação de ferro. Para além disso, verificou-se que o conteúdo em ferro do gel tanínico melhora a sua afinidade para o arsénio. Com um gel tanínico contendo 24 mg de ferro por g de adsorvente, obteve-se uma capacidade máxima de adsorção de 1.92 e 2.3 mg g^{-1} de As(III) e As(V), respetivamente, a 20 ºC e pH 3.5. O adsorvente sintetizado neste trabalho apresenta-se como uma potencial alternativa para a remoção de arsénio de soluções aquosas por adsorção.

Keywords: taninos, arsénio, biopolímero, adsorção, tratamento de águas e águas residuais.

Acknowledgments

This thesis was the labor of a year, however, to me, it seemed like the labor of a lifetime. Not because I did not enjoy it, on the contrary; but because it required a huge amount of work and seemed like the culminating of my academic career (which is kind of accurate). What I mean by this is that I feel I ought to thank not only the people who helped me directly and indirectly while I was doing this but also the people who helped and were important for me in previous periods of my life. Thus, let's begin.

First, I would like to thank the Chemical Engineering Department of FEUP and the associated laboratory LSRE where it was made available for me the space, materials and equipment required for the experimental assays of this thesis. I thank also my colleagues of laboratory E404A who always were available to help when I needed it, with a special thanks to Ana Isabel Gomes, who was always the kindest person to me since my first day there. I also would like to thank Eng. Liliana Pereira (DEQ/FEUP) for the help provided through borrowed equipment and to Prof. Fernão Magalhães and to Eng. Luís Carlos (DEQ/FEUP) for making possible the use of the particle size analyzer.

Second, I thank Dra. Sílvia Santos for her guidance, support, teachings, availability, and so on. You were an outstanding thesis's advisor; it was a pleasure working with you. Thanks also to Prof. Cidália Botelho, who also made the time for revising my writings and providing me with suggestions to make it better. I am glad I had the opportunity to work with you as well; you are one the nicest teachers I ever met.

And last but certainly not least, I thank my best friend Daniel Santos, of almost two decades, who always inspired me to be a better person and with who I spent innumerable joyful moments; without you my life would be incredible dull. And also to my cousin Marisa Bacelo, who always were a life advisor to me and who always were present in my weakest moments. I do not know how I would make it so far without your friendship.

And as a closing note, I do not want to forget the gang of noobs that nagged me with silly messages over on Skype pretty much the whole time I was writing this thesis. So… thanks, I suppose.

Contents

List of Figures

List of Tables

Abbreviations

FAAS	Flame Atomic Absorption Spectrosmetry
FTIR	Fourier Transformed Infrared Spectroscopy
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
rpm	Rotations per minute
TBA	Tannin-based adsorbent
TE	Tannin extract
TG	Tannin gel
TG-Fe	Iron-loaded tannin gel without oxidation
TG-Ox2-40-Fe	Iron-loaded tannin gel oxidised with HNO_3 2 M for 90 min at 40ºC
TG-Ox2-60-Fe	Iron-loaded tannin gel oxidised with HNO_3 2 M for 90 min at 60ºC
TG-Ox1-30-Fe	Iron-loaded tannin gel oxidised with HNO_3 1 M for 30 min at 60ºC
TG-Ox1-50-Fe	Iron-loaded tannin gel oxidised with HNO_3 1 M for 50 min at 60ºC
TG-Ox1-120-Fe	Iron-loaded tannin gel oxidised with HNO_3 1 M for 120 min at 60ºC
PZC	Point of zero charge

Nomenclature

C_{in}	Initial concentration of arsenic (mg L^{-1})
C_t	Arsenic concentration at t minutes (mg L^{-1})
C_{eq}	Equilibrium concentration of arsenic (mg L^{-1})
k_1	Pseudo first order kinetic constant (min^{-1})
k_2	Pseudo second order kinetic constant (g mg^{-1} min^{-1})
K_L	Langmuir equilibrium constant (mg L^{-1})
K_F	Freundlich equilibrium constant ($mg^{(n-1)/n}$ $L^{1/n}$ g^{-1})
w	Adsorbent mass (g)
q	Amount of arsenic adsorbed per g of adsorbent (mg g^{-1})
q_{eq}	Amount of arsenic adsorbed per g of adsorbent at equilibrium (mg g^{-1})
q_t	Amount of arsenic adsorbed per g of adsorbent at t minutes (mg g^{-1})
Q_m	Maximum adsorption capacity, predicted by Langmuir model (mg g^{-1})
n	Freundlich constant related to the adsorption intensity
R^2	Coefficient of determination
SE	Standard error
T	Temperature (ºC)
V	Volume of solution (L)

1. Introduction

The principal objective of the work presented here is to produce a tannin-based adsorbent, with tannins extracted from pine bark and to test its applicability in arsenic removal from water.

Adsorption processes are viewed as relatively simple methods, effective for the removal of various contaminants from aqueous solution. Depending on the water characteristics, adsorption can be applied as an alternative to conventional treatment processes (coagulation/flocculation, biological treatment) or as a final step, at a post-treatment level [1, 2], in water or industrial wastewater treatment. Commercial adsorbents include mainly activated carbon and activated alumina. The manufacture of these materials involves high energy costs, due to the high temperatures required, which has implications for the acquisition price of the adsorbents and for the environment. In fact, to reduce the environmental impact of adsorption processes, adsorbents should be ideally effective, renewable and abundant materials, and should require minimal processing before use. Biosorption gives a key contribution to reach these goals. It is defined as the property of certain biomolecules, or types of biomass (biosorbents), to bind and concentrate selected ions or molecules from aqueous solutions [3]. The mechanisms of biosorption are generally based on physicochemical interactions between adsorbates and the functional groups present on the biomass surface, such as electrostatic interactions, ion exchange, metal ion chelation or complexation [4]. In the last years, biosorption on marine seaweeds, agricultural wastes, forest residues and industrial by-products, in native or modified forms, has been indicated as a promising technology for the uptake of heavy metals and organic contaminants from waters [5-9]. In addition to water remediation, biosorption technology has also recognized applications in the recovery of metals from effluents and hydrometallurgical processes [4, 10, 11]. Adsorbents derived from lignocellulose and tannin materials, seaweeds and chitosan, have shown great potential to selectively uptake precious and critical metals, and to be used in added value applications, such as catalysis [4].

Tannins are inexpensive and ubiquitous natural polymers [12], polyphenolic secondary metabolites of higher plants, mainly present in soft tissues (sheets, needles or bark) [13, 14]. After cellulose, hemicellulose, and lignin, tannins are the most abundant compounds extracted from biomass [14], leaves, roots, bark, seeds, wood and fruits [15].

1

The most common tannin feedstocks are mimosa bark (*Acacia mearnsii*, or *mollissima*), quebracho wood (*Schinopsis balansae* and *Schinopsi lorentzii*), pine bark (*Pinus radiata*) and Gambier shoot and leaf (*Uncaria gambir*). However, multiple trees and shrubs contain significant amounts of tannins [16]. Noteworthy, maritime pine (*Pinus pinaster*) is one of the most common trees in Portugal, making the bark of these trees one of the preferable tannin sources for the production and application of tannin-based adsorbents nationally. Tannin contents reported in literature for some vegetable sources are presented in Table 1.

Table 1. Tannin contents reported for some vegetable materials.

Plant material	%
Quebracho heartwood [17, 18]	20-30
Wattle (acacia bark) [17]	15-50
Black oak [17]	8-12
Pinus pinaster bark [18]	22.5
Eucalyptus bark [19, 20]	16-40
Mangrove bark [17]	15-42
Chestnut (endodermics/hull) [21]	2.50 / 0.94
Chestnut wood [17]	4-15
Grey and black Alder [22]	12

Tannins are important commercial substances, traditionally used as tanning agents in the leather industry, allowing the transformation of hide into leather. Other uses include adhesives (as phenol substitutes in the formulations), medical, cosmetic, pharmaceutical and food industrial applications [15, 23]. Regarding the woodland conservation, particularly to avoid the fell of trees such as quebracho, mimosa and chestnut, alternative tannin sources, such as locally available residues or by-products, should be selected. Possible sources include wine wastes (grapeseed), chestnut peels (from chestnut industry processing), forest exploitation wastes, timber, pulp and paper mills residues. Some of these biomass residues are incinerated, landfilled, used in horticulture or as energy source. It is however known that their use for heat/power generation has operational, economic and environmental limitations [24]; in addition, these options despise the valuable chemical content of the biomaterials. The extraction of tannins from vegetable residues constitutes then an important contribute for their reuse and valorisation, and for tannins sustainable production.

Tannins are historically classified into two groups: hydrolysable or non-hydrolysable (condensed). On the basis of their structural characteristics, however, a classification into four major groups is preferable: gallotannins, ellagitannins, complex tannins, and condensed tannins [14, 15]. Hydrolysable tannins can be fractionated into simple components, by treatment with hot water or by enzymes [15]. Condensed tannins have a higher activity towards aldehyde, being chemically and economically more interesting for the preparation of resins, adhesives and other applications apart from the leather [16]. Fig. 1 presents the structures of a catechin unit and a condensed tannin [16].

The presence of phenolic groups in tannins clearly indicates its anionic nature [25]. Phenolic groups act as weak acids, thus are able to deprotonate, being good hydrogen donors, to form phenoxide ion which is resonance-stabilized.
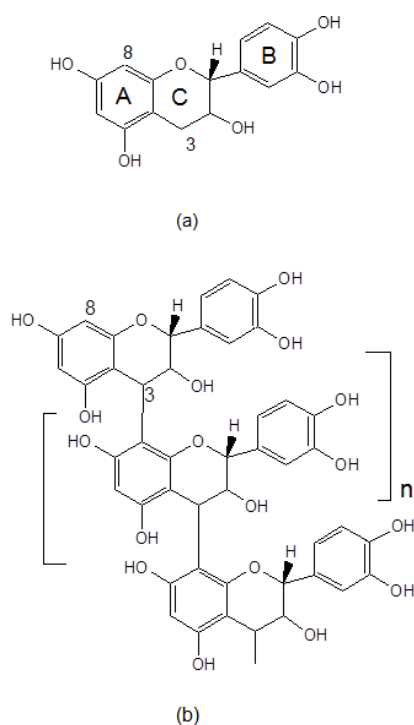
Fig. 1. Structures of (a) a catechin unit and (b) a condensed tannin.

The anionic nature of tannins surface groups opens the possibility to use them as adsorbents for cationic species. However, by chemical surface modifications, adsorption of soluble anionic species, which arsenic is an example of, can also be possible. Arsenic (As) is a steel-gray, brittle, toxic, non-degradable metalloid which is ubiquitous in the environment and highly toxic to all forms of life. Arsenic

3

leaches to ground water through natural weathering reactions, biological activity, geochemical reactions and volcanic emissions [26]. Moreover, anthropogenic sources as mining activity, combustion of fossil fuels, smelting of metals, use of arsenical compounds in agriculture (insecticides, pesticides and herbicides) and in livestock feed are additional pathways for environmental arsenic problems [27, 28]. Long-term exposure to arsenic may contribute to the development of several types of cancer as well non-carcinogenic diseases such as the diseases of vascular systems, dysfunction of respiratory system and injury to central nervous system [29, 30]. The main reason for chronic arsenic poisoning worldwide is the consumption of As-contaminated water and food [31, 32]. It is, therefore, crucial the removal of arsenic from contaminated waters.

Thus, taking all the above information into account, it is of extreme importance the existence of cost-effective and environmentally-benign remediation techniques specific for arsenic-contaminated water incidents. There are several methods for As removal from contaminated waters: coagulation/flocculation, membrane processes (microfiltration, ultrafiltration, nanofiltration, and reverse osmosis), electrochemical methods, phytoremediation, bioremediation, adsorption and ion exchange. Ungureanu et al. [27] recently reviewed and compared their advantages and disadvantages. Although adsorption is a relatively simple method, the adsorptive As removal is not easy using many low-cost adsorbents, due to the anionic nature of the contaminant and its difficult complexation with many functional groups. Iron-based adsorbents (iron oxides, iron impregnated materials and bimetal oxides) have been identified as promising adsorbents [27]. Based on that, this work aims to assess the arsenic removal from aqueous solutions using a lab-produced pine-tannin-based adsorbent. This way, the advantages of the adsorption process, in terms of simplicity and costs, accumulates with the advantages of using a source-material, for the adsorbent production, that is widely and cheaply available in the region. To the author's knowledge, there is no report evaluating the possibility of using a tannin-based adsorbent to remove arsenic from water; hence, this is a novel study which augments its relevance. Furthermore, this thesis has also the goal of characterize the adsorbent obtained in order to correlate some of its properties with production conditions and adsorption capacities.

This dissertation is structured by chapters as:

Chapter 2 - describes the state of the art, presenting first a brief overview about tannins extraction from vegetable sources, following a summary of the chemical methods commonly reported in literature to prepare tannin-based adsorbents (TBAs). Moreover, it also contains a revision of the literature concerning the evaluation of tannin-based materials as adsorbents for inorganic contaminants from aqueous solution, as well as concerning the recovery of substances by biosorption on TBAs.

Chapter 3 - lists and explains the materials and methods, respectively, used in the experimental part of the dissertation.

Chapter 4 - presents the results obtained in this work, along with their discussion. Chapter 5 - contains the concluding remarks and also suggestions for future works.

2. State of the art[1]

As it was mentioned, in this work a tannin-based adsorbent will be produced with tannins extracted from pine bark and its applicability in arsenic removal from water will be studied. Therefore, in this chapter there is a summary of different tannin extraction methods and different TBA production methods and treatments, and several studies that focus on the application of these kind of materials as adsorbents, either for water and wastewater treatment or for recovery of substances, are listed.

2.1. Tannin extraction

There are no universal conditions for extracting tannins from vegetable sources [14]. The yield and the composition of extracts depends on the source, type of solvent, extraction time, temperature, solid-liquid ratio, and preparation of the sample, which is commonly milled, used in fresh, frozen or dried state. The extraction procedure should be optimized in a case-specific basis.

The polar nature of water makes it possible for use as an extraction solvent for many compounds [33]. The traditional industrial method for tannin extraction from vegetable matter is exactly based on hot/boiling water, with temperatures ranging from 50 to 110 °C, using autoclaves working in counter-current, contact times of several hours (6–10 h) and water/tannin-containing material ratios equal to 2–2.4 in mass. Tannins are then concentrated, by evaporation under vacuum, to limit the oxidation [14, 34].

Extraction procedures commonly followed by researchers to obtain tannins for subsequent production of TBAs have been centred on the use of alkaline solutions, containing sodium hydroxide. NaOH solutions were found to increase the tannin extraction yield from *pinus pinaster* bark by 2.5-6 times, in comparison to water [35]. The optimum conditions to extract the highest formaldehyde-condensable polyphenols content from *pinus pinaster* bark were found to be: 5% NaOH (of bark weight), solid/liquid ratio of 1/6 and temperature of 90 ºC [35]. These conditions have been also used to extract tannins from other sources, such as from *C. sempervivens* (Cypress) bark and *Acacia nilotica* leaves [36, 37]. Alkaline solutions

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[1] Adapted from "Hugo A.M. Bacelo, Sílvia C.R. Santos, Cidália M.S. Botelho, *Tannin-based biosorbents for environmental applications – a review*, Chemical Engineering Journal 303, 575-587. doi:10.1016/j.cej.2016.06.044"

containing sodium sulphite have been also used as extraction solvent. In the case of solid wastes from chestnut industry processing, solutions at 1% Na_2SO_3 were recommended to favour the extraction of condensed tannins, whilst hydrolysable tannins were extracted efficiently using 1% NaOH [38].

The extraction efficiency can be also improved by organic solvents, such as ethanol, methanol, acetone and hexane [39-42]. It is however important to consider the principles of green extractions and one of them advocates for the "use of alternative solvents and principally water or agro-solvents" [33]. The use of petrochemical solvents should be avoided, considering the related negative environmental effects and flammability and toxicity risks. In the last years, new extraction methods have been also developed, such as microwave-assisted extraction (MAE), ultrasound-assisted extraction (UAE) and pressurized liquid extraction (PLE), which can bring important improvements for the extraction of these bio-compounds [14]. It is however noteworthy that for the purpose of preparation of biosorbents, which are expected to be eco-friendly, a simple and inexpensive processing is desired. Moreover, for the preparation of biosorbents it is not required a thorough purification. Sugar, organic acids or other plant components are known to occur as impurities in tannin extracts [14]. In some cases, the presence of polyphenolic compounds, other than tannins, can even improve the adsorption ability, as suggested by the results of Palma et al. [7].

2.2. Preparation of tannin-based adsorbents

Tannins are water-soluble compounds and require a process of immobilization/insolubilization before use as biosorbents for aqueous phase applications. Different insolubilization procedures have been successfully performed, under a few different set of conditions. Different products, here generally termed as TBAs, have been obtained. Additionally, some authors were beyond that and further chemically modified the TBAs in order to increase its efficiency towards certain types of adsorbates. Table 2 summarizes the immobilization/insolubilization methods and the additional modifications that have been undertaken for tannins.

Table 2. Summary of literature reported methods for TBAs production.

Designation	Immobilization/insolubilization method		Further modification	Ref.
Resin/Gel	Polymerization	Formaldehyde	None	[37, 43]
			Iron loading	[44]
			Ammonia	[12]
			Amine group	[45, 46]
	Polymerization	Sulphuric acid	None	[47-49]
			Amine group	[50]
Immobilized tannins	Collagen/Collagen fiber		None	[42, 51, 52]
	Silica beads		None	[53, 54]
Foam	Polymerization	Formaldehyde, furfuryl alcohol	Ethyl ether, p-toluensulfonic acid	[55, 56]

2.2.1. Tannin gels

Insolubilization of tannins can be achieved through their reaction with formaldehyde (or other aldehyde), a step-growth polymerization reaction that can be either acid- or base-catalysed [37, 57, 58]. In such reaction, an aldehyde compound establishes links between the tannin monomers, acting as a cross-linking agent. Thus, a tannin non-linear insoluble polymer, known as tannin resin or gel, is synthesized. The experimental procedure in basic medium generally involves the dissolution of tannin extract in sodium hydroxide solution, addition of formaldehyde, gelation reaction conducted at high temperature (80ºC), for 8-12 h [37, 43, 59, 60], and, finally, washing, drying and sieving. The amount of aldehyde required is dependent on the specific conditions and the tannins source, but in general, values between 1 and 5.7 mmol of formaldehyde per g of tannin extract have been reported for successful gelations [37, 43, 59, 60]. It is also clear that acetaldehyde presents a weak polymerization action, when compared with formaldehyde. Weibull black tannins, for instance, were successfully gelified with formaldehyde amounts of 1 and 3.68 mmol g^{-1}, but did not gelified with acetaldehyde dosages of 1.3 and 4.85 mmol g^{-1} [37]. In order to simplify the synthesis procedures, some works [47, 58, 61] report the preparation of tannin-gels using the vegetable materials (e.g.: persimmon powder, raw peels) without extracting the tannins.

On the other hand, tannins can also be immobilized by mixing them with sulphuric acid, which catalyses a spontaneous condensation reaction (crosslinking between hydroxyl groups), as carried out for tannins from astringent persimmons [48, 49].

Tannin gels present an acidic surface characterized by different groups (carboxylic, lactonic, phenolic and carbonyl groups) and no basic groups [57]. The measurements of the zeta potentials at several pH values characterized the adsorbents in terms of their surface charge. Points of zero charge (PZC), or isoelectric points, have been identified at very low pH values, approx. 2 [57, 62]. This confirms the anionic nature of tannin-resins, and unless further treatment, a much higher electrostatic affinity is predicted for cations than anions.

2.2.2. Modified tannin gels

As previously referred, tannin resins can be used directly as adsorbents or subjected to further modifications prior to application. The phenolic groups present in tannins grant them an anionic feature, due to the possibility of releasing protons, which in turn renders these molecules suitable to cations adsorption, but not for anionic ones. HSAB theory [63] states that hard acids prefer binding to hard bases and soft acids prefer binding to soft bases. Hydroxyl groups are hard bases and then are not amenable to interact with soft metal acids. Amino groups have higher affinity and selectivity for soft metal ions, because the nitrogen atom is a softer base than oxygen [64]. One of the modifications reported in literature is then the amine-functionalization of tannin-resins [45]. Fig. 2 presents schematically several ways to obtain an amine-modified TBA. The simplest procedure involves an ammonia treatment of the tannin resin (after polymerization with formaldehyde) [12, 65]. Kim et al. [64] optimized ammonia treatment procedure, in terms of ammonia concentration, time and temperature, in order to get a maximum amount of amino groups introduced into tannin gels. 10 wt.% solution, 333 K and 6 h of treatment were found enough to get ca. 3% of nitrogen. Evidences, based on the decrease in oxygen content and based in ^{13}CNMR (Carbon-13 nuclear magnetic resonance) spectra, suggested the replacement of hydroxyl groups of the tannin gel by amino groups during the ammonia treatment [64, 65]. Slightly more complex procedures, involving an intermediate chloromethylation step, were performed in order to anchor bisthiourea (BTU) [46], N-aminoguanidine (AG) [59], tetraethylenepentamine (TEPA) [45], dimethylamine (DMA) [61], diethylamine (DEA) and triethylamine (TEA) ligands [50]. The introduction of nitrogen ligands is catalysed by sodium carbonate in dimethylformamide (DMF) or by formaldehyde, according to how the polymerization was achieved (Fig. 2). TEA-tannin resin, for instance, presented a pH_{PZC} of 7.72 [50], which in comparison to the typical values

reported for unmodified tannin resins (pH$_{PZC}$=2), shows a significant improvement on the surface charge by the chemical modification.
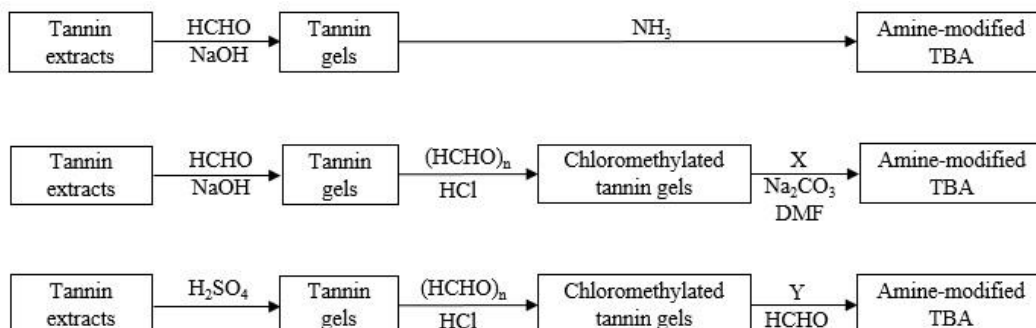
Fig. 2. Schematization of the production methods for different types of amine-modified TBAs. X= BTU, AG, TEPA; Y= DMA, DEA, TEA.

Besides the modification with amine groups, it has been also reported the modification of TBAs with iron, yielding an iron-loaded biosorbent [44]. Tannin gel was firstly subjected to an oxidation by nitric acid, followed by the iron adsorption from a stirred Fe(III) solution. The results presented by Ogata et al. [44] showed the importance of performing the oxidation step, where hydroxyl groups of the tannin gels were oxidized to carbonyl ones, which have a higher affinity to adsorb iron. The results also showed the importance of optimizing the oxidation time and the nitric acid concentration, in order to avoid excessive oxidation and decomposition of the gel. In fact, iron materials were known to be good adsorbents for many metal oxyanions [66] and phosphates, but the difficulty to handle with very fine particles of iron oxides has dictated the exploitation of iron-based adsorbents, using different support media, such as activated carbons [67], activated alumina [68], graphene oxide sheets [69], agro-wastes [70]. Regarding tannin-based materials, iron-treatments were not still conveniently explored, although the interesting results presented by Ogata et al. [44] show good perspectives for their application.

2.2.3. Immobilized tannins

A different approach to convert tannins in adsorbents is to immobilize them in a tridimensional structure. Collagen fiber has been proposed as a possible immobilization material. This natural biomass is abundant (obtained from skins of

domestic animals) and exhibits excellent mechanical strength. It has several functional groups that can react with many other chemicals, tannins included. Collagen fibers covalently immobilize tannins through a cross-linking reaction of aldehydes. In addition to the creation of a water-insoluble matrix, the process gives unique fibrous structure and hydrophility properties to the adsorbent [52]. The reported immobilization procedures for tannins from bayberry [71] or bark of *Myrica rubra* [42] consisted in the preparation of the collagen fibers, by the removal of the non-collagen fraction of skins, reaction with tannin, followed by a cross-linking reaction with oxazolidine, which facilitates the covalent reaction between tannin and collagen. In another attempt, collagen, rather than collagen fiber, was employed as supporting matrix [51]. It exhibited higher tannin immobilizing capacity (1.5 g g^{-1} collagen, approx. 3 times the value obtained for collagen fiber), suggesting a better performance as biosorbent.

Mesoporous silica was also proposed in literature as a supporting matrix for tannins immobilization [53, 54]. Silica was chosen since it shows excellent swelling resistance in different solvents and a good mechanical, thermal and chemical stability, and, according to the authors, improves the adsorption kinetics, considering its mesoporous structure [54]. Of note, the silica beads had to be aminated prior to tannin immobilization, i.e. an amine group was introduced in the beads in order to establish a chemical link with the tannin molecules. After, the synthesis involves the beads mixing with bayberry tannins and glutaraldehyde (cross-linking agent), which reacts with the amino group of mesoporous matrix establishing covalent bonds [54].

Whatever the way of immobilization (silica, collagen or other water-insoluble matrices), it is important to bear in mind that for the preparation of biosorbents, the interest lies in relatively simple and inexpensive processing.

2.2.4. Tannin foams

Tannin rigid foams are known for a long time, but their possible application as another type of TBA was only recently exploited [55, 56]. The procedure of preparation of tannin foams basically involves the mixing of reagents (tannins, furfuryl alcohol, distilled water and formaldehyde, blowing agent, additives), followed by the expansion step catalysed by a strong acid, and finally, a curing (aging) step to harden and stabilize the network [56]. Optimization of the variables

involved in the process can be performed to improve the economy of the synthesis. For instance, Sanchez-Martin et al. [55] optimized the amounts of reagents involved in the foaming process of Weibull black tannin foams, considering the resultant sorption properties of the biosorbent. Pine tannins, on the other side, are known to have a very high reactivity with formaldehyde under acidic conditions [72], causing significant difficulties in the foaming process. The preparation of pine tannin foams was however made possible by Lacoste et al. [72], although the materials were not still evaluated as TBAs.

2.3. Tannin-based adsorbents for water and wastewater treatment applications

Several pollution problems should be avoided by prevention and that it is happening increasingly with ever changing thinking ways. Nevertheless, there are still many problems that need to be subjected to remediation strategies. For example, effluents from textile, chemical, mining or metal finishing industries, if not properly treated, represent harmful and noxious menaces for the environment, disrupt ecosystems and harm human health [73, 74]. Thus, water remediation is a crucial issue to the scientific community. Also surface and ground water need suitable treatment to be considered for drinking-water production, which can mean to remove priority and emerging pollutants from trace levels. Adsorption has been considered a cost-effective method, and biomaterials heralded as promising adsorbents. Production of TBAs meant to be used for the removal of dangerous pollutants from aqueous solutions has been assessed, to some extent, by many authors in recent years. Table 3 presents maximum adsorption capacities (Q_m), reported in literature, for different TBAs on the uptake of inorganic pollutants. It is important to note that Q_m values are primarily dependent on the temperature and pH, but their calculation is also dependent on the adsorbent dosage used. In Table 3 and whenever possible, Q_m values are then provided together with the most relevant experimental conditions. TBAs have been also applied for the removal of organic pollutants from aqueous solutions but such data is not presented here; a more detailed literature revision of application of TBAs can be found in Bacelo et al [75].

Table 3. Maximum adsorption capacities for different adsorbates, reported for TBAs.

Adsorbent	Adsorbate	Q_m (mmol g^{-1})	Conditions[a]	Ref.
Condensed-tannin gel		5.52	pH 2.0, 303 K, 5-50[b] g L^{-1}, 19.7 mmol L^{-1}	[60]
Persimmon tannin gel		5.27	pH 3.0, 303 K, 0.2 g L^{-1}, 0.2-2 mmol L^{-1}	[76]
Black wattle tannin-gel	Cr(VI)	9.39	pH 1.0, 298 K, 2.0 g L^{-1}, 9.6-96 mmol L^{-1}	[57]
Persimmon waste gel		7.18	pH 1.0, 303 K, 1.0 g L^{-1}, 0-10* mmol L^{-1}	[49]
Tannin-immobilized mesoporous silica bead	Cr(III)	1.3	pH 5.5, 303 K, 1.0 g L^{-1}, 0.1-4.0 mmol L^{-1}	[77]
Wattle tannin gel		0.56	pH 4.2, 1.0 g L^{-1}, 0-0.4* mmol L^{-1}	[78]
Quebracho tannin resin	Pb(II)	0.42	pH 5.0, 296 K, 1.0 g L^{-1}, 0.05-0.7 mmol L^{-1}	[62]
Valonia tannin resin		0.67	pH 5.0, 1.0 g L^{-1}, 0.2-0.5 mmol L^{-1}	[79]
Valonia tannin resin		0.71	pH 5.0, 1.0 g L^{-1}, 0.08-1.6 mmol L^{-1}	[79]
Mimosa tannin gel	Cu(II)	0.69	pH 5.0, 298 K, 1.0 g L^{-1}, 0.2-2.3 mmol L^{-1}	[80]
Valonia tannin resin		0.54	pH 5.0, 1.0 g L^{-1}, 0.1-0.6* mmol L^{-1}	[79]
Pinus tannin gel	Zn(II)	1.0	pH 7.0, 293 K, 0-0.4 mmol L^{-1}	[37]
Bayberry tannin-immobilized collagen fiber	Hg(II)	0.99	pH 7.0, 303 K, 1.0 g L^{-1}, 0.25-5 mmol L^{-1}	[52]
Wattle Tannin gel		1.05	pH 8.8, 303 K, 2.0 g L^{-1}, 0.9-19 mmol L^{-1}	[12]
Amine-modified Wattle tannin gel	B	2.25	pH 8.8, 303 K, 2.0 g L^{-1}, 0.9-19 mmol L^{-1}	[12]

a – experimental conditions: pH, temperature, adsorbent dosage and initial (* or equilibrium) adsorbate concentration range.

2.3.1. Removal of heavy metals and toxic metalloids

Tannin gels have shown great affinity for toxic heavy metals under aqueous conditions, such as chromium [49, 57, 60, 76], lead [62, 78, 79], copper [79, 80] and zinc [37, 79]. The adsorption of these adsorbates is usually assessed in acidic pH range, conditions commonly found in the wastewaters generated in electroplating industry wastewaters, and also to avoid precipitation of the metals that occurs in basic conditions.

Lead, copper and zinc are metals which present a positive charge (mainly as a double charged metal ion, M^{2+}) under acidic pHs. As can be seen in Table 3, tannin resins from different vegetable sources have provided considerable adsorption capacities (36-250 mg g^{-1}, 0.4-1.0 mmol g^{-1}) for the removal of these elements from water. Many studies provided evidences that tannin resins uptake metals by complexation and ion exchange, with metals complexes being established with two adjacent hydroxyls (catechols), whose stability increase if a third adjacent hydroxyl (pyrogallols) is presented [81]. The dissociation of surface groups in tannins with

the increase in pH, leads to stronger complexing ability and higher electrostatic attraction (between the positive adsorbate and the negative biosorbent surface). These are the reasons why the patterns observed in pH influence assays carried out for Pb(II), Cu(II), Ni(II) and Zn(II) which show an increase of the adsorbed amounts with the increase of pH, in acidic range, with highest removals reached at pH 4 or 5 [62, 78, 79]. Through competitive adsorption assays, carried out with Pb(II), Cu(II) and Zn(II), it was concluded that valonia tannin resins had an affinity towards lead over other metals ($Pb^{2+} > Cu^{2+} > Zn^{2+}$) [79].

In aqueous solution, chromium is found in the two most stable oxidation states, Cr(III) and Cr(VI). The hexavalent form is of particular concern because of its great toxicity [82], known to be carcinogenic and mutagenic to living organisms. Regarding Cr(III), this element appears in acidic solutions under positively charged species (Cr^{3+}, $CrOH^{2+}$, $Cr_3(OH)_4^{5+}$ and $Cr(OH)_2^+$), and then its adsorption behavior is expected to be quite similar to lead, copper and zinc. In fact, using tannin-immobilized mesoporous silica beads, Huang et al. [53] reported an increase in Cr(III) removal with the increase in pH from 2.5 to 5.5. The pH_{PZC} of the biosorbent was 4.01 and thus the chelating interaction of Cr(III) with phenolic hydroxyls was especially promoted for pH above this value. The maximum adsorption capacity was also quite considerable (68 mg g^{-1}, 1.30 mmol g^{-1}) and, considering the molar value, even higher than the values reported for other cationic heavy-metals.

The hexavalent chromium form has a different aqueous chemistry. In acidic aqueous solutions, Cr(VI) is mostly presented under the species of $HCrO_4^-$, or as CrO_4^{2-} for pH close to the neutrality. The prevalence of these anionic forms is impeditive for electrostatic attraction, when pH conditions are above pH_{PZC} (as previously referred, the PZC of tannin resins is usually near pH 2). However, at strong acidic conditions (pH 1-3) several studies [57, 60, 76] reported great adsorption capacities for Cr(VI). Rodrigues et al. [57] reported a strong decrease in Cr(VI) adsorbed amount with increasing pH, with optimum removals found at pH 1, which was explained on the basis of electrostatic attraction between the positively charged surface of the TBA and the negatively charged ion ($HCrO_4^-$). As can be seen in Table 3, tannin gels from different sources have been provided excellent adsorption capacities, ranging from 274 to 488 $mg_{Cr(VI)}$ g^{-1}. A four reaction step mechanism (illustrated in Fig. 3) was proposed for Cr(VI) uptake by mimosa (*Acacia mollissima*) tannin gel [60]: (a) the esterification of chromate with tannin molecules, (b) the reduction of Cr(VI) into Cr(III) and the formation of carboxyl group by the

oxidation of tannin molecules and (c) the ion exchange of Cr(III) with hydroxyl and/or carboxyl groups created in tannin gel particles. These results were obtained at too low pH (mainly at pH 1) and using too high chromium concentrations (1 g L^{-1}), which favour the oxidation ability of chromate. For that reason, in a different study [76], less acidic conditions (pH 3) and lower Cr concentrations ($\approx$10 mg L^{-1}) were evaluated, using a persimmon tannin resin. The results corroborated the previous findings, with similar high efficiency (Q_m = 274 mg g^{-1}), but with no evidences of the presence of Cr(III) adsorbed in the gel.
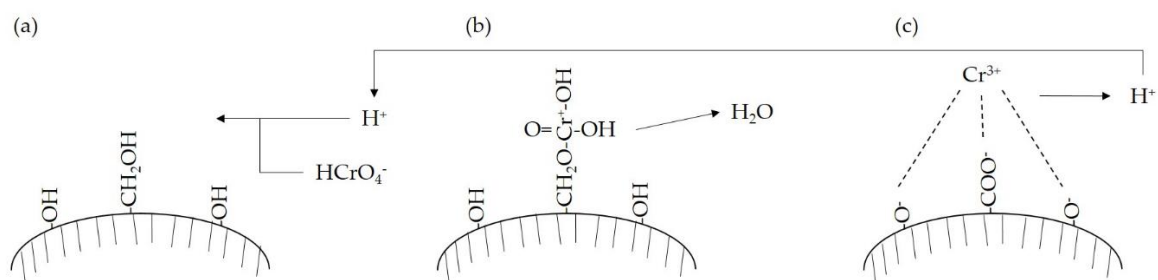
Fig. 3. Schematic diagram of the adsorption mechanism of Cr(VI) within the tannin gel (adapted from [60]): (a) attack on tannin-gel by protons and chromate; (b) esterification of chromate with tannin surface groups, with release of water; (c) reduction of Cr(VI) into Cr(III) and formation of carboxyl group by the oxidation of tannin molecules, with Cr^{3+} adsorption by electrostatic attraction.

A persimmon waste gel obtained through acid-catalysed polymerization was also evaluated in terms of its biosorption capacity for Cr(VI), through a selective adsorption assay [49]. The optimal pH value for chromium adsorption was found to be 3, however it was at pH 1 that the highest selectivity towards Cr against other metals, such as Fe(III), Pb(II), Cd(II) and Zn(II) was observed.

From an environmental point of view, the ability of tannin gels to promote Cr(VI) reduction in solution, early observed in many studies [60, 76] and also recently corroborated for a black wattle tannin gel [57], is beneficial, since it leads to decrease in the toxicity of the treated water. On the other hand, the high efficiency observed for Cr(VI) removal at strong acidic pHs can be favourable since many effluents from metal finishing processes present pH values in the range 1-3 [57, 83], and then can be adequately treated with no need of additional expenses in base additions for pH corrections.

Desorption and regeneration of exhausted adsorbents is usually an important factor to be considered in the design of an adsorption process. The possibility of

regeneration should decrease the overall process cost and its dependency on the continuous supply of the biomass [84]. The desorption would be especially beneficial if the metal (in the eluent) can be reused directly and if the eluent did not cause serious structural damage on the adsorbent during regeneration. However, many times strong acid or alkaline solutions are needed to find adequate desorption levels and not always the direct reuse is possible. In addition, the high polluting character of these residues and the drop in the biosorptive capacity that is occasionally observed following regeneration, discourage desorption procedures when low-cost adsorbents are used. Rodrigues et al. [57], for instance, evaluated Cr desorption from an exhausted black wattle tannin gel and found a limited desorption level: 24 % desorption using 0.1 M NaOH as eluent.

As explained in chapter 3, chemical modifications (post-polymerization) are common in studies with TBAs, when there is the need to increase the affinity of the adsorbent towards the desired adsorbate. An example of this is the targeting of boron by an amine-modified TBA, prepared by ammonia treatment of the tannin resin [12]. Boron is an element that occurs naturally, but it is also present in wastewaters from several industrial plants and, above certain concentrations, it is harmful for life beings. In aqueous solution, boron is mostly present under the species of $B(OH)_3$ (for pH below 9) or $B(OH)_4^-$ (pH above 9). By comparison with an unmodified tannin gel, it was shown that the amine modification does indeed increase the boron removal efficiency of the adsorbent, by doubling the maximum adsorption capacity of tannin gel towards boron (Table 3). The boron adsorbed amounts were relatively small and almost constant for pH values below 7, whereas increased with increasing pH above 7. Importantly, the pH value where the adsorption started to increase is also the point where the predominant species of boron started to shift from the neutral molecule ($B(OH)_3$) to the oxyanion ($B(OH)_4^-$). This means that boron was adsorbed under the anionic form. The proposed adsorption mechanism involves the chelate formation between tetrahydroxyborate ion and hydroxyl and amino groups of the adsorbents. The more stable coordination bonds between boron and nitrogen justify the higher affinity of the amine-treated tannin gel to boron, in comparison to the unmodified tannin gel [12].

The removal of mercury(II) from aqueous solution was assessed using bayberry tannin-immobilized collagen fiber adsorbent [52]. High adsorbed amounts were found in a wide pH range of 4-9, reaching 198 mg g^{-1}. A two-step adsorption mechanism was proposed: first, a deprotonation process occurs, leading adjacent

phenolic hydroxyls to become negatively charged; then, a chelating reaction takes place, with the two hydroxyls acting as a ligand for one mercury ion.

The toxicity of arsenic is referred in the first chapter of this thesis. Arsenic exists in four oxidation states: As(-III) (arsines), As (elemental arsenic), As(III) (arsenite) and As(V) (arsenate) [85, 86]. In natural environment, arsenic appears in trivalent and pentavalent oxidation states, being As(V) the most stable form [87-89]. As(V) is thermodynamically stable state in aerobic water, while As(III) is predominant in reduced redox environment [90]. Environmental species of arsenic include arsenious acids (H_3AsO_3, $H_3AsO_3^{2-}$), arsenic acids (H_3AsO_4, $H_3AsO_4^{-}$, $H_3AsO_4^{2-}$), arsenites, arsenates, methylarsenic acid, dimethylarsinic acid, arsine, etc [26]. Arsenic speciation in aqueous solution depends of the solution pH and involves the presence of neutral and negative oxyanions (Fig. 4). It is known that arsenite is more toxic than arsenate, with inorganic As being more toxic than organic As [91]. There are no reports in the literature revised for the preparation of this dissertation that evaluates the adsorption of arsenic onto TBAs. In fact, it is expected an untreated TBA not to be efficient whatsoever for arsenic. The predominant species of arsenic are neutral or negative, and ideally should be positive in order to be attracted to the negatively-charged surface of TBAs. To avoid this obstacle, the TBA should be subjected to a treatment to shift its surface charge; an example of such treatment is presented in this work.
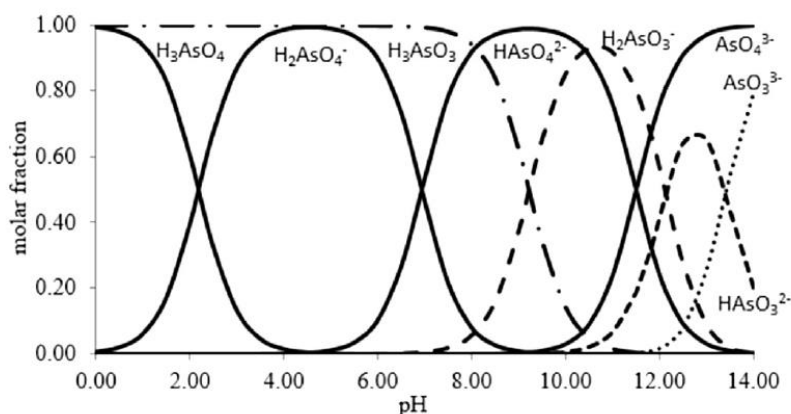
Fig. 4. Arsenate and arsenite speciation as a function of pH [27].

2.4. Tannin-based adsorbents for recovery of substances

Several metals are considered critical and precious due to their importance for our economy and lifestyles (in chemical industries, development of new advanced materials and related industries) and to the risks of supply shortage (related to rising demands and scarcity risks) [4, 92, 93]. Such critical and precious elements include gold, silver, platinum, palladium, molybdenum, among others [94]. Nowadays, there is a rising concern about these elements sustainability around the globe [4]. The driving force of this concern is, of course, its economic value, as there is a demand for such elements in several industrial and technological applications. In fact, many of these applications generate wastes containing the critical and precious metals, which in order to mitigate the risk of supply, should be viewed as valuable resources ready for exploitation [94]. The creation of a circular economy approach to recycle these elements promotes their sustainability [4]. An example of such wastes are the obsolete electric and electronic devices, or e-wastes, which contain large amounts of precious metals. Indeed, e-wastes contain more gold per ton of scrap than gold ores do per ton of ore, being considered a secondary ore of gold [58].

There are several approaches to recover critical and precious elements, including chemical precipitation, coagulation, ion exchange and membrane technologies [4]. In particular, hydrometallurgical techniques involving chemical leaching have been preferred for recovery of metals from e-wastes. Adsorption appears again as a strong alternative to recover these metals, and biosorbents, in particular, have been attracting researchers as potential materials to be applied in sustainable metal recovery technologies [4]. Moreover, adsorption is able to be applicable for dilute solutions, an important property for the recovery of scarce and precious elements, owing to their low concentrations in a wide range of waste streams [94, 95]. With that in mind, TBAs have attracted many researchers and have been studied for the recovery of aforementioned elements from aqueous solutions. The maximum adsorption capacities reported in literature for TBAs, on the uptake of several precious and rare metals (batch mode experiments) are listed in Table 4. As can be seen, gold is one of the precious metals more extensively targeted, and persimmons the most common tannin source.

Table 4. Maximum adsorption capacities of several precious and rare metals by TBAs.

Adsorbent	Adsorbate	Q_m (mmol g^{-1})	Conditions[a]	Ref.
Immobilized persimmon tannin		≈ 5 [b]	pH 3.0, 303 K, 0.05 g L^{-1}, 0.05-1.0 mmol L^{-1}	[96]
Persimmon powder-formaldehyde resin		9.1	pH 2.0, 323 K, 0.3 g L^{-1}, 0.8-1.8 mmol L^{-1}	[58]
Persimmon peel gel		≈ 9 [b]	0.1 M HCl, 303 K, 1.0 g L^{-1}, 0-60* mmol L^{-1}	[47]
Crosslinked persimmon tannin gel		7.7	0.1 M HCl, 303 K, 1.0 g L^{-1}, 0.5-24 mmol L^{-1}	[48]
Tannin-immobilized mesoporous silica bead		3.3	pH 2.0, 323 K, 1.0 g L^{-1}, 0.25-4 mmol L^{-1}	[54]
BTU persimmon tannin gel	Au(III)	5.18	0.1 M HCl, 303K, 1.3 g L^{-1}, 0.2-15 mmol L^{-1}	[46]
AG persimmon tannin gel		8.90	pH 2.5, 323 K, 1.0 g L^{-1}, 0-35* mmol L^{-1}	[59]
TEPA persimmon tannin gel		5.63	0.1 M HCl, 303K, 1.0 g L^{-1}, 0-6* mmol L^{-1}	[45]
DMA persimmon waste gel		5.6	0.1 M HCl, 303K, 1.0 g L^{-1}, 0-23 mmol L^{-1}	[61]
Bayberry tannin-immobilized collagen fiber		7.6	pH 2.5, 323 K, 0.2 g L^{-1}, 0.5-2.4 mmol L^{-1}	[97]
Valonea tannin-formaldehyde resin		0.82	pH 2.0, 293 K, 1 g L^{-1}	[98]
Bayberry tannin-immobilized collagen fiber		0.31	pH 4.0, 313 K, 1.0 g L^{-1}, 0-0.33* mmol L^{-1}	[71]
BTU persimmon tannin gel	Pd(II)	1.80	0.1 M HCl, 303K, 1.3 g L^{-1}, 0.2-10 mmol L^{-1}	[46]
AG persimmon tannin gel		2.01	0.1 M HCl, 303K, 1.0 g L^{-1}, 0-10* mmol L^{-1}	[59]
TEPA persimmon tannin gel		1.76	0.1 M HCl, 303K, 1.0 g L^{-1}, 0-6 mmol L^{-1}	[45]
DMA persimmon waste gel		0.42	0.1 M HCl, 303K, 1.0 g L^{-1}, 0-4.5* mmol L^{-1}	[61]
BTU persimmon tannin gel		0.67	0.1 M HCl, 303K, 1.3 g L^{-1}, 0.2-10 mmol L^{-1}	[46]
AG persimmon tannin gel		1.01	0.1 M HCl, 303K, 1.0 g L^{-1}, 0-8* mmol L^{-1}	[59]
TEPA persimmon tannin gel	Pt(IV)	1.48	0.1 M HCl, 303K, 1.0 g L^{-1}, 0-4* mmol L^{-1}	[45]
DMA persimmon waste gel		0.28	0.1 M HCl, 303K, 1.0 g L^{-1}, 0-6* mmol L^{-1}	[61]
Bayberry tannin-immobilized collagen fiber		0.21	pH 3.0, 313 K, 1.0 g L^{-1}, 0-0.23 mmol L^{-1}	[71]
Persimmon tannin gel	V(IV)	4.84	pH 3.75, 303 K, 0.2 g L^{-1}, 0.2-2.5 mmol L^{-1}	[99]
	V(V)	3.81	pH 6.0, 303 K, 0.2 g L^{-1}, 0.2-2.5 mmol L^{-1}	[99]
Valonea tannin-formaldehyde resin	Rh(III)	0.11	pH 2.0, 293K, 1 g L^{-1}	[98]
TEA persimmon waste gel	Mo(VI)	3.0	pH 3.0, 303 K, 2 g L^{-1}, 0-4.2* mmol L^{-1}	[50]

a – experimental conditions: pH, temperature, adsorbent dosage and initial (* or equilibrium) adsorbate concentration range; b – maximum adsorbed amount obtained experimentally

2.4.1. Gold

The importance of gold is not restricted to its role as a value standard or a metal for jewellery, but also to its very special properties and industrial applications, such as in high-tech electronics [100].

As can be seen from the Q_m values summarized in Table 4, TBAs are clearly able to preconcentrate gold from strong acidic solutions in very high biosorbed amounts (ranging from 3.3 to 9.1 mmol g^{-1}).

Regarding tannin-resins (with no further chemical modifications, apart from the gelation reaction), the mechanism proposed in literature for gold uptake by TBAs is based on Au(III) reduction to elemental gold, by a three-step mechanism [47, 101]: ligand exchange of AuCl$_4^-$ by hydroxylphenyl groups in the adsorbent, reduction of Au(III) to Au(0) by the adsorbent, and adsorption of the resulting Au(0) by the adsorbent; simultaneous to the reduction of trivalent gold ions, the oxidization of the hydroxyl groups of the tannin gel to carbonyl groups takes place [43]. The optimum pH conditions for gold uptake are usually evaluated under a narrow acidic range (practical interest conditions), using HCl solutions or HNO$_3$/HCl mixtures (acids of aqua regia, commonly used in leaching processes). Optimum uptake of gold in tannin-derived resins has been found at pH 2 [43, 58] or 3 [96]. In addition to the pH, the acids present in solution (HCl or HNO$_3$) are also variables to be considered, exerting different effects on the amount of gold adsorbed. Fan et al. [102], for example, analyzed the influence of hydrochloric and nitric acid concentrations on gold adsorption by persimmon residual based bio-sorbent resins and concluded that HNO$_3$ exerted a higher impact on gold adsorption than HCl: sharp decrease in the adsorption percentage was recorded for HNO$_3$ concentrations above 3 mol L^{-1}, whereas for HCl, the decrease was observed only above 5.8 mol L^{-1}. However, below the aforementioned acid concentrations, Au(III) was extensively preconcentrated in the TBA. In addition to a great capacity to uptake gold, the selectivity is an important property when a biosorbent is considered for the recovery of a metal. Tannin resins have also showed a selective uptake of gold, against negligible or weakly uptakes of other metals present in the solution (Fe^{3+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+} Pd^{2+}, Pt^{4+}) [47, 48, 58, 102]. In general, literature has been mostly focused in batch adsorption studies, with few studies reporting results in continuous mode fixed-bed columns [58, 101]. The column studies carried out by Xie et al. [58] suggested that the resin was effective for the uptake of Au(III) from aqueous solutions, but during the adsorption step, and even after 8,000 bed volu-

mes, adsorption equilibrium (saturation) was not achieved. Based on the observations, the researchers suggested that the loaded Au(III) was being aggregated at the upper surface layer of the bed as nanoscale gold particles form, and the separation of the reduced gold particles from the biosorbent was generating new active sites in the persimmon powder-formaldehyde resin. The elution of the gold from the loaded-biosorbent was found to be easy using an acidic thiourea solution (1.0 mol L^{-1}). Results presented by Fan et al. [102] also show that during adsorption in a packed-bed column, the outlet gold concentration has never reached the inlet value, which corroborates the previous observations. In this study, however, the researchers proposed incineration to recover gold from the loaded-adsorbent. The authors reported an amount of 50.6 mg of gold (99.9 % purity), obtained by incineration of 100 mg of tannin resin, after saturation.

Immobilized bayberry tannins onto collagen fibers were also able to uptake gold extensively from an acidic solution, with adsorbed amounts reaching 1500 mg g^{-1} of gold [97]. However, in this study, desorption was proven to be impossible through the use of a desorbent; many eluents were tested (sodium bicarbonate, sodium carbonate, hydrochloric acid, urea, and thiourea) and all failed. This is a drawback for this adsorbent, limiting the subsequent recovery to burning, as suggested by the authors. Another possible way but limited to specific applications (catalysis, for instance) is the direct reuse of gold loaded in the adsorbent.

Chemical modified resins with amine compounds (BTU, AG, TEPA, DMA) have been also synthesized and evaluated for gold recovery [45, 46, 59, 61]. With respect to the maximum uptake capacities (Table 4), these treatments are not very advantageous, with no (or little) improvements when compared to unmodified resins [10, 48]. Even though, Gurung et al. [59] reported an outstanding selectivity of AG-modified persimmon tannin gel (Q_m = 8.90 mmol g^{-1}, i.e., 1753 mg g^{-1}), stating that the amine treatment creates positively charged sites, due to amine protonation in acidic medium, able to electrostatically attract the negative charged gold chloro-anionic species. Gold concentration in these amine-modified adsorbents has been reported as a result of anion exchange coupled electrostatic interaction, with simultaneous reduction of adsorbed Au(III) to elemental form [45, 46, 59], as it was happening to unmodified tannin gels.

Several results regarding gold adsorption and recovery in continuous-mode experiments have been also presented in literature and validate the batch-mode promising results. DMA-persimmon waste gel presented a maximum loading

capacity for Au(III) of 5.96 mol kg^{-1} in packed-bed adsorber, similar to the value reported for batch-mode, and 98% being eluted and recovered [61]. The regeneration and reuse of TEPA-modified tannin gels was examined by adsorption/elution cycles using 0.1 M HCl and found to be feasible for at least four repeated cycles, with 83-97 % recoveries and undiminished metal uptake capacities [45].

2.4.2. Palladium and Platinum

Literature also presents some studies reporting TBAs for palladium and platinum recovery.

The mechanism for Pd(II) adsorption on tannin gels was found to proceed through the inner sphere redox reaction: the Pd(II) ionic species are reduced to metallic Pd(0) and adsorbed, while the hydroxyl groups of the tannin gel are oxidized, which is accompanied by the formation of a ligand-substituted Pd(II)–tannin complex for a two-electron transfer [103, 104]. The adsorption experiments with palladium should be carried out at pH 2, aiming to prevent metal precipitation [98, 103]. At pH 2, Pd(II) adsorbed amounts on wattle condensed-tannin gel particles reached approx. 200 mg g^{-1} (0.002 mol L^{-1} Cl$^-$, 333 K, from Pd(II) 100 mg L^{-1} solution) [103], whereas a maximum capacity of 87.1 mg g^{-1} (1 mol L^{-1} HCl, from 200 mg L^{-1} Pd(II)) was reported for a valonea tannin–formaldehyde resol resin [98].

As explained in subchapter 3.2, compared with hydroxyl groups, amino groups have higher affinity and selectivity for soft metal ions. Then, a stronger bond with soft acidic precious metal ions, such as Pd(II) and Pt(IV), is expected if an amine-treatment is performed in tannin gels. Several works clearly demonstrated [46, 59, 64, 65] the significant enhancement in the adsorbability of both precious metals. The adsorbed amounts of Pt(IV) were however found to be much smaller than the values obtained for Pd(II). The difference is not so significant if we take the maximum adsorbed amounts in mg g^{-1}, but it is clearly visible if we consider the molar amounts adsorbed. The amine-treated tannin gels can then selectively adsorb Pd(II) from a Pd(II)/Pt(IV) mixture, although being also effective for Pt(IV) uptake in single metal solution [65].

In the previous subchapter, we had seen that Au(III) was reduced to the elemental form, in the presence of both unmodified and amine-modified tannin resins. Here, in the case of Pd(II), which was also found to be reduced by unmodified tannin

resins, in the presence of amine-treated gels, literature suggested that it is not reduced to Pd(0) [45].

The adsorption behavior of Pd(II) and Pt(IV) in modified/unmodified tannin resins was found to be influenced by pH and total chloride ion concentration [65, 103], since the speciation of both elements, chloropalladium(II) and chloroplatinum(IV) complexes, is dependent on these two parameters [65]. Higher chloride concentrations in aqueous solutions were found to decrease the adsorbed amounts of Pd(II) [65, 103] and Pt(IV), which means that complexes with fewer chloride ligands are more favorable for being adsorbed.

Considering that the unmodified tannin gels have shown high selectivity and capacity for gold, while the amine-modified gels have shown high selectivity for palladium, continuous-mode experiments to recover precious metal from industrial samples have been conducted using a setup consisting of two sequential packed-bed columns: a first one packed with unmodified adsorbent (tannin gel), in order to selectively recover gold, and a second column packed with amine-modified adsorbent, to recover palladium and platinum. Xiong et al. [61], employing a persimmon waste-gel (first column) achieved Au(III) uptake of 139 mg g^{-1}, and null uptake of Pd, Pt and other metal ions in solution; using a DMA-persimmon waste-gel (second column), they found adsorbed amounts of 20.1 and 13.2 mg g^{-1}, respectively for Pd(II) and Pt(IV). Using a mixture of thiourea/hydrochloric acid solution, 93-96% of recoveries were found from the loaded adsorbents. Gurung et al. [46] also conducted a similar experiment, using persimmon-tannin gel, in the first column, and BTU persimmon tannin gel in the second one; the amount of Au(III) adsorbed in the first column was 167 mg of Au(III) per g, and 94.2% was recovered using acidic thioureia solution; in the second column, Pd(II) was selectively preconcentrated in BTU-persimmon tannin gel (9.6 mg g^{-1}) and 98% was recovered after elution. These results show adsorption capacities for Au, Pd and Pt, significantly lower than the values reported for batch mode experiments (Table 3), but even though quite considerable; in addition, excellent recoveries from the loaded adsorbents were found. In another study [45], Pd and Pt adsorption and desorption from TEPA-modified tannin resins using 0.1 mol L^{-1} HCl as eluent was found to be quantitative (or near to quantitative) for at least four repeated cycles (recoveries above 79%).

2.4.3. Molybdenum

Molybdenum is another important metal to be recovered, considering its expanding demanding in industry, its major use in high performance stainless steel [94] and the negative effect to flora and fauna if molybdenum-containing wastes are not adequately disposed. TBAs have also been reported as possible biosorbents for the preconcentration of Mo(VI). Astringent persimmon gel, prepared with formaldehyde, exhibited high selectivity towards Mo(VI), in presence of Ca(II) and Re(VII). For increasing HCl concentrations (1 and 3 mol L^{-1}), it was also selectively removed in the presence of other metals, such as Cu(II), Pb(II), Fe(III), Zn(II), Mn(VII) and Ni(II) [105]. A remarkably high adsorption capacity of 101 mg g^{-1} was found, with an inferred adsorption mechanism based on molybdenum esterification with catechol or pyrogallol groups. In another study, persimmon waste gel, prepared by crosslinking with concentrated sulfuric acid, also showed ability to preconcentrate Mo(VI) (Q_m=54 mg g^{-1}) [106], with high Mo/Re separation factors ranging from 14 to 164, depending on the HCl concentration.

Amine-treatments of tannin gels were found to further enhance the adsorption ability towards molybdenum. Shan et al. [50] synthetized DEA and TEA-tannin gels from persimmon waste. As explained before, the new positively charged nitrogen groups were able to interact with negatively charged Mo ions, and then improve the uptake of this metal. Maximum adsorption occurred at pH 3-6, since at higher pH (or lower), electrostatic repulsion between negative charged adsorbent and Mo oxyanions (or positive charge adsorbent and positive/neutral Mo species) prevents the adsorption. Both DEA and TEA-adsorbents were found to preconcentrate molybdenum extensively, but TEA, due to the higher steric hindrance presented a higher selectivity towards Mo(VI), against rhenium. TEA-tannin gel showed experimental maximum adsorption capacities for Mo(VI) of 191 mg g^{-1} (pH 1) and 235 mg g^{-1} (pH 3), with Langmuir model predicting slightly higher monolayer capacities, 258-287 mg g^{-1}. An excellent selectivity was obtained, with a separation factor Mo/Se above 10^4. Continuous-mode fixed-bed adsorption-elution experiments were conducted to recover Mo(VI). The breakthrough took place after about 50 bed volumes (initial concentration 50 mg L^{-1}), and the bed was found to be saturated after 735 bed volumes. Six consecutive adsorption–elution cycles were run and the results showed that biomass waste can be repeatedly used in the biosorption process without significant losses of adsorption capacity.

2.4.4. Vanadium and Rhodium

Vanadium is one of the rare metals, extensively used as an alloying element in steel and iron and titanium alloys, and as catalyst [107]. Vanadium is widely distributed, but not in high concentrations. The low grade of vanadium in the processed ores and the depletion of concentrated ore deposits in the world justifies the increasing interest for the recovery of this element from various sub-products [108].

Regarding the use of TBAs for vanadium recovery, a persimmon tannin gel was used to study the uptake of V(IV) and V(V), from VO^{2+} and VO_3^- solutions, respectively [99]. Electron spin resonance analysis was used to infer the adsorption mechanisms. As it can be seen from Table 4, considerable values for maximum uptakes were found for both species. The pH influence assay showed negligible adsorption for pH values below 2 and an extensive removal in the pH range 2-8. For V(IV), optimum adsorption was found at pH 5-6, as a result of the highly stable complex formation between VO^{2+} (a hard acid) and the hard bases, catechol and pyrogallol, in the tannin polymer. For V(V), a sharp maximum was found at pH 3.75, but a second broad maximum was also observed at around pH 5-6. In this case, the adsorption took place via the neutral molecule, H_3VO_4, which according to the predicted V(V) speciation in water has its maximum at pH 3.75. At pH 6, the reduction of VO_3^- to VO^{2+} was found to occur prior to vanadium adsorption.

Rhodium is another precious metal, able to be recovered in valonea tannin resins [98]. Adsorption of aquachlororhodium(III) species, $[RhCl_5H_2O]^{2-}$ and $[RhCl_2(H_2O)_4]^{2-}$, mostly took place via ligand exchange mechanism. Under the conditions studied, and in opposite to the observed for palladium or gold, reduction of Rh(III) species to metallic form did not occur. The maximum adsorption capacity of valonea tannin resin was 10.86 mg g^{-1}.

2.4.5. Phosphates

For the reasons that have already been stated, most of the literature studies have been focused on the use of TBAs for the recovery of critical metals. The recovery of other substances, such as phosphate is not usual. Phosphorous is a macronutrient, essential for plant growth and for the modern agricultural techniques. An interesting study concerning the recovery of phosphates in an iron-treated TBA (see subchapter 2.2.2.) and its further direct reuse as a fertilizer is reported by Ogata et al. [44]. The possible direct use of phosphate-loaded TBAs in

agriculture is a challenging way to close the loop. Through an iron loading treatment, a TBA with affinity to uptake phosphate was obtained. A maximum adsorption capacity of 14.7 mg-P g^{-1} (predicted by Langmuir modeling) was found. In the pH range 3-12, pH did not influence phosphate adsorption.

This kind of iron-loaded biosorbent seems to be an interesting option, not only for phosphate, but also for any other solutes that behave similarly in aqueous solution. According to the author's knowledge, for instance, there are not studies regarding arsenic, or other toxic metalloids, removal using TBAs, and the results showed here are clearly promising.

3. Materials and Methods

3.1. Adsorbent preparation

3.1.1. Tannin extraction

Pinus pinaster bark was collected and used in this work. This species was chosen due to its abundance in Portugal. The tannin extraction procedure applied here was adapted from the one described by Sánchez-Martín et al. [37]. The tannins were extracted according to the following procedure: the bark was broken up, producing pieces roughly ranging from 2 mm to 2 cm, and they were put in distilled water (600 mL per 100 g of bark). Then, sodium hydroxide (analytical grade, pellets, *Absolve*) was added (5 g per 100 g of bark) and the mixture was stirred and heated in a magnetic stirrer/heating plaque at 85 °C for 90 minutes. Solids were separated from the liquid fraction by filtration (qualitative filter paper, *Whatman*). Finally, the liquid fraction was evaporated in a heating plate until the sample contained almost no water. Importantly, during the evaporation procedure the temperature was controlled with a thermometer so it did not surpass 65 °C and promote the oxidation of the tannins as a consequence. For the evaporation of the liquid fraction, other techniques (spray drying, rotary evaporator and freeze-drying) were considered in order to reduce the time required, but, in the end, these other options were disregarded due to their disadvantages. Spray drying had high losses and it was only suitable for low volumes; the rotary evaporator would lead to a precipitate of difficult recovery; and freeze-drying was also only suitable for low volumes. The humid precipitant was dried in an oven at 65 °C. The resultant material, considered the tannin extract, was denoted as TE (Fig. 5).
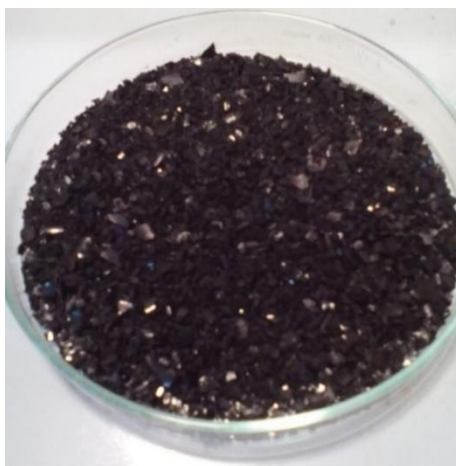

Fig. 5. Tannin extract.

3.1.2. Tannin gelification

The tannin gelification procedure applied here was adapted from the one described by Xie et al. [58] and Nakano et al. [109]. The tannin extract was dissolved in 0.25 mol L^{-1} NaOH solution (4 mL per g of tannin extract) at room temperature, which was followed by addition of 0.4 mL of formaldehyde (37 wt %, analytical grade, *Labsolve*) per g of tannin extract, as a crosslinking reagent. After gelification at 80 °C for 12 hours, the product was dried in an oven at 65 °C, following by washing successively with HNO_3 solution (0.05 mol L^{-1}) and distilled water to remove unreacted substances. Finally, the obtained adsorbent was once more dried at 65 °C. The resultant product was considered the tannin-based adsorbent gel and denoted in the present work as TG. The procedure from bark to the adsorbent gel is schematized in Fig. 6.
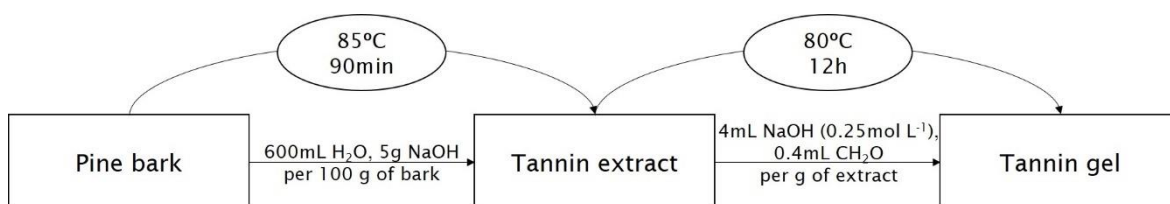
Fig. 6. Schematization of the tannin extraction from pine bark and its gelification procedure.

3.1.3. Preparation of iron-loaded adsorbent

Based on the results previously obtained [110], an unmodified tannin gel does not present significant arsenic uptake ability (6% of As(III) removal was found from a 24 mg L^{-1}, at pH 4, 20 °C and using a TG dosage of 10 g L^{-1}). However, the literature revision performed for this dissertation allowed to infer the possibility of using chemically modified tannin gels to treat arsenic-contaminated waters.

Indeed, Ogata et al [44] have shown that an iron-loaded TBA was efficient for the removal of phosphates from water. Phosphates have a chemical behavior in aqueous conditions, in terms of speciation, that is quite similar to that of arsenic(V). Hence, it was presumed that such adsorbent would have potential to remove arsenic from aqueous solutions and it was decided to evaluate such potential in the present work. The iron-loading procedure proposed by the researchers was developed for a wattle-tannin extract. It consisted in the oxidation

of the tannin gel with nitric acid solution (2 mol L^{-1}, 120 min, 60 ºC), followed by a 5-day contact with $FeCl_3$ solution 1 mol L^{-1} at initial pH 1.

This procedure was here optimized, to some extent, for the pine tannins used in this work. The following variables were studied in order to maximize the amount of iron impregnated in the tannin gel: nitric acid concentration (1 and 2 mol L^{-1}), temperature (40 and 60 ºC) and time of oxidation (30-120 minutes). One gram of TG was added to 100 mL of nitric acid solution with a concentration of 1 mol L^{-1}, being kept under stirring and at 60 ºC for 30, 50 or 120 minutes, or 2 mol L^{-1}, also kept under stirring and at 40 or 60 ºC for 90 minutes. Next, the adsorbent was washed with water to remove the remaining HNO_3 from the particles. Finally, the adsorbent was dried in an oven at 65 ºC. The resultant products were considered the oxidized tannin-based adsorbent gels.

One gram of the oxidized tannin-based adsorbent gel particles was added to 50 mL of $FeCl_3 \cdot 6H_2O$ solution with a concentration of 1 mol L^{-1} at pH 2 (adjusted with HNO_3). Also, non-oxidized gel was also subjected to same iron treatment. The mixture was kept under stirring at room temperature for 48 h, followed by washing with water to remove unreacted species. Finally, the adsorbent was dried in an oven at 65 ºC. The resultant product was considered the iron-loaded tannin-based adsorbent gel (Fig. 7). The different types of TBA obtained are listed in Table 5.

Table 5. Specifications of each TBA obtained.

Designation	Oxidation conditions	Iron-treatment
TG	-	-
TG-Fe	-	+
TGOx1-30-Fe	1 M, 30 min, 60 ºC	+
TGOx1-50-Fe	1 M, 50 min, 60 ºC	+
TGOx1-120-Fe	1 M, 120 min, 60 ºC	+
TGOx2-40-Fe	2 M, 90 min, 40 ºC	+
TGOx2-60-Fe	2 M, 90 min, 60 ºC	+

Fig. 7. Tannin-based iron-loaded adsorbent gel.

3.2. Adsorbent characterization

3.2.1. Determination of iron content

Iron content present in the iron-loaded tannin-based adsorbents and in the tannin gel was determined by digesting 0.5 g of adsorbent in glass tubes at 150 ºC for 2h with 5.0 mL of distilled water, 12.0 mL of HCl and 4.0 mL of HNO_3 (concentrated acids, 37% and 65% respectively, analytical grade, *Merck*) [111], which were placed in a digester (*DK6 Heating Digester Velp Scientifica*, Fig. 8).

Fig. 8. Digester equipment used in the acid digestion of adsorbent samples.

Seven samples of TBAs were analysed: TG, TG-Fe, TGOx1-30-Fe, TGOx1-50-Fe, TGOx1-120-Fe, TGOx2-40-Fe and TGOx2-60-Fe (Table 5). Samples were digested in duplicate and a blank digestion was also performed. After digestion, solutions were filtered through cellulose acetate membrane filters (0.45 µm porosity). Iron concentrations were determined by flame atomic absorption spectrometry (FAAS) - equipment: *GBC 932 Plus* (Fig. 10) - using a single-element cathode lamp and the conditions defined in Table 6. The results obtained were used to calculate the amount of iron present in the gel matrix per g of adsorbent.

Table 6. Instrumental analytical parameters and calibration curve details for iron content analysis by FAAS.

Working range (mg L^{-1})	0.5–10
Wavelength (nm)	248.3
Lamp current (mA)	5.0
Flame	Air–Acetylene
R^2	>0.995

3.2.2. Determination of point of zero charge pH

The determination of the zero point charge pH (denoted as pH_{PZC}) procedure was based on the mass titration method, at constant ionic strength, described by Noh and Shwarz [112]. The zero point charge represents the pH value under which a surface of an adsorbent has a global electric charge equal to zero. This property should allow one to predict the electrostatic attractions between the adsorbent surface and the adsorbate at different pH values, depending if it is above or below its pH_{PZC}. A sample of the adsorbent was added to 10 mL of NaCl solution (0.01 M) with different dosages: 1, 5, 10, 15, 20 g L^{-1}. Samples were made in duplicate and a blank was also performed, in order to discount the possible effect of CO_2 from air. The mixtures were kept under room temperature with stirring for 24 hours. Then, the pH of each solution was measured and the plot pH vs dosage was drawn. The pH_{PZC} represents the pH limit value when the dosage tends to infinite [112].

3.2.3. Determination of particle size

Particle size distribution of each adsorbent was determined by laser diffraction spectroscopy (*Coulter LS 230* analyzer) using water as the dispersion medium.

3.2.4. Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) analyses were undertaken in order to evaluate the surface functional groups at the different TBAs prepared. Infrared spectra were obtained in duplicate, in a wavenumbers range of 400 – 4000 cm^{-1}, number of scans of 50 and a resolution of 8.0 cm, using the FTIR *Shimadzu IRAffinity-1* spectrophotometer (Fig. 9), equipped with *PIKE Easidiff* module (PIKE Technologies) for solid samples. The samples were crushed until they were almost thin powders.

Fig. 9. FTIR spectrometer and support module for solid samples.

3.3. Adsorption assays

3.3.1. Arsenic solutions

Arsenic was studied under the trivalent (arsenite, As(III)) and the pentavalent (arsenate, As(V)) oxidation state. As(III) solutions were prepared by diluting a commercial standard solution (*SCP Science*, 1003 ± 3 mg mL^{-1}, 4% HNO_3) and As(V) solutions were prepared by diluting a lab-made standard prepared with $HAsNa_2O_4 \cdot 7H_2O$ (994 ± 10 mg mL^{-1}, 2% HCl).

3.3.2. Analytical methods

The samples were analyzed for its arsenic content by flame atomic absorption spectrosmetry (*GBC 932 Plus*, Fig. 10) and, for As levels below 7 mg L^{-1}, graphite furnace atomic absorption spectrosmetry (GFAAS, *GBC SenAADual*, equipped with the automatic sampler *PAL 3000*, Fig. 10). The matrix of solution to be analyzed by GFAAS was constituted by 150 µL of HNO_3 and 3.0 mL of H_2O_2 per 100 mL of sample. The instrumental and analytical conditions are defined in Table 7 and Table 8. Moreover, the samples were also analyzed for its iron content by FAAS under the conditions defined in Table 5 in order to evaluate iron leaching.

Table 7. Instrumental analytical parameters and calibration curve details for arsenic content analysis.

Spectrometry	GFAAS	FAAS
Working range	3–50 µg L^{-1}	5–50 mg L^{-1}
Wavelength (nm)	193.7	193.7
Lamp current (mA)	5.0	5.0
Flame	-	N_2O–Acetylene
R^2	>0.995	>0.995
Detection limit	3 µg L^{-1}	2 mg L^{-1}
Quantification limit	10 µg L^{-1}	7 mg L^{-1}

Table 8. GFAAS analysis program conditions.

Step	T_{final} (ºC)	Ramp time (s)	Hold time (s)
1		Sample inject	
2	90	10	15
3	120	15	10
4	800	5	5
5	800	0	1
6	2400	0.8	1.2
7	2500	1	2

Fig. 10. Atomic Absorption Spectrometers used for As and Fe analysis: GBC 932 plus, used for FAAS determinations (left) and GBC SensAA Dual used for GFAAS measurements (on the right).

3.3.3. Effect of pH

The adsorption assays were executed through the application of the adsorbent in As(III) or As(V) solutions (10 mg L^{-1}) with a dose of 5 g L^{-1}, which was kept under stirring in constant temperature (20 ˚C) and pH for 24 h (more than enough to reach the equilibrium). The adsorbents used in this assay were three: TG-Ox2-40-Fe, TG-Ox2-60-Fe and TG-Ox1-50-Fe. The samples were made in duplicate and several pH values were evaluated: 2.0, 3.5, 4.5, 5 and 7. There was a preference towards pH

in the acid region since the arsenic-contaminated waters generally present an acidic feature. Thus, in order the obtain results in conditions close to those of real situations, those pH values were chosen. After equilibrium was reached, cellulose acetate filters were used to filter every sample. The liquid samples were then analyzed for their content of arsenic, to determine the amount of metalloid removed per mass unit of adsorbent (q), and of iron, to determine the amount of iron leached from the adsorbent to the solution.

3.3.4. Kinetic assay

To study the adsorption kinetics the following assay was executed. An arsenic (III or V) solution of 500 mL, with a concentration of 10 mg L^{-1}, was placed in contact with 5.0 g of adsorbent (TG-Ox1-50-Fe) at pH 3.5, 20 °C and under stirring. Samples were retrieved at 5, 15, 30, 60, 120 and 240 minutes after the start of the assay and were immediately filtrated with cellulose acetate filters. Then, the samples were analysed in terms of arsenic and iron content.

3.3.5. Equilibrium assay

In order to determine adsorption isotherms and establish the maximum adsorption capacities of TG-Ox1-50-Fe, for As(III) and As(V), equilibrium experiments were performed. 0.3 g of adsorbent was applied to 30 mL of arsenic (III or V) solutions of 1, 2.5, 5, 25 and 40 mg L^{-1} at pH 3.5 and 20 °C. After the equilibrium was reached (stirring time: 24 h), the samples were filtrated with cellulose acetate filters. Finally, the arsenic and iron content in the liquid phase was evaluated and pH measured.

4. Results and Discussion

4.1. Preparation of iron-loaded tannin-based adsorbents

Several tannin extractions from pine bark were executed, in separate four batch operations, having extracted tannins from almost 4 kg of bark. From each extraction it was obtained a certain mass of tannin extract, which in turn was used to determine the extractable content in the bark sample used. From the four operations that were carried out, an average extractable content was calculated: 109±55 mg per g of bark (average ± standard deviation), which corresponds to an extractable content of 11±6 %, under the experimental conditions used (alkaline extraction, at 85 ºC, for 90 min). This value is in agreement with what is reported in the literature, which is around 10% [113].

Tannin gelification is a chemical procedure that immobilizes tannins in an insoluble matrix, maintaining their properties, such as metal chelation, so they can be used as an efficient adsorbent agent. This procedure involves a polymerization reaction with formaldehyde through methylene bridges linkages at reactive positions on the tannin flavonoid molecules, which means there is an incorporation of CH_2 groups from the formaldehyde and loss of OH groups by the tannins. Tannins gelification was carried out in four separate batches. In these operations, global mass losses (evaluated comparing the TE mass used and the final TG mass obtained) between 28 and 79 % were reached (average: 58 %). The considerable variability observed between the different batches was probably related to the separation and washing procedures (loss of fine particles) that were carried out after the reaction; also, the different particle sizes of TE influence the ease with which tannin extract solubilizes in the alkaline medium, where the gelification reaction takes place, which in turn influences the degree of conversion of the reaction. Since the time and the temperature was the same for the four batches, it is not believed that these factors influence the different yields obtained in the four batches. Additionally, it is to be noted that a contact time of 12 hours was used, which gives enough time to complete the reaction, considering many researchers report reaction times of 8 hours [37]. In fact, during the reaction time, and after 4-7 hours of reaction, it was possible to observe a sudden change in the appearance of the mixture, from liquid to a gummy product. Based on the results here obtained, it is expected to be synthesized around 42 g of tannin gel per 100 g of tannin extract.

As explained in subchapter 3.1.3, few different sets of conditions for the oxidation procedure were tested in order to maximize the iron uptake by the adsorbent and minimize the mass losses during oxidation. The conditions stated in the original procedure presented in Ogata et al. [44] (nitric acid 2 M, 120 min, 60 ºC) proved in this work to be too aggressive for the adsorbent. Using this high concentration, and oxidation time of 90 min, a great portion of adsorbent was dissolved and an excessive oxidation occurred, causing a 53% loss in mass (from the comparison of the amounts of TG used and TG-Ox2-60 obtained). Ogata et al. had also observed that excessive oxidation can occur using HNO_3 5 mol L^{-1} for an hour and 2 mol L^{-1} for four hours, but in the present work, it was verified that less severe conditions can effectively oxidize excessively pine-tannin gels.

Although it does not favour oxidation, a lower temperature (40 ºC) was assessed in an attempt to diminish losses and then, adsorbent TG-Ox2-40-Fe was produced; indeed, in this case, the mass loss during the oxidation was lower, about 22%. The use of a lower acid concentration (1 mol L^{-1}) at 60 ˚C and for an oxidation time of 50 minutes leads to a reduced mass loss (8%), being the best result achieved. The optimization of the procedure to prepare iron-loaded TBAs should take in account not specifically this mass loss, but the amount of iron impregnated in the adsorbent. In the next subchapter, these results will be presented and the optimum oxidation conditions will be selected based on the outcome of the acid-digestions performed.

4.2. Characterization of the adsorbent

4.2.1. Iron content

To optimize the oxidation conditions (nitric acid concentration and time), a correlation between these parameters and the iron content of the adsorbents was evaluated. Seven kinds of adsorbents were subjected to acid digestion and results presented in Table 9: TG, TG-Fe, TG-Ox1-30-Fe, TG-Ox1-50-Fe, TG-Ox1-120-Fe, TG-Ox2-40-Fe and TG-Ox2-60-Fe. The TG sample was used as a control, presenting, as expected, negligible iron content. Comparing the iron content of the non-oxidized iron-loaded adsorbent (TG-Fe) with the content of any of the oxidized adsorbents (TG-Ox-Fe samples), it is possible to conclude the importance of the oxidation step to maximize the iron uptake. In the different conditions studied, the oxidation step was responsible for 3-12 times greater Fe levels in the adsorbents. Furthermore, it

can be seen that too little or too much oxidation decreases the iron uptake by the TBA. Therefore, the optimal oxidation conditions for posterior iron treatment was found to be 50 min in 1 mol L^{-1} HNO_3 at 60 °C, where a content of 24.4 ± 0.7 mg of iron per g of adsorbent was achieved. This iron content value is much lower than that obtained by Ogata et al. that, with an oxidation with HNO_3 2 mol L^{-1} for 120 minutes, managed to load the adsorbent with 85.1 mg of iron per g of tannin gel. Such discrepancy of iron content values can be explained with the lack of accurate optimization of the oxidation procedure in the present work, but also to the different particle sizes of the TG samples used and, of course, different tannin sources. Indeed, to achieve true optimization, a factorial planning should be executed including the three variables here studied (time, temperature and acid concentration).

Finally, the overall average yield of the whole adsorbent production procedure was found to be 40 grams of iron-loaded tannin gel per 100 g of tannin extract. Tracking back the production route to the extraction, the average yield was 4.3 g of iron-loaded tannin gel per 100 g of bark.

Table 9. Iron content of several TBAs (value ± deviation between average and duplicate measurements).

Adsorbent	Iron content (mg g^{-1})
TG	0.20 ± 0.01
TG-Fe	2.1 ± 0.4
TG-Ox2-40-Fe	5.9 ± 0.1
TG-Ox2-60-Fe	13 ± 1
TG-Ox1-30-Fe	10 ± 1
TG-Ox1-50-Fe	24.4 ± 0.7
TG-Ox1-120-Fe	7.8 ± 0.2

4.2.2. Particle size

Particle size is an important property to an adsorbent because it influences its surface area which in turn influences the adsorption capacity; in general, the greater the specific surface area, the higher the adsorption capacity. The distribution of the particle size of the adsorbent TG-Ox1-50-Fe is presented in Fig. 11. The particle size presents a large distribution, with a mean particle diameter

estimated as 733 µm and a median of 624 µm. 25% of the particles have a diameter greater than 1.1 mm and 25% below 0.27 mm. As referred, the use of fine particles would enhance the adsorption capacity; however, considering the future scale-up of the process and the application of the adsorbent in a continuous system (fixed-bed), higher size particles are preferred to avoid high head losses in the column and clogging problems.
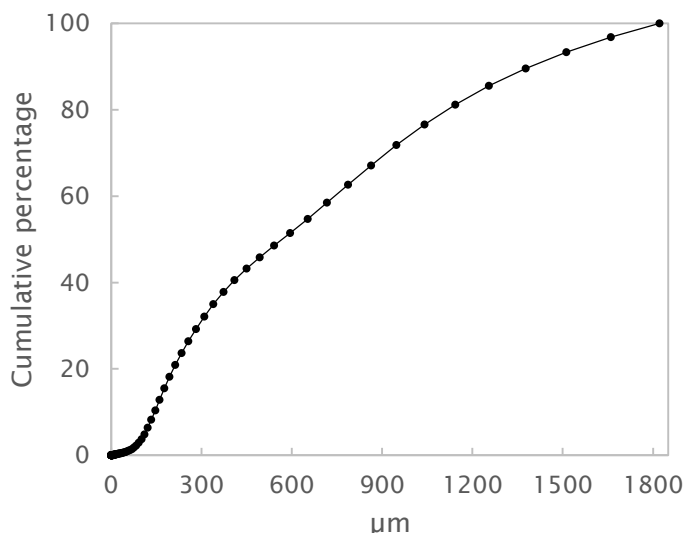
Fig. 11. Particle size distribution of adsorbent TG-Ox1-50-Fe.

4.2.3. pH_{PZC}

The pH_{PZC} is an important parameter for an adsorbent since it allows to predict the influence of pH on adsorption. The adsorbent surface will be charged negatively or positively if the solution pH is above or below the pH_{PZC}, respectively. Thus, manipulating such parameter can significantly alter the adsorption ability and behaviour of an adsorbent.

The results obtained in the determination of pH_{PZC} of TG, TG-Ox1-50-Fe and TG-Ox2-40-Fe are presented in Fig. 12. As it can be observed, the incorporation of iron within the tannin gel matrix radically decreases the pH_{PZC} of the adsorbent. Indeed, while for the untreated tannin gel pH_{PZC} was found to be 7.22±0.09, the values for the iron-loaded tannin gels iwere 2.93 ± 0.02 (TG-Ox1-50-Fe) and 3.0 ± 0.3 (TG-Ox2-40-Fe). Hence, it is expected for the adsorbent to have affinity through electrostatic attraction towards negatively charged species only in solutions which

pH is below 3. This result indicates a narrow pH interval to the adsorbent to be efficient towards anions through electrostatic attraction. As it can be observed in the speciation diagram (Fig. 4), for pH below 9 As(III) is mostly under the species H_3AsO_3, while As(V) is under the form $H_2AsO_4^-$, for pH 2-7. None of those species is oppositely charged to the adsorbent surface, thus adsorption is not expected to occur by electrostatic attraction. Therefore, according to these results, it seems that the incorporation of iron by the tannin gel may debilitate its ability to uptake arsenic, at least through electrostatic attraction.
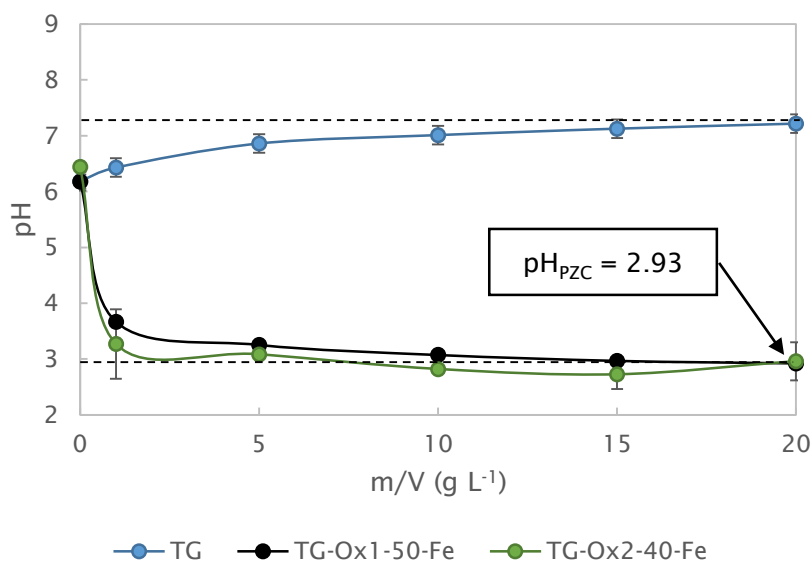
Fig. 12. Graph displaying the pH_{PZC} assay results.

4.2.4. FTIR

FTIR analysis allows to detect the presence of functional groups on the adsorbent, making it possible to compare the differences or similarities between tannin gels produced in different conditions. Moreover, it allows to infer on the evolution of the adsorbent, in terms of functional groups, throughout its preparation, since the tannin extract to the iron-loaded tannin gel.

The FTIR spectra obtained for several samples are presented on Fig. 13. Comparing TE and TG (Fig.13a), the following observations can be made: (i) the decrease in the relative intensity of the broad O-H absorption band (3200-3800 cm^{-1}) observed from TE to TG suggests a higher presence of OH groups in the extract, which was expected due to the loss of some OH groups during the formation of the gel (with

inclusion of CH_2 groups to link the different units); (ii) differences in the shape were observed for the absorption bands corresponding to C=O (1630-1820 cm^{-1}); in TE the band is sharper than in TG, which suggests some kind of modification during the gelification in some of these groups (probably a partial oxidation of hydroxyl groups occurred and generated carbonyl groups).

Between TG and TG-Ox1-50-Fe (Fig. 13a), there is no difference in the absorption band O-H but a slightly difference was observed in C=O, suggesting that carbonyl group was the one to interact with iron particles, as proposed by Ogata et al. [44].

Regarding the comparison between non-oxidized and oxidized adsorbents, it was expected a decrease in the intensity of O-H band from TG-Fe to TG-Ox forms, due to the supposed oxidation of hydroxyl groups and their conversion to carbonyl ones. Lower intensities of OH bands and higher intensities of C=O absorption were expected for higher oxidation times. However, the differences between the spectra are not so significant (Fig. 13b). In fact, comparing the C=O bands of the spectra for 30, 50 and 120 min, it seems that the higher intensity was found for 50 min, suggesting a higher amount of C=O groups in this sample, a low degree of oxidation for 30 min and an excessive oxidation for 120 min. This corroborates the previous findings and explains the higher amount of iron that was found to be impregnated in TG-Ox1-50-Fe in comparison to the other oxidized samples.
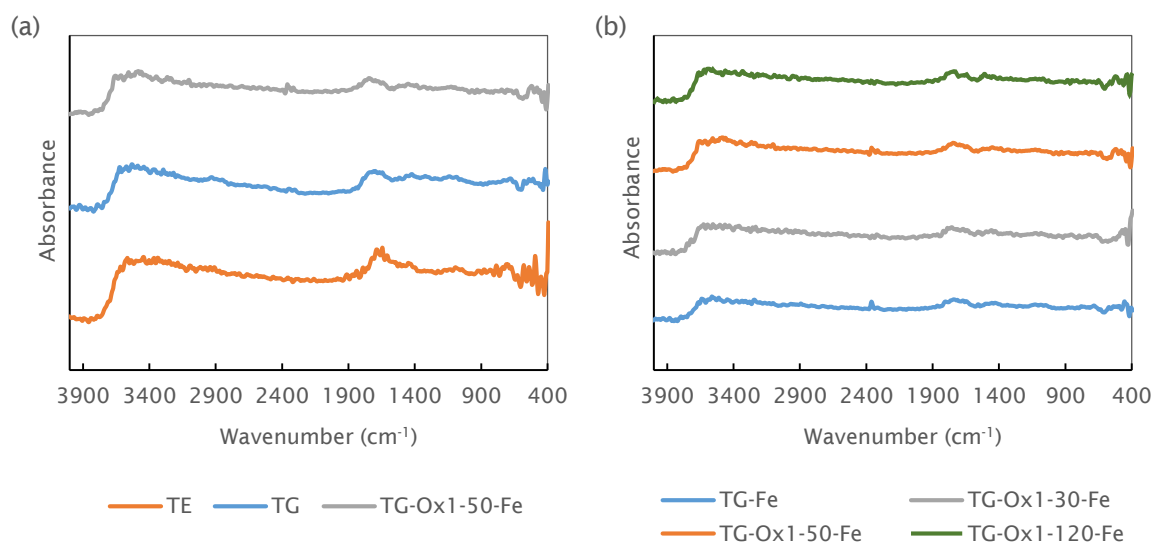

Fig. 13. FTIR spectra: (a) comparison between the tannin extract, tannin gel and iron-loaded tannin gel; (b) comparison between different, in terms of oxidation, iron-loaded tannin gels.

4.3. Adsorption assays

4.3.1. Effect of pH

In order to evaluate the influence of pH on adsorption, the adsorbent was added to arsenic solutions with different pH. Furthermore, adsorbents with different iron contents were also used in order to infer the effect of iron on the arsenic uptake by the tannin gels. The results were presented as adsorbed amounts (q, mg g^{-1}) which are determined by the following mass balance equation (Eq. 1):

$$q = \left(C_{in} - C_{eq}\right) \times \frac{V}{w} \quad (1)$$

where C_{in} (mg L^{-1}) is the initial arsenic concentration, C_{eq} (mg L^{-1}) is the equilibrium arsenic concentration in bulk solution, V (L) is the volume of solution, and w (g) is the adsorbent mass. q allows to determine the adsorbent removal efficiency: the higher q, the more efficient the adsorbent is. Moreover, the lixiviated iron was also analysed to consider secondary pollution. For that, it was determined the total iron concentration dissolved in solution.

Three adsorbents were added to arsenic solutions, TG-Ox2-40-Fe, TG-Ox2-60-Fe and TG-Ox1-50-Fe, that presented iron contents of 6, 13 and 24 mg per g of adsorbent, respectively. The results obtained are presented in Fig. 14. The TG-Ox2-40-Fe adsorbent was the first to be produced; its very low iron content suggested an also very low efficiency to uptake arsenic. The assay was executed under four different pH: 2, 3.5, 5 and 7. At higher pH, the results obtained were negligible, meaning that the adsorbent was not able to uptake arsenic. The best results were achieved under pH 2, for both arsenic species, where q was measurable but still modest: 0.4 and 0.25 mg g^{-1} for As(III) and As(V), respectively (Fig. 14a).

With the optimization of the preparation of the adsorbent, tannin gels with a higher iron content were obtained, TG-Ox2-60-Fe and TG-Ox1-50-Fe. These two adsorbents were added to arsenic solutions at pH 2, 3.5 and 4.5. Both TG-Ox2-60-Fe and TG-Ox1-50-Fe achieved their maximum adsorbed amount at pH 3.5 (close to the pH$_{PZC}$) for the pentavalent arsenic, which was 1.3 and 1.8 mg g^{-1}, respectively. The trivalent form of arsenic was better removed at pH 3.5 by TG-Ox2-60-Fe (q=0.71 mg g^{-1}) and at pH 4.5 by TG-Ox1-50-Fe (q = 1.7 mg g^{-1}).

Such results indicate an optimal pH for adsorption between 3.5 and 4.5, being required further studies to determine that value. Additionally, it is clear that there is an overall increase in adsorption capacity with the increase of the iron content
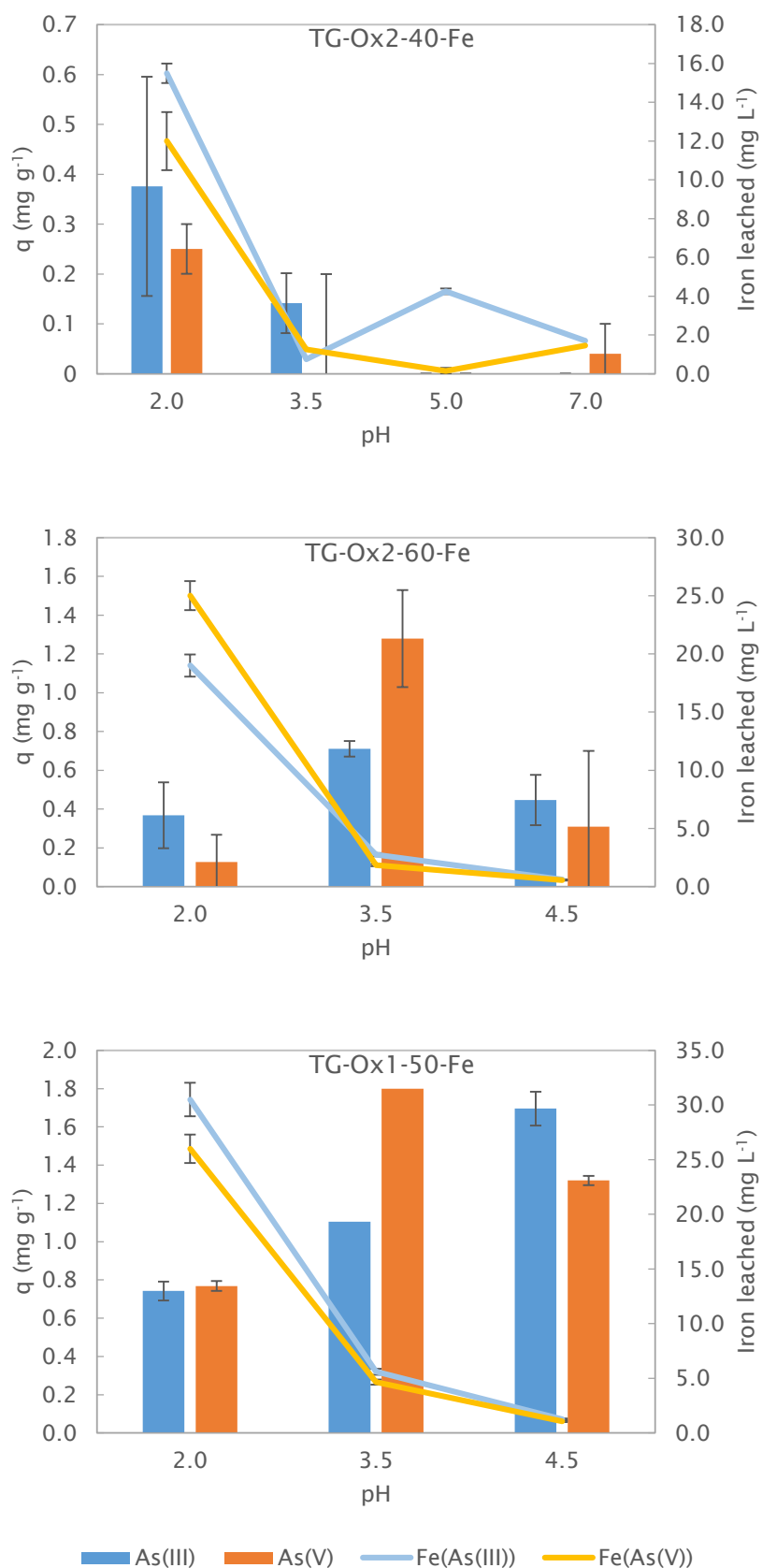
Fig. 14. The effect of pH on the amount of As adsorbed by different tannin-based adsorbents and on the iron leached to the solution: C_{in} = 10 mg L^{-1}; adsorbent dosage = 5 g L^{-1}; T = 20 °C; contact time = 24 h.

of the tannin gel, suggesting that an efficiently iron-loaded tannin gel can indeed remove arsenic from aqueous solutions through adsorption. Considering the impossibility to establish electrostatic interactions between As(III) and As(V) species and the iron-loaded adsorbents (explained in subchapter 4.2.3), the present results suggest that the iron provides sites for specific As adsorption. As(V) has been reported to adsorb onto iron sites by the formation of surface complexes and As(III) to the same mechanism, by previous oxidation to the pentavalent form [114, 115].

Vieira prepared an iron-loaded seaweed (using the brown alga *S. muticum*) and evaluated it on the uptake of arsenic from aqueous solutions [114]. The researcher reported several evidences of the occurrence of As(III) oxidation to As(V) simultaneously to Fe(III) reduction to Fe(II). In that work, it was achieved slightly higher adsorbed amounts, around 2 mg g^{-1} of As(V) for pH values between 2 and 7 and almost 2 mg g^{-1} of As(III) at pH 7. However, it is important to note that on the assays where it was obtained those adsorption capacities the initial arsenic concentration was 2.5 fold higher that the one used here. Moreover, the algae had an iron content of about 50 mg g^{-1}, twice as much to what was achieved here with the tannin gel. If the presence of iron does indeed enhance the ability of an adsorbent to uptake arsenic, the better results achieved with the algae can be justified by that.

In terms of leached iron, all three adsorbents tested promoted a similar behaviour with the increase of pH. As expected, for all three tannin gels, it was verified the highest leached iron at pH 2 (12-30 mg L^{-1}) and generally decreasing with the increase of pH. That is one reason why the adsorption tests were performed in acidic range. Iron(III) in solution easily precipitates as hydroxide (solubility product for $Fe(OH)_3$, Kps, is very low). So, it is expected that high pH values produce falsified adsorption results due to As adsorption on $Fe(OH)_3$ particles instead of on the tannin adsorbent. However, the presence of the characteristic, and easily visible, Fe(OH)3 redish fine particles, was not observed in any of the pH conditions evaluated, which indicate no (or insignificant) precipitation. If all the dissolved

iron measured corresponded to Fe^{3+}, theoretical calculations, based on Kps, indicate precipitation for pH values higher than 3.5. This calculation does not account with other iron forms (Fe^{2+} and complexed iron species), which decrease the possibility of iron hydroxide precipitation.

The same behaviour was also observed in another work [114]. For TG-Ox1-50-Fe, at pH 3.5 (optimum for As(III) uptake) the dissolved iron was limited to 5 mg L^{-1} and

at pH 4.5 (optimum for As(V)), it was 1 mg L^{-1}. These values, obtained under the optimum conditions for adsorption, are much more acceptable than the obtained at strong acidic conditions. On the other hand, as expected the use of an adsorbent with higher iron content causes a higher amount of iron lixiviated. However, between the assays with TG-Ox2-60-Fe and TG-Ox1-50-Fe, and although the iron content is twofold higher, the amount of iron lixiviated was only slightly higher, suggesting also a better stability of the selected adsorbent. This represents an advantage for TG-Ox1-50-Fe because while the adsorption capacity of arsenic was significantly increased with the increase of iron content of the adsorbent, the leaching of iron did not significantly increase. Nevertheless, depending on the pH conditions, the final concentrations of iron in the water can be still too high to be safe. In fact, the Decree-Law 236/98 of Portugal states that the maximum iron concentration for water discharged is 2 mg L^{-1}. Though, in the end, that may not be a problem; since arsenic-contaminated waters generally present an acid pH, they will have to be alkalinized before discharge in order to also respect safety directives. One consequence of such procedure is the precipitation of iron that can be easily removed before discharge, automatically eliminating, therefore, the source of secondary pollution.

In almost every set of conditions studied, it was in the trivalent arsenic solutions that a higher amount of iron leached was observed. Such observation corroborates the recently proposed [114] adsorption mechanism for As(III), which states that oxidation of arsenic into As(V) occurs prior to adsorption. Thus, the reduction of Fe(III) into Fe(II) is promoted, causing a higher leaching of iron. However, in the present study, the adsorbed amount of As(V) was not always greater than the obtained for As(III), which may indicate that As(III) can also be directly adsorbed by the iron-loaded TBA. To conclude, the present results do not show the same evidences reported by Vieira [114]. To have greater certainty about the adsorption mechanisms, further work should be conducted. Voltammetric measurements and X-ray absorption spectroscopy can be used in the future to assess the oxidation state of As present in the liquid phase and adsorbed onto the solid surface, respectively.

The results obtained and also the ease to control the pH during the experiment were used as criterions to choose 3.5 as the pH for the kinetic and equilibrium assays, which were performed with the TG-Ox1-50-Fe for both As(III) and As(V).

4.3.2. Adsorption kinetics

The adsorption kinetics assay for both the trivalent and pentavalent species of arsenic were performed using 10 mg L^{-1} as the initial concentration and 10 g L^{-1} as adsorbent dosage (TG-Ox1-50-Fe). Kinetic models of pseudo-first and second-order were fitted to the experimental data using the software *CurveExpert 1.4*. The kinetic parameters were determined by non-linear adjustment of the experimental data.

The kinetic model of pseudo first order [116] has been used to describe the adsorption of pollutants of effluents. The application of this model implies the assumption that the adsorption only occurs in one active site of the adsorbent surface and its sites have the same affinity towards the ion. Equation (2) describes the adsorption phenomena through a pseudo first order model:

$$q_t = q_{eq}(1 - e^{-k_1 t}) \quad (2)$$

where q_t is the amount of arsenic adsorbed at t minutes per mass of adsorbent (mg g^{-1}), q_{eq} is the amount of arsenic adsorbed at equilibrium per mass of adsorbent (mg g^{-1}), k_1 is the pseudo first order kinetic constant (min^{-1}) and t is time (min).

The kinetic model of pseudo second order [117] has been applied to adsorption studies of metallic ions, dyes and other chemical substances. The basis of this model is the assumption that the adsorption occurs in two active sites of the adsorbent surface and its sites have the same affinity towards the adsorbate. Equation (3) expresses the pseudo second order kinetic model:

$$q_t = \frac{k_2 q_{eq}^2 t}{1 + k_2 q_{eq} t} \quad (3)$$

where q_t is the amount of arsenic adsorbed at t minutes per mass of adsorbent (mg g^{-1}), q_{eq} is the amount of arsenic adsorbed at equilibrium per mass of adsorbent (mg g^{-1}) and k_2 is the pseudo second order kinetic constant (g mg^{-1} min^{-1}).

The variation of the normalized concentration (C/C$_{in}$) through time is presented in Fig. 15 for both As(III) and As(V). A clear observation for both arsenic species is the somewhat stagnation after the two hours mark, achieving similar final values with a slightly better performance for arsenate uptake. In these experimental conditions, two hours can then be defined as the contact time necessary to reach adsorption equilibrium. Additionally, it is also clear that As(V) is adsorbed faster that As(III). In fact, the concentration of As(V) is halved after 30 minutes of contact

with the adsorbent, while that only happens with As(III) after 60 minutes. Finally, in four hours the adsorbent was able to remove 85% of As(V) while it removed 80% of As(III).
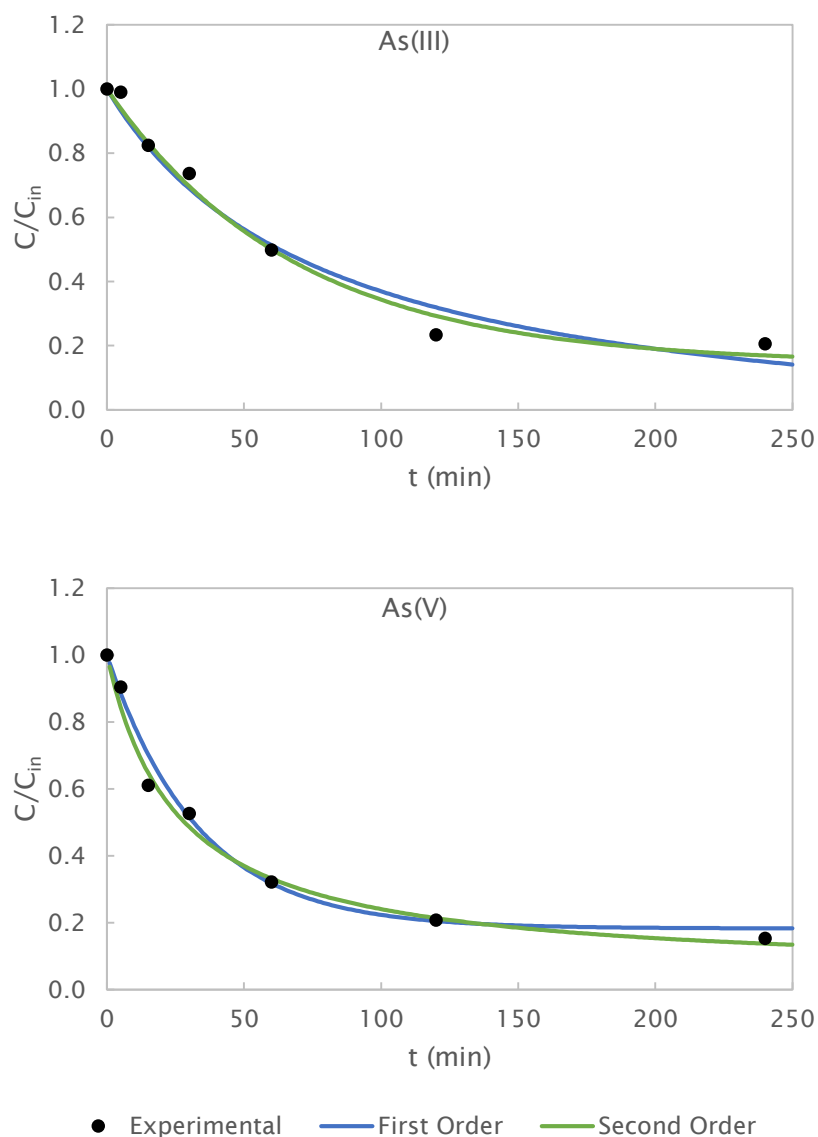
Fig. 15. Kinetic assay results. Variation of the normalized concentration of arsenic (C/C_{in}) throughout time. $C_{in} = 10$ mg L^{-1}; adsorbent dosage = 10 g L^{-1}; T = 20 °C.

The kinetic parameters determined here are presented in Table 10. As it can be seen, both models adjust very well the experimental data for As(III) and As(V) since the coefficient of determination (R^2) is very high (0.98 or higher). From the standard error (SE) values, it is possible to conclude which is the kinetic model that better applies to the experimental data: lower error means better adjustment (better

accuracy in the model prediction). It happens to be that for arsenite the pseudo first order model is the optimal, with a lower SE and lower uncertainty in the model parameters; it should be noticed that the kinetic constant for pseudo-second order presented a high uncertainty, which make its value statistically not significant. In the case of arsenate, pseudo second order model described better its adsorption kinetics. It is also possible to conclude that the adsorption of As(V) occurs much faster than that of As(III) since the associated kinetic constant is much greater. This difference indicates a possible extra step in the As(III) adsorption, such as it oxidation into As(V) as previously discussed.

Table 10. Kinetic parameters for the pseudo first and second order kinetic models for As(III) and As(V) adsorption by TG-Ox1-50-Fe (values ± confidence interval for 95%).

	Pseudo first order			
	q_{eq} (mg g^{-1})	$k_1 \times 10^2$ (min^{-1})	R^2	SE
As(III)	0.8 ± 0.1	1.5 ± 0.5	0.99	4.1×10^{-2}
As(V)	0.83 ± 0.08	3.0 ± 1.0	0.99	4.4×10^{-2}
	Pseudo second order			
	q_{eq} (mg g^{-1})	$k_2 \times 10^2$ (g mg^{-1} min^{-1})	R^2	SE
As(III)	1.1 ± 0.3	1.0 ± 1.0	0.98	5.5×10^{-2}
As(V)	1.0 ± 0.1	4.0 ± 2.0	0.99	3.8×10^{-2}

4.3.3. Adsorption equilibrium

In order to determine the maximum adsorption capacity of As(III) and As(V) by the adsorbent here studied and define the equilibrium relation between As in the liquid and solid phases, equilibrium assays were performed. Langmuir and Freundlich models were adjusted to the experimental values (q_{eq} as a function of C_{eq}) using the software *CurveExpert 1.4*. The isotherm parameters were determined by non-linear adjustment of the experimental data.

The Langmuir model [118] is based on the principle of the existence of free sites where biosorption of the ion occurs and it is a model that was developed for monolayer adsorption. In this model, each active site can only accommodate one adsorbate entity, being connected in fixed sites. Of note, the adsorption is energetically equal in all active sites and does not depend on the presence of

adsorbed species in the vicinity. The Langmuir model is described by the following expression (Eq. 4):

$$q_{eq} = \frac{K_L Q_m C_{eq}}{1 + K_L C_{eq}} \quad (4)$$

where Q_m is the maximum adsorption capacity (mg g^{-1}), q_{eq} is the amount of arsenic adsorbed at equilibrium per mass of adsorbent (mg g^{-1}), C_{eq} is the concentration of arsenic in equilibrium (mg L^{-1}) and K_L is the Langmuir equilibrium constant (mg L^{-1}).

The Freundlich model [119] is empiric and it is based on the occurrence of heterogeneous adsorption along the surface with different active sites. This model is ruled by the following equation (Eq. 5):

$$q_{eq} = K_F C_{eq}^{\frac{1}{n}} \quad (5)$$

where q_{eq} is the amount of arsenic adsorbed at equilibrium per mass of adsorbent (mg g^{-1}), C_{eq} is the concentration of arsenic in equilibrium (mg L^{-1}), K_F is the Freundlich equilibrium constant (mg L^{-1}) and n is the adsorption intensity identification constant (if n>1 the isotherm if favourable, if n≤1 the isotherm is unfavourable).

The results of the equilibrium assays are presented in Fig. 16 and the isotherm parameters are listed in Table 9.

Table 11. Equilibrium model parameters for As(III) and As(V) adsorption by TG-Ox1-50-Fe (values ± confidence interval for 95%).

	Langmuir			
	Q_m (mg g^{-1})	$K_L \times 10^1$ (mg L^{-1})	R^2	SE
As(III)	1.92 ± 0.09	3.2 ± 0.5	0.99	2.6×10^{-2}
As(V)	2.3 ± 0.2	4.0 ± 0.1	0.99	5.7×10^{-2}
	Freundlich			
	$K_F \times 10^1$ (mg$^{(n-1)/n}$ L$^{1/n}$ g^{-1})	n	R^2	SE
As(III)	5.0 ± 2.0	2.3 ± 0.9	0.96	1.6×10^{-1}
As(V)	6.0 ± 3.0	2.4 ± 1.2	0.94	2.2×10^{-1}

The maximum adsorbed amount of As(III) was found to be 1.7 ± 0.2 mg g^{-1} at an equilibrium concentration of 25.35 mg L^{-1}. On the other hand, the maximum adsorption capacity for As(V) was a bit higher: 2.0 ± 0.3 mg g^{-1} at an equilibrium concentration of 21.4 mg L^{-1}. In the conditions studied, the removal percentages ranged from 40 to 83 % and from 49 to 90 % for As(III) and As(V), respectively. These values indicate very significant perspectives for use iron-loaded TBAs on the uptake of As from contaminated waters.
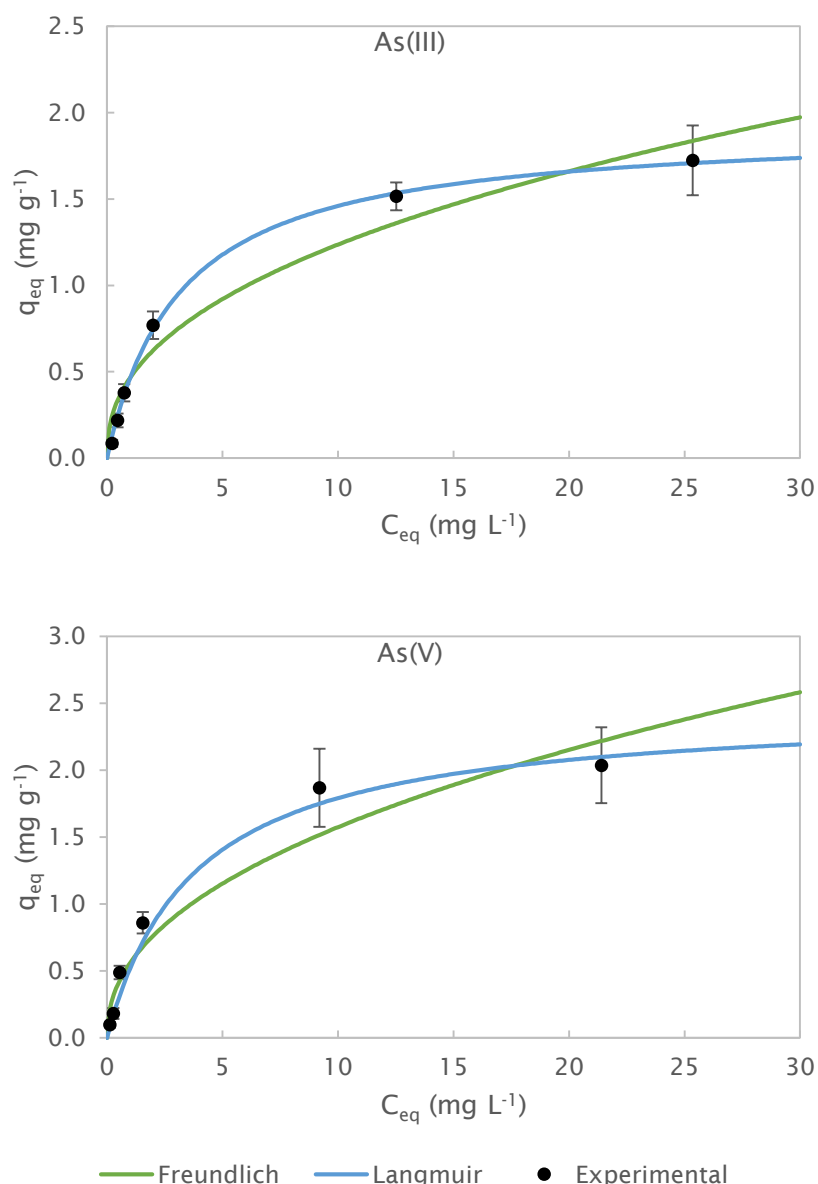

Fig. 16. Equilibrium assay results. Variation of adsorption capacity (q$_{eq}$) as a function of the concentration of arsenic (C$_{eq}$) for different initial concentrations. Adsorbent dosage = 10 g L^{-1}; T = 20 ºC; contact time = 24 h.

The experimental data was adjusted to the Freundlich model with low R^2 values, suggesting that the adjustment was poor. Moreover, the SE is about 5 times higher for the Freundlich model than for the Langmuir one. Thus, the Langmuir model better adjusts the experimental data for both As(III) and As(V). The Langmuir constant is somewhat greater for the As(V) than for As(III), hinting at the bigger affinity of the adsorbent towards arsenate.

The maximum adsorbed amounts obtained experimentally are lower than those presented by the Langmuir model for both As(III) and As(V). This suggests that the monolayer coverage of the adsorbent surface was not attained for the concentration range used. To achieve (or to confirm) experimentally the values of maximum adsorption capacities given by the Langmuir model it would be necessary to extend the equilibrium assays for higher initial concentrations of arsenic. In the present work, it was decided to not do that, since there would be no practical interest to assess the removal of arsenic above the concentrations here used. In real circumstances, arsenic concentrations can reach 12 mg L^{-1} [27]. The use of As solutions with concentrations much higher than 40 mg L^{-1}, would be completely out of the typical values that are found in real contaminated waters.

The Langmuir model indicated Q_m values of 1.92 ± 0.09 and 2.3 ± 0.2 mg g^{-1} for As(III) and As(V), respectively. The values for maximum adsorption capacity here obtained fit somewhat reasonably with those reported in the literature (summarized in Table 12). Q_m values are dependent on the experimental conditions used (temperature, pH and initial adsorbate concentration). Taking into account the influence of the initial concentrations on Q_m and the variability found in the C_{in} values used by different researchers (from few µg L^{-1} to 600 mg L^{-1} levels), it is necessary to do these comparisons carefully. It is expected to achieve greater values the higher are the initial concentrations. Thus, it can be said that the iron-loaded tannin gel TG-Ox1-50-Fe presents considerable Q_m values.

In Fig. 17, the values for iron leaching found in the equilibrium assays are plotted against the initial As concentrations. Once more, it is observed a greater leaching in the As(III) samples than in the As(V) samples. It is another hint to the proposed adsorption mechanism based on the oxidation of arsenite into arsenate prior adsorption, causing the reduction of iron and, in turn, promoting its leaching. Additionally, considering that the equilibrium assays were done at the same pH and adsorbent dosage (the two variables that usually govern the degree of metals leaching from a solid sample), it would be expected that the dissolved iron concen-

Table 12. Maximum adsorption capacities (Q_m) reported in the literature for arsenic removal from aqueous solutions.

| Adsorbent	Range of C_{in} (mg L^{-1})	Oxidation state	pH	Q_m (mg g^{-1})	Ref.
Cod fish scales	0-0.3	As(III)	7	0.027	[120]
	0-0.2	As(V)		0.025	
Activated alumina (AA)	0-1	As(III)	7.6	0.18	[121]
Chitosan	0.025-2	As(V)	5.6-6.2	0.730	[122]
Iron oxide impregnated AA	1.4	As(III)	12	0.73	[123]
Iron chitosan granules	1-10	As(III)	7	2.32	[124]
		As(V)		2.24	
Activated carbon (GAC)	0.10-30	As(V)	4.7	0.038	[125]
GAC-Fe	0.10-30	As(V)	4.7	2.96	
Iron-coated *S. muticum* algae	1-40	As(III)	7	4.19	[114]
		As(V)		7.30	
S. Xylosus using Fe(III)-treated biomass	10-300	As(III)	7	54.35	[126]
		As(V)	3	61.34	
Green algae (*Maugeotia genuflexa*)	10-400	As(III)	6	57.5	[127]
Lessonia nigrescens algae	50-600	As(V)	2.5	45.2	[128]
Iron-loaded tannin gel	1-40	As(III)	3.5	1.92	This work
		As(V)		2.31	
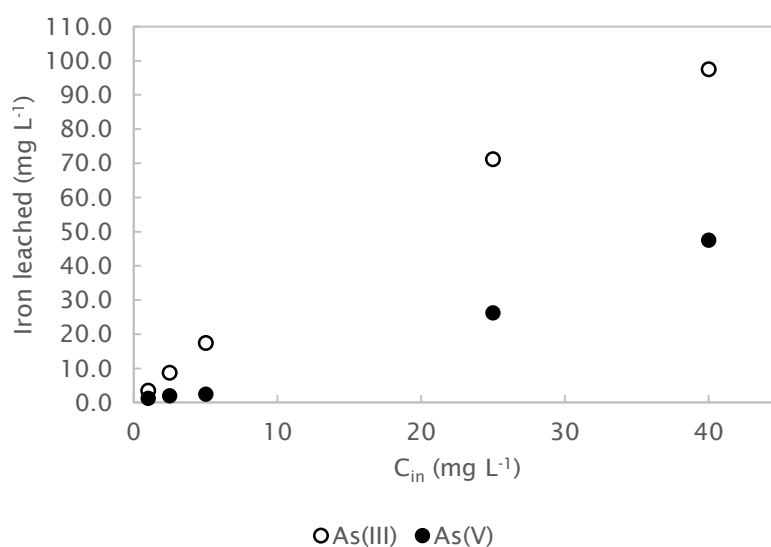
Fig. 17. Iron leaching in the equilibrium assay.

tration did not present significant variations from different initial As concentrations. As can be seen from Fig. 17, the iron leached from the TG-Ox1-50-Fe showed to be strongly dependent on C_{in} which suggest that some kind of interaction takes place between these two elements.

5. Concluding remarks

In this work, the ability of an iron-loaded tannin gel to uptake arsenic from aqueous solutions was assessed. The iron-loading modification was intended to enhance the affinity of the adsorbent towards arsenic, thus maximizing the iron content of the adsorbent was a goal. It was concluded that an oxidation step prior treatment with iron is of great importance to the optimization of the preparation of the adsorbent. Indeed, it was observed that not enough or too much oxidation negatively influences the impregnation of iron on the adsorbent. The optimal conditions for the oxidation step were found to be 60 ºC, 1 mol L^{-1} of HNO_3 and 50 min of contact time. Under these conditions, it was produced an Fe-loaded tannin gel adsorbent (TG-Ox1-50-Fe) with an iron content of 24.4 ± 0.9 mg g^{-1}.

Using the adsorbent TG-Ox1-50-Fe, slightly acidic conditions showed to favour the adsorption of As(III) and As(V), with optimum pH of 3.5 (for arsenite) and 4.5 (for arsenate). Since the pH_{PZC} was found to be 2.93 ± 0.02, such behaviour along the pH indicates that the adsorption must be happening mostly through chemical interaction with iron and not through electrostatic attraction. Of note, the adsorbent seems to have affinity towards both oxidation states of arsenic, making it advantageous for real scenario applications. This is true because some arsenic-contaminated waters, like those leached by mines, contain both species of arsenic.

Furthermore, adsorption isotherm of arsenic on the adsorbent followed the Langmuir equation for As(III) and As(V). Adsorption of arsenite had a maximum predicted capacity of 1.92 mg g^{-1} while adsorption of arsenate presented a maximum capacity of 2.3 mg g^{-1} (20 ºC, pH 3.5). For both As oxidation states, the adsorption equilibrium was reached in two hours, although the pentavalent form is adsorbed significantly faster in the first hour. In almost every case, samples of As(III) promoted more iron leaching than its As(V) counterpart. The evidences found in the present work are in general agreement with an adsorption mechanism proposed in literature for other iron-based adsorbents (stating that oxidation of As(III) into As(V) occurs prior to adsorption). However, future work need to be done to prove the occurrence of As(III) conversion to As(V) and Fe(III) to Fe(II).

6. Suggestions for future works

The adsorbent here produced and evaluated displayed potential for applications involving the removal of arsenic from aqueous solutions. However, the synthesis of this biomaterial can and must be subjected to further optimization. The iron content should be maximized through a detailed optimization of the oxidation step.

The iron-loading step should also be studied, considering the contact time, tannin gel dosage, pH and iron $FeCl_3$ concentration. Therefore, it is expected that better adsorption results could be achieved. Beyond that, another suggestion for future work is to study the adsorbent performance for different initial concentrations of arsenic (levels of µg L^{-1}, commonly found in groundwater samples from regions of abandoned mines). The same applies to the kinetic and equilibrium assays, where in order to obtain more reliable data, different adsorbent dosages, initial arsenic concentrations and pH values should also be studied.

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