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Use of cork byproducts in the removal of arsenic from water and wastewater

Master Thesis

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Abstract

The cork oak is one of the most common trees in the Mediterranean landscape and the Portuguese cork industry represents 50% of the worldwide production. From the manufacturing of raw cork products, there is a great part that is converted into byproducts. The most part of byproducts consist of cork granules which can be used for other purposes.

As cork granules are byproducts, they may be used for pollutant removal from water and wastewater with lower cost. There are already some applications of cork in this field for the removal of organic pollutants and heavy metals but there are none for arsenic removal.

Arsenic in drinking water is one of the most serious environmental health problems in history and affects about 100 million people. The regions of south and east of Asia are the most overwhelmed by arsenic toxicity. There are also regions in Portugal like the abandoned mining area of Segura, near Castelo Branco and the area of the heap of Cabeço do Pião, in Fundão that are affected by this problem.

The existent treatment solutions still present many disadvantages. In general, they are too expensive and need trained personnel for their maintenance and operation. Adsorption using cork granules is proposed in the present work as a solution to minimize these concerns.

Laboratorial tests were performed to evaluate the As sorption capacity of cork. Firstly, cork characterization assays were done, such as FTIR analysis and determination of the pH zero point charge (pH_{zpc}). FTIR results showed that there are no significant differences between the cork samples analyzed, with and without treatment with hexadecyltrimethylammonium bromide (HDTMA-Br) or after sorption of As. The pH_{zpc} was determined as 5.2 for white cork (WC) and 8.0 for treated white cork (TWC).

Then, As(V) sorption tests were made in order to evaluate different conditions, such as type of cork (black and white), pH (1.5 – 10), granulometry (0.2 – 0.3, 0.8 – 1.0 mm for white cork and 1 – 2 mm for black cork), pretreatment with HDTMA-Br (5 and 50 g/L). The best adsorption results were reached at pH 3 for WC, pH 5 – 8 for TWC 5 g/L and pH 7 for TWC 50 g/L. In general, for smaller granulometry, the adsorption capacity increases.

Kinetics and equilibrium isotherms were studied at pH 6. Pseudo 1st and 2nd order models were fitted to kinetics experimental results and the best adjustment (higher R^2) was obtained using a 1st order model for TWC. Equilibrium time was considered to be 8 h and the equilibrium adsorption capacities obtained were 113 ± 24 μg/g for WC and 140 ± 14 μg/g for TWC. Langmuir and Freundlich models were fitted to the experimental data of equilibrium studies. In this case the best adjustment (higher R^2) was obtained using the Langmuir model for both WC and TWC

and maximum adsorption capacities of 123 ± 87 μg/g and 212 ± 49 μg/g were obtained, respectively.

As(III) was briefly studied and the adsorption capacities were similar to those of As(V) for WC at pH 3.4 and 5.2, while for TWC the As(V) adsorption capacity was always better than that for As(III).

Finally, toxicity assays using Microtox® were done. Samples after adsorption with TWC have shown higher toxicity than the initial solution of As, pointing to a toxicity increase when the surfactant is used as a cork pretreatment.

Summing up, cork showed low adsorption capacities for As. Even though the pretreatment increased As removal capacity, the treated solutions exhibited toxicity, which means that cork treated with HDTMA-Br is not recommended for the treatment of drinking water.

Keywords: cork granulates, arsenic removal, adsorption, HDTMA-Br, water.

Sumário

O sobreiro é uma das árvores mais comuns na paisagem mediterrânica, sendo que a indústria portuguesa representa cerca de 50% da produção mundial de cortiça. Do fabrico de produtos de cortiça, é gerada uma grande quantidade de subprodutos, que podem ser transformados em grânulos e usados para outros fins.

Sendo os granulados de cortiça subprodutos da indústria, o seu preço é mais baixo e portanto podem constituir uma alternativa para a remoção de poluentes das águas. Há já algumas aplicações da cortiça nesta área, tanto para poluentes orgânicos como para metais pesados, contudo a remoção de arsénio ainda não foi estudada.

O arsénio na água de consumo afigura-se como um dos problemas ambientais mais sérios da história e afeta cerca de 100 milhões de pessoas em todo o mundo. As regiões mais afetadas por este problema são o sul e o este da Ásia. Contudo existem algumas áreas de Portugal em que a presença de arsénio também se verifica. São exemplos, a área mineira de Segura, agora abandonada, perto de Castelo Branco ou a também área mineira de Cabeço do Pião, no Fundão.

As soluções de tratamento existentes até agora ainda apresentam muitas desvantagens. No geral, são caras e necessitam de pessoal preparado para a sua manutenção e operação. Assim sendo, a adsorção em cortiça foi considerada como hipótese, por minimizar estas preocupações.

Foram realizados testes laboratoriais com o intuito de avaliar a capacidade de adsorção de As por parte da cortiça. Em primeiro lugar, foram efetuados ensaios para a caracterização da cortiça. Foram eles análise com FTIR e determinação do pH no ponto de carga zero (pH_{zpc}). Os resultados do FTIR não evidenciaram diferenças entre as várias amostras de cortiça analisada: com e sem tratamento com HDTMA-Br e depois da adsorção com As(V). O pH_{zpc} obtido para a cortiça branca foi de 5.2, enquanto para a cortiça branca tratada foi de 8.0.

De seguida, foram feitos testes de adsorção com As(V) de forma a avaliar diferentes condições, como o tipo de cortiça (branca ou preta), o pH (1.5 – 10), a granulometria (0.2 – 0.3 e 0.8 – 1.0 mm para a cortiça branca e 1 – 2 mm para a cortiça preta) e o pré-tratamento com HDTMA-Br (5 e 50 g/L). Os melhores resultados foram obtidos para pH 3 no caso da cortiça branca, pH 5 – 8 para a cortiça branca tratada com 5 g/L e pH 7 para a cortiça branca tratada com 50 g/L. No geral, a capacidade de adsorção da cortiça aumentou para a granulometria mais baixa.

Foram estudadas a cinética e as isotérmicas de equilíbrio a pH 6. Modelos de pseudo 1ª e 2ª ordens foram ajustados aos resultados experimentais da cinética, sendo que o melhor ajuste (R^2 mais alto) obtido foi para o modelo de 1ª ordem no caso da cortiça branca tratada. O tempo de equilíbrio foi de 8 horas e as capacidades de adsorção de equilíbrio foram de 113 ± 24 µg/g para a cortiça branca e de 140 ± 14 µg/g para a cortiça branca tratada. No caso das isotérmicas de equilíbrio, os modelos de Langmuir e Freundlich foram ajustados aos dados experimentais. O melhor ajuste (R^2 mais elevado) foi para o modelo de Langmuir, tanto para a cortiça branca como para a cortiça branca tratada, e as capacidades máximas de adsorção foram de 123 ± 87 µg/g e 212 ± 49 µg/g, respetivamente.

O As(III) foi estudado brevemente, sendo que as capacidades de adsorção registadas foram semelhantes às obtidas para o As(V) para a cortiça branca pH 3.4 e 5.2. Para a cortiça branca tratada as capacidades de remoção de As(V) foram sempre superiores às de As(III).

Finalmente, foram realizados testes de toxicidade usando o Microtox®. Estes testes mostraram que, depois da adsorção com cortiça branca tratada, a solução apresentava maior toxicidade que a solução inicial, indiciando um aumento de toxicidade quando o surfactante é usado no pré-tratamento.

Assim, conclui-se que a cortiça apresentou baixas capacidades de remoção de arsénio. Apesar do pré-tratamento ter aumentado a capacidade de remoção de arsénio, estas soluções apresentaram toxicidade, o que significa que cortiça tratada com HDTMA-Br não é recomendada para a purificação de água de consumo.

Palavras-chave: granulados de cortiça, remoção de arsénio, adsorção, HDTMA-Br, água.

Contents

List of Figures

List of Tables

Abbreviations and symbols

Abbreviations

AAS – Atomic Absorption Spectroscopy

BC – Black Cork

DNA – Deoxyribonucleic Acid

FTIR – Fourier Transform Infrared Spectroscopy

HDTMA-Br – Hexadecyltrimethylammonium bromide

IS – Initial Solution

LOD – Limit Of Detection

LOQ – Limit Of Quantification

pH_{zpc} – Zero Point of Charge

TBC – Treated Black Cork

TOC – Total Organic Carbon

TWC – Treated White Cork

WC – White Cork

Symbols

C_a – Acid concentration (mol/L)

C_b – Base concentration (mol/L)

C_e – Equlibrium concentration (mg/L)

C_i – Initial concentration (mg/L)

K – Kinetic constant

k_F – Freundlich constant ($\mu g\ g^{-1}(\mu g.L^{-1})^{-1/n}$)

k_L – Langmuir constant (L/g)

n – Freundlich model parameter

q – Adsorptive capacity (µg/g or mg/g)

q_e – Equilibrium adsorption capacity (µg/g)

Q_{max} – Maximum adsoption capacity (µg/g or mg/g)

q_s – Superficial charge (mmol/g)

R^2 – coefficient of determination

T – Temperature (°C)

t – Time (h)

t_C – Contact time (h)

V – Volume (L or mL)

v – Rotation velocity (rpm)

V_a – Acid volume (mL)

V_b – Base volume (mL)

V_T – Total volume (mL)

%w/v – weight/volume (g/L)

Δq – Difference between natural and pretreated maximum adsorption capacity (mg/g)

1. Introduction

Cork forest is important not only because of the material humans obtain from it, but also because it brings contributions to the environment, acting in carbon dioxide fixing, helping with hydrology regulation, preventing desertification and preserving wildlife. This way, cork forests may help to reduce the impact of climate changes and protect biodiversity (Rives et al., 2012).

Cork by itself is a biomaterial that can act as a sorbent because it contains several functional groups that are able to interact with water contaminants in different ways, such as adsorption, chemisorption, complexation and ion exchange. For the removal of metal ions from waters, sorption has been found to be an effective method, due to its efficiency, simplicity, easy applicability, and cost-effectiveness. Cork industry generates wastes and byproducts that have been considered for pollutants removal from water (Dias et al., 2013; Pintor et al., 2012).

On the other hand, arsenic (As) occurs in water, from both natural and anthropogenic sources, in more than 70 countries, causing health problems to the population (Meliker et al., 2008).

In the last years, low-cost adsorbents have been widely studied for arsenic removal from water. These products are obtained from agricultural and industrial waste and byproducts, soils and its constituents, oxides, hydrotalcites and phosphates, among others. Biosorbents such as chitin and chitosan, cellulose sponge, plants, algae and even human hairs have also been used (Mohan et al., 2007a).

1.1. The Cork Industry

Cork used in industry is the outer bark from the species *Quercus suber* L. This tree has a thick bark that regenerates over time and, for that reason, it may be extracted several times from the same tree for human use, usually in intervals of 9 years (Anjos et al., 2014; Rives et al., 2012).

The cork oak forests have been very common in the Mediterranean area for thousands of years, with special incidence in the Iberian Peninsula, due to environmental and climate conditions. In fact, there are 2 227 700 ha of cork oak forest in the world and, from those, 61% are in the Iberian Peninsula. In Portugal, the oak forests represent more than 700 thousand ha and they are concentrated in Alentejo. The annual production of cork in Portugal is about 100 thousand tons, corresponding to 49.6% of the world's production (APCOR, 2014). This is a very

important sector in the Portuguese economy since the exports correspond to around 835 million euros and the net exports to 700 million euros in 2013. These data indicate that the majority of the produced cork in Portugal is for foreign consumption (APCOR, 2014; Lima, 2011; Rives et al., 2012).

The origin of cork may vary and it is divided in three different categories: the virgin cork, the second cork and the reproduction cork. The virgin cork is collected from trees aged between 25 and 30 years and it represents the first extraction. It shows a deformed structure with deep fractures. The second cork, as the name indicates, originates from the second extraction and, as the first one, presents deep fractures. The reproduction cork represents the following extractions in which the material has the best quality. For this reason, the price per kg of reproduction cork is five times higher than the other sources and as the extraction price is the same, this is the more commercialized type with 86.5% against 13.5% of the others. The virgin and the second cork usually go directly to cork granulate production (Rives et al., 2012).

1.2. Cork Granulates

Cork granulates are byproducts from the cork industry and their size varies from 0.25 to 8 mm. There are two types of cork granulates: the white and the black. The white cork granulate is submitted to a treatment or preparation in order to clean the raw material. The main process of this treatment is boiling in clean water, which allows the cleaning of cork, the removal of water-soluble substances and the improvement of cork flexibility and elasticity. This way, the material will satisfy the health requirements of the end product that will be probably used in the food or drink industry (Rives et al., 2012). The black cork granulate is a byproduct of black agglomerate production, which is carried out in a chamber at 380 °C with the injection of steam (Pintor et al., 2013).

To produce granulate, cork is subjected to a crush reception and then it is triturated or grinded until the cork is divided in pieces with the convenient size. Finally, the granulates are sorted by different specifications according to their use (Rives et al., 2012).

As it was mentioned before, cork granulates are created from product rejects and these can be formed in the preparation of the natural cork products, in their production or from their recycling. More than 70% of the raw material is converted into byproducts, so it is necessary to find useful applications for granulates in order to minimize the loss (Rives et al., 2012).

1.3. Cork Properties

Cork presents some unique properties that make its use very attractive, such as being a natural and renewable material, having very low permeability to both liquids and gases, being compressible and flexible and having a low cellular density, a very low thermal conductivity, energy-absorbing capacity, an apparent lack of chemical reactivity and high durability (Anjos et al., 2014; Rives et al., 2012).

In terms of its structure, cork has a honeycomb cellular structure, formed by hexagonal prismatic closed cells that are stacked orderly base by base without intercellular voids. This structure presents some macroscopic pores across the planks in a radial direction that are called lenticular channels. Cork cells have high flexibility given by wall undulation and corrugation (Anjos et al., 2014).

In Figure 1, it is possible to observe the honeycomb structure of cork through scanning electron micrographs of cork cells.

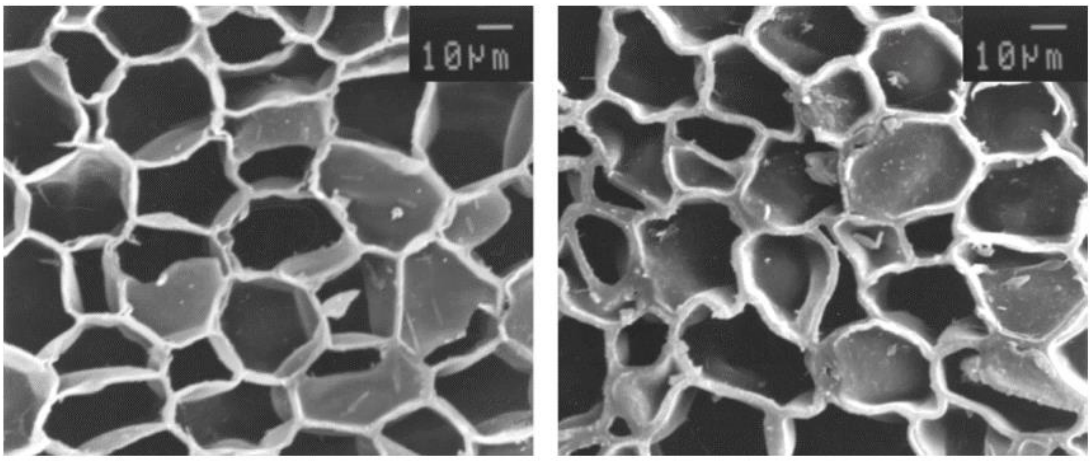

Figure 1 - Scanning electron micrographs of cork cells (tangential section).

Source: Anjos et al. (2014)

According to its geometry, cork has three distinct sections (axial, radial and tangential). Cork is generally organized under different classes depending on the proportion of lenticular channels (responsible for its macroporosity). The increase of lenticular channels corresponds to a lower cork quality (Lagorce-Tachon et al., 2015).

Cork is generally composed by suberin, around 40 – 45%, and lignin, around 20 – 25%, (both hydrophobic polymers); polysaccharides, around 12 – 20%, (cellulose and hemicellulose, that are hydrophilic) and waxes, tannins and other extractives. Although different authors report different proportions of each compound, usually suberin is the most prevalent and the second

major constituent is either lignin or polysaccharides, depending on the origin of the tree and the cork age (Dias et al., 2013; Olivella et al., 2013; Pintor et al., 2012).

1.4. Applications of cork

Humans have been using cork for some centuries. The mechanical behavior of cork is an important feature for its choice in various applications (Rives et al., 2012).

The products are divided in two classes according to the way they are produced. The natural cork products are made from solid cork with minimum transformation of raw cork. On the other hand, granulate-agglomerate products can be manufactured by individual molding or by extrusion using glues, therefore consist of joined cork. The first ones are more profitable for the industry and natural cork stoppers are the most representative products of this type. When considering the granulate-agglomerate products, the raw material is granulate that is then used to manufacture the body of technical stoppers, pads, boards, floorings, insoles and insulated panels (Rives et al., 2012).

The Portuguese industry suffered a drop in cork sales and exports in the last years due to the economic crisis affecting Portugal as well as other western European countries, which are the biggest consumers of this product. For this reason there was a need for innovation and the companies started to create new products and to improve the existing ones, therefore searching for new markets. Examples of new designs include stoppers with sophisticated heads, new visual models of flooring, clothes, jewelry, furniture and even applications in the aerospace industry (APCOR, 2014; Lima, 2011).

Cork granules have also been commercialized in the last years as sorbents for oil spill management (Corticeira Amorim).

1.5. Arsenic chemistry

Arsenic (As) is the 33rd element of periodical table of elements and it occurs in the 3rd position of group 15. It is a metalloid due to its metallic and non-metallic properties. Arsenic has four oxidation states, As(V), As(III), As(0) and As(-III), and can be present in inorganic or organic forms. The inorganic ones, more commonly found in water, are arsenite (As(III)), predominant under reducing conditions, and arsenate (As(V)), predominant under oxidizing conditions. The rate of conversion to each other depends on the environmental parameters such as temperature, pH, presence of iron and exposure to light (Meliker et al., 2008; Sharma et al.,

2014). The speciation diagram in aqueous solution is shown in Figure 2. It presents the forms arsenic may assume in aqueous solution according to pH.

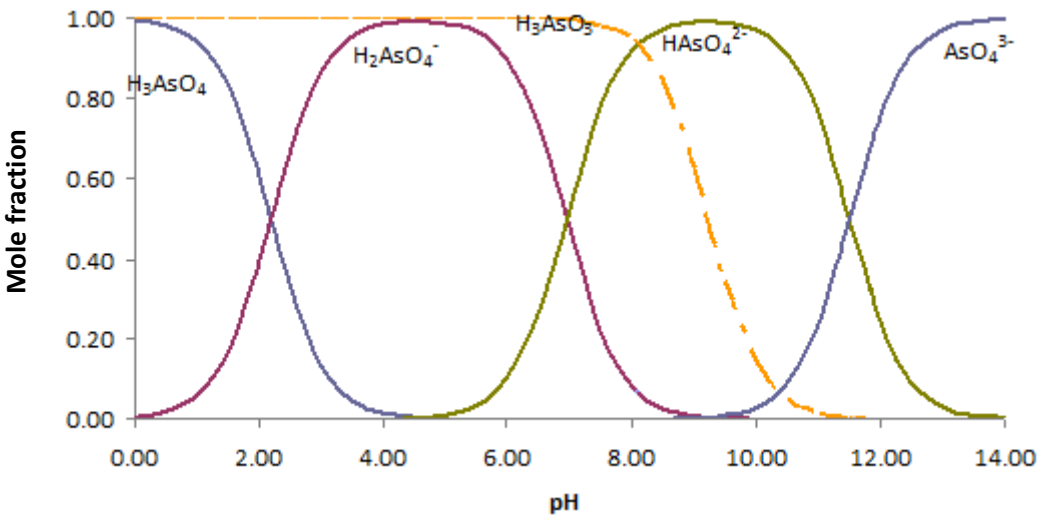

Figure 2 - Arsenic speciation diagram in aqueous solution.

Source: Ungureanu et al. (2015)

1.6. Arsenic Sources

Arsenic is the 20th most abundant element in earth's crust and it circulates and occurs in water due to both natural and anthropogenic sources. The natural sources can be mineral weathering, biologically aided mineralization, volcanic emissions and the anthropogenic ones count mining and mineral-processing activities (Antunes et al., 2013; Meliker et al., 2008; Sharma et al., 2014).

Arsenic has been used for centuries in diverse areas. Among its utilizations are pesticides and herbicides, wood preservatives, constituents of organic and inorganic pigments and feed additives, as well as medicinal uses. In the latest years its use has been phased out (Meliker et al., 2008).

1.7. Arsenic Problems

Worldwide, arsenic contamination was found in more than 70 countries and the regions more affected by the presence of this element in water are developing countries, located in South and East of Asia, more specifically, the Bengal delta and other parts of India, Nepal, Pakistan, Myanmar, Vietnam, Cambodia and China. These are poor regions, with high population

density, where contaminated water is used to drink, to cook and for irrigation of the fields, making this one of the most serious environmental health problems in history (Sharma et al., 2014). The distribution of the aquifers with high concentrations of arsenic around the world is presented in Figure 3.

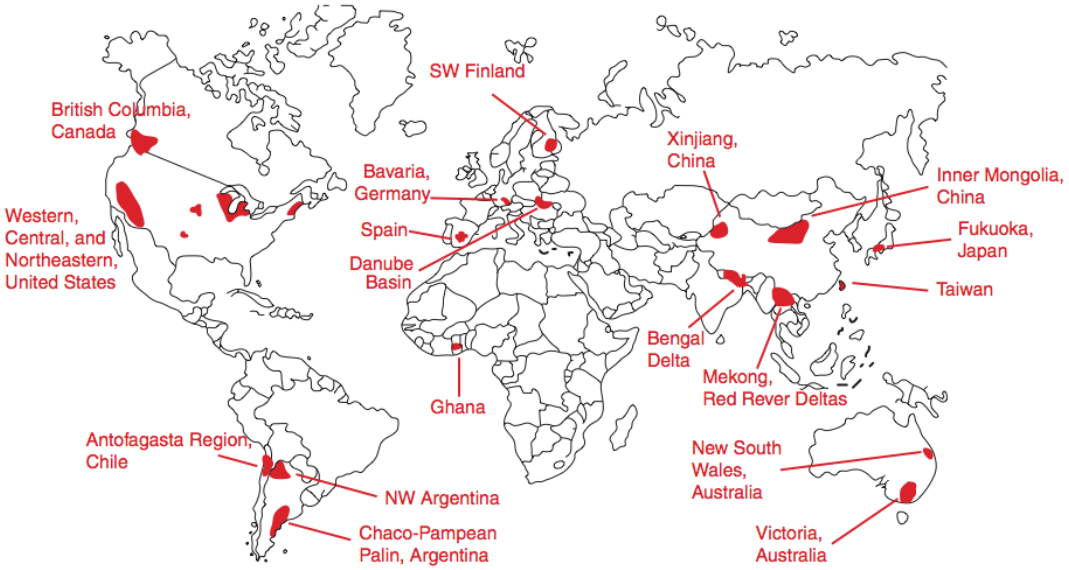

Figure 3 - Principal aquifers with high arsenic concentrations worldwide.

Source: Sharma et al. (2014)

In Portugal, at the abandoned mining area of Segura, near Castelo Branco, studies show that the probability of exceeding the arsenic background value is high, but it is even higher the probability of contamination of water that is commonly used in agriculture, the primary activity of the region (Antunes et al., 2013).

In 2010, a study was performed at some points of river Zêzere, next to heap of Cabeço do Pião, in Fundão, to evaluate the presence of metals in water. As shown in Figure 4, the arsenic levels in water are above the recommended limits on the winter months due to the higher rainfall levels that drag the contaminants to the river water (Gonçalves, 2011/12).

The human exposure to arsenic occurs essentially from ingestion of water or food cultivated with contaminated water, but there are other ways, such as inhalation or absorption trough dermal contact. Its presence is impossible for the consumer to detect since it has no taste, odor or color (Antunes et al., 2013).

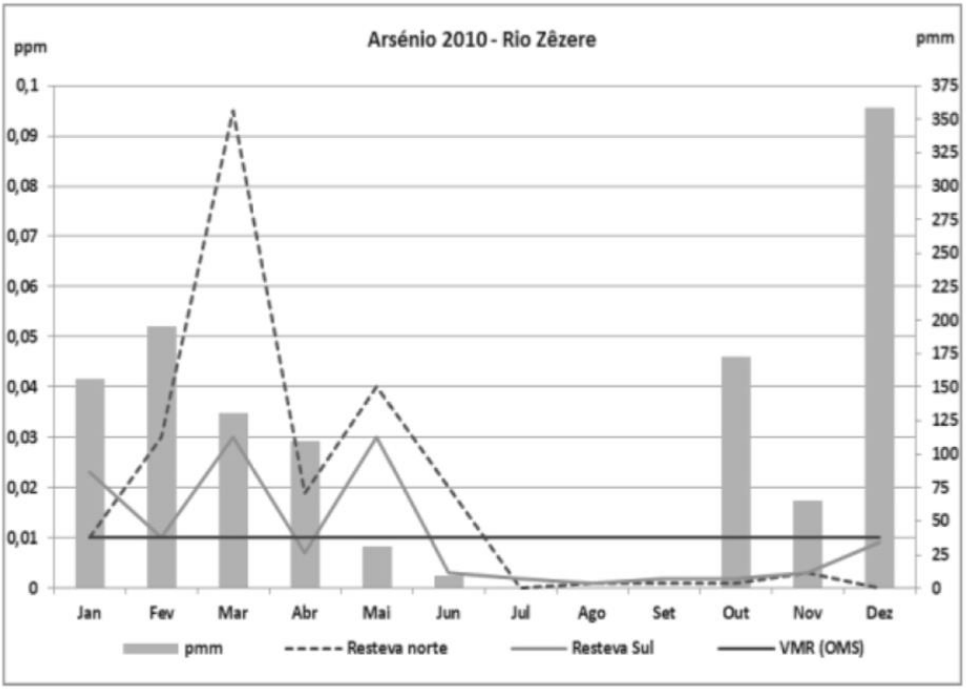

Figure 4 - Arsenic concentrations at river Zêzere in 2010.

Source: Gonçalves (2011/12)

With a long-term exposure (5 – 10 years) to arsenic, ingested in the inorganic forms soluble in water, it is fast and extensively absorbed (80 – 90%) and it can bind to bioactive molecules such as proteins or DNA, causing arsenicosis. This poisoning is disfiguring, disabling, and leads to potentially fatal diseases like skin and internal cancers, diseases of the blood vessels of the legs and feet, and possibly diabetes, high blood pressure and reproductive disorders (Meliker et al., 2008; Sharma et al., 2014).

When this pollutant is ingested in food, it is less harmful since it is capable to bind to thio-groups in peptides and proteins and for this reason is it less absorbed by the gastrointestinal tract than when it is in the water forms. After intake, arsenic is removed by excretion in urine but also by sweat, faeces, skin and hair. The biological half-life of this toxin is around 4 days (Sharma et al., 2014).

As the species present in major quantities in water are As(V) and As(III), these are the most important ones to human exposure. As(III) is the one that reacts more with tissue contents and which is more slowly excreted by the body, but As(V) also reduces to As(III). So, it is important to remove both forms from water, since once they enter human body, their reducing capacity is high and the metabolite distribution will be similar, regardless of which form entered the body (Sharma et al., 2014).

According to the Portuguese legislation and the World Health Organization, the maximum value of arsenic permitted in drinking water is 10 µg/L (Decreto-Lei nº 306/2007). In

1983, it was considered a Provisional Tolerable Weekly Value of 15 µg inorganic As/kg body weight, but then it was decided that this level was not appropriate, and a new international value was never defined (Sharma et al., 2014).

In Asia, arsenic concentration values of 4000 µg/L were found in well water and in Portugal values of 1190 µg/L and 636 µg/L were registered (Antunes et al., 2013). It is estimated that 100 million people are exposed to a concentration above the legal parameters (Sharma et al., 2014).

1.8. Project presentation

The objective of this work is to evaluate cork byproducts, obtained at low cost from cork industry, as As adsorbents in aqueous solution.

This is an innovative field since there are no records of cork having ever been studied for As removal (according to the author's knowledge). Due to this lack of previous results to predict cork behavior in presence of As, literature publications of As removal by other sorbents and cork as a sorbent to metals and other pollutants were considered as a basis for this work.

For this reason, some tests related to cork characterization, such as pH_{zpc} and FTIR analysis, were done. The sorption tests were performed under different conditions (pH, granulometry, type of cork) and a pretreatment with a surfactant was also analyzed. Kinetics and equilibrium isotherms were studied. Not only As(V) was tested but As(III) was also briefly evaluated in order to find out if its behavior was similar to As(V). Finally, toxicity assays were done to verify if the removal of As coincided with less harmful solutions to the organisms.

2. State of the art

2.1. The use of cork to remove water pollutants

When the aim is to remove pollutants from water or wastewater and it is necessary to choose a sorbent, several parameters must be taken in consideration, such as its thermal, chemical and mechanical stability and its capacity for fast sorption (Nurchi et al., 2014).

Cork has been widely used to remove heavy metals and there are also some studies about its capacity to remove organic compounds. In the next paragraphs, a state of the art of the existing applications of cork for pollutant removal from water will be presented.

Olivella et al. (2013) studied the capacity of cork to remove aromatic compounds, specifically phenanthrene. They used ten cork samples with different compositions and submitted them to sorption studies with the goal of establishing relationships between cork components and their sorption capacity for phenanthrene. They concluded that lignin is the main biopolymer responsible for the good sorption process. Contrarily, dichloromethane extractives block the interaction lignin-phenanthrene. Suberin, holocellulose, ethanol and water extractives do not influence the sorption of the pollutant by cork. It was also shown that the lignin-phenanthrene interaction is mostly hydrophobic in nature.

Krika et al. (2012) explored the use of cork biomass to remove cadmium, a toxic metal. In this study, the parameters selected, after testing their effect, were a pH of 6 and a diameter of particles of 0.08 mm. The temperature varied between 20 °C, 30 °C and 40 °C. The maximum adsorption capacity (Q_{max}) improved with the temperature increase, between 20 – 40 °C, from 9.65 to 14.77 mg/g.

Machado et al. (2002) examined the removal of chromium (III) by adsorption in cork powder. 6 ranges of particle size were used, from < 0.1 mm to > 0.9 mm. When it comes to temperature, the values of 22 °C, 30 °C and 40 °C were tested and the increase of this factor led to an improvement in pollutant removal of 8%. Two values of pH, 4 and 6, were tested. At lower pH, adsorption of the metal did not occur, only at pH 6 chromium was removed. The adsorption capacity increased from 3.43 to 3.86 mg/g as the temperature increased from 22 to 40 °C.

Other heavy metals such as copper and nickel were studied, at pH 7, 25 °C and with size particles of 0.42 - 0.84 mm by Villaescusa et al. (2002). The maximum adsorption capacities obtained were 2.64 mg/g for copper and 4.09 mg/g for nickel. The removal of lead by cork residues was also investigated by Mota et al. (2004), being the Q_{max} equal to 5.3 mg/g.

Fiol et al. (2003) and Sen et al. (2012) studied the removal of Cr(VI) from water using cork. In the first study for a contact time of 24 h, at 25 °C and pH 3.0, for a concentration range

of 10 – 1000 mg/L, the maximum adsorption capacity was 17.0 mg/g. In the later study, Q_{max} of 22.98 mg/g for black agglomerate and 21.69 mg/g for untreated *Q. cerris* cork were obtained. The ideal pH was 2.0 and 3.0, respectively.

The removal of antibiotics from water was analyzed by Crespo-Alonso et al. (2013). In this case the compound used was ofloxacin, the temperature was 25°C, and three different pH values (4, 7 and 9) and two sizes of cork (nominal diameter inferior to 0.42 mm and between 0.42 and 0.84 mm) were chosen to evaluate the best conditions. The best sorption capacity was found with the larger particles at pH 9 and it was 37.9 mg/g. Despite this, for the smaller granulometry, Q_{max} decreases from 31.3 to 24.9 mg/g as the pH increases.

Nurchi et al. (2014) investigated the application of raw cork as sorbent of chrysoidine, an azo-dye. The parameters under study were the pH (4 and 7), the initial concentration of the pollutant and the particle size (nominal diameter inferior to 0.42 mm and between 0.42 and 0.84 mm). It was concluded that the maximum sorption of 57.3 mg/g was achieved for smaller particle size at pH 7.

Pintor et al. (2012) reviewed the use of cork powder and granules to remove pollutants and in Appendix A.1 it is exhibited a summary table that consists in an adaptation of their studies updated with some of the values of saturation capacity for the different pollutants referred above, according to the Langmuir adsorption equilibrium model.

As previously stated and illustrated by bibliographic research, there are no studies available about As adsorption from a solution using cork. On the whole cork has been applied as an adsorbent for some cationic metals, presenting a substantial adsorption capacity.

2.2. Arsenic removal techniques

Nowadays, the preferred technologies for arsenic removal are coagulation, precipitation or coprecipitation, adsorption, ion exchange and membrane technologies such as reverse osmosis (Kwok et al., 2014).

Comparing As(III) to As(V), due to a low surface charge of the first one, As(V) is usually more easily removed (Kwok et al., 2014).

Several processes have been used for arsenic removal from water solutions as coagulation/flocculation followed by disinfection, ion exchange with strong-base chloride form resins, membrane filtration, oxidation, electrocoagulation or even a combination some of the referred methods. However, despite their good As removal down to values below maximum admissible concentrations, there are disadvantages to these methods, such as the use of

chemicals and formation of toxic sludge, the influence of competitive ions or the high costs of material and maintenance (Ungureanu et al., 2015).

In the following section, the state of the art for arsenic removal by adsorption will be discussed, focusing on low cost processes.

Shafique et al. (2012) used a biosorbent, pine leaves from *Pinus roxburghii*, to remove As (V) from water. The influence of some parameters was investigated in order to determine optimum conditions at 25 °C. The pH was studied from 1 to 10, finding the ideal value at 4. The contact time between sorbent and solution varied from 5 to 50 min and the agitation speed from 25 to 250 rpm, concluding that 35 min and 100 rpm were the right choices, respectively. The adsorbent dose was also studied using a range from 4 to 40 g/L. The adsorption efficiency generally decreased with the increase in adsorbent concentration, while the adsorption capacity increased. There was a need to balance the two factors and 20 g/L was selected as the best concentration of pine leaves.

Kumari et al. (2005) considered the use of *Moringa oleifera*'s seed to remove As(III) and As(V) from the aqueous system. The optimum conditions obtained by adsorption studies were 60 min of contact time, 10 g/L of plant seeds and a pH of 7.5 for As(III) and 2.5 for As(V).

Hansen et al. (2006) researched the use of the algae *Lessonia nigrescens* at 3 different pH values (2.5, 4.5 and 6.5) for the removal of As(V) from wastewaters. It was verified that adsorption worked better at lower pH.

Pehlivan et al. (2013) analyzed the capacity of sugarcane treated with hydrous ferric oxide in the removal of As(V). The ideal conditions were found to be pH 4, a contact time of 3 hours, temperature of 22°C and concentration of sorbent 0.25 g/50 mL solution.

The use of biomass from anaerobic sludge treatment to remove arsenic from contaminated water was studied by Chowdhury et al. (2011).

Some of the values of maximum adsorption capacity in arsenic removal, applying the Langmuir adsorption isotherm equilibrium model (Equation 6), according to the methods described above, are shown in Table 1.

Table 1 - Maximum adsorption capacity values for arsenic removal by different sorbents according to Langmuir adsorption isotherm equilibrium model.

Sorbent	Form of Arsenic	pH	Temperature (°C)	Arsenic concentration	Q_{max} (mg/g)	Source
Pine leaves	As(V)	4	25	n.s.	3.27	Shafique et al., 2012

Seed of *M. oleifera*	As(III)	7.5	n.s.	10 - 100 µg/L	0.00313	Kumari et al., 2005
Seed of *M. oleifera*	As(V)	2.5	n.s.	10 - 100 µg/L	0.00833	Kumari et al., 2005
L. nigrescens;	As(V)	2.5	25	50 - 600 mg/L	45.2	Hansen et al., 2006
L. nigrescens;	As(V)	4.5	25	50 - 600 mg/L	33.3	Hansen et al., 2006
L. nigrescens;	As(V)	6.5	25	50 - 600 mg/L	28.2	Hansen et al., 2006
Sugarcane bagasse	As(V)	4	22	50 mg/L	22.1	Pehlivan et al., 2013
Anaerobic biomass	As(V)	5	22±2	200 – 500 µg/L	0.164	Chowdhury et al., 2011
Pine wood char	As(III)	3.5	25	10 – 100 µg/L	0.0012	Mohan et al., 2007b
Oak wood char	As(III)	3.5	25	10 – 100 µg/L	0.006	Mohan et al., 2007b
Oak bark char	As(III)	3.5	25	10 – 100 µg/L	0.0074	Mohan et al., 2007b
Pine bark char	As(III)	3.5	25	10 – 100 µg/L	12	Mohan et al., 2007b
Agricultural residue “rice polish”	As(III)	7	20	n.s.	0.139	Ranjan et al., 2009
Agricultural residue “rice polish”	As(V)	4	20	n.s.	0.147	Ranjan et al., 2009
Green algae (*Maugeotia genuflexa*)	As(III)	6	20	10 – 400 mg/L	57.5	Sari et al., 2011
Green algae (*Ulothrix cylindricum*)	As(III)	6	20	10 – 400 mg/L	67.2	Tuzen et al., 2009

As mentioned previously, the adsorption of pollutants may be higher when the temperature increases or the pH is lower. However, these could be extreme conditions for the environment in which arsenic is present, so that kind of values may not be feasible in practice.

2.3. Pretreatments

To understand how cork might remove arsenic from water it is necessary to comprehend the role of chemical components that form cork and how they interact with arsenic.

The cork particle size is an important factor in the adsorption of pollutants. The smaller the granules are, the higher the interaction between cork and adsorbates will be, as the contact area and the number of active adsorption sites increase. (Chubar et al., 2004).

Sometimes, with adequate pretreatment of the adsorbent, the capacity to remove pollutants improves greatly. Chubar et al. (2004) studied the effect of pretreatment on cork for the biosorption of heavy metals, through Fisher esterification, with calcium and sodium chlorides, with acidic and alkaline solutions, with oxidizing agents and by thermal activation. The influence of some of these pretreatment procedures are shown in Table 2.

Table 2 - Comparison between adsorption capacity of original and pretreated cork biomass.

Pretreatment	Pollutant	Pollutant Concentration (mg/L)	q (mg/g)		Δq (%)
			Original	Pretreated	
Boiling in 0.1M NaOH	Cu	100	12.0	16.1	33
Heating 90 °C in 0.5M NaOH	Cu	200	14.0	18.8	34
Boiling in laundry detergent	Cu	200	12.0	19.0	58
Boiling in laundry detergent	Ni	10	2.9	4.5	55
Boiling in 0.7% NaClO 5 h	Cu	100	12.0	16.0	33
Heating 60 °C in 1% NaClO	Cu	200	14.0	16.8	20
Contact 0.7% NaClO 12 h	Cu	100	12.0	16.6	38
Contact 7% NaClO 35 min	Cu	100	12.0	21.6	80

Adapted from Chubar et al., 2004

After observation of the table above, it is possible to conclude that the pretreatments always improved the sorption capacity of cork for both copper and nickel. The best improvement rates were obtained for cork biomass treated in contact with 7% NaClO for 35 min, regardless of the concentration of pollutant present on the sample.

An equally important pretreatment was boiling in laundry detergent, which exhibited more than 50% improvement of removal capacity not only for copper but also for nickel.

Yusof et al. (2009) and Chutia et al. (2009) use HDTMA-Br, a surfactant (as laundry detergent) as a pretreatment in zeolites to remove As(V). It was reported that, with this

treatment, arsenic removal capacity improved from 1.30 mg/g to 6.99 mg/g (using modernite as sorbent) and from 0.70 mg/g to 3.40 mg/g (when clinoptilolite was the sorbent).

Hereupon, HDTMA-Br was considered as a possible pretreatment, due to its cationic proprieties. Since cork is hydrophobic, it will attract the hydrophobic tail of the surfactant and leave the cations at the surface so higher number of positive charges can be expected. This way cork may interact better with negatively charged pollutants such as As.

Information was gathered from the literature of other occasions where this compound was used as pretreatment. In Table 3 some conditions of HDTMA-Br use are described.

Table 3 - Summary of HDTMA-Br treatment conditions found in the literature.

Sorbent	Pollutant	Sorbent quantity (g)	Solution volume (mL)	HDTMA-Br concentration	Conditions	Source
zeolite Y	As(V) Cr(VI)	n.s.	n.s.	50%, 100% and 200% of cation exchange capacity (CEC)	n.s.	Yusof et al., 2009
kaolinite	Cr(VI)	10	50	1 g/L	30°C, 24h	Jin et al., 2014
clinoptilolite glauconite montmorillonite	Cr(VI)	7	300	1.0 – 2.0 CEC	Stirring: 2h, 60°C Resting: 24h, 25°C	Bajda et al., 2013
mordenite clinoptilolite	As(V)	10	100	10.9 g/L	Room temperature 24h	Chutia et al., 2009
Red clay	Cr(VI) phenol	1	100	5.1 g/L	4h, 60°C stirring	Gładysz-Płaska et al., 2012

3. Materials and methods

3.1. Cork Treatment

White and black cork granulates from Corticeira Amorim were used in this work. The diameter of the granules was 0.2 – 0.3 and 0.8 – 1 mm for white cork and 1 – 2 mm for black cork. 10 g/L of cork were washed in distilled water at 60 °C during 2 h. This process was repeated 3 times for the two major granulometries and 5 times for the 0.2 – 0.3 mm one in order to assure that the total organic carbon (TOC) in the contact water was inferior to 10 mg/L. Subsequently 10 g/L of cork were submitted to treatment in HDTMA-Br solution 5 g/L or 50 g/L (acquired from Acros Organics, purity >99%) during 24 h, at room temperature. Drying was performed overnight at 60 °C. Summing up, four different adsorbents were used: white cork (WC), treated white cork (TWC), black cork (BC) and treated black cork (TBC) with several granulometries.

3.2. Analytical Methods

Arsenic concentration was measured using a flame atomic absorption spectrometer (mod. GBC 932 plus) at a wave length of 193.7 nm, a slit width of 1.0 nm and a lamp current of 5.0 mA. Acetylene and dinitrogen monoxide were used as combustible/oxidant gases. Each sample was read 3 times. Standard solutions of arsenic in ultrapure water were prepared with concentrations of 3, 6, 10, 20, 30, 40 and 50 mg/L. These standards as well as the other As(V) solutions used in this work were prepared from a work solution of 100 mg/L obtained from a stock solution of As(V) (bought from SPC Science with a concentration of 1001±3 µg/ml and 4% of HNO_3) and ultrapure water.

For samples whose concentration was inferior to 5 mg/L, an atomic absorption spectrometer equipped with graphite furnace (mod. GBC GF3000) was used. Arsenic was determined using a calibration line in the range 2-50 µg/L. Samples matrices contained 1.50 mL/L of HNO_3 (68-70%, analytical grade, Scharlau ACS Basic) and 30 mL/L of H_2O_2 (30%, analytical grade, Merck). Nickel with a concentration of 150 mg/L (prepared from Nickel(II) nitrate hexahydrate, Merck) in ultrapure water was used as matrix modifier. The analysis was performed with 217.6 nm wavelength, slit 0.2 nm, 10 mA lamp current and background correction.

3.3. Adsorbent characterization assays (FTIR and pH_{zpc})

FTIR analyses were performed with cork with a diameter of 0.2 – 0.3 mm with and without treatment with 5 g/L HDTMA-Br. The cork granules were also examined after a sorption test with the initial concentration of 45 mg/L of As(V) and the FTIR spectrum of pure HDTMA-Br was also obtained. All the analyses were done in a FTIR Spectrophotometer (IRAffinity-1, Shimadzu) with a diffuse reflectance accessory (PIKE EasiDiff, PIKE Technologies), using the absorbance mode, in the range of wavenumbers 400 – 4000 cm^{-1}, with a number of scans of 50 and a resolution of 8.0.

Each sample was tested in duplicate.

To evaluate the HDTMA-Br treatment effect, the pH_{zpc} of WC and TWC with 5 g/L HDTMA-Br was determined. This way, the surface charge of cork granules during As removal assays could be predicted.

A cork concentration of 20 g/L was contacted with a solution of 30 mL of 0.01 M KNO_3 (Merck) (the electrolyte was used to maintain the ionic strength constant) and stirred for 2 h at 20 rpm and 25 °C. After this time 0.1, 0.2, 0.3, 0.4 or 0.5 mL of 0.1 M HCl (prepared from 33% Sigma-Aldrich) or 0.3, 0.6, 0.9, 1.2, or 1.5 mL of 0.1 M NaOH was added and they were kept 24 h in agitation under the same conditions.

After this time the final pH was read using a pH meter (Metrohm 702 SM Titrino) and a calibrated glass electrode (Metrohm 6.0255.100).

A blank assay (without cork addition) was also performed to discount the atmospheric CO_2 influence.

3.4. Preliminary tests

For initial studies of arsenic removal, a temperature of 25 °C, a pH of 5, stirring at 20 rpm using a rotating shaker, a contact time of 24 h, a concentration of cork of 5 g/L and 30 mL of an As initial concentration of 25 mg/L were used.

In order to compare the different adsorbents, white (0.8 – 1.0 mm) and black cork both with and without treatment with HDTMA-Br of 5 g/L were used.

In all experiences, the pH was adjusted in the beginning of the assay and checked in the end with a pH meter (mod. HANNA Instruments HI83141). When it was necessary to adjust the pH (± 0.5), diluted solutions of HNO_3 and NaOH were used.

In this and all the other assays, the cork was separated from the solution by filtration using a cellulose acetate membrane with a 0.45 µm pore size.

Each condition was tested in triplicate.

3.5. Effect of pH, granulometry and treatment with HDTMA-Br

Arsenic removal was studied using white cork, with the conditions of temperature of 25 °C, agitation at 20 rpm during 24 h, a concentration of cork of 5 g/L and using 30 mL of an initial solution of 25 mg/L As. Different values of pH (1.5, 2.5, 3, 4, 5, 6, 7, 8 and 10), %w/v of HDTMA-Br (0, 5 and 50 g/L) and granulometry (0.2 – 0.3 and 0.8 – 1.0 mm) were used in order to find out the ideal conditions to perform this experiment. The detailed conditions that are varied for each assay are shown in Table 4.

The pH was adjusted at the beginning of the assay and verified 3 times during the experiment, and corrected when there was a variation superior to 0.5. Each condition was tested in triplicate.

Table 4 - Variable conditions of each assay (pH, granulometry and %w/v HDTMA-Br).

Adsorbent	%w/v HDTMA-Br (g/L)	Granulometry (mm)	pH
white cork	0	0.8 – 1.0	1.5, 2.5, 3, 4, 5, 6, 7, 8 and 10
white cork	5	0.8 – 1.0	1.5, 2.5, 3, 4, 5, 6, 7, 8 and 10
white cork	50	0.8 – 1.0	1.5, 2.5, 3, 4, 5, 6, 7 and 8
white cork	0	0.2 – 0.3	3 and 5
white cork	5	0.2 – 0.3	5 and 7

3.6. Kinetics

Kinetic studies were performed with white cork (0.2 – 0.3 mm) before and after treatment with 5 g/L of HDTMA-Br. The conditions in which the experiment was performed were 25 °C, pH = 6 and agitation speed of 20 rpm, a concentration of cork of 5 g/L using 30 mL of an initial solution of 25 mg/L As. The test was done in separate vials and for each one was settled a different contact time of 0.25, 0.5, 1, 2, 3, 5, 8 and 20 h.

The pH was adjusted at the beginning of the assay and checked at the end. Each condition was tested in duplicate.

3.7. Equilibrium studies

Isothermal equilibrium studies were performed with white cork (0.2 – 0.3 mm) before and after treatment with 5 g/L of HDTMA-Br. The conditions in which the experiment was performed were 25 °C, pH = 6 and agitation speed of 20 rpm, a concentration of cork of 5 g/L using 30 mL of an As initial solution and a contact time of 24 h. The different As concentrations of the initial solution were in the range 0.5- 45 mg/L.

The pH was adjusted at the beginning of the assay and checked at the end. Each condition was tested in duplicate.

3.8. As(III) tests

Although As(V) is more commonly observed in water, As(III) is more toxic to organisms. For this reason, As(III) removal using white cork (0.2 – 0.3 mm) was also studied, at 25 °C and 20 rpm during 24 h, a concentration of cork of 5 g/L using 30 mL of an initial solution of 25 mg/L As. Different values of pH (3, 5 and 7) were used. The pH was adjusted at the beginning of the assay and verified 3 times during the experiment, and corrected when there was a variation superior to 0.5. Cork with and without treatment with HDTMA-Br was used.

As(III) solutions were prepared from a standard solution 1000±3 mg/L (Chem-Lab), preserved with HCl.

Each condition was tested in triplicate.

3.9. Microtox®

The toxicity of multiple samples was studied using a Microtox® Model 500 Analyzer in order to find out if the removal of As from water was effective not only in concentration but also in harmfulness for the organisms present in water. The organism studied was the bacterium *Vibrio fischeri* and the goal was to measure its luminescence under contact with the different concentrations of As of the studied solutions. The process of bioluminescence is a biochemical process that is inhibited in presence of toxic agents. Microtox® is a standard test that quickly determines water toxicity. It has a calibrated photometer to record the cells' luminescence. Firstly, a blank sample is measured (cells in water without pollutants) and then the samples' inhibition is calculated comparing to the blank one.

Solutions of As(III) and As(V) were tested before and after sorption with white cork (0.2 – 0.3 mm). For As(III) both natural and HDTMA-Br treated cork were used while for As(V) only natural cork was examined. All the samples had a pH close to 7 in order to minimize the pH effect on the cells' luminescence. Two concentrations of samples (2% and 4%) and two contact times (5 min and 15 min) were used.

Each condition was tested in duplicate.

4. Results and discussion

4.1. Preliminary tests

In order to start the analyses and find out which type of cork could be the best to further exploration, and given that no other studies using cork as a biosorbent for As were reported in literature, the two types of cork (BC and WC) were tested. The closest granulometries available were used to better compare the results. The two types of cork treated with HDTMA-Br (TBC and TWC) were also used to have a preliminary idea if this would improve As adsorption by cork.

After the measurement of initial and equilibrium concentrations by atomic absorption spectroscopy (AAS), the results were analyzed using Equation 1 and are presented in Figure 5.

$$q = \frac{C_i - C_e}{m} \times V_T \quad (1)$$

Where q is the adsorbed amount, per unit mass of adsorbent (mg/g), C_i is the initial concentration (mg/L), C_e is the equilibrium concentration (mg/L), m is the cork mass (g) and V_T is the solution volume (mL).

The deviation bars present in the graphs correspond to the maximum and minimum values.

Taking a general look at the results, a high deviation to the mean associated to each one is visible. This can be caused by the fact that the difference of concentration between the initial solution and the one after contact with the adsorbent is low and close to the error of AAS measure. On top of that, there is a heterogeneity associated to all natural adsorbents and cork is no exception. Observing the results we can conclude that both WC and TWC remove As(V) from water better than BC and TBC. When it comes to the effect of the treatment with HDTMA-Br there was no significant difference in white cork samples, although in black cork a difference can be observed.

After analyzing these results, it was decided to continue the tests only with white cork, both treated and untreated, and to increase the w/v to 20 g/L in order to intensify the difference between initial and equilibrium concentrations and in this way minimize the error associated to AAS measurements.

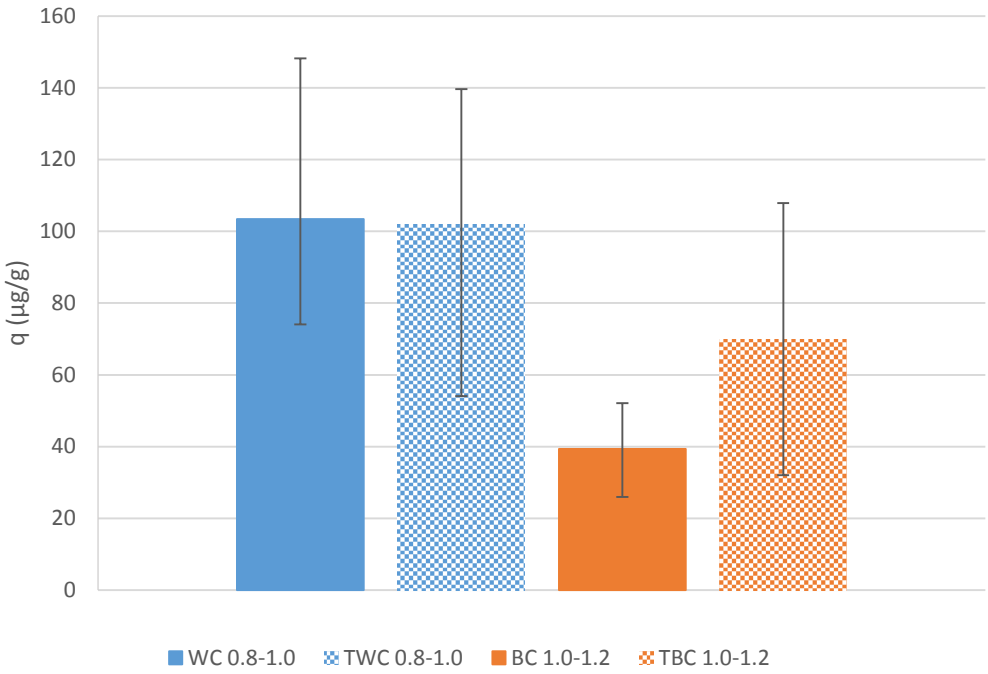

Figure 5 - Preliminary tests of As removal using the two types of cork (black and white) with and without treatment with HDTMA-Br.

(Experimental conditions: T = 25 °C, pH = 5, t_c= 24 h, C_i(As) = 25 mg/L, V = 30 mL, w/v = 5 g/L, v =20 rpm)

4.2. pH_{zpc}

Once decided which type of cork to work with, potentiometric titration tests were made in order to understand the behavior of cork surface and its interaction with the ions present in the solution. The WC was submitted to contact with different concentrations of NaOH and HCl, as described earlier, and the data were analyzed according to Equations 2 and 3, where C_a and C_b are the acid and base concentrations (mol/L), V_a and V_b are the volumes acid and base added (L), V_T is the total volume (L) and ΔNB is the function ΔN vs pH for the blank assay (mmol).

$$\Delta N = C_b V_b - C_a V_a - ([OH^-] - [H^+]) \times V_T \quad (2)$$

$$q_s = -\frac{\Delta N - \Delta NB}{m} \quad (3)$$

The results obtained can be observed in Figure 6.

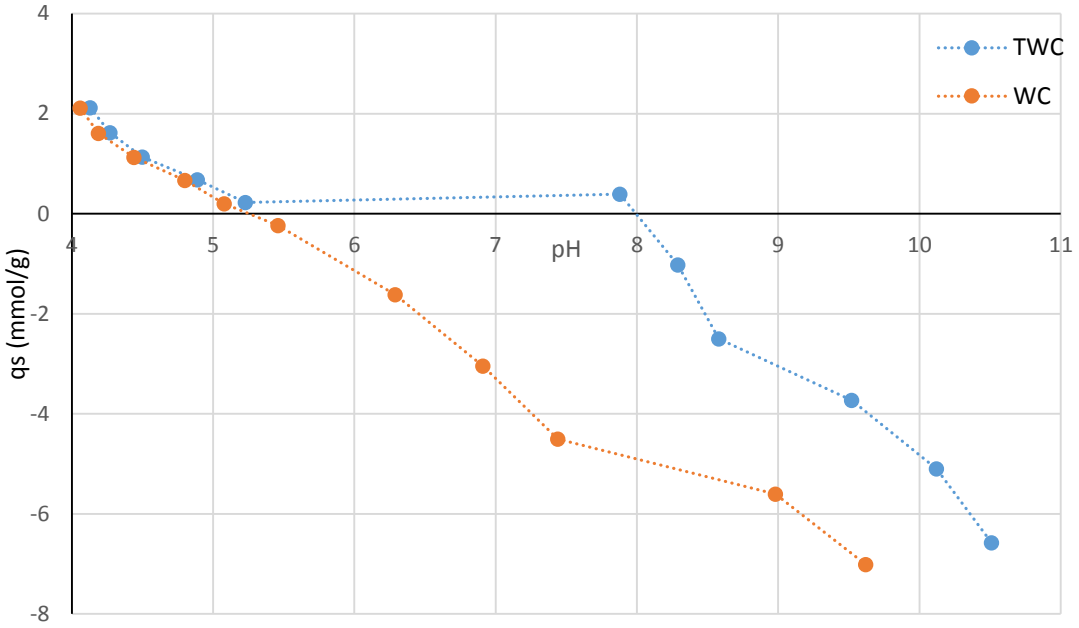

Figure 6 - pH_{zpc} for WC and TWC.

(Cork granulometry = 0.8 – 1.0 mm)

The pH_{zpc} (zero point of charge) means the pH value in which the number of positive surface charges equals the number of negative surface charges in the material. This is an important information because the pH influences not only the charges present at the sorbent surface but also the chemical speciation of As in solution. Thus, it is possible to infer the likelihood of attraction and repulsion between sorbent and sorbate (Fiol et al., 2009).

Analysing the graph, it can be observed that the pH_{zpc} for WC is around 5.2, which means that for pH values below 5.2, cork has a positive charge at the surface and for this reason will attract anions. When the pH is above 5.2, cork will attract cations. Meanwhile, for TWC, the pH_{zpc} is 8.0 and, similarly, when pH is below 8.0, cork will attract anions, and when the pH is higher than 8.0, the cork surface has a net negative charge, having more affinity to cations. Summing up, considering the anionic characteristic of As, a better interaction of TWC and As is predictable when comparing to WC, especially above pH 5.2.

4.3. Effect of pH, granulometry and pretreatment with HDTMA-Br

The pH effect was tested as well as the influence of the treatment with HDTMA-Br and its concentration. The pH was settled to a specific value between 1.5 and 9.5, and WC and TWC submitted to two different concentrations of the surfactant (5 and 50 g/L) with a diameter of

0.8 – 1.0 mm were used. After the measurement by AAS, the results were analyzed using Equation 1 and they are illustrated in Figure 7.

The pH values were adjusted at the beginning of the experiment, then verified (and corrected when needed) 3 times during the running time of the assay and quantified again at the end. The pH values of 1.5 and 2.9 were never adjusted in the middle of the experiment because a change superior to 0.5 was not verified. pH values of 3.4, 4.3 and 9.5 varied a lot, and consequently, a lot of adjustments were needed, causing small errors in the final measurement of As concentration. For values of pH between 5.3 and 7.8 only a few adjustments were necessary.

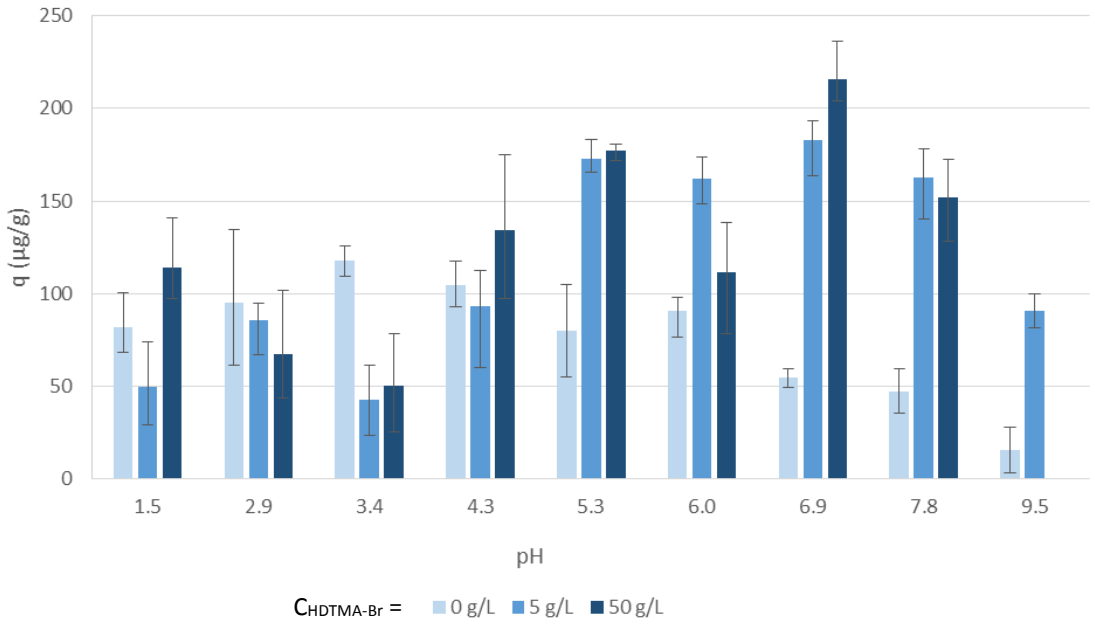

Figure 7 – The effect of pH and treatment with HDTMA-Br.

(Experimental conditions: T = 25 °C, t_c =24h, C_i(As) = 25 mg/L, V = 30 mL, w/v = 20 g/L, v =20 rpm)

Analyzing the data, both the treatment with HDTMA-Br and the pH influence the removal of As(V) with cork.

Starting by looking only at WC results and the influence of pH on them, it is verify that the higher values of removal capacity correspond to pH of 3.4 and 4.3 and from this point an increase of pH value corresponds to a diminution of adsorption capacity. This can be explained if we look at pH_{zpc} value of WC (5.2), which means that for pH below this value the cork surface is positively charged. In addition, looking at Figure 2 (arsenic speciation), for As(V) between pH 2 and 7, its form is $H_2AsO_4^-$, having a negative charge and in this way a better attraction towards

cork. On the other hand, for values superior to 5.2, cork becomes more negatively charged and therefore more repulsive for As(V), which is also charged negatively.

Concentrating now in TWC results (for both concentrations), the adsorption capacity of cork increases with the pH, reaching a maximum around 6.9, and then starts to drop. For the same reason as in WC, considering the value of pH_{zpc} for TWC (8.0), below 8.0 cork is charged positively and As(V) presents a negative charge. Moreover, as the pH becomes closer to 7, the most abundant As(V) form is $HAsO_4^{2-}$, which means more negative charges and a higher interaction with cork. However, when pH gets closer to 8.0, the negative charges at the cork surface increase and start to dominate, so when pH gets over 8.0 the interaction with As(V) becomes weaker.

As the differences in the treatment concentration (5 or 50 g/L) were not significant at the most common pH of natural water (5 – 7) and due to the cost increase caused by a 10x more concentrated treatment, only the lowest concentration of HDTMA-Br was considered for further examinations.

The effect of granulometry was also studied since, as reported, lower granulometries have often better adsorption rates due to a higher superficial area available for the binding of As. In addition, since cork cells are closed and consequently there is poor accessibility to inner pores, this increase of superficial area could have a significant impact on the results.

A value of pH of 5 was used since it is normal commonly found pH of water and mining drainage containing As and the best values of As(V) removal according to the previous graph were used for both WC (pH = 3.4) and TWC (pH = 6.9). The results of this study, that were analyzed using Equation 1, can be seen in Figure 8.

Observing the graph, we can say that, in general, the smallest granulometry has a better As(V) adsorption. The only exception is for WC at pH = 3 in which there is not a significant difference between the two sizes tested.

As it was mentioned before, these results were expected and are concordant with the literature, since as the superficial area increases and the number of possible bonding sites grows, the adsorption capacity of cork also becomes higher.

Therefore, it was decided to carry out the kinetics and equilibrium tests with the smaller granulometry since it has proved to be more effective in As(V) removal and this way the errors of AAS measurement would have less impact on the final results.

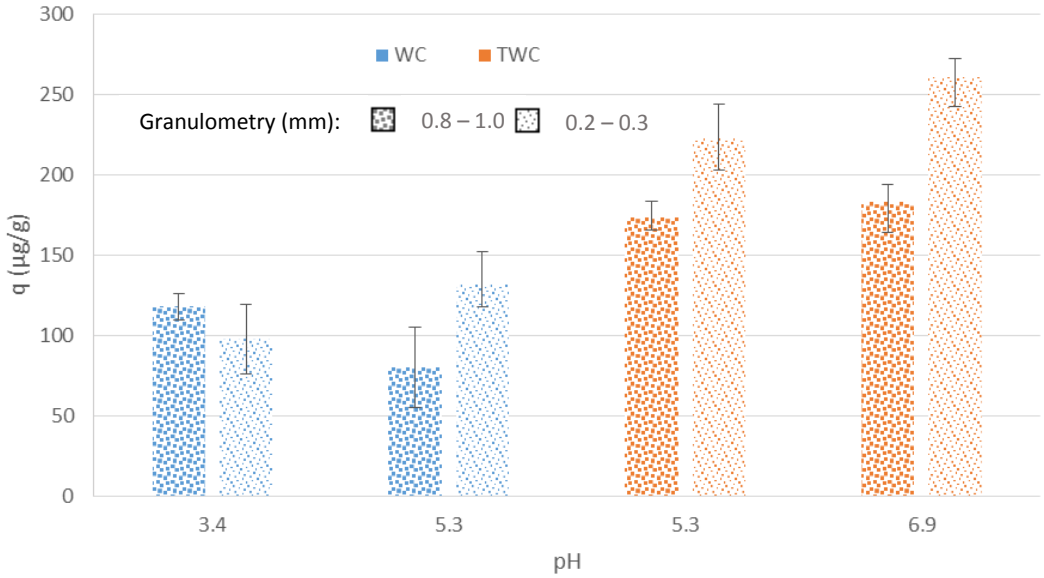

Figure 8 - Granulometry effect in WC and TWC at different pH.

(Experimental conditions: T = 25 °C, t_c =24h, C_i(As) = 25 mg/L, V = 30 mL, w/v = 20 g/L, v =20 rpm)

4.4. Kinetics

Adsorption kinetic studies were conducted for WC and TWC with 5 g/L HDTMA-Br, both with a granulometry of 0.2 – 0.3 mm. The experimental data were analyzed using Equation 1 and fitted to pseudo 1st (Lagergren, 1898) and 2nd order models (Ho, 1995), according to Equations 4 and 5, respectively. CurveExpert software was used for the non-linear fittings.

Pseudo 1st order: $q = q_e\left(1 - e^{(-kt)}\right)$ (4)

Pseudo 2nd order: $q = \frac{q_e^2 kt}{1+q_e kt}$ (5)

Where q is the adsorption capacity (µg/g), q_e is the equilibrium adsorption capacity (µg/g), k is the kinetic constant (h^{-1} for 1st order and g μg^{-1} h^{-1} for 2nd order) and t is the time (h).

The experimental results as well as the modeled curves are represented in Figure 9 for WC and in Figure 10 for TWC. The parameters of both models and materials are shown in Table 5.

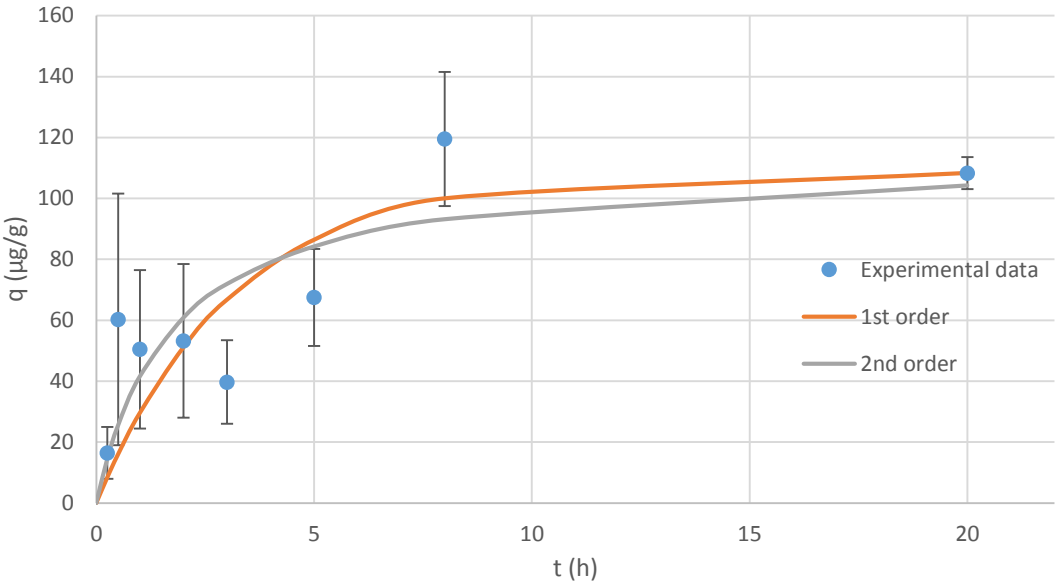

Figure 9 - Adsorption kinetics for WC and the adjustment to models of 1st and 2nd orders.

(Experimental conditions: T = 25 °C, pH = 6, C_i(As) = 25 mg/L, V = 30 mL, w/v = 20 g/L, v =20 rpm)

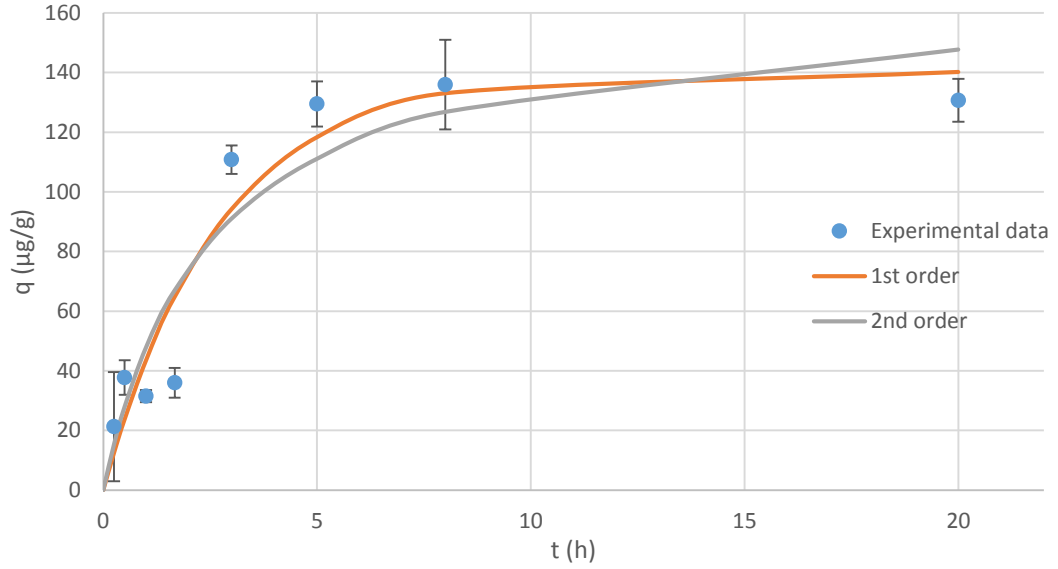

Figure 10 - Adsorption kinetics for TWC and the adjustment to models of 1st and 2nd orders.

(Experimental conditions: T = 25 °C, pH = 6, C_i(As) = 25 mg/L, V = 30 mL, w/v = 20 g/L, v =20 rpm)

Looking at the results, it is possible to conclude that the pseudo 1st order model has a higher coefficient of correlation when describing the behavior of the TWC. At the same time, pseudo 1st order model also predicts a maximum adsorbed amount (q_e = 140 µg/g) closer to the experimental value (131 µg/g). For WC, the experimental data and respective errors justify the poor R^2 values obtained for both models. The dispersion of experimental data points in the first three hours (Figure 9) precluded the calculation of statistically significant values of the kinetic

constants. Then, K values presented on table 5, for WC are subjected to very considerable standard error.

Analyzing both graphs, it is possible to estimate the equilibrium time, which is around 8 h for both treated and untreated cork.

Table 5 - Kinetics parameters from 1st and 2nd order model adjustments. (value ± standard error)

		1st order	2nd order
WC	R^2	0.53	0.60
	q_e	109 ± 22 µg/g	113 ± 24 µg/g
	K	0.3 ± 0.2 h^{-1}	0.005 ± 0.004 g μg^{-1} h^{-1}
TWC	R^2	0.91	0.87
	q_e	140 ± 14 µg/g	166 ± 25 µg/g
	K	0.4 ± 0.1 h^{-1}	0.002 ± 0.001 g μg^{-1} h^{-1}

The adsorbed amount of arsenic at equilibrium is better for cork with HDTMA-Br treatment, 140 ± 14 µg/g, comparing with cork without treatment, 113 ± 24 µg/g, which corresponds to an improvement of 24%.

On the whole, it is shown that both models suit TWC experimental data much better than WC ones (comparing R^2), which reflects the low homogeneity of cork particles (as could be seen in the significant extent of error bars, Figure 9) which is minimized with the surface treatment.

4.5. Isotherms

The smallest granulometry of WC and TWC with 5 g/L of HDTMA-Br was used. The Langmuir and Freundlich models were fitted to the experimental data (previously analyzed by Equation 1) according to Equation 6 (Langmuir, 1918) and Equation 7 (Freundlich, 1907), respectively.

Langmuir: $q = \frac{Q_{max} K_L C_e}{1 + K_L C_e}$ (6)

Freundlich: $q = K_F C_e^{1/n}$ (7)

Where q is the adsorption capacity (µg/g), Q_{max} is the maximum adsorption capacity (µg/g), C_e is the equilibrium concentration, K_L is the Langmuir constant (L/g), K_F is the Freundlich constant (µg g^{-1}(µg.L^{-1})$^{-1/n}$) and n is Freundlich model parameter.

The Langmuir model describes a non-competitive adsorption on the material in which a monolayer of ions is formed at the material's surface. The Freundlich model considers that the surface is heterogeneous and consequently that there are sites with different affinities. Therefore, the sites with higher affinity to the adsorbate are occupied in first place.

Experimental results as well as the curves adjusted according to the aforementioned models are represented for WC and TWC in Figures 11 and 12, respectively. The parameters obtained from these adjustments are presented in Table 6.

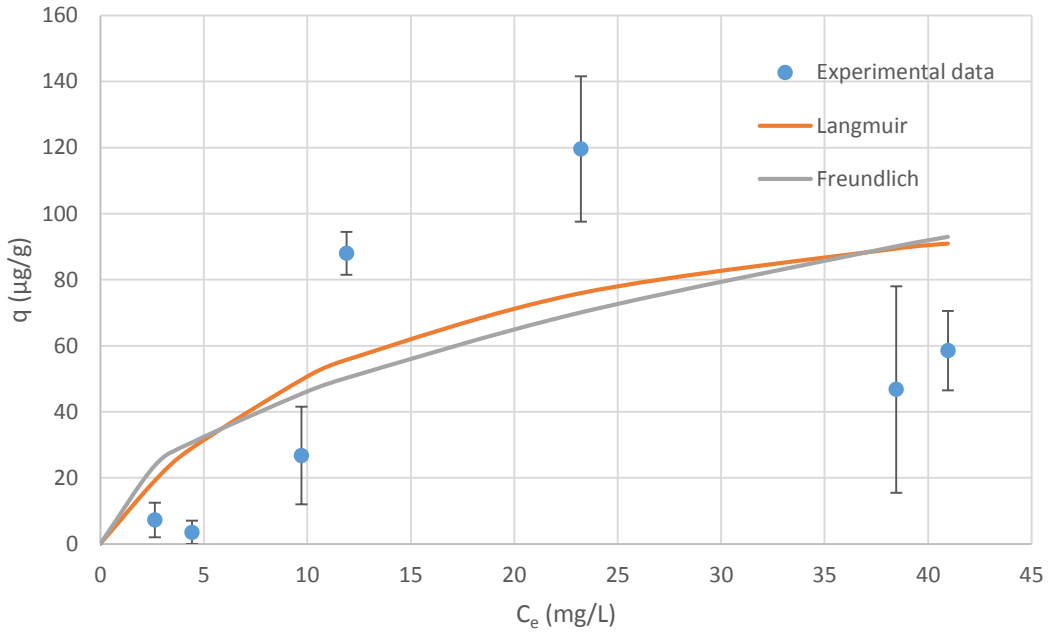

Figure 11 - Equilibrium isotherm for WC and the adjustment to Langmuir and Freundlich models.

(Experimental conditions: T = 25 °C, pH = 6, t_c = 24h, V = 30 mL, w/v = 20 g/L, v =20 rpm)

As it happened before for kinetics, both models fit the TWC experimental data much better than WC (comparing R^2) which, once more, reflects that the homogeneity of natural cork is poor and it is improved with the treatment with HDTMA-Br. Moreover, the errors associated to WC experimental points are higher than those of TWC, which supports the assumption of the lack of homogeneity in natural cork. It is important to note that Langmuir and Freundlich parameters presented for WC are not statistically significant.

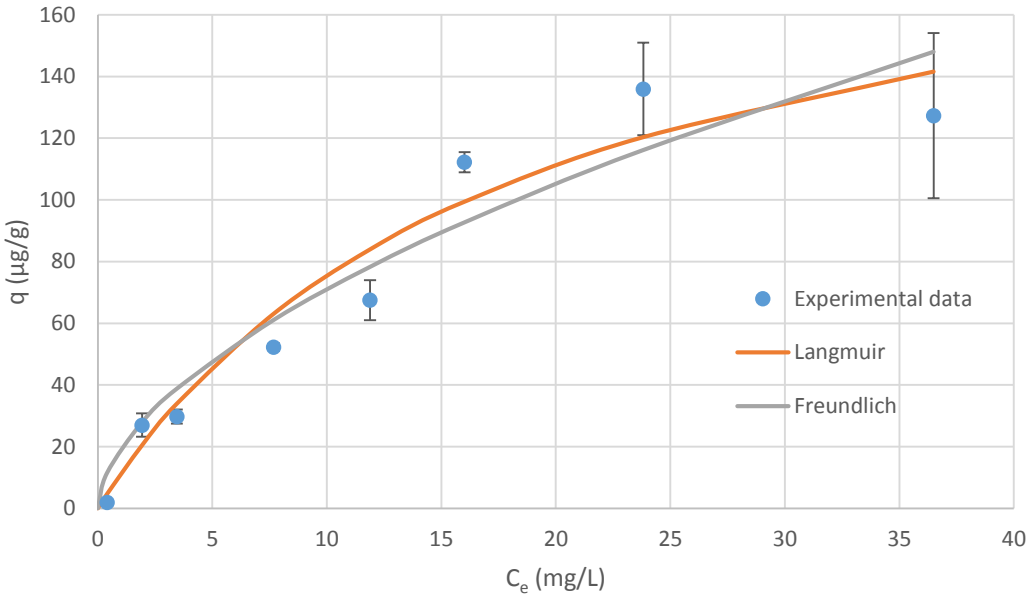

Figure 12 – Equilibrium isotherm for TWC and the adjustment to Langmuir and Freundlich models.

(Experimental conditions: T = 25 °C, pH = 6, t_c = 24h, V = 30 mL, w/v = 20 g/L, v =20 rpm)

As the data illustrate, the Langmuir model has a greater R^2 than the Freundlich model for both WC and TWC. This means that the adsorption of As(V) into cork probably occurs in a monolayer.

The maximum adsorption capacity of cork seems to be better for cork treated with HDTMA-Br than for the one without treatment. The value grows from 123 ± 87 µg/g to 212 ± 49 µg/g, corresponding to an increase of 73%. However, if we take into account the error associated to this parameter, it is not possible to conclude for certain if there is actually an increase.

Adsorption capacities obtained for As removal by WC and TWC are low and present a high deviation associated to each value. When comparing the Q_{max} to the literature ones, using cork as a sorbent and for As sorption (Table 1), it is verified that cork is a better sorbent to other compounds than As(V). This fact was already predicted since negative species adsorption is always a challenger. When it comes to As(V) sorption by other materials, in general cork has a lower Q_{max}: pine leaves, 3.27mg/g (Shafique et al. 2012), *L. nigrescens*, 45.2 mg/g (Hansen et al., 2006). However cork still presents a higher Q_{max} than *M. oleifera* seeds, 8.33 µg/g (Kumari et al., 2005), pine wood char, 1.2 µg/g (Mohan et al., 2007b) and also oak wood char, oak bark char and agricultural residue “rice polish”.

Table 6 - Isotherm parameters from Langmuir and Freundlich adjustments. (value ± standard error)

	Langmuir		Freundlich	
WC	R^2	0.51	R^2	0.41
	Q_{max} (µg/g)	123 ± 87	K_F (µg $g^{-1}(\mu g.L^{-1})^{-1/n}$)	15 ± 18
	K_L (L/g)	0.07 ± 0.11	1/n	0.5 ± 0.4
TWC	R^2	0.92	R^2	0.89
	Q_{max} (µg/g)	212 ± 49	K_F (µg $g^{-1}(\mu g.L^{-1})^{-1/n}$)	19 ± 7
	K_L (L/g)	0.06 ± 0.03	1/n	0.6 ± 0.1

4.6. As (III) tests

All the analyses so far were performed with As(V) because this is the form of As that is more commonly present in water. However, as As(III) is a more toxic form (about ten times), the lower granulometry forms of TWC and WC were tested at 3 different pH values to find out how well As(III) interacts with cork.

In Figure 13 the results of these assays are shown, after being analyzed according Equation 1, along with the previous ones done with As (V) for a better comparison.

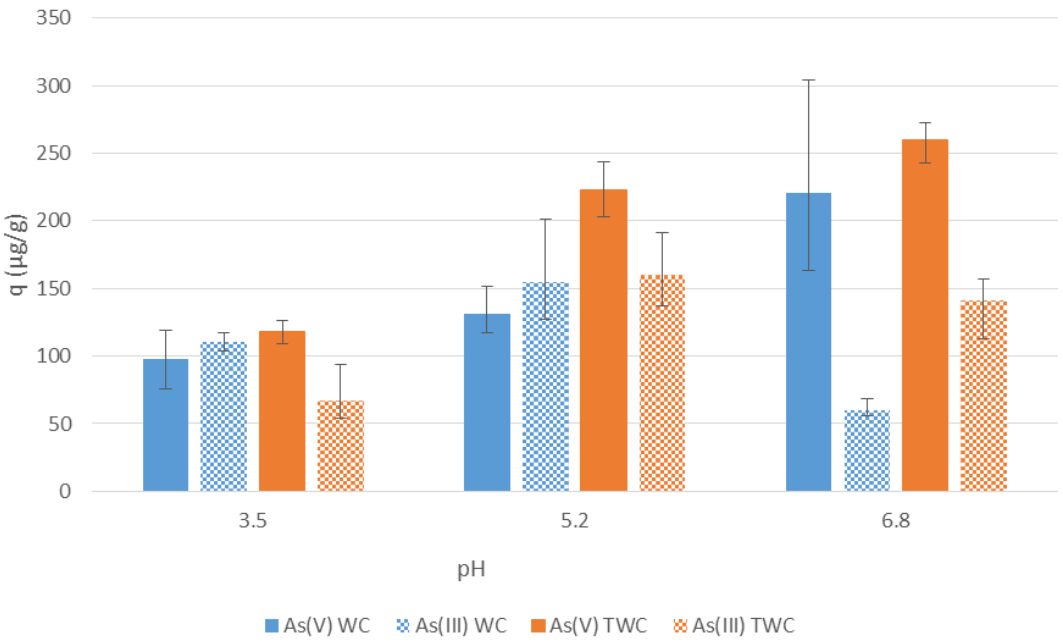

Figure 13 - Comparison between As(III) and As(V) removal by cork with and without treatment with HDTMA-Br at different pH.

(Experimental conditions: T = 25 °C, t_c =24h, C_i(As) = 25 mg/L, V = 30 mL, w/v = 20 g/L, v =20 rpm)

Observing the graph, we can say that for pH 3.5 and 5.2, the removal of As was similar for both compounds, when it comes to WC. For TWC, the sorption of As(V) by cork was slightly higher than that of As(III). For the highest pH, the differences in sorption capacity are much more meaningful, As(V) having a much increased sorption on cork when compared to As(III).

Unlike As(V), which for the shown concentrations increases the sorption in cork with the pH, for As(III) the sorption is better at pH 5.2 for both treated and untreated cork. The difference in the adsorbed amount of As(III) between pH 5.2 and 6.8 were most significant for the untreated cork. This can be explained considering that As(III) is expected to be predominantly under neutral form (H_3AsO_3) for pH < 10 (Figure 2). Its removal by WC will then be more favorable in pH conditions where it is also neutral, around 5. In the case of TWC, the differences in As(III) adsorbed between pH 5.2 and 6.8 were not significant, because, regarding the potentiometric titration results (Figure 6), in the pH range 5.2 – 8, the adsorbent charge is near zero. Thus, while for WC the worst sorption occurs at pH 6.8, for TWC this happens for pH 3.5.

4.7. FTIR characterization

In order to characterize the sorbent, cork before and after treatment with 5 g/L of HDTMA-Br as well as after 24 h contact with a 45 mg/L As(V) solution, and pure HDTMA-Br, were subjected to FTIR analysis.

FTIR was used to obtain an infrared spectrum of absorption. The results of this analysis are represented in Figure 14.

The results demonstrate that there is no substantial difference between the spectra of the three cork samples. This reveals that neither treatment with HDTMA-Br nor the adsorption of As(V) cause substantial change in the functional groups of cork.

Combining these results with the ones obtained by kinetics and isotherms studies, we can infer that the treatment improved slightly cork's removal capacity of As, with no significant change the functional groups of cork.

López-Mesas et al. (2011) also performed a FTIR analysis to cork before and after adsorption with cadmium and lead and, as in the present case, there were no significant differences between the samples. The cork structure is not affected in the process which is good since cork can be reused (López-Mesas et al., 2011).

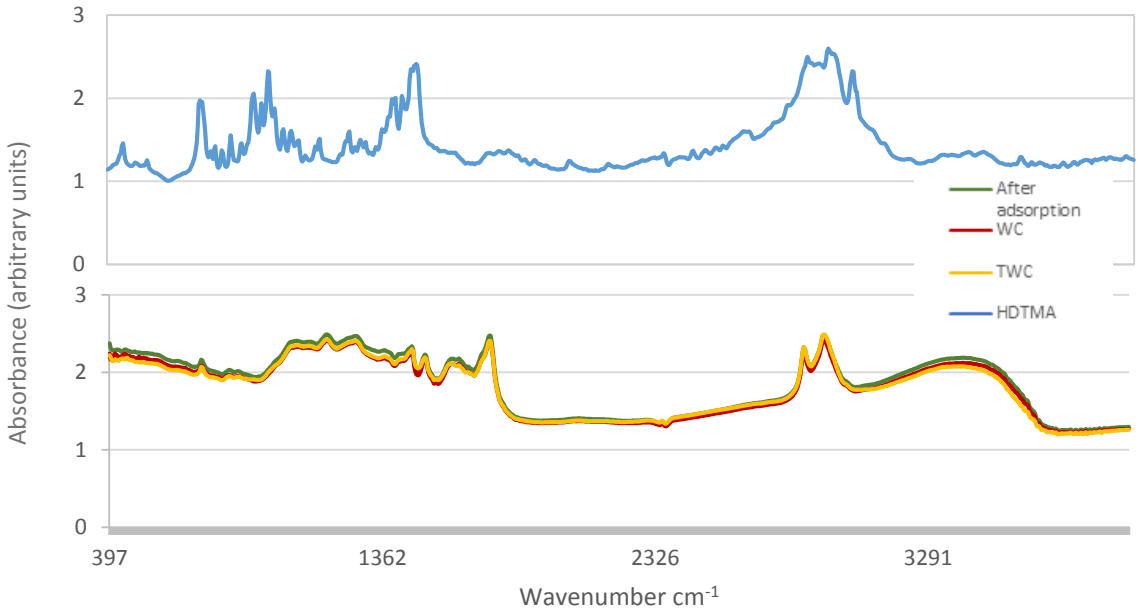

Figure 14 - FTIR analysis of HDTMA-Br and cork with and without treatment with HDTMA-Br and after As(V) adsorption

4.8. Microtox®

With the purpose of evaluating the effectiveness of As removal in terms of toxicity, a Microtox® assay was performed on initial and after adsorption As solutions. Microtox® is a test for rapid toxicity screening and analysis, based in bioluminescence technology to monitor contamination of water. In this case, two concentrations of the samples were used and after a certain time (5 min and 15 min), the luminescence of a sample without any pollutant (blank sample) and the samples containing As were measured. The % of inhibition of the samples containing As was calculated compared to the blank sample.

The results of the effect of As solutions on the luminescence of the cells are presented in Figure 15.

Observing how the solutions affect the luminescence of the cells, it was noticed that a few results that do not correspond to what was expected. Firstly, As(V) appeared as more toxic for cells than As(III), which does not correspond to what is commonly reported in literature. This toxicity difference is significant for a concentration of 2% but it is smaller for a 4% concentration. As the toxicity depends on the organism and on the tests, this particular one shows a different result from what was anticipated.

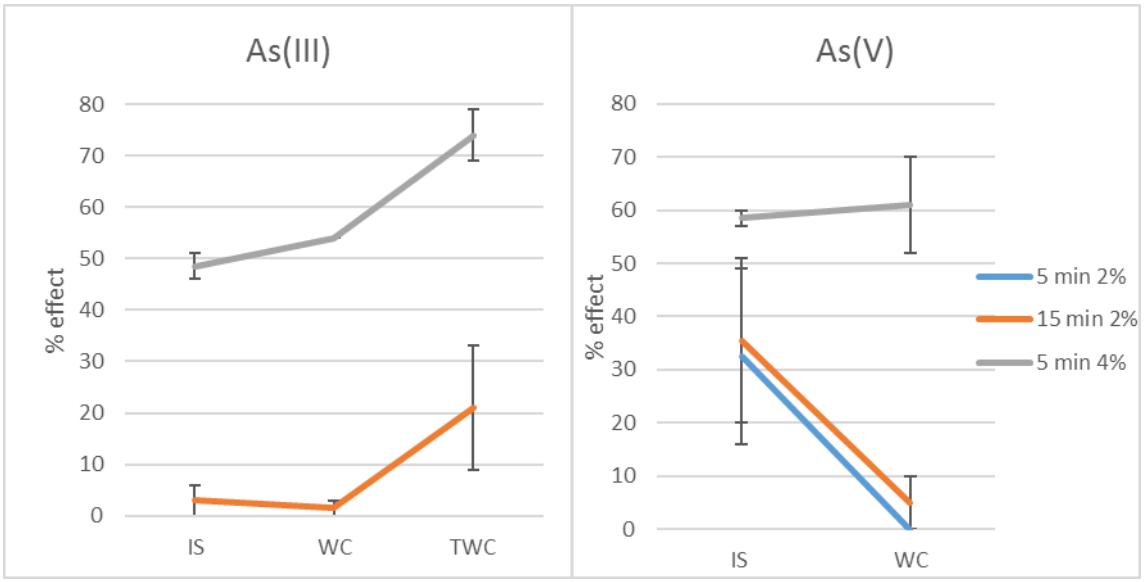

Figure 15 - Toxicity results of As(III) and As(V) solutions before and after adsorption with cork.

(Experimental conditions: pH = 7; CAs(III) (mg/L): IS = 23.04, WC = 21.93, TWC = 20.79; CAs(V) (mg/L): IS = 25.61, WC = 23.66)

Then, another surprising but negative aspect occurred for a concentration of 4% of solution and after 5 min. Both solutions of As(V) and As(III) after treatment present a slightly higher toxicity than the initial solution. Finally, both solutions of As after adsorption with TWC have a greater effect in the inhibition of luminescence, suggesting that the adsorbent releases some kind of harmful substance to the solution. This is an important result since surfactant treatments have been reported in many studies as a way to enhance the adsorption ability of the adsorbent while their real impact on the treated water toxicity remains unstudied. This way, it can be concluded that an alternative treatment for cork should be found.

On the other hand the results using 2% of As solution for both molecules show that for adsorption with WC, the toxicity of the solution improved.

5. Conclusions

5.1. General conclusions

This work presented an exploratory study on the capacity of cork granulates for the adsorption of arsenic.

Observing all the adsorption results, a high deviation to the mean was visible in most of them. This may be explained by the small difference between the initial solution and the one after adsorption, close to the error associated with AAS measurements, and the cork's heterogeneity.

Samples of white cork presented a higher adsorption capacity when compared to the black cork ones.

The pH_{zpc} was determined as being 5.2 for WC and 8.0 for TWC which means that a better interaction between As and WC is predictable below pH 5.2 while for TWC this value increases to 8.0.

For WC the higher values of removal capacity corresponded to pH of 3.4 and 4.3 while for TWC the adsorption capacity of cork increased with the pH, reaching a maximum around 6.9.

Differences in the treatment concentration (5 or 50 g/L) were not significant in the most common pH of natural water (5 – 7).

In general, the smallest granulometry had a better As(V) adsorption since superficial area increases and the number of possible bonding sites grows.

Kinetics of sorption on TWC was better described using the 1^{st} order model. The equilibrium time was estimated as 8 h for both WC and TWC and the equilibrium adsorption capacity was 113 ± 24 μg/g and 140 ± 14 μg/g, respectively.

For equilibrium isotherms, Langmuir model presented the best fit. The maximum adsorption capacity was 123 ± 87 μg/g for WC and 212 ± 49 μg/g for TWC.

The study of As(III) removal by cork showed that the adsorption capacities were similar to those of As(V) for WC at pH 3.4 and 5.2 while for TWC the As(V) adsorption capacity was always better than that of As(III).

FTIR analysis demonstrated that there is no substantial difference between the spectra of the cork samples with and without treatment and after As(V) adsorption. Therefore, neither treatment with HDTMA-Br nor the adsorption of As(V) cause substantial change in the functional groups of cork.

Arsenic solutions after contact with TWC presented a higher inhibition of the organism than the initial solution of As, which indicates that HDTMA-Br increases the solutions toxicity.

The experimental work done provided relevant information about the cork behavior as a sorbent for As solutions.

Both WC and TWC had low adsorption capacities for As. Even though the pretreatment increased As removal capacity, the treated solutions exhibited toxicity, which means that cork treated with HDTMA-Br is not recommended for the treatment of drinking water.

5.2. Future work

Since the adsorption capacities obtained were low and the pretreated samples showed higher toxicity, other pretreatment solutions need to be found, that can improve cork adsorption capacity while not being harmful to organisms, for example with one of the pretreatments referred in pretreatment section or even and iron one that is also commonly used for As removal.

Another point that can be tested is the ability of cork to adsorb other anionic species besides As, as antimony, molybdenum or selenium.

If good adsorption capacities are obtained using ultrapure water, assays with effluents and natural water contaminated with As should also be tested. Finally, a good and simple support for cork, as for example a column, needs to be projected so the system can operate in continuous mode.

References

Anjos, O., Rodrigues, C., Morais, J., & Pereira, H. (2014). Effect of density on the compression behaviour of cork. *Materials and Design, 53*, 1089-1096.

Antunes, I., & Albuquerque, M. (2013). Using indicator kriging for the evaluation of arsenic potential contamination in an abandoned mining area (Portugal). *Science of the Total Environment, 442*, 545-552.

APCOR. (2014). *Cortiça/Cork 2014.*

Badja, T., & Kłapyta, Z. (2013). Adsorption of chromate from aqueous solutions by HDTMA-modified clinoptilolite, glauconite and montmorillonite. *Applied Clay Science, 86*, 169-173.

Chowdhury, M., & Mulligan, C. (2011). Biosorption of arsenic from contaminated water by anaerobic biomass. *Journal of Hazardous Materials, 190*, 486-492.

Chubar, N., Carvalho, J., & Correia, M. (2003). Cork biomass as biosorbent for Cu(II), Zn(II) nad Ni(II). *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 230*, 57-65.

Chubar, N., Carvalho, J., & Correia, M. (2004). Heavy metals biosorption on cork biomass: effect of the pre-treatment. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 238*, 51-58.

Chutia, P., Kato, S., Kojima, T., & Satokawa, S. (2009). Adsorption of As(V) on surfactant-modified natural zeolites. *Journal of Hazardous Materials, 162*, 204-211.

Corticeira Amorim. (s.d.). Obained on 18th January 2015, from Corksorb: http://www.corksorb.com/downloads/file91_pt.pdf

Crespo-Alonso, M., Nurchi, V., Biesuz, R., Alberti, G., Spano, N., Pilo, M., & Sanna, G. (2013). Biomass against emerging pollution in wastewater: Ability of cork for the removal of ofloxacin from aqueous solutions at different pH. *Journal of Environmental Chemical Engineering, 1*, 1199-1204.

Decreto-Lei nº 306/2007. (27th August 2007). *(164)*. Diário da República.

Dias, A., Simão, V., Merib, J., & Carasek, E. (2013). Cork as a new (green) coating for solid-phase microextraction: Determination of polycyclic aromatic hydrocarbons in water samples by gas chromatography–mass spectrometry. *Analytica Chimica Acta, 772*, 33-39.

Domingues, V., Alves, A., Cabral, M., & Delerue-Matos, C. (2005). Sorption behaviour of bifenthrin on cork. *Journal of Chromatography A, 1069*, 127-132.

Domingues, V., Priolo, G., Alves, A., Cabral, M., & Delerue-Matos, C. (2007). Adsorption behaviour of alpha-cypermethrin on cork and activated carbon. *Journal of*

Environmental Science and Health. Part B, Pesticides, Food Contaminants, and Agricultural Wastes, 42, 649-654.

Feundlich, H. (1907). Üeber die adsorption in Loesungen. *Zeitschrift Für Physikalische Chemie, 57*, 385-470.

Fiol, N., & Villaescusa, I. (2009). Determination of sorbent point zero charge: usefulness in sorption studies. *Environmental Chemistry Letters, 7*, 79-84.

Fiol, N., Villaescusa, I., Martínez, M., Miralles, N., Poch, J., & Serarols, J. (2003). Biosorption of Cr(VI) using low cost sorbents. *Environmental Chemistry Letters, 1*, 135-139.

Gładysz-Płaska, A., Majdan, M., Pikus, S., & Sternik, D. (2012). Simultaneous adsorption of chromium(VI) and phenol on natural red clay modified by HDTMA. *Chemical Engineering Journal, 179*, 140-150.

Gonçalves, A. (2011/12). Riscos associados à exploração mineira. O caso das minas da Panasqueira. *Cadernos de Geografia, 30/31*, 131-142.

Hansen, H., Ribeiro, A., & Mateus, E. (2006). Biosorption of arsenic(V) with *Lessonia nigrescens*. *Minerals Engineering, 19*, 486-490.

Ho, Y. S. (1995). *Adsorption of heavy metals from waste streams by Peat.* Ph.D Thesis , University of Birmingham, Birmingham.

Jin, X., Jiang, M., Du, J., & Chen, Z. (2014). Removal of Cr(VI) from aqueous solution by surfactant-modified kaolinite. *Journal of Industrial and Engineering Chemistry, 20*, 3025-3032.

Karbowiak, T., Mansfield, A., Barrera-García, V., & Chassagne, D. (2010). Sorption and diffusion properties of volatile phenols into cork. *Food Chemistry, 122*, 1089-1094.

Krika, F., Azzouz, N., & Ncibi, M. (2012). Adsorptive removal of cadmium from aqueous solution by cork biomass: Equilibrium, dynamic and thermodynamic studies. *Arabian Journal of Chemistry*, doi: 10.1016/j.arabjc.2011.12.013

Kumari, P., Sharma, P., Srivastava, S., & Srivastava, M. (2005). Arsenic removal from the aqueous system using plant biomass: a bioremedial approach. *Journal of Industrial Microbiology and Biotechnology, 32*, 521-526.

Kwok, K., Koong, L., Chen, G., & McKay, G. (2014). Mechanism of arsenic removal using chitosan and nanochitosan. *Journal of Colloid and Interface Science, 416*, 1-10.

Lagergren, S. (1898). About the theory of so-called adsorption of soluble substances. *Kungliga Svenska Vetenskapsakademis, 24*, 1-39.

Lagorce-Tachon, A., Karbowiak, T., Loupiac, C., Gaudry, A., Ott, F., Alba-Simionesco, C., Gougeon, R., Alcantara, V., Mannes, D., Kaesther, A., Lehmann, E., & Bellat, J. (2015). The cork viewed from the inside. *Journal of Food Engineering, 149*, 214-221.

Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society, 40*, 1361-1403.

Lima, J. (2011). *A Importancia da cortiça no panorama nacional*. Obtained on 22nd December 2013, de Instituto Superior de Agronomia: http://ae.isa.utl.pt/attachments/article/123/Apresentação%20JL%20ISA%2021%20Março%202011.pdf

López-Mesas, M., Navarrete, E., Carrillo, F., & Palet, C. (2011). Bioseparation of Pb(II) and Cd(II) from aqueous solution using cork waste biomass. Modeling and optimization of the parameters of the biosorption step. *Chemical Engineering Journal, 174*, 9-17.

Machado, R., Carvalho, J., & Correia, M. (2002). Removal of trivalent chromium(III) from solution by biosorption in cork powder. *Journal of Chemical Technology and Biotechnology, 77*, 1340-1348.

Meliker, J., & Nriagu, J. (2008). Arsenic. (K. Heggenhougen, & S. Quah, Edits.) *International Encyclopedia of Public Health*, 233-238.

Mohan, D., & Pittman Jr., C. (2007a). Arsenic removal from water/wastewater using adsorbents - A critical review. *Journal of Hazardous Materials, 142*, 1-53.

Mohan, D., Pittman Jr, C., Bricka, M., Smith, F., Yancey, B., Mohammad, J., Steele, P., Alexandre-Franco, M., Gómez-Serrano, V., & Gong, H. (2007b). Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. *Journal of Colloid and Interface Science, 310*, 57-73.

Mota, D., Marques, P., Pereira, C., Gil, L., & Rosa, M. (2004). *Lead Bioremoval by Cork Residues as Biosorbent.* INETI.

Nurchi, V., Crespo-Alonso, M., Biesuz, R., Alberti, G., Pilo, M. , Spano, N., & Sanna, G. (2014). Sorption of chrysoidine by row cork and cork entrapped in calcium alginate beads. *Arabian Journal of Chemistry, 7*, 133-138.

Ollivella, M., Jové, P., & Oliveras, A. (2011). The use of cork waste as a biosorbent for persistent organic pollutants - study of adsorption/desorption of polycyclic aromatic hydrocarbons. *Journal of Environmental Science and Health, Part A, 46*, 824-832.

Ollivella, M., Jové, P., Bianchi, A., Bazzicalupt, C., & Cano, L. (2013). An integrated approach to understanding the sorption mechanism of phenanthrene by cork. *Chemosphere, 90*, 1939-1944.

Pehlivan, E., Tran, H., Ouédraogo, W., Schmidt, C., Zachmann, D., & Bahadir, M. (2013). Sugarcane bagasse treated with hydrous ferric oxide as a potential adsorbent for the removal of As(V) from aqueous solutions. *Food Chemistry, 138*, 133-138.

Pintor, A., Ferreira, C., Pereira, J., Correia, P., Silva, S., Vilar, V., Botelho, C., & Boaventura, R. (2012). Use of cork powder and granules for the adsorption of pollutants: A review. *Water Research, 46*, 3152-3166.

Pintor, A., Silvestre-Albero, A., Ferreira, C., Pereira, J., Vilar, V., Botelho, C., Rodríguez-Reinoso, F., & Boaventura, R. (2013). Textural and surface characterization of cork-based sorbents for the removal of oil from water. *Industrial & Engineering Chemistry Research, 52*, 16427–16435.

Ranjan, D., Talat, M., & Hasan, S. (2009). Biosorption of arsenic from aqueous solution using agricultural residue 'rice polish'. *Journal of Hazardous Materials, 166*, 1050-1059.

Rives, J., Fernandez-Rodriguez, I., Gabarrell, X., & Rieradevall, J. (2012). Environmental analysis of cork granulate production in Catalonia – Northern Spain. *Resources, Conservation and Recycling, 58*, 132-142.

Sari, A., Uluozlü, O., & Tüzen, M. (2011). Equilibrium, thermodynamic and kinetic investigations on biosorption of arsenic from aqueous solution by algae (*Maugeotia genuflexa*) biomass. *Chemical Engineering Journal, 167*, 155-161.

Sen, A., Olivella, A., Fiol, N., Miranda, I., Villaescusa, I., & Pereira, H. (2012). Removal of chromium(VI) in aqueous environments using cork and heat-treated cork samples from *Quercus cerris* and *Quercus suber*. *BioResources, 7*, 4843-4857.

Shafique, U., Ijaz, A., Salman, M., Zaman, W., Jamil, N., Rehman, R., & Javaid, A. (2012). Removal of arsenic from water using pine leaves. *Journal of the Taiwan Institute of Chemical Engineers, 43*, 256-263.

Sharma, A., Tjell, J., Sloth, J., & Holm, P. (2014). Review of arsenic contamination, exposure through water and food and low cost mitigation options for rural areas. *Applied Geochemistry, 41*, 11-33.

Tuzen, M., Sari, A., Mendil, D., Uluozlu, O., Soylak, M., & Dogan, M. (2009). Characterization of biosorption process of As(III) on green algae *Ulothrix cylindricum*. *Journal of Hazardous Materials, 165*, 566-572.

Ungureanu, G., Santos, S., Boaventura, R., & Botelho, C. (2015). Arsenic and antimony in water and wastewater: Overview of removal techniques with special reference to latest advances in adsorption. *Journal of Environmental Management, 151*, 326-342.

Villaescusa, I., Fiol, N., Cristiani, F., Floris, C., Lai, S., & Nruchi, V. (2002). Copper(II) and nickel(II) uptake from aqueous solutions by cork wastes: a NMR and potentiometric study. *Polyhedron, 21*, 1363-1367.

Villaescusa, L., Fiol, N., Poch, J., Bianchi, A., & Bazzicalupi, C. (2011). Mechanism of paracetamol removal by vegetable wastes: the contribution of [pi]-[pi] interactions, hydrogen bonding and hydrophobic effect. *Desalination, 270*, 135-142.

Yusof, A., & Malek, N. (2009). Removal of Cr(VI) and As(V) from aqueous solutions by HDTMA-modified zeolite Y. *Journal of Hazardous Materials, 162*, 1019-1024.

Appendix

A. Cork as an adsorbent

Table A 1 - Table of maximum sorption capacity values for the different pollutants removed by cork according to Langmuir adsorption isotherm model

Pollutant	Cork granulometry (mm)	pH	Temperature (°C)	Q_{max} (mg/g)	Source
Ofloxacin	< 0.42	4	25	31.1	Crespo-Alonso et al., 2013
Ofloxacin	< 0.42	7	25	26.0	Crespo-Alonso et al., 2013
Ofloxacin	< 0.42	9	25	24.9	Crespo-Alonso et al., 2013
Ofloxacin	0.42 - 0.84	4	25	31.1	Crespo-Alonso et al., 2013
Ofloxacin	0.42 - 0.84	7	25	26.0	Crespo-Alonso et al., 2013
Ofloxacin	0.42 - 0.84	9	25	37.9	Crespo-Alonso et al., 2013
Chrysoidine	< 0.42	4	n.s.	36.3	Nurchi et al., 2014
Chrysoidine	< 0.42	7	n.s.	57.3	Nurchi et al., 2014
Chrysoidine	0.42 - 0.84	7	n.s.	44.6	Nurchi et al., 2014
Guaiacol	20 x 10 x 2	n.s.	n.s.	125	Karbowiak et al., 2010
4-Methylguaiacol	20 x 10 x 2	n.s.	n.s.	159	Karbowiak et al., 2010
4-Ethylguaiacol	20 x 10 x 2	n.s.	n.s.	164	Karbowiak et al., 2010
4-Propylguaiacol	20 x 10 x 2	n.s.	n.s.	180	Karbowiak et al., 2010
4-Vinylguaiacol	20 x 10 x 2	n.s.	n.s.	237	Karbowiak et al., 2010
4-Ethylphenol	20 x 10 x 2	n.s.	n.s.	134	Karbowiak et al., 2010

Bifenthrin	1 – 2	n.s.	n.s.	260	Domingues et al., 2005
Bifenthrin	3 – 4	n.s.	n.s.	55	Domingues et al., 2005
α-cypermethin	1 – 2	n.s.	n.s.	303	Domingues et al., 2007
α-cypermethin	3 - 4	n.s.	n.s.	136	Domingues et al., 2007
Paracetamol	0.63 – 0.75	n.s.	n.s.	990	Villaescusa et al., 2011
Eugenol	20 x 10 x 2	n.s.	n.s.	306	Karbowiak et al., 2010
Acenaphthene	0.25 – 0.42	n.s	n.s	46±25	Olivella et al., 2011
Fluorene	0.25 – 0.42	n.s	n.s	49±26	Olivella et al., 2011
Phenanthrene	0.25 – 0.42	n.s	n.s	32±5	Olivella et al., 2011
Anthracene	0.25 – 0.42	n.s	n.s	26±18	Olivella et al., 2011
Pyrene	0.25 – 0.42	n.s	n.s	32±4	Olivella et al., 2011
Benz(a)anthracene	0.25 – 0.42	n.s	n.s	26±8	Olivella et al., 2011
Chrysene	0.25 – 0.42	n.s	n.s	23±5	Olivella et al., 2011
Benzo(b)fluoranthene	0.25 – 0.42	n.s	n.s	28±12	Olivella et al., 2011
Benzo(K)fluoranthene	0.25 – 0.42	n.s	n.s	21±7	Olivella et al., 2011
Benzo(a)pyrene	0.25 – 0.42	n.s	n.s	21±5	Olivella et al., 2011
Indeno(1,2,3-cd) pyrene	0.25 – 0.42	n.s	n.s	20±18	Olivella et al., 2011
Dibenz(a,h)anthracene	0.25 – 0.42	n.s	n.s	16±3	Olivella et al., 2011
Benzo(ghi)perylene	0.25 – 0.42	n.s	n.s	23±2	Olivella et al., 2011
Cadmium	0.04	6	20	9.65	Krika et al., 2012
Cadmium	0.04	6	30	12.48	Krika et al., 2012
Cadmium	0.04	6	40	14.77	Krika et al., 2012
Cadmium (II)	0.5 - 1	5	n.s.	2.4	López-Mesas et al., 2011
Chromium(III)	0.200 – 0.355	4	22	6.30	Machado et al., 2002
Chromium (VI)	1.0 – 1.5	2.0 – 4.7	n.s.	17.0	Fiol et al., 2003
Copper(II)	0.42 - 0.84	6	25	2.64	Villaescusa et al., 2002

Copper(II)	0.050 – 0.100	5	n.s.	20	Chubar et al., 2003
Nickel(II)	0.42 - 0.84	6	25	4.09	Villaescusa et al., 2002
Nickel(II)	0.050 – 0.100	5	n.s.	10	Chubar et al., 2003
Lead(II)	1 – 2	3 – 3.5	n.s.	5.3	Mota et al., 2006
Lead (II)	0.5 - 1	5	n.s.	13.6	López-Mesas et al., 2011
Zinc (II)	0.050 – 0.100	5	n.s.	25	Chubar et al., 2003

Adapted from Pintor et al. 2012.

B. Validation parameters of the analytical method

Table B 1 - Validation parameters of the analytical method.

Working range	3 – 50 mg/L
Coefficient of determination	≥ 0.995
Limit of detection (LOD)[a]	2- mg/L
Limit of quantification (LOQ)[b]	7 mg/L
b±s	0.30±2.05
Precision [As] = 20 mg/L; N = 10	RSD = 1.53%
Intermediate Precision [As] = 20 mg/L; N = 8	RSD = 4.16%
TWC* spiked with [As] = 12 mg/L	113%
WC* spiked with [As] = 12 mg/L	111%
TBC* spiked with [As] = 12 mg/L	109%
BC* spiked with [As] = 12 mg/L	112%

a LOD is defined as 3 times the standard deviation of the blank

b LOQ is defined as 10 times the standard deviation of the blank

* Water solutions after contact with the respective adsorbent.