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da Silva Dias**

Produção de carvões ativados por pirólise em micro-ondas de resíduos industriais para a remoção de fármacos da água

Production of activated carbons by microwave pyrolysis of industrial wastes for the removal of pharmaceuticals from water



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Dissertação apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Mestre em Estudos Ambientais, realizada sob a orientação científica da Professora Doutora Maria Isabel da Silva Nunes, Professora Auxiliar do Departamento de Ambiente e Ordenamento da Universidade de Aveiro e sob a co-orientação científica da Doutora Vânia Maria Amaro Calisto, Estagiária de Pós-Doutoramento do Departamento de Química da Universidade de Aveiro, e do Professor Doutor Valdemar Inocêncio Esteves, Professor Auxiliar do Departamento de Química da Universidade de Aveiro.

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À minha avó pelo exemplo de humildade e resiliência, por todo o carinho e por cada palavra amiga. Deixou muitas saudades... Até um dia, com amor, da sua Raquelinha.

“Not everything that counts can be counted, and not everything that can be counted counts” Albert Einstein

o júri

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palavras-chave

Adsorção; Carvões ativados; Ativação química; Pirólise por micro-ondas; Fármacos; Ambiente; Tratamento de água; Valorização de resíduos.

resumo

Sendo os fármacos compostos biologicamente ativos, a sua presença nos recursos hídricos tem gerado preocupações devido aos efeitos adversos em organismos não-alvo. Sendo os tratamentos convencionais, aplicados nas estações de tratamento de águas residuais (ETARs), ineficientes para a remoção destes contaminantes, as ETARs são apontadas como a principal fonte de fármacos no meio ambiente. O processo de adsorção, enquanto tratamento avançado para a remoção de fármacos da água, em particular com o uso de carvões ativados (CAs), tem-se mostrado um processo de fácil aplicação e eficiente, sem formação de subprodutos.

Como a produção de CAs pode ser um processo dispendioso, devido aos requisitos energéticos e ao uso de precursores de elevado custo, a alternativa pirólise em micro-ondas (MO) de lama primária (LP) da indústria papelreira pode ser uma solução promissora, contribuindo simultaneamente para a valorização de resíduos industriais. Neste trabalho, os CAs foram produzidos por pirólise em MO de LP impregnada com KOH (agente ativante) durante 10 min a 800 W, lavados com ácido clorídrico e crivados para obtenção da fração de partículas com dimensão inferior ou igual a 180 μm . Obtiveram-se diferentes CAs alterando as razões de agente ativante:precursor, nomeadamente 0.5:1, 1:1 e 1.5:1. Os CAs produzidos foram física e quimicamente caracterizados. No sentido de avaliar o desempenho dos CAs produzidos, realizaram-se testes de adsorção em descontinuo com água ultra-pura para determinar a percentagem de adsorção do anti-epilético carbamazepina (CBZ). O efeito da concentração de CA e o efeito do tempo de contacto também foram testados.

Os resultados obtidos demonstraram que, de um modo geral, os CAs produzidos numa razão de 0.5:1 de agente ativante:precursor apresentaram áreas superficiais específicas (S_{BET}) entre 773 e 1190 m^2/g e elevadas percentagens de remoção de CBZ de soluções de água ultra-pura, acima de 80 %, para concentrações de CA de 0.1 g/L e tempos de contacto de 24 h. Os CAs produzidos em laboratório demonstraram ter uma estrutura porosa mais desenvolvida do que o CA comercial de referência e S_{BET} comparáveis. Todavia, para as mesmas condições experimentais, diferentes lotes de produção originaram CAs com propriedades e desempenhos diferentes, denotando que mais trabalho de investigação deve ser investido de modo a otimizar o seu processo de produção, tornando-o repetível.

keywords

Adsorption; Activated Carbons; Chemical activation; Microwave pyrolysis; Pharmaceuticals; Environment; Water treatment; Waste valorisation.

abstract

The presence of pharmaceuticals in water bodies, being biologically active compounds, have raised concerns due to the adverse effects in non-target organisms. With the conventional treatments, applied in the wastewater treatment plants (WWTPs), being inefficient for the removal of these contaminants, WWTPs are pointed out as the main source of pharmaceuticals into the environment. The use of adsorption, as an advanced treatment for the removal of pharmaceuticals from water, in particular by using activated carbons (ACs), has shown to be an easy-handling and cost-efficient process, without sub-products formation.

Since the production of ACs can be an expensive process, due to the high energy requirements and the use of expensive precursors, the alternative microwave (MW) pyrolysis of paper mill primary sludge (PS) can be a promising solution, contributing simultaneously for industrial waste valorisation. In the scope of this work, ACs were produced by MW pyrolysis of PS impregnated in KOH (activating agent) for 10 min at 800 W, washed with hydrochloric acid and sieved to obtain the fraction of particles with a size up to 180 μm . Different ACs were obtained by changing activating agent:precursor ratios, namely 0.5:1, 1:1 and 1.5:1. The produced ACs were physico-chemically characterised. In order to assess the performance of the produced ACs, batch adsorption experiments were performed with ultra-pure water to determine the adsorption percentages of the anti-epileptic carbamazepine (CBZ). The effect of AC dosage and the effect of contact time were also tested.

The obtained results have shown that, overall, the ACs produced with an activating agent:precursor ratio of 0.5:1 presented specific surface areas (S_{BET}) between 773 and 1190 m^2/g and high percentages of CBZ removed from ultra-pure water solutions, above 80 %, for AC dosages of 0.1 g/L and a contact time of 24 h. The lab-made ACs have shown a more developed porous structure than the reference commercial AC and comparable S_{BET} . Nevertheless, under the same experimental conditions, different production batches resulted in ACs with different properties and performances, highlighting that further research work is required to optimise its production process, making it repeatable.

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Nomenclature

A_{CBZ}	CBZ peak area
A_{IS}	IS peak area
AC	Activated carbon
AOP	Advanced oxidation processes
BET	Brunauer–Emmett–Teller
BS	Biological sludge
CBZ	Carbamazepine
CZE	Capillary zone electrophoresis
D	Average pore diameter (nm)
EC	Emerging contaminant
EOF	Electroosmotic flow
HPLC	High performance liquid chromatography
IC	Inorganic carbon
IR	Impregnation ratio
IS	Internal standard
IUPAC	International Union of Pure and Applied Chemistry
K_{ow}	Octanol-water partitioning coefficient
L	Average micropore width (nm)
LOD	Limit of detection
LOQ	Limit of quantification
MEKC	Micellar electrokinetic chromatography
MW	Microwave
OC	Organic carbon
PS	Primary sludge
PZC	Point of zero charge
RSD	Relative standard deviation
S_{BET}	Specific surface area (m^2/g)
SDS	Sodium dodecyl sulphate

TC	Total carbon
TOC	Total organic carbon
V_p	Total pore volume (cm^3/g)
W_0	Total micropore volume (cm^3/g)
WWTP	Wastewater treatment plant

CHAPTER 1: INTRODUCTION

1.1. WATER CONTAMINATION BY EMERGING CONTAMINANTS: THE PROBLEMATIC OF PHARMACEUTICALS

Pharmaceuticals are biologically active agents designed to induce physiological responses in humans or animals (Calisto, 2011; Halling-Sorensen et al., 1998; Klatte et al., 2017; Vasquez et al. 2014). These organic compounds are synthesized for the prevention, treatment and reduction of diseases symptoms, which contributes for the improvement of health and quality of life. The continuous and increasingly consumption of pharmaceuticals worldwide is related to factors such as population growth, increase of life expectancy, population ageing, increase of chronic diseases, development of new and less expensive drugs, to name a few (Calisto, 2011; Jelic et al., 2012; Kalaji & Rastogi, 2017; OECD, 2015).

After ingestion, pharmaceuticals are not completely metabolised by the human or animal organism, and are excreted as unchanged substances (parent compounds) or transformed products (metabolites) (Calisto, 2011; Halling-Sorensen et al., 1998; Rivera-Utrilla et al., 2013). Pharmaceuticals excreted by humans or animals, in their original or metabolised form, follow different pathways as illustrated in Figure 1. Human excreted medicines, usually pass through wastewater treatment plants (WWTPs) before they enter into the environment. Unused or expired medications are also inappropriately disposed into sinks/toilets or trash containers, ending up going to WWTPs or to landfills, respectively. In what concerns veterinary medicine, excreted pharmaceuticals are more likely to enter directly into the environment through soil and/or water contamination without a prior treatment at a WWTP (Halling-Sorensen et al., 1998; Khetan & Collins, 2007; Klatte et al., 2017; Kümmerer, 2001; Li et al., 2015; Ternes et al., 2004; Vasquez et al., 2014; Wang & Wang, 2016; Wilkinson et al., 2017; Zhang et al., 2008). Regardless of their degree of metabolization, excreted compounds can continue to be transformed by biotic and abiotic processes (by physico-chemical reactions such as oxidation, reduction and hydrolysis) in both WWTPs and receiving water bodies (Halling-Sorensen et al., 1998; Rivera-Utrilla et al., 2013; Vasquez et al., 2014; Verlicchi et al., 2012; Wilkinson et al., 2017). Pharmaceuticals may be referred to as emerging contaminants (ECs), since they are degradation-resistant synthetic or natural compounds, that are still unregulated in what concerns environmental

allowed levels, and have the potential to cause adverse effects to non-target organisms, including humans (Rivera-Utrilla et al., 2013; Rodriguez-Narvaez et al., 2017; Wilkinson et al., 2016).

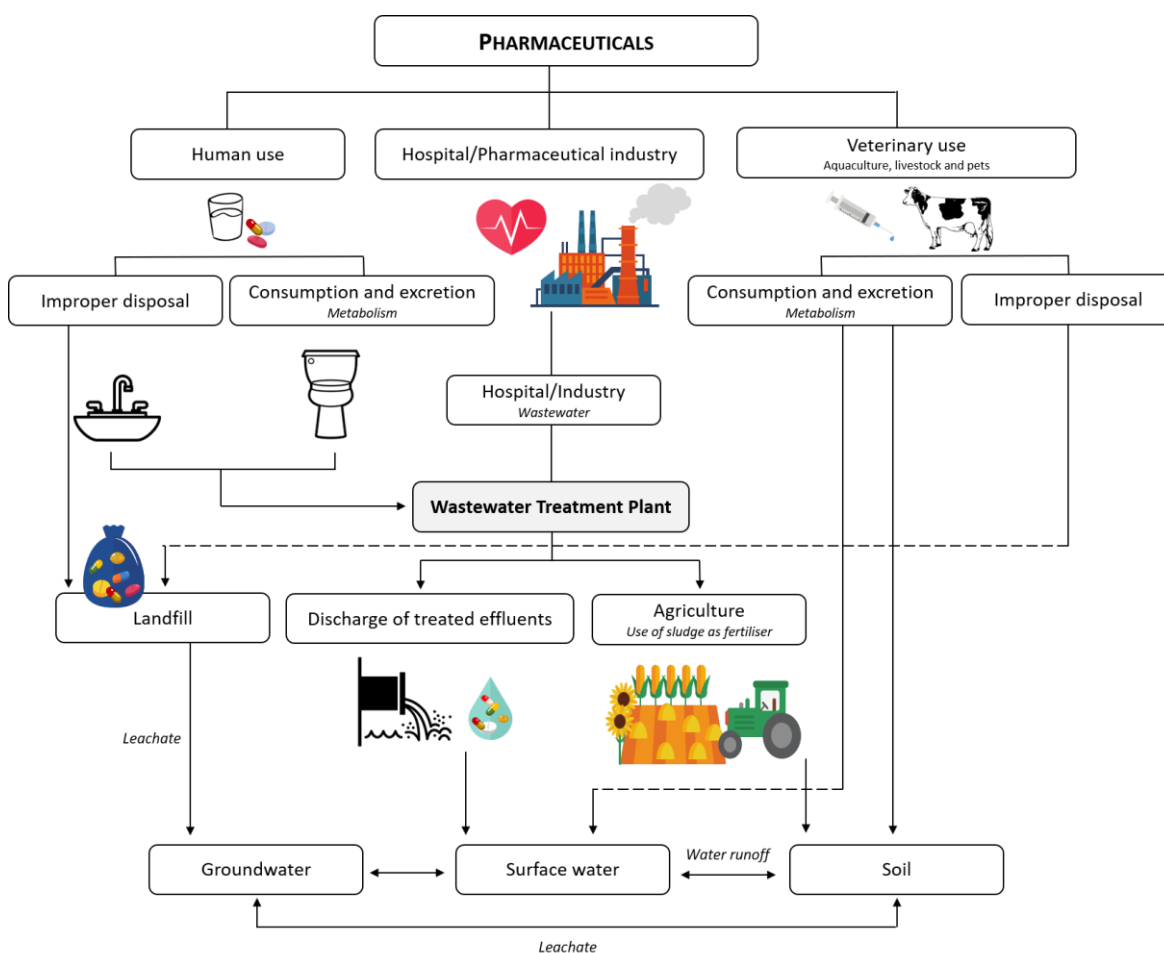


Figure 1. Pathways for the entrance of pharmaceuticals into the environment (adapted from Calisto, 2011)

WWTPs are designed to remove regulated contaminants such as pathogens, organic and inorganic compounds (in concentrations at mg/L range), by primary and secondary treatments, in order to meet the effluent quality standards for its disposal into the water bodies (Bolong et al., 2009; Deblonde et al., 2011; Jelic et al., 2012; Verlicchi et al., 2012). Nevertheless, WWTPs are considered to be the main point sources of pharmaceuticals into the environment, since the conventional treatments are inefficient to remove ECs from the wastewaters, which results in their discharge and contamination of aquatic and terrestrial ecosystems (Bolong et al., 2009; Jelic et al., 2012; Klatte et al., 2017; Petrie et al., 2015;

Petrović et al., 2003; Rivera-Utrilla et al., 2013). Tertiary treatments are optional and more expensive processes, that can be applied at WWTPs in order to improve the quality of the discharged effluent. These advanced treatments can be chemical, biological and physical processes (also addressed as phase-changing processes) (Jelic et al., 2012; Luo et al., 2014; Rodriguez-Narvaez et al., 2017; Wang & Wang, 2016). Advanced oxidation processes (AOP), membrane processes, biological processes and adsorption onto activated carbon (AC), are commonly addressed in literature as promising solutions to remove ECs from water, including pharmaceuticals (Bo et al., 2015; Luo et al., 2014; Rodriguez-Narvaez et al., 2017; Wang & Wang, 2016).

Due to the development of analytical methodologies, pharmaceuticals were detected in the environment as complex mixtures of several different classes of pharmaceuticals, in their transformed or original form. Some of the detected classes include analgesics, antibiotics, anti-inflammatory, diuretics, beta-blockers, anti-hypertensive, hormones, psychiatric, anti-histamines, anti-epileptics and lipid regulators, which even in small quantities (ng to µg/L range) can adversely impact ecosystems (Calisto, 2011; Rivera-Utrilla et al., 2013; Rodriguez-Narvaez et al., 2017; Vasquez et al., 2014). Klatte *et al.* (2017) highlight the problem of disease resistance to pharmaceuticals due to the exposure to low concentration of ECs and warn about the low levels at which hormones start having effects. The World Health Organization (WHO, 2014) also points out the problem related to antibiotic resistance, since the projections indicate that, in the future, even infections from small injuries may lead to death. The presence of pharmaceuticals in drinking water does not exceed trace levels (ng/L), so they would not cause an acute reaction (Klatte et al., 2017; Kümmerer, 2001; Rivera-Utrilla et al., 2013; Wilkinson et al., 2016, 2017), however it increases the possibility of potential impacts due to a cumulative effect and life-cycle exposures (Gaffney et al., 2016; Rivera-Utrilla et al., 2013; Vasquez et al., 2014; Wilkinson et al., 2016).

Carbamazepine (CBZ), the pharmaceutical studied under the scope of this work, is an anti-epileptic used for the treatment of mental disorders whose molecular structure is illustrated in Figure 2. It is a commonly detected pharmaceutical in WWTPs and surface waters due to high ingestion levels (around 1000 mg per patient per day) and its high

recalcitrance to the conventional wastewater treatments (Bahlmann et al., 2014; Brezina et al., 2017; Donner et al., 2013; Jelic et al., 2012; Luo et al., 2014; Zhang et al., 2008).

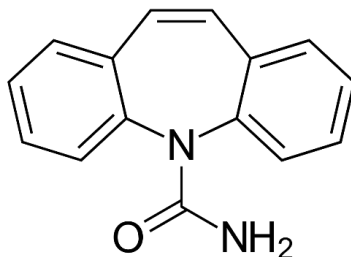


Figure 2. Molecular structure of CBZ

CBZ is highly metabolised by the liver, presenting metabolites as biologically active as the parent compound (Bahlmann et al., 2014; Jelic et al., 2012; Zhang et al., 2008). Biological treatments at WWTPs are associated to the conversion of CBZ metabolites into their original forms, which can be related to higher concentrations of parent compound in the effluent when compared to the influent (Luo et al., 2014). It is known that CBZ is responsible to harmfully impact aquatic ecosystems, including invertebrates, fish and algae (Brezina et al., 2017), being crucial to develop feasible processes for its removal.

1.2. REMOVAL OF PHARMACEUTICALS FROM CONTAMINATED WATER BY ADSORPTION ONTO ACTIVATED CARBONS

1.2.1. BASIC DESCRIPTION OF THE ADSORPTION PROCESS

Adsorption is a surface phenomenon, which consists of the accumulation of particles (atoms, ions or molecules) on a surface or interface, when it occurs between two distinct physical states of matter such as liquid-solid, gas-solid or gas-liquid interfaces. The adsorbed component is the adsorbate, while the material in which particles are concentrated is referred as the adsorbent (De Gisi et al., 2016; Snoeyink, 1990; Weber Jr., 1972). Only adsorption between liquid-solid interfaces will be focused, since this work, as described below, is aimed to study the adsorptive removal of pharmaceuticals from water by using AC.

Since the adsorbate can be polar or non-polar and neutral or electrically charged, the adsorption process can occur due to electrostatic attraction, Van der Waals attraction or by covalent bond (Jaria, 2014; Weber Jr., 1972). Adsorption processes based on electrostatic interaction, also called exchange adsorption, result from the concentration of ions on charged sites of the adsorbent where they remain fixed. When results from weaker interactions, such as Van der Waals interactions, adsorption is considered to be physical, physisorption. If the adsorbate interacts with the adsorbent through stronger interactions, such as covalent bonds, the adsorption process is known as chemisorption. Physisorption, as opposed to chemisorption, is a reversible process, making it suitable for separation/extraction methods (De Gisi et al., 2016; Weber Jr., 1972).

Molecules accumulate onto a solid surface until the amount of solute in the solution reaches a dynamic equilibrium with the amount of solute adsorbed onto the adsorbent, that is, when the number of adsorbed and desorbed molecules is equal. In the equilibrium, the amount of solute concentrated onto the adsorbent as a function of the adsorbate's concentration, at constant temperature, can be described by an adsorption isotherm, as shown in Figure 3 (Bansal & Goyal, 2005; De Gisi et al., 2016; Snoeyink, 1990; Weber Jr., 1972). It expresses q_e as a function of C_e where, q_e is the adsorption capacity, that is, the amount of adsorbed solute per unit of mass of adsorbent at the equilibrium (mg/g) and C_e is the concentration of solute in solution at the equilibrium (mg/L). A higher value of q_e represents a more efficient adsorption, that is, more solute is accumulated onto the solid surface, resulting in a lower concentration of adsorbate in the solution (De Gisi et al., 2016; Snoeyink, 1990; Weber Jr., 1972). The adsorption of solute molecules onto the surface of an adsorbent may occur in single or multimolecular layers. Langmuir, Brunauer-Emmett-Teller (BET) and Freundlich are some adsorption models that can be used to describe this accumulation process (Snoeyink, 1990; Weber Jr., 1972).

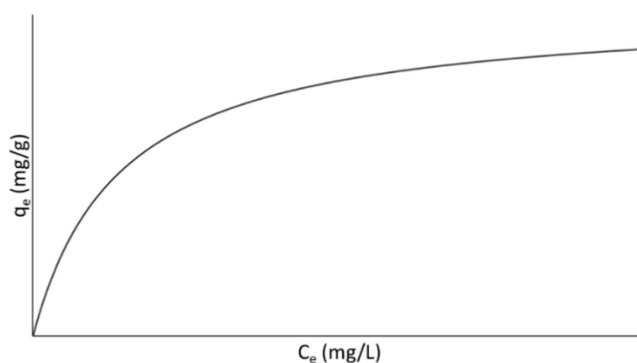


Figure 3. Example of the graphical representation of an adsorption isotherm

The adsorption process is influenced by factors related to the adsorbate/adsorbent properties and operating conditions, as identified in Figure 4 (Ferreira, 2017; Luo et al., 2014; Mansour et al., 2017; Snoeyink, 1990; Weber Jr., 1972), that are decisive for the removal of contaminants, including pharmaceuticals.

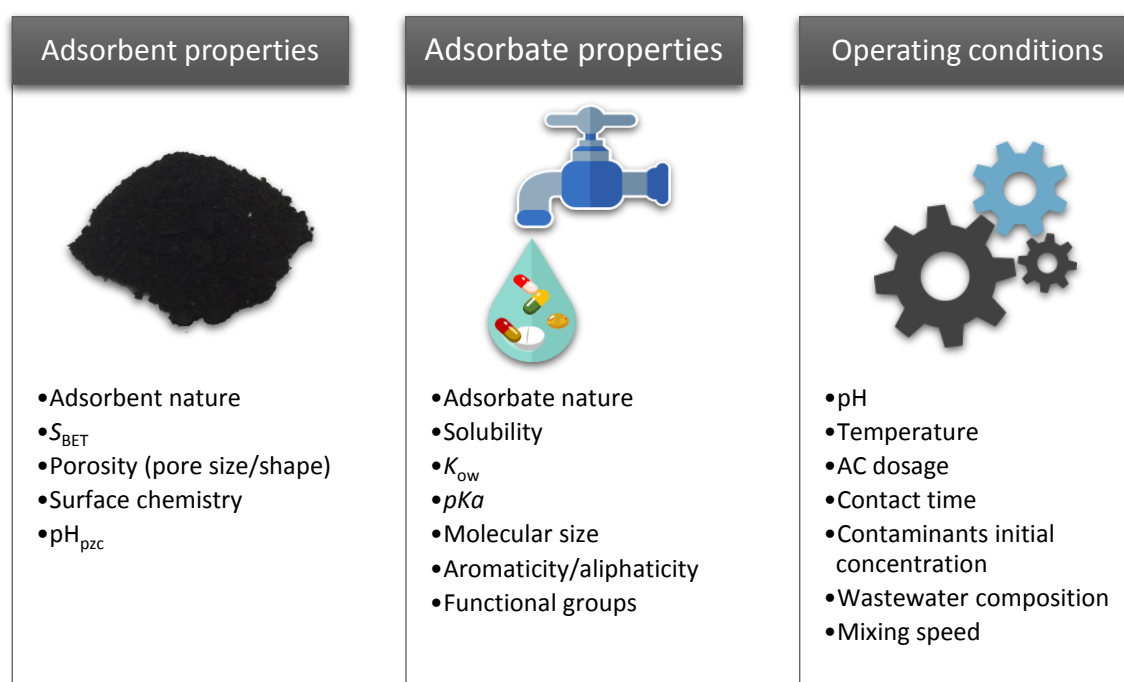


Figure 4. Examples of adsorbent/adsorbate physico-chemical properties and operating conditions that influence the adsorption mechanism

Calisto *et al.* (2015) observed that the pH strongly affected the adsorption mechanism of pharmaceuticals onto the produced adsorbent and therefore, the

pharmaceutical uptake was determined by the adsorbent surface chemistry. Mestre *et al.* (2014) referred the effect of the adsorbate molecular size on the adsorption process, in which the physically activated adsorbent presented the appropriate textural properties to adsorb the pharmaceutical with higher molecular weight. Bolong *et al.* (2009) addressed the competition for the same adsorption active sites and/or pore blocking, which could reduce the rate of adsorption and/or imply the use of a higher dosage of adsorbent (Bolong *et al.*, 2009; Snoeyink, 1990). Considering the complexity of the adsorption process, only some factors that affect the adsorption mechanism were briefly described.

Being a surface process, adsorption is favoured by adsorbents with high specific surface area (S_{BET}) and well-developed porosity (Hesas *et al.*; Peláez-Cid *et al.*, 2012; Rodriguez-Narvaez *et al.*, 2017). According to their nature, adsorbents may be carbonaceous, such as AC, graphite and carbon nanotubes, or non-carbonaceous, like clay and silica (Akhtar *et al.*, 2016; Baccar *et al.*, 2012; Mansour *et al.*, 2017; Rodriguez-Narvaez *et al.*, 2017). In the context of this work, only carbon-based adsorbents, namely ACs, will be addressed.

The adsorbate solubility is a determining factor, since a low solubility in the aqueous solution induces higher adsorption (Weber Jr., 1972). The octanol-water partitioning coefficient (K_{ow}) is related to the interaction of a solute with the adsorbent. In aqueous solutions, high values of K_{ow} are associated with adsorbates with lower affinity for water and therefore, a higher adsorption capacity. Contrarily, solutes with low K_{ow} preferably remain in the liquid phase due to their higher affinity for water and therefore, are less available to adsorb (Kushwaha *et al.*, 2013; Mansour *et al.*, 2017). Considering the particle size, adsorbates with a higher molecular weight, usually, tend to have lower uptake rates by microporous adsorbents, due to a limited access to the active sites of the adsorbent (Snoeyink, 1990; Weber Jr., 1972).

The pH value is an important factor since it determines the ionization degree of the adsorbate in solution and the surface charge of the adsorbent, influencing the interactions between them (Kushwaha *et al.*, 2013; Weber Jr., 1972). The point of zero charge (PZC) is related to the pH value at which the adsorbent surface charge is neutral ($\text{pH} = \text{pH}_{\text{pzc}}$). Positively charged adsorbents can be related to surface protonation (in acidic media) when

$\text{pH} < \text{pH}_{\text{pzc}}$. The presence of basic surface functional groups also contributes for a net of positive charge at the adsorbent surface. In alkaline media, the negatively charged adsorbent surface is caused by the ionization of acidic functional groups when $\text{pH} > \text{pH}_{\text{pzc}}$ (Bansal & Goyal, 2005; Kushwaha et al., 2013; Luo et al., 2014; Mansour et al., 2017; Moreno-Castilla, 2004).

1.2.2. ACTIVATED CARBON: DEFINITIONS AND APPLICATIONS

ACs, also called solid sponges, are the most commonly used adsorbents due to their ability to cope with a great diversity of different molecules, organic and inorganic contaminants, of different sizes (De Gisi et al., 2016; Foo & Hameed, 2010; Peláez-Cid et al., 2012). ACs are characterised by a system of micropores, S_{BET} and a surface chemistry, which are the basis for their adsorption capacity. Because of their high adsorption capacity, ideal for small molecules, their applications include air purification, water treatment, colour, odour and taste removal (Jaria, 2014; Peláez-Cid et al., 2012; Sarici-Ozdemir & Onal, 2016; Yahya et al., 2015). Commercial AC can be obtained from several carbonaceous sources such as coal, lignite, wood and bones (Mansour et al., 2017; Peláez-Cid et al., 2012; Weber Jr., 1972). It is commonly produced as powder AC or granular AC, being the main difference the particle's size and, subsequently, their distinct applications. Regarding the size, the powder form has a dimension smaller than 0.1 mm, while granules comprise sizes between 0.6 and 4.0 mm (Bansal & Goyal, 2005; Mansour et al., 2017). AC is mainly composed by carbon, conventionally between 85 and 95 % for commercial AC, being the remaining components oxygen, hydrogen, sulphur, nitrogen and inorganic ash. The amounts of these elements depends on the precursor and production process (Bansal & Goyal, 2005). The ACs S_{BET} can range between 500 and 3000 m^2/g (Jaria, 2014; Peláez-Cid et al., 2012; Weber Jr., 1972).

ACs adsorptive properties result from the thermal transformation of a carbonaceous raw material, in which pores are formed due to the loss of volatile compounds and the random rearrangement of the carbon structure. The adsorption capacity improvement relies not only in the surface chemistry of the material, but also on the ACs internal surface (Jaria, 2014; Peláez-Cid et al., 2012; Weber Jr., 1972).

The internal surface is related to the well-developed porous structure of the AC, which indeed is the reason for its designation as activated (Jaria, 2014). According to the International Union of Pure and Applied Chemistry (IUPAC), pores can be classified as micropores, mesopores and macropores if they are smaller than 2 nm, between 2 and 50 nm, and bigger than 50 nm, respectively (IUPAC, 2014). A system of pores with different sizes and shapes, randomly distributed, contributes for the increase of the area available for adsorption, in which meso and macropores act as transport channels, allowing the adsorbate to access to micropores (Calisto et al., 2015; Jaria, 2014; Peláez-Cid et al., 2012; Weber Jr., 1972).

Regarding the chemical surface, ACs are composed by functional groups chemically bonded at the edges of the crystalline structure. The basicity of the AC surface is provided by functional groups such as carbonyls, chromenes, and pyrones, while the carboxylic groups, lactones, phenols and anhydrides (oxygen-based groups) are responsible for the surface acidic behaviour. Other groups such as hydroxyl, ether, quinone and anhydride can be found at the carbon surface (Foo & Hameed, 2012b, 2012a; Hesas et al., 2013; Yahya et al., 2015), as shown in Figure 5. The presence of these acidic and basic groups affects the surface charges and the adsorbate/adsorbent interactions (Akhtar et al., 2016; Jaria, 2014; Kushwaha et al., 2013; Yahya et al., 2015). Additionally, the reactivity of these functional groups allows the surface functionalization of the ACs (Jaria, 2014).

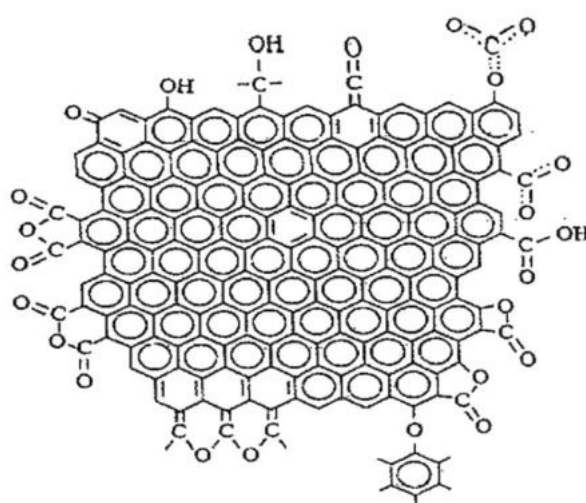


Figure 5. Typical functional groups that can be present on the AC surface (Yahya et al., 2015)

Available literature has pointed out the adsorption of pharmaceuticals onto AC as an attracting solution, highlighting advantages such as non-formation of by-products, versatility, good removal efficiency (at low concentrations of contaminants), low operational energy, non-selectivity and possibility for regeneration/reuse (Álvarez-Torrellas et al., 2016; Antunes et al., 2012; Calisto et al., 2017; Mansour et al., 2017; Mestre et al., 2014; Sotelo et al., 2014). Nonetheless, these adsorbents are not widely used due to their high costs (De Gisi et al., 2016; Mansour et al., 2017) and because contaminants are not mineralised (Pereira, 2017; Rodriguez-Narvaez et al., 2017).

1.2.3. PRODUCTION OF ACTIVATED CARBON

ACs porous structure, S_{BET} and surface chemistry, are highly influenced by the production process, that is, carbonaceous starting materials, carbonisation, activation and operating conditions (Hesas et al., 2013; Jaria, 2014; Peláez-Cid et al., 2012; Wahi et al., 2017; Weber Jr., 1972).

The production of ACs combines the carbonisation of a starting carbonaceous material with an activation process, that can be applied before, during or after carbonisation. Carbonisation is the thermal degradation (around 800 °C) of the precursor organic fraction, that is, the elimination of most of the non-carbon species, such as oxygen, hydrogen and nitrogen, released as gaseous and liquid by-products. The remaining elemental carbon forms a rigid carbon skeleton, composed of aromatic irregularly arranged structures and a rudimental porous structure (small and closed pores). In that sense, an amorphous, lower density material is formed, exhibiting similar characteristics to the starting material. Carbonisation is also referred to as pyrolysis, when it is carried out in an inert atmosphere (oxygen-free), provided by gases such as nitrogen (N_2 , commonly used) or argon, which also lead to a good porosity development. The activation of the carbonaceous structure, which can be physical or chemical, promotes the porosity development by creating new pores, unblocking obstructed pores, enlarging and/or merging the existing pores (Hesas et al., 2013; Jaria, 2014; Peláez-Cid et al., 2012; Wahi et al., 2017; Weber Jr., 1972).

In the physical or thermal activation, the AC is produced in two distinct phases: carbonisation and then activation. Carbonisation takes place in an inert atmosphere at temperatures that can vary from 400 to 950 °C. The resulting carbon structure is then activated, that is, pores are enlarged through a partial oxidation (gasification process) in an oxidizing atmosphere of air, steam (H_2O), carbon dioxide (CO_2) or a combination of these gases at temperatures ranging from 800 to 1100 °C (Jaria, 2014; Mansour et al., 2017; Peláez-Cid et al., 2012).

In the chemical activation, carbonisation and activation (usually) occur simultaneously. The precursor is impregnated with solutions of phosphoric acid (H_3PO_4), nitric acid (HNO_3), sodium hydroxide (NaOH), potassium hydroxide (KOH), zinc chloride (ZnCl_2) or potassium carbonate (K_2CO_3), to name a few activating agents, dried at 100 - 120 °C (or used as a paste, slurry), and then pyrolysed at temperatures between 400 and 800 °C. Activating agents differ in relation to the shape and size of the generated pores (since they act as template) and the nature of the functional groups added onto the AC surface, which is also related to the activating agent:precursor ratio. After the activation process, ACs need to be washed in order to remove residual activating agent and unblock obstructed pores. Some environmental disadvantages include the corrosiveness and hazardousness of activating agents, metal contamination (Jaria, 2014; Mansour et al., 2017; Peláez-Cid et al., 2012) and eutrophication potential caused by the presence of phosphorous (Mestre et al., 2011). Under these circumstances, K_2CO_3 is highlighted as being one of the most environmentally friendly chemical activating agent (Peláez-Cid et al., 2012).

Chemical activation provides ACs with a higher S_{BET} , lower energy demands, higher control of the pore size distribution and shorter activation times when compared to physical activation. However, the latter stands out for being cheaper, free from corrosive reagents and with no impurities coming from the activating agent (Jaria, 2014; Peláez-Cid et al., 2012).

1.2.4. THE USE OF ALTERNATIVE PRECURSORS FOR ACTIVATED CARBON PRODUCTION

In the past few years, more attention has been given to the use of lignocellulosic materials for the production of AC, such as fruit peels/shells/stones, wood, grape bagasse, sisal, cork and cereal wastes, to name a few (Antunes et al., 2012; De Gisi et al., 2016; Mestre et al., 2011, 2014; Peláez-Cid et al., 2012; Yahya et al., 2015). At a given point, these sources of biomass acted as a carbon dioxide sequester and their energy content resulted from solar radiation storage during the photosynthesis process, in which carbon dioxide and water were converted into oxygen and carbonaceous sources, including simple sugars, lipids and polymers such as starch, proteins, cellulose, hemicellulose and lignin (Peláez-Cid et al., 2012; Zhang et al., 2010). The use of these starting materials aroused interest due to their renewable nature, high carbon content, low cost and their large abundance, making them more affordable than the commercial AC precursors (obtained from expensive and/or non-renewable sources) (Ahmed & Theydan, 2014a; Jaria, 2014; Kushwaha et al., 2013; Mansour et al., 2017; Peláez-Cid et al., 2012; Yahya et al., 2015). The expensiveness of the ACs includes factors such as the starting material source, the high energy requirements for the production/regeneration process, costs related to the activation process and low production yields (Calisto et al., 2015; Peláez-Cid et al., 2012; Rodriguez-Narvaez et al., 2017).

Besides agricultural precursors, the production of ACs from industrial wastes can be favourable from both economic and environmental point of view. In the context of the present work, paper mill primary sludge (PS), a waste derived from treatment of the effluents generated by the paper mill industry, was used for AC production purposes.

Paper mill industry operates with large amounts of fresh water, generating high volumes of effluents that require a prior treatment to assure the effluent quality standards before its disposal into water bodies (Adhikari & Bhattacharyya, 2015; Pervaiz & Sain, 2015; Soucy et al., 2014). PS is a carbon-rich waste, mainly composed by cellulose, hemicellulose and lignin, that results from flocculation/sedimentation operations applied during a primary treatment. Then, the effluent is subjected to a biological treatment, in which the organic matter is degraded by the action of microorganism, from which biological sludge (BS) is obtained (Adhikari & Bhattacharyya, 2015; Buruberri et al., 2015; Calisto et al., 2014;

Pervaiz & Sain, 2015; Soucy et al., 2014). Paper mill industry is responsible for the production of significant amounts of sludge, around 45 kg of dry sludge per ton of paper produced (Adhikari & Bhattacharyya, 2015; Soucy et al., 2014). With an annual production higher than 200 000 tons, sludge was pointed out as being the major fraction of solid waste produced in the Portuguese mills from 2014 to 2016 (CELPA, 2016).

The cruciality in reducing the volume of waste and the development of valorisation measures, in order to avoid landfilling, have been emphasised by the Waste Framework Directive (2008/98/EC) (European Parliament and the Council of the European Union, 2008). Paper mill solid wastes are commonly landfilled, incinerated (for energy recovery) and used for agricultural purposes. Landfilling has been reducing over time and is discouraged due to environmental impacts (Buruberri et al., 2015; Monte et al., 2009; Pervaiz & Sain, 2015). To tackle with the high amounts of paper mill sludge, some waste management/valorisation measures include its incorporation in building materials, road building, composting (Monte et al., 2009), its use as wood adhesive and for biofuels production (Pervaiz & Sain, 2015). Moreover, due to its carbonaceous nature, paper mill sludge can also be converted into ACs, contributing for the production of a cost-efficient adsorbent (Calisto et al., 2014; Jaria et al., 2017; Jiang & Ma, 2011; Namazi et al., 2015; Pervaiz & Sain, 2015). A process in which waste is re-inserted in the production chain and used as a secondary raw material for the production of value-added products, is fitted within a circular economy context. Contrarily, in a linear economy context, goods are produced from primary sources, used and end-of-life products are disposed as useless wastes, according to a non-sustainable life cycle (Khalili et al., 2000; Liguori & Faraco, 2016).

Considering the removal of pharmaceuticals from water, the ACs produced from both agricultural (Álvarez-Torrellas et al., 2016; Mestre et al., 2011, 2014) and industrial wastes, specifically PS (Jaria et al., 2015, 2018), have shown results regarding S_{BET} , adsorption capacity and adsorption kinetics, comparable to those obtained for commercial ACs. The AC produced by Jaria *et al.* (2018) from conventional pyrolysis of PS, has shown to be more efficient than the commercial AC to remove pharmaceuticals, even using a low dosage of absorbent, presenting a S_{BET} between 1389 and 1627 m²/g and a removal capacity around 78 % (overnight shaking at 80 rpm, 25 °C and an AC dosage of 0.015 g/L).

1.3. MICROWAVE PYROLYSIS: AN ALTERNATIVE TO CONVENTIONAL PYROLYSIS FOR ACTIVATED CARBON PRODUCTION

Microwave (MW) heating is a thermochemical process in which the heat is produced by electromagnetic waves (frequency ranging from 300 MHz to 300 GHz). Overall, published studies address the production of ACs by MW pyrolysis in 2.45 GHz adapted domestic MWs (Foo & Hameed, 2012c; Jones et al., 2002; Liu et al., 2010).

In the conventional pyrolysis in a muffle furnace, samples are heated by conduction and convection mechanisms, from an external source, occurring a temperature gradient from the hot surface to the interior of the particle (Ahmed & Theydan, 2014b; Ania et al., 2005; Foo & Hameed, 2012c; Hesas et al., 2013; Wahi et al., 2017). Since precursors with different sizes and shapes are not uniformly heated during conventional heating, the release of the volatile compounds (gas diffusion) is not so effective, which can compromise the AC properties (Ahmed & Theydan, 2014b; Yang et al., 2010). Moreover, non-uniform heating requires higher heating times and energy inputs, and may also generate hotspots, that is, regions in the precursor where the temperature can reach extremely high values (Hesas et al., 2013; Jones et al., 2002; Yang et al., 2010).

Contrarily, MW radiation allows a rapid, uniform and selective heating. MWs are converted into heat at the molecular level of the precursor. When a carbonaceous material is subjected to MW radiation, with a certain frequency, its molecules (with an induced or permanent dipole) react through a dipole rotation. In order to be oriented towards the opposite direction of the applied field, the movement of the molecules causes a molecular agitation, which generates heat (Ania et al., 2005; Jones et al., 2002; Liu et al., 2010; Yang et al., 2010). Heating occurs by energy transference instead of heat transference (Hesas et al., 2013). In this context, temperature gradient occurs from the internal particles of the precursor to its cold surroundings, allowing a volumetric, effective (energy saving) and faster heating (Hesas et al., 2013; Saucier et al., 2015; Wahi et al., 2017; Yang et al., 2010). Thus, this thermal gradient allows higher temperatures in the precursors interior, which provides the volatilisation of low molecular weight compounds and the further development of pores (Hesas et al., 2013). Other advantages that can be pointed out

include: (1) easiness of heating control, (2) higher production yield with well-developed porosity and S_{BET} , (3) does not involve heating by convection, (4) it is a safer and easier methodology to manipulate, (5) the equipment is smaller, (6) requires lower energy demands and (7) produces less waste (Hesas et al., 2013; Jones et al., 2002; Li et al., 2009; Wahi et al., 2017).

Such as for the conventional pyrolysis, the starting material, heating temperature, gaseous atmosphere (gas type and flow rate), reaction time, physical/chemical activation agent, impregnation ratio (IR) and time, oxidative atmosphere, are some conditions that need to be considered when applying MW radiation (Hesas et al., 2013; Wahi et al., 2017). The main difference between conventional and MW heating is that, the sample heating occurs by manipulation of the MW power, which is indirectly related to the temperature. Radiation time is a determinant parameter given that longer heating periods can cause porous structure shrinkage, carbon burning and/or pores rupture, resulting in lower S_{BET} . In opposition, shorter radiation times and higher MW power favours porosity and S_{BET} development (Hesas et al., 2013; Liu et al., 2010; Wahi et al., 2017).

Contrarily to conventional pyrolysis, MW pyrolysis requires a prior activation since carbonaceous precursors are transparent to MW radiation (Hesas et al., 2013; Liu et al., 2010; Namazi et al., 2015; Saucier et al., 2015). The production of AC by MW pyrolysis can be achieved in two different ways:

- i. It can be produced by one-step chemical activation, in which the precursor is impregnated with a chemical agent that acts as absorber of MW radiation. A paste, referred to as slurry, is formed which can be directly carbonised by MW pyrolysis or can be previously dried (Hesas et al., 2013; Liu et al., 2010; Zaini & Kamaruddin, 2013);
- ii. It can be a two-steps production, in which the precursor is activated by conventional pyrolysis, forming a rudimental carbon skeleton that acts as MW radiation absorber allowing the precursor to carbonise. Then, the carbonised material can be physically/chemically activated and subjected to MW pyrolysis (Saucier et al., 2015; Zaini & Kamaruddin, 2013).

As shown in Table 1, the production of ACs in one-step requires lower heating times and therefore, are less energy demanding than ACs produced by two-steps MW pyrolysis (Table 2). Results found in literature have shown that S_{BET} values for ACs produced by conventional pyrolysis range between 600 and 1300 m^2/g (Baccar et al., 2012; González et al., 2009; Mestre et al., 2011, 2014; Rajapaksha et al., 2014; Tay et al., 2009), while ACs produced by MW pyrolysis exhibit higher S_{BET} with values ranging between 700 and 2000 m^2/g (Ahmed & Theydan, 2012; Deng et al., 2009; Foo & Hameed, 2012d, 2012b; Huang et al., 2011; Li et al., 2008, 2009; Liu et al., 2010; Saucier et al., 2015; Yang et al., 2010).

Despite of the good properties attained for ACs produced by MW pyrolysis of alternative precursors, few studies address the use of paper mill sludge as precursor for the production of ACs by MW radiation. Jiang and Ma (2011) applied MW radiation to paper mill sludge for waste disposal purposes, that is, to reduce the mass of sludge. Namazi *et al.* (2015) produced ACs by combining PS and BS (1:1 ratio); Nevertheless, the authors did not test the adsorption capacity of the produced materials. As far as it is known, there are no studies of paper mill sludge-based ACs, obtained through MW pyrolysis, to remove pharmaceuticals from water. Taking into account the large availability of this carbonaceous waste and the limitations related to the use of expensive ACs for water treatment, the production of ACs by MW pyrolysis of PS seems to be an optimist solution.

Table 1. Production yield and textural properties of ACs produced by one-step MW pyrolysis of alternative precursors

Precursor	Mass of precursor (g)	Activating agent	Activating agent:precursor ratio	MW power (W)	MW radiation time (min)	AC yield (%)	S_{BET} (m^2/g)	V_p (cm^3/g)	Adsorbate	Reference
Cocoa shell	30	Lime + ZnCl_2 + FeCl_3	1:1	360 - 1200	80 – 160 (s)	20	619	0.315	Diclofenac Nimesulide	(Saucier et al., 2015)
Siris seed pods	3	K_2CO_3	1.5:1	540	8	26.19	1676.61	0.708	Metronidazole	(Ahmed & Theydan, 2013)
Siris seed pods	3	KOH	1:1	620	8	22.48	1824.88	0.782	Ciprofloxacin Norfloxacin	(Ahmed & Theydan, 2014a)
Lotus stalks	-	H_3PO_4	1:2	700	15	40.01	1431	1.337	Oxytetracycline	(Huang et al., 2011)
Giant reed	1.5	KOH	2:1	620	10	9.1	1065.3	0.643	Amoxicillin	(Chayid & Ahmed, 2015)
Bamboo	5	H_3PO_4	1:1	350	20	47.8	1432	0.696	-	(Liu et al., 2010)
Paper mill sludge	-	NaOH	2:1	1200	5	13	660	-	-	(Namazi et al., 2015)
Cotton stalk	-	ZnCl_2	1.6:1	560	9	37.92	794.84	0.63	Methylene blue Iodine	(Deng et al., 2009)

Table 2. Production yield and textural properties of ACs produced by two-steps MW pyrolysis of alternative precursors

Precursor	Pyrolysis	Activating agent	Heating time (min)	Temperature / MW power	AC yield (%)	S_{BET} (m^2/g)	V_p (cm^3/g)	Adsorbate	Reference
Coconut shell	Conventional	-	120	1000 °C	22	702	0.532		(Yang et al., 2010)
	Conventional followed by MW	Steam	75	900 °C	42.2	2079	1.212	-	
		Steam + CO ₂			39.2	2194	1.293		
Jatropha hull	Conventional	-	60	600 °C	40	480	0.42	Iodine	(Xin-Hui et al., 2011)
	Conventional followed by MW	Steam	19	900 °C	16.56	1350	1.07		
Empty fruit bunches	Conventional	-	-	700 °C	43.17	256	0.14	Methylene blue	(Foo & Hameed, 2012c)
	Conventional followed by MW	KOH	7	600 W	73.78	1372	0.76		
Tobacco stems	Conventional	-	120	450 °C	-	-	-	Methylene blue Iodine	(Li et al., 2008)
	Conventional followed by MW	K ₂ CO ₃	30	700 W	16.65	2557	1.647		
Wood sawdust	Conventional	-	-	700 °C	-	159.48	0.102	Methylene blue	(Foo & Hameed, 2012b)
	Conventional followed by MW	K ₂ CO ₃	5	600 W	80.75	1496.05	0.864		
Waste tea	Conventional	H ₃ PO ₄	60 min	350 °C	-	928.8	0.285	-	(Yagmur et al., 2008)
	MW followed by conventional	H ₃ PO ₄	30 s	900 W	-	1157	0.228		

1.4. ANALYTICAL QUANTIFICATION OF PHARMACEUTICALS: BASIC DESCRIPTION OF CAPILLARY ELECTROPHORESIS

In the scope of this work, the quantification of CBZ in aqueous phase was carried out through capillary electrophoresis. Capillary electrophoresis is a separation technique that lays down in the separation of charged molecules through their movement in a fluid when subjected to a constant external electric field. A thin capillary, with a thickness in the μm range, is used as a physical support for the molecules to get separated (Calisto, 2011; Oliveira, 2017). The electrophoretic separation requires an electric current input, vials containing samples and electrolytes, two metallic electrodes at the inlet and outlet, a silica capillary (and therefore composed by silanol functional groups suitable for functionalisation purposes), a detection system and a software to operate the instrument and manage data acquisition and processing (Calisto, 2011), as illustrated in Figure 6.

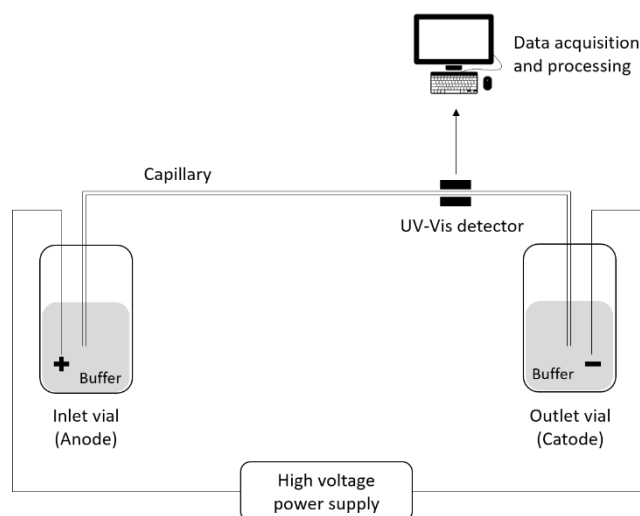


Figure 6. Schematic representation of capillary electrophoresis system

High performance liquid chromatography (HPLC), is a separative technique that could also be considered for pharmaceutical quantification purposes. Nevertheless, when compared to HPLC, capillary electrophoresis exhibits advantages such as (Calisto, 2011; Oliveira, 2017):

- The use of smaller amounts of reagents;
- Capillaries are less expensive than HPLC columns;

- Capillaries are more versatile, in the sense that the stationary phase can be modified through capillary coatings or by adding a pseudostationary phase;
- Allows the separation of molecules in a wide range of molecular weights and charges;
- Presents a higher separation resolution than HPLC.

The electrophoretic separation is a consequence of two driving forces, electrophoretic mobility and electroosmotic flow (EOF). Electrophoretic mobility is related to the movement of charged molecules due to an electrostatic force originated by the applied electric field. Moreover, as a result of the applied electric field, a liquid flow known as EOF is formed when the electrolyte contacts the charged inner walls of the capillary.

Capillary electrophoresis can occur in several separation modes, being the simplest one known as capillary zone electrophoresis (CZE). In CZE, sample is injected into a capillary filled with electrolytic solution, also mentioned as buffer, to allow the analyte molecules to be separated. A constant electric field is applied when the two extremities of the capillary are immersed in the buffer, generating an electric potential difference, which causes the migration of the charged molecules along the capillary towards the detector. Since this separation mode was limited to charged molecules, it was necessary to adopt measures to assure the mobility of neutral molecules. Electrokinetic capillary chromatography was developed in order to overcome this constraint, by introducing a pseudostationary phase in the separation buffer, combining concepts of both CZE and chromatography. Surfactants are commonly added to the separation buffer, in which the surfactant molecules involve the neutral molecules in the aqueous solution by forming micelles, referred to as pseudostationary phase. This separation mode is named micellar electrokinetic chromatography (MEKC). The neutral analytes, involved in the micelles, also migrate through electrophoretic mobility and EOF. Sodium dodecyl sulphate (SDS) is commonly used as surfactant, which allows the formation of negatively charged micelles that migrate towards the outlet vial (Calisto, 2011; Oliveira, 2017).

1.5. MAIN GOALS OF THE PRESENT WORK

This work aims to produce ACs by MW pyrolysis of paper mill PS to remove CBZ from water. Specific goals of this work include:

- To evaluate the effect of IR between precursor and activating agent in the resulting AC;
- To evaluate the repeatability of the AC production process;
- To characterise the produced ACs by determining the total organic carbon (TOC) content, the S_{BET} and total pore volume (V_p);
- To assess the adsorptive performance of the produced ACs to remove CBZ, through batch adsorption tests in ultra-pure water for different dosages of AC;
- To evaluate how the mass of AC and the contact time between adsorbent/adsorbate affect the adsorption of CBZ onto the AC, through adsorption experiments in batch mode.

CHAPTER 2: MATERIALS AND METHODS

2.1. REAGENTS

PS was chemically activated with KOH (Akzo Nobel) in pellets form. The produced ACs were washed with a solution of hydrochloric acid ($\geq 37\%$, Fluka).

The adsorption tests were performed with CBZ (99%, Sigma-Aldrich), which was quantified by capillary electrophoresis using the following chemicals: sodium dodecyl sulphate PA-ACS (Panreac), sodium tetraborate (borax, Riedel-de Haen), hexadimethrine bromide (polybrene, Sigma-Aldrich), sodium chloride, sodium hydroxide (VWR), ethylvanillin (99%, Aldrich), acetonitrile (Chem-Lab, HPLC grade).

For IC determination a diluted solution of phosphoric acid (85 % for analyses -ACS-ISO, Panreac) was used.

Except the washing acid solution, that was prepared with distilled water, all the solutions were prepared with ultra-pure water obtained from a Milli-Q Millipore system (Milli-Q plus 185).

2.2. PRODUCTION OF ACTIVATED CARBONS

ACs were produced by one-step chemical activation and MW pyrolysis of paper mill PS. The precursor was provided by a Portuguese paper mill industry that applies a chemical process (chlorine free) known as kraft process, to eucalyptus wood (*Eucalyptus globulus*). According to the procedure described by Calisto *et al.* (2014), PS was collected and subjected to two drying steps: dried at room temperature for several days and then dried at 60 °C in an oven for 24 h. Subsequently, PS was grinded with a blade mill (Figure 7).



Figure 7. Dried paper mill primary sludge

PS was then chemically activated with KOH and three activating agent:precursor ratios were tested: 0.5:1, 1:1 and 1.5:1 (w/w). For each carbon produced, a mixture was prepared in a proportion of 9 mL of ultra-pure water per 3 g of precursor and the corresponding mass of KOH for each IR. Both precursor and activating agent were weighted on an analytical balance with an uncertainty of ± 0.0001 g. After homogenisation, the sample was impregnated for 1 h in an ultrasonic bath at room temperature.

The slurry (precursor impregnated with activating agent) was placed into a cylindrical quartz reactor (2.2 cm diameter x 38.5 cm length), which was held in the reactor with a folded cone-shaped glass fibre filter (Whatman, 47 mm). The reactor was inserted vertically, as shown in Figure 8, into a modified Samsung MW furnace (2.45 GHz) with an adjustable power between 100 and 800 W.



Figure 8. Experimental apparatus used in this work: (a) Quartz reactor; (b) Experimental setup used for MW pyrolysis; (c) Slurry placed inside the quartz reactor in the MW furnace

The bottom of the reactor was tapered and connected to a N₂ flow. The top of the reactor was surrounded by a removable metallic cover (7.5 cm length), which was attached to a silica exhaust pipe (0.8 cm diameter x 38 cm length) from which the pyrolysis gases were expelled (Figure 8). The MW pyrolysis was performed under an inert atmosphere after a 15 min purge with a N₂ flow, ensuring the removal of oxygen from the reaction system.

The slurry was pyrolysed for 10 min at a radiation power of 800 W. The N₂ flow was kept until the carbonised sample was cooled to room temperature, for about 10 min.

The carbonised material was removed from the reactor, milled and soaked with a 1.2 M HCl solution at a 50 mL/g liquid to solid ratio. This procedure, not only allowed the removal of residual KOH activating agent, but also promoted the unblocking of the obstructed pores by inorganic material (ashes). The material remained suspended in the acid solution for 1 h, similarly to the procedure described in Oliveira (2017), after which it was vacuum filtered and repeatedly washed with distilled water until neutral pH of the washing solution was achieved. The AC was then dried at 105 °C for 48 h, weighed, sieved to obtain the fraction of particles with a size up to 180 µm and stored in polypropylene vessels for further experiments. The production of ACs is summarised in Figure 9.



Figure 9. Stages of the ACs production performed in the present work

The production yield was determined as the ratio between the mass of the produced AC and the initial mass of precursor, both weighted in dry basis,

$$\text{Yield (\%)} = \frac{m_i}{m_0} \times 100 \quad (1)$$

where m_0 is the mass of PS and m_i is the mass of the produced carbon after activation, grinding, washing and drying.

All the materials were produced in triplicate to evaluate the repeatability of the process, resulting in a total of nine ACs. The produced materials were named according to the production conditions, namely, precursor (PS), activating agent (KOH), activating agent:precursor ratio and the production batch (first, second or third production). For example, PS-KOH-0.5:1-1batch is related to the AC obtained from PS, chemically activated with KOH in a 0.5:1 (activating agent:precursor) ratio during the first production (1 batch). The same analogy was considered to name the remaining produced ACs.

Preliminary tests were performed, consisting of the MW pyrolysis of the PS without activating agent or with lower quantity of activating agent (in a proportion of 0.1:1) and no carbonisation was achieved.

2.3. CHARACTERISATION OF ACTIVATED CARBONS

2.3.1. TOTAL ORGANIC CARBON

Total organic carbon (TOC) was determined for the precursor and for the produced ACs by difference between total carbon (TC) and inorganic carbon (IC), which were analysed in a TOC-VCPH Shimadzu analyser, with a solid sample module SSM-5000A. For both TC and IC determination, a blank test was carried out at the beginning of each work session, using an empty porcelain crucible. Glucose ($\text{C}_6\text{H}_{12}\text{O}_6$, corresponding to 40 % of carbon), was used to test the calibration curve previously made for TC determination, while sodium carbonate (Na_2CO_3 , corresponding to 11% of carbon) was the control standard used for IC determination. The carbon content of the precursor and ACs was determined as the

average of three replicates whenever the amount of AC allowed it. For IC determination, 4 mL of phosphoric acid:water (1:2) was added into the porcelain crucibles (blank and samples). The samples were weighed in a microbalance with an uncertainty of ± 0.001 mg.

2.3.2. SPECIFIC SURFACE AREA (S_{BET}) AND POROSITY

The determination of S_{BET} and porosity were accomplished through a collaboration with Instituto Nacional del Carbón (INCAR – CSIC), Oviedo, Spain. S_{BET} was obtained from a Micromeritics equipment (Gemini VII 2380) using nitrogen adsorption isotherms at -196 °C and applying the BET model in the relative pressure range of 0.01 to 0.1. Samples were submitted to a degasification process at 120 °C overnight. V_p was determined from the amount of nitrogen adsorbed at a relative pressure of 0.99. Dubinin-Astakhov equation was applied to the lower relative pressure zone of the nitrogen adsorption isotherm to obtain total micropore volume (W_0). S_{BET} and V_p were determined for all the materials except for the precursor.

2.4. BATCH ADSORPTION TESTS

2.4.1. BATCH ADSORPTION TESTS WITH THE PRODUCED ACTIVATED CARBONS

Adsorption tests in batch mode were carried out to assess the adsorption of CBZ onto the nine produced ACs. For that purpose, solutions of CBZ were prepared in ultra-pure water, with an initial concentration of 5 mg/L. CBZ and ACs were weighed in a microbalance with an uncertainty of ± 0.001 mg.

Studies were carried out for each AC at different dosages, namely 0.025, 0.05 and 0.1 g/L. The weighed carbon (1 mg) was transferred to polypropylene tubes with a total capacity of 50 mL, and the corresponding volume of 5 mg/L pharmaceutical solution was added in order to achieve the intended AC dosage, as summarised in Table 3. All the tests were performed, at least, in triplicate.

Table 3. Mass of carbon weighed and volume of 5 mg/L CBZ solution used for the three AC dosages under study

AC dosage (g/L)	Mass of AC (mg)	Volume of CBZ solution (mL)
0.025	1	40
0.05	1	20
0.1	1	10

A control experiment consisting of pharmaceutical solution without the adsorbent, was carried out simultaneously with each adsorption test in order to assess the (possible) pharmaceutical adsorption onto the polypropylene tubes and/or its thermal degradation. The samples and control were shaken in an overhead shaker (Heidolph, Reax 2) at 80 rpm under a controlled temperature of 25.0 ± 0.1 °C for 24 h. Then, control and samples were filtered through a 0.22 μ m PVDF syringe filter (13 mm diameter, Whatman), as shown in Figure 10, to stop the adsorption process by removing the adsorbent.

**Figure 10.** On the left, samples and the control after conclusion of an adsorption test; On the right, the syringe filter system

Control and samples were analysed by capillary electrophoresis, as described in Section 2.5., in order to determine the concentration of pharmaceutical that remained in the aqueous phase. The percentage of CBZ adsorbed was determined by the difference between the initial concentration of pharmaceutical, given by the control test, and the concentration of CBZ that remained in the aqueous phase of each sample after filtration,

$$\text{Adsorption (\%)} = \frac{C_0 - C_f}{C_0} \times 100 \quad (2)$$

where C_0 is the initial concentration of CBZ provided by the control test and C_f is the concentration of CBZ that remained in the aqueous phase. The adsorption percentage of each AC was determined as the average of all replicates.

Due to the small masses of AC used to achieve the desired AC dosage in the described experiments, some tests were performed to assess the possibility of AC adhesion onto the walls and lids of the propylene tubes, which might have a significant impact in the AC that is effectively in contact with the pharmaceutical solution. For this purpose, and maintaining the same final AC dosage, higher masses of AC were used and some of the described batch adsorption tests were repeated. Due to the limited quantities of AC produced, tests using 2 mg of adsorbent were applied to only four ACs, namely, PS-KOH-0.5:1-2batch, PS-KOH-1:1-2batch, PS-KOH-0.5:1-3batch and PS-KOH-1:1-3batch, to achieve the final AC dosage of 0.05 and 0.1 g/L. Experiments using 3 mg of AC could only be performed for PS-KOH-0.5:1-3batch and PS-KOH-1:1-3batch, for an AC dosage of 0.1 g/L, as shown in Table 4. Tests were not performed for an AC dosage of 0.025 g/L, since the maximum volume of 50 mL of the polypropylene tubes would inevitably require 1 mg of AC per 40 mL of pharmaceutical solution, considering that the concentration of the pharmaceutical solution was not changed.

Table 4. Mass of AC weighed and the corresponding volume of 5 mg/L CBZ solution

AC	AC dosage (g/L)	Mass of AC (mg)	Volume of CBZ solution (mL)
PS-KOH-0.5:1-2batch PS-KOH-1:1-2batch	0.05	2	40
PS-KOH-0.5:1-3batch PS-KOH-1:1-3batch	0.1	2	20
PS-KOH-0.5:1-3batch PS-KOH-1:1-3batch	0.1	3	30

The weighed ACs were transferred to the polypropylene tubes and the corresponding volume of 5 mg/L CBZ solution was added. The adsorption tests were carried

out for 24 h in triplicate, under controlled temperature and shaking. After capillary electrophoresis analyses, the adsorption percentages were determined according to Equation 2.

2.4.2. EVALUATION OF THE EFFECT OF CONTACT TIME

In order to confirm if the adsorbent/adsorbate contact time was enough for attaining the maximum removal percentages at the studied conditions, 49 and 72 h adsorption tests were also performed for the ACs PS-KOH-0.5:1-2batch and PS-KOH-0.5:1-3batch. The experiments were performed using 1 and 2 mg of AC to achieve the final AC dosage of 0.05 and 0.1 g/L. The experimental conditions were the same as described in Section 2.4.1.

2.5. QUANTIFICATION OF CARBAMAZEPINE BY CAPILLARY ELECTROPHORESIS

The quantification of the CBZ was performed in a Beckman P/ACE MDQ electrophoresis equipment, equipped with a UV-Vis photodiode array detector, operated with the software 32 Karat. The pharmaceutical was quantified according to a MEKC method by using a dynamically coated capillary and an electrolyte buffer consisting of 30 mM of SDS and 15 mM of sodium tetraborate (borax).

Before the first usage, a silica capillary of 40 cm length (75 μ m inner diameter and 375 μ m external diameter), 30 cm to the detection window, was coated, as described in Table 5. A 1 M NaOH solution was used for the activation of the silanol groups and hexadimethrine bromide (polybrene) was responsible for adding positively charged functional groups. In order to avoid the capillary blocking, all the reagents (buffer, polybrene and NaOH), samples including, were previously filtered through 0.22 μ m PVDF filters (Whatman).

Separation was carried out at 25 °C by applying an electric field of 25 kV, for approximately 3.6 min. The detection of CBZ occurred at 214 nm, according to the pharmaceutical absorption spectra. Ethylvanillin was used as internal standard (IS) and added to all the samples at an initial concentration of 167 mg/L. Samples were injected by

pressure, implying non-repeatable injection volumes; For that reason, the IS was used for pharmaceuticals quantification purposes through the ratio between the CBZ peak area and the IS peak area (A_{CBZ}/A_{IS}). The experimental conditions used for capillary electrophoresis analysis are listed in Table 5. Each sample, that is, control and each replicate from the adsorption experiments, was analysed in triplicated.

Table 5. MEKC experimental steps and conditions

MEKC quantification method	
Sample/standard vials preparation	
Each vial of sample/standard had: 150 μ L borax 100 mM + 30 μ L ethylvanillin 167 mg/L + 1350 μ L sample/standard	
Coating of the bare silica capillary	
Before the usage of a new capillary.	<u>Experimental conditions:</u> NaOH 1 M (30 min); H ₂ O (15 min); Polybrene 0.5% (w/v) in NaCl 0.5 M (20 min); H ₂ O (2 min); Buffer consisting of 30 mM of SDS and 15 mM of borax (20 min);
Washing steps	
Daily, in the beginning (initial washing) and at the end (final washing) of the working session.	<u>Experimental conditions:</u> Initial washing: Buffer (20 min) Final washing: H ₂ O (10 min)
Electrophoresis conditions	
T = 25 °C, ΔV = 25 kV, λ = 214 nm, P = 20 psi	
Separation method	
Separation occurred in vials with 1350 μ L of electrolyte buffer (30 mM of SDS and 15 mM of borax). Separation buffer was renewed every six runs.	<u>Experimental conditions:</u> Washing with H ₂ O (1 min at 20 psi); Washing with buffer (1.5 min at 20 psi); Sample injection (4 s at 0.5 psi); Injection of H ₂ O (3 s at 0.5 psi); Separation (3.2 - 3.6 min)

To integrate the obtained electropherograms, Matlab 9.0 (R2016a) compiler was used. Figure 11 represents an example of an electropherogram, in which the first peak represents EOF, the peak with a migration time around 1.7 min corresponds to the IS, and around 2.7 min there is the peak corresponding to CBZ that remained in the aqueous phase.

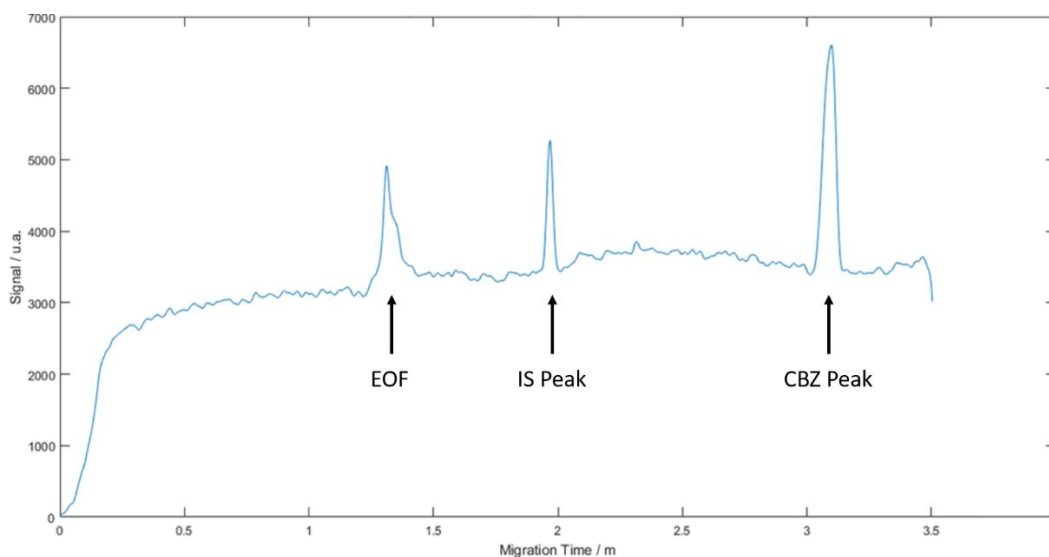


Figure 11. Electropherogram of a control test of a 5 mg/L CBZ solution

2.5.1. CALIBRATION CURVE

To estimate the concentration of CBZ a calibration curve was performed for each capillary renewal.

Seven standards with concentrations of 0.25, 0.5, 1, 2, 3, 4 and 5 mg/L were prepared by dilution of a 5 mg/L stock solution in 5 mL volumetric flasks. The standards were quantified by MEKC according to the experimental conditions described in Table 5 (Section 2.5.). The standards were analysed in quadruplicate. A linear calibration curve was obtained by applying the least-squares linear regression, in which the A_{CBZ}/A_{IS} ratio was represented as a function of the pharmaceutical concentration, according to the equation:

$$y = mx + b \quad (3)$$

where y is A_{CBZ}/A_{IS} , x is the concentration of CBZ, m is the slope and b is the intercept on the y -axis.

The limit of detection (LOD) and quantification (LOQ) were determined by the calibration curve method, according to International Conference on Harmonization (2005) guidelines. LOD and LOQ were obtained through the equations:

$$\text{LOD} = 3.3 \times \frac{\sigma}{S} \quad (4)$$

$$\text{LOQ} = 10 \times \frac{\sigma}{S} \quad (5)$$

where σ is the standard deviation of the intercept and S is the slope of the calibration curve.

CHAPTER 3: RESULTS AND DISCUSSION

3.1. PRODUCTION OF ACTIVATED CARBONS

As mentioned previously, three production batches were carried out, in the exact same experimental conditions for three different IRs, from which nine ACs resulted. During the slurry carbonisation it was observed the formation of flame and incandescence, whose intensity and duration varied with the IR, being more pronounced for lower concentrations of activating agent. For the slurry with an IR of 0.5:1 (activating agent:precursor), flame formation/incandescence occurred intense and continuously in the initial heating minutes (3 – 4 min), becoming intermittent over the process, until at the end it was not observed. Considering the slurry with the IR of 1:1, when flame formation/incandescence occurred, it was observed for smaller periods of time, when compared to 0.5:1 ratio. Finally, for the 1.5:1 slurry carbonisation no flame was observed, and when incandescence occurred, it was intermittent and for short periods of time. These experimental occurrences may be related to the carbonisation rate, in the sense that for the materials in which the flame formation/incandescence was more intense (0.5:1 ratio), the final ACs presented a more blackish appearance, which may be related to a more complete carbonisation (Figure 12). The achievement of a “complete” carbonisation with lower concentrations of KOH can be an advantageous feature in the economic point of view.



Figure 12. ACs produced in the activating agent:precursor ratio of 0.5:1

For the materials in which the flame formation/incandescence was less intense, 1:1 and 1.5:1 ratios, the final ACs still presented some brownish fractions, probably due to the incomplete carbonisation of the precursor as shown in Figure 13 and Figure 14, respectively.



Figure 13. ACs produced in the activating agent:precursor ratio of 1:1



Figure 14. ACs produced in the activating agent:precursor ratio of 1.5:1

As shown in Figure 15, the production yield (calculated by Equation 1) did not varied significantly for ACs within the same IR, nevertheless, there was a slight difference for ACs produced with different IRs, being PS-KOH-0.5:1, the AC obtained with higher product yield.

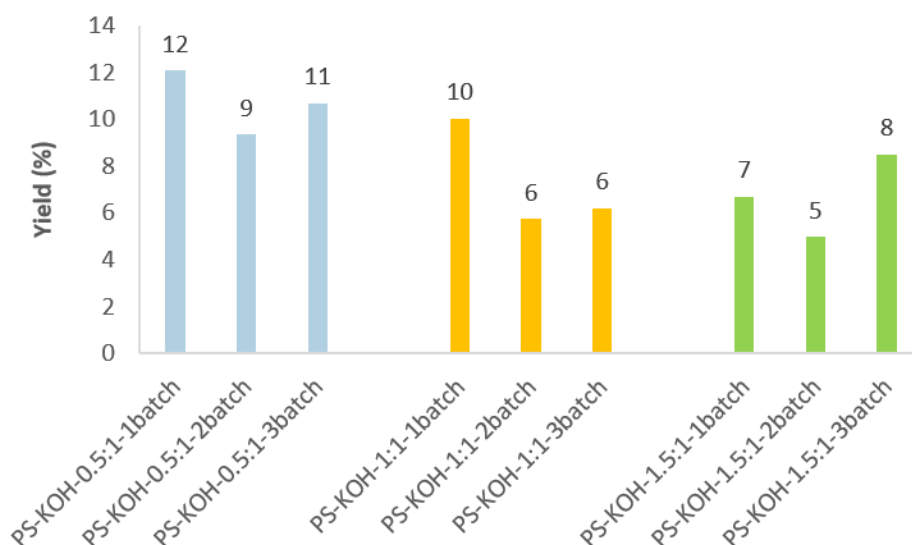


Figure 15. Production yield (%) of the produced ACs

Table 1 (Section 1.3.) summarises the production conditions, yield and textural properties of ACs available in literature, produced by one-step MW pyrolysis of alternative precursors, similarly to those used in the present work. For comparative purposes, PS-KOH-0.5:1 was considered with an average yield of 11 ± 1 %, which is slightly lower than the production yields reported in literature.

Overall, losses during the production are significant, in the way that 3 g of PS originated approximately 300 mg of AC. Besides the inevitable losses that occurred throughout the production stages, it was found that the step that had major influence in the obtained yield was the acid washing. As mentioned in previous studies (Calisto et al., 2017; Jaria et al., 2015, 2017; Pereira, 2017), these losses can be related to the removal of the inorganic material, such as ashes, improving microporosity and S_{BET} due to the unblocking of obstructed pores.

It should be noted that the chemical activation of carbonaceous materials produces adsorbents with a well-developed porosity, which may result in lighter materials and therefore, lower production yields. Nevertheless, the production yield of the produced ACs decreases by increasing the concentration of the activating agent, which was not attributed to a well-developed porous structure since V_p also decreases with the increase of KOH

concentration, as shown in Table 6 (Section 3.2.2.). These losses may be related to a higher decomposition of the precursor due to the reaction with KOH.

Preliminary experiments of the MW pyrolysis of PS in the absence of the activating agent or lower quantity of activating agent (activating agent:precursor of 0.1:1), demonstrated that no carbonisation was achieved. These results are an evidence that the activating agent not only promotes structural changes through the formation of new pores and/or widening the existing ones, but also promotes the production of char by acting as MW radiation absorber.

The production process of the ACs by MW pyrolysis presented some inherent variables difficult to control, such as:

- The equipment used for MW pyrolysis was a domestic MW, in which the heating process was assisted by a rotatory plate. The modifications to the MW, described in Section 2.2., did not allowed the sample to be heated in a rotatory movement, which means that uniformity of radiation inside the equipment could not be guaranteed;
- The quartz reactor was built analogously to other reactors described in literature allowing small dosages of slurry. Also, due to its shape, it was difficult to assure a homogeneous sample packaging for each production;
- Contrarily to conventionally heated experiments in muffle furnaces, the reaction temperature could not be measured;
- To assure oxygen-free conditions, the system was purged with N₂ before pyrolysis. When regulating the N₂ flow the slurry was slightly vertically dislocated. According to the experiments carried out, it is not possible to assure if this displacement could (or not) move the slurry, to a position out of the optimal radiative field. Similarly, the carbonised material could be displaced by the N₂ flow during heating.

3.2. CHARACTERISATION OF ACTIVATED CARBONS

3.2.1. TOTAL ORGANIC CARBON

The ACs were produced from a starting material composed by 30.5 ± 0.3 % of TC, 4.4 ± 0.2 % of IC and therefore 26.0 ± 0.4 % of TOC. Figure 16 shows that MW pyrolysis promoted an increase of the OC content in the obtained ACs. The results reinforce that MW pyrolysis, along with the acid washing, is responsible for the removal of most IC content, reducing it to negligible values (under 0.2 %).

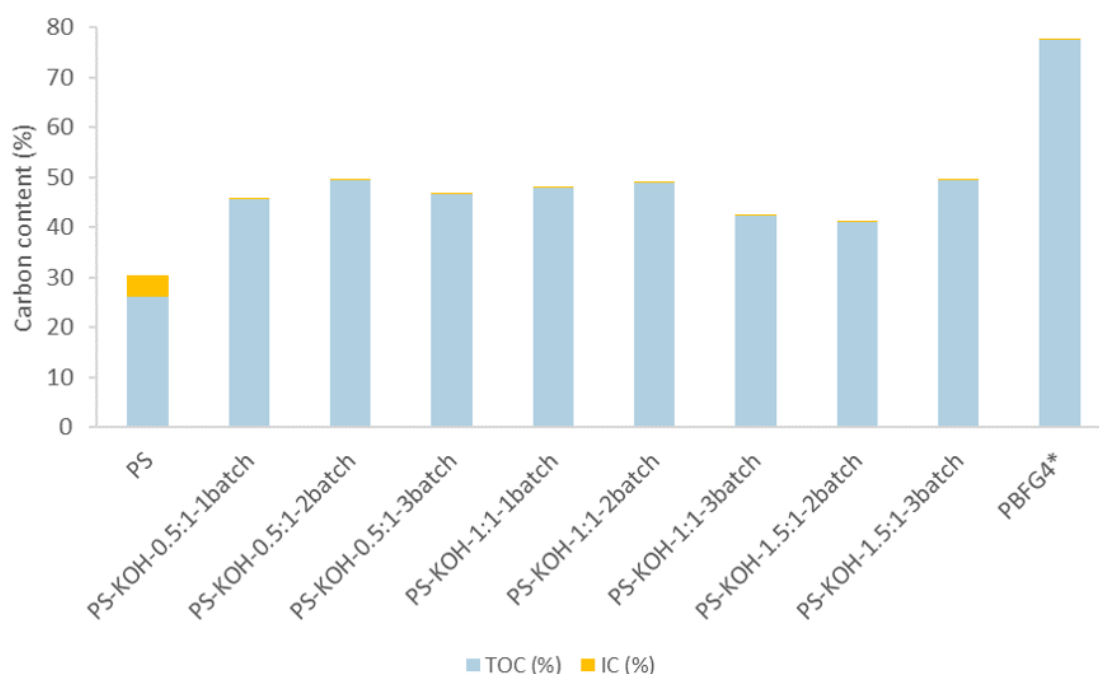


Figure 16. Carbon content of the PS, produced ACs and the commercial AC (PBFG4) used as reference.

*Data published in Jaria *et al.* (2018)

The carbon content of the ACs produced by MW pyrolysis were compared to ACs produced by conventional pyrolysis of PS. According to the production conditions described in Jaria *et al.* (2018), the ACs were named as CPy-PS800-150KOH-1:1, CPy-PS800-60KOH-1:1, CPy-PS650-150KOH-1:1 and CPy-PS650-60KOH-1:1, corresponding to the conventional pyrolysis of PS impregnated with KOH (1:1 ratio), at temperatures of 650 or 800 °C for 60

or 150 min. Also for comparison purposes, it was considered a commercial powder AC named PULSORB FG4 (PBFG4), provided by ChemViron Carbon.

Overall, the MW pyrolysed ACs have TOC values ranging between 42.5 ± 0.5 % and 49.6 ± 0.4 %, representing low values when compared to the commercial AC PBFG4 with 77.5 ± 0.1 % of TOC (data published in Jaria *et al.*, 2018). The ACs produced by conventional pyrolysis present higher TOC than the ACs produced by MW radiation, with CPy-PS650-150KOH-1:1 and CPy-PS650-60KOH-1:1 presenting around 54.9 ± 0.1 % and CPy-PS800-150KOH-1:1 and CPy-PS800-60KOH-1:1 around 67 ± 1 % (Jaria *et al.*, 2018). Considering the ACs obtained by conventional pyrolysis, the increase in temperature resulted in an increase of TOC, raising the question of whether or not the increase of MW radiation time could increment the carbon content. Contrarily to conventional pyrolysis, the temperature to which the sample was subjected during the MW heating could not be measured. As mentioned in Section 1.3., the MW power is indirectly related to the temperature, which in this particular case could not be increased since the maximum power of the equipment is 800 W. Therefore, the only variable that could be manipulated during the carbonisation process would be radiation time.

3.2.2. SPECIFIC SURFACE AREA (S_{BET}) AND POROSITY

Table 6 summarises the results obtained for S_{BET} and porous structure of the produced ACs. Both Table 6 and Figure 17 support the high variability within ACs with the same IR from different batches that were obtained under the same experimental conditions. The variability of S_{BET} (and V_{P}) is more pronounced for ACs obtained with higher concentration of activating agent (1.5:1 ratio), showing a relative standard deviation (RSD) of 48 %. Within the ACs produced with a 0.5:1 ratio, the variability of S_{BET} in relation to the mean was less pronounced, showing a RSD of 23 %. One observes some consistency of the obtained results for both PS-KOH-0.5:1 and PS-KOH-1:1 from the second and third batches.

The AC with the lower IR (PS-KOH-0.5:1) presents better textural properties, with an average S_{BET} of 946 ± 217 m²/g and an average V_{P} of 0.72 ± 0.13 cm³/g. PS-KOH-0.5:1-batch stands out from the other two batches under the same experimental conditions with a S_{BET} of 1190 m²/g, which may be due to some experimental constraints, in which the

precursor remained impregnated in the activating agent for 4 h instead 1 h. Overall, S_{BET} and V_p decrease with the increase of the activating agent concentration, which is in line with data published by Saucier *et al.* (2015) and Thue *et al.* (2016).

Table 6. Textural properties of the produced ACs

AC	S_{BET} (m^2/g)	V_p (cm^3/g)	W_0 (cm^3/g)	D (nm)	L (nm)
PS-KOH-0.5:1-1batch	1190	0.87	0.57	1.46	1.67
PS-KOH-0.5:1-2batch	773	0.62	0.38	1.59	1.73
PS-KOH-0.5:1-3batch	875	0.68	0.43	1.55	1.73
PS-KOH-1:1-1batch	354	0.36	0.18	2.03	1.91
PS-KOH-1:1-2batch	820	0.68	0.42	1.66	1.88
PS-KOH-1:1-3batch	816	0.63	0.41	1.55	1.82
PS-KOH-1.5:1-1batch	213	0.27	0.11	2.55	1.93
PS-KOH-1.5:1-2batch	603	0.52	0.30	1.72	1.83
PS-KOH-1.5:1-3batch	414	0.42	0.20	2.00	1.84
PBFG4 *	848	0.36	0.36	-	1.72
CPy-PS800-150KOH-1:1 *	1627	1.07	0.73	-	1.74
CPy-PS800-60KOH-1:1 *	1531	0.96	0.69	-	1.73

*Data published in Jaria *et al.* (2018)

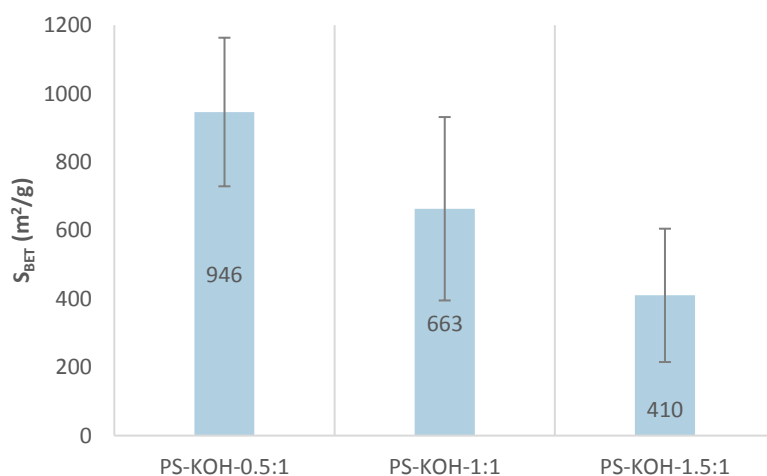


Figure 17. Variability of S_{BET} for the produced ACs considering the average of three replicates

The nine produced ACs have an average pore diameter smaller than 2 nm, which according to IUPAC (2014) classification, are attributed to micropores. Overall, the adsorbents exhibit a well-developed microporous structure, allowing the enhancement of the S_{BET} , which is complemented by some mesoporosity that can act as channels allowing the access to the micropores.

Both PS-KOH-0.5:1 and PS-KOH-1:1, except PS-KOH-1:1-1batch, present S_{BET} values comparable to the commercial AC PBFG4. Considering the ACs obtained by conventional pyrolysis, the adsorbents produced at 800 °C have better textural properties than the same ACs produced at 650 °C, with CPy-PS650-150KOH-1:1 and CPy-PS650-60KOH-1:1 presenting a S_{BET} of 473 m²/g and 523 m²/g, respectively (Jaria et al., 2018). Moreover, the ACs produced at 800 °C by conventional pyrolysis present a more developed porosity and higher S_{BET} when compared to MW pyrolysed ACs. It is noteworthy that the textural properties of PS-KOH-0.5:1 here produced were achieved in less time and with less activating agent than the ACs produced by conventional pyrolysis. However, poor levels of reaction control such as lack of temperature monitorisation and non-homogeneous radiation inside the equipment, as mentioned in Section 3.1., limit the comparison with conventionally produced ACs.

The results summarised in Table 1, Section 1.3., related to ACs chemically activated by one-step MW pyrolysis, were considered for comparison purposes. Overall, PS-KOH-0.5:1 presents satisfying S_{BET} when compared to ACs produced from giant reed (Chayid & Ahmed, 2015), cocoa shell (Saucier et al., 2015), cotton stalk (Deng et al., 2009) and paper mill sludge (containing PS and BS in a ratio of 1:1) (Namazi et al., 2015). However, when compared to ACs obtained from siris seed pods (Ahmed & Theydan, 2013, 2014b), lotus stalks (Huang et al., 2011) and bamboo (Liu et al., 2010), PS-KOH-0.5:1 exhibit lower S_{BET} . These results reinforce the cruciality of developing further work towards the optimisation of ACs production by MW pyrolysis of PS, evaluating, besides the effect of IR, the effect of MW power, radiation time and the resulting effects on the adsorption percentages of adsorbate.

3.3. BATCH ADSORPTION TESTS

3.3.1. QUANTIFICATION OF CARBAMAZEPINE BY CAPILLARY ELECTROPHORESIS

The adsorption tests were carried out for the nine produced ACs with three different carbon dosages (as listed in Table 3, Section 2.4.1.) suspended in a stock solution of CBZ with a concentration of 5 mg/L. When the adsorption tests were concluded the amount of CBZ that remained in the aqueous phase was quantified by MEKC. The correlation coefficient of the calibration curves was above 0.995. LOD and LOQ values were 0.042 and 0.129 mg/L, respectively.

Figure 18 shows two electropherograms, where electropherogram (a) represents the control test corresponding to ≈ 5 mg/L of CBZ, and electropherogram (b) relates an experiment in which the amount of pharmaceutical that remained in the aqueous fraction was relatively low.

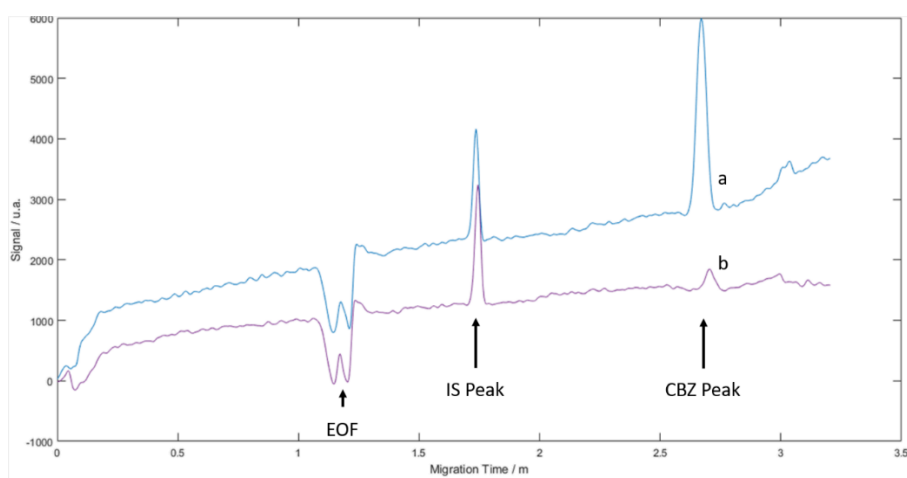


Figure 18. Electropherogram examples: (a) control test, [CBZ] ≈ 5 mg/L and (b) sample

3.3.2. PRELIMINARY ADSORPTION EXPERIMENTS

Preliminary adsorption tests, following the description from Section 2.4.1, were performed for non-washed ACs, for a carbon dosage of 0.1 g/L (24 h shaking at 80 rpm and 25 °C). The results showed that without washing with HCl 1.2 M, the ACs were not able to remove CBZ from ultra-pure water solutions, exhibiting adsorption percentages lower than

10 %. These experiments reinforce previous observations regarding the importance of the washing procedure to unblock obstructed pores.

Saucier *et al.* (2015) concluded similarly in the studies performed for the removal of nimesulide. The authors observed, for adsorbent dosages of 2.5 g/L, that the AC achieved a removal percentage of 98.75 % when washed with an acid solution, while the corresponding non-washed AC removed 40.25 % of pharmaceutical (contact time of 120 min, at 25 °C for a 100 mg/L nimesulide solution).

In this sense, the adsorption experiments in the present work were carried out with the produced ACs previously washed with a HCl solution.

3.3.3. BATCH ADSORPTION TESTS WITH THE PRODUCED ACTIVATED CARBONS

The removal percentages of CBZ have a pronounced variability within ACs with the same IR from different batches, obtained under the same experimental conditions, similarly to what was observed for S_{BET} , as illustrated in Figure 19. It can be noted that the increase of the carbon dosage from 0.025 to 0.1 g/L results in higher removal percentages of CBZ, in which 0.1 g/L is, generally, the dosage that exhibits larger removal percentages. The variability is also reflected in the concentration of KOH, in which the adsorption percentages of CBZ decreased for ACs with higher concentration of activating agent, with PS-KOH-1.5:1 presenting less consistency and lower adsorption percentages. According to Ahmed and Theydan (2013), the increase in the concentration of activating agent can lead to the micropores degradation due to an excessive widening of the pores, which is reflected in a lower adsorption efficiency.

PS-KOH-0.5:1-1batch has the best CBZ removal rate, with values of 90 ± 3 % and 97.1 ± 0.5 %, for adsorbent dosages of 0.05 and 0.1 g/L, respectively. These results are consistent with the high S_{BET} and well-developed porosity of this AC. According to the textural properties of PS-KOH-0.5:1-2batch and PS-KOH-0.5:1-3batch it would be expected better removal performances for the latter, due to its higher S_{BET} ($875 \text{ m}^2/\text{g}$), which is not confirmed by the adsorption percentages, that are lower for PS-KOH-0.5:1-3batch.

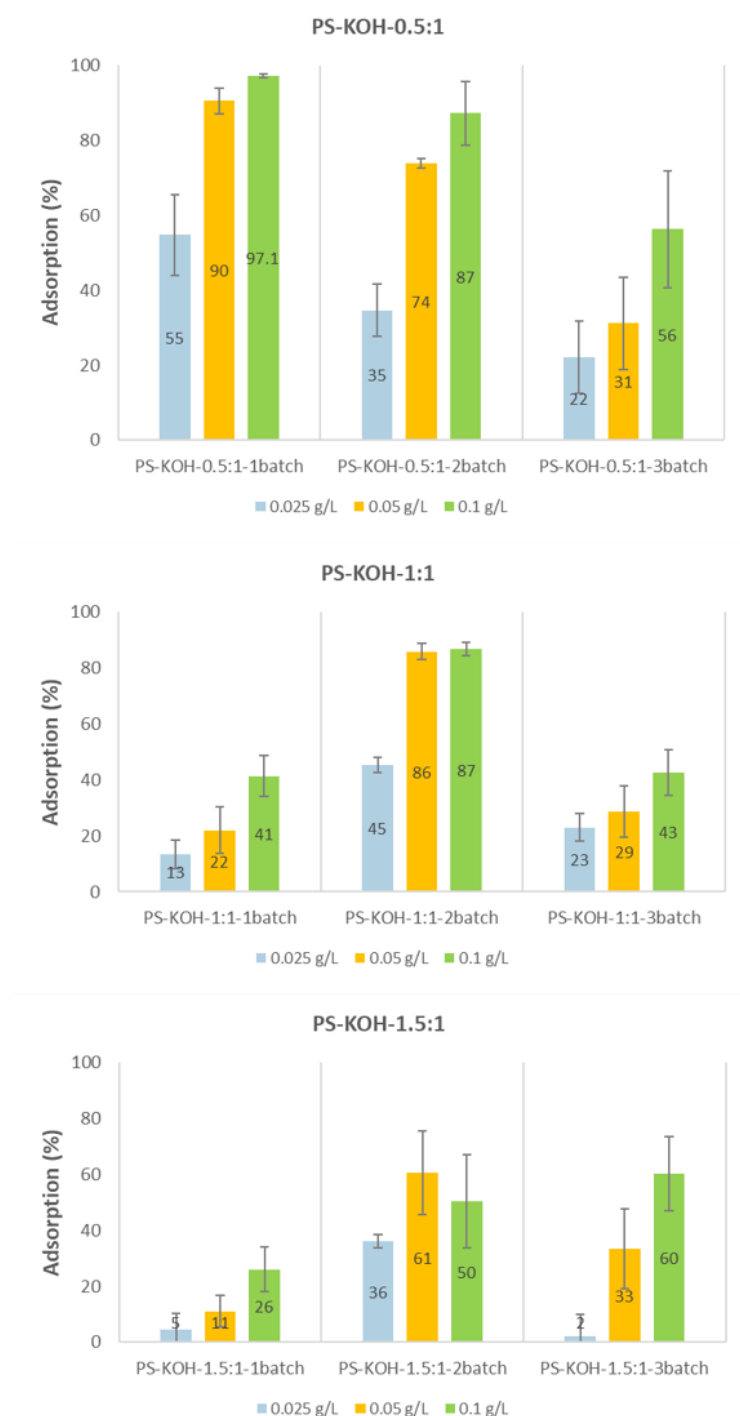


Figure 19. Adsorption percentages for all the produced ACs, considering a contact time of 24 h and AC dosages of 0.025, 0.05 and 0.1 g/L

PS-KOH-1:1-1batch and PS-KOH-1:1-3batch have analogous adsorption percentages for the same AC dosages, which was not expected considering that the first batch has smaller S_{BET} and V_p than the third batch. Taking into account the similarities between S_{BET}

and V_p of PS-KOH-1:1-2batch ($820 \text{ m}^2/\text{g}$, $0.68 \text{ cm}^3/\text{g}$) and PS-KOH-1:1-3batch ($816 \text{ m}^2/\text{g}$, $0.63 \text{ cm}^3/\text{g}$), it would be expected that both removed CBZ from the aqueous phase similarly, which is not confirmed by the adsorption percentages in which the third batch presents remarkably lower percentages than the second batch, being more pronounced for the AC dosage of 0.05 g/L .

When compared to the produced ACs by MW pyrolysis, ACs conventionally heated stands out with good CBZ removal uptakes (Table 7), presenting adsorption percentages around 80 % for lower AC dosages (0.015 g/L), as described in Jaria *et al.* (2018). The authors performed adsorption tests in similar conditions to those applied in the present work, however, instead of 24 h, the samples remained under overnight shaking. The ACs produced at 800°C have higher adsorption percentages, as it would be expected due to their high S_{BET} and well-developed porous network, as summarised in Table 6 (Section 3.2.2.). CPy-PS800-60KOH-1:1 is the more promising AC, since it has the same adsorption percentage for lower energy consumption, hence lower costs. In addition, the use of lower AC dosages to achieve analogous outcomes for the removal of CBZ from water raises the adsorbent interest for being cost-efficient.

Table 7. CBZ adsorption percentages for ACs produced by conventional pyrolysis. Adsorption tests performed by Jaria *et al.* (2018) (5 mg/L CBZ solution, AC dosage of 0.015 g/L , overnight shaking at 80 rpm and 25°C)

AC	Adsorption (%) CBZ
CPy-PS800-150KOH-1:1	81 ± 3
CPy-PS800-60KOH-1:1	81 ± 1
CPy-PS650-150KOH-1:1	8.8 ± 0.1
CPy-PS650-60KOH-1:1	6 ± 1
PBFG4	18 ± 5

The commercial AC (PBFG4) used as reference presents lower adsorption percentages when compared to the ACs produced conventionally and those produced in the scope of this work. However, one should consider that PBFG4 uptakes were achieved for AC dosages of 0.015 g/L , which is almost two times inferior than the smaller AC dosage used in this work (0.025 g/L). Even though, considering the well-developed microporous

structure of the produced ACs, it would be expected better CBZ removal percentages for PS-KOH-0.5:1 when compared to PBFG4, considering that the tests would be performed under the same experimental conditions.

As mentioned in Section 2.4.1., the use of small masses of AC to perform the adsorption tests could be an influencing factor in the CBZ uptake percentages, in the sense that the effect of any small variation, such as adhesion of the adsorbent onto the tubes walls/lid, will be more evident when using low masses of AC than would be for higher masses. Therefore, and maintaining the same final AC dosage, batch adsorption tests were performed weighing 2 mg and 3 mg of AC as summarised in Table 4 (Section 2.4.1.). Since one of the raised doubts was related to the heterogeneity between batches obtained under the same experimental conditions, the tests were performed for PS-KOH-0.5:1-2batch, PS-KOH-0.5:1-3batch, PS-KOH-1:1-2batch and PS-KOH-1:1-3batch. The amount of AC was limited due to the low production yields, as shown in Figure 15 (Section 3.1.), which resulted in masses of AC that could vary between 140 and 300 mg, needed for physico-chemical characterisation of the ACs and adsorption tests. The small amount of AC produced for each batch conditioned the number of experiments that could be performed, which also explains why the experiment with 3 mg was carried out for only two ACs from the third batch.

The CBZ adsorption percentages are more consistent within ACs with the same IR from different batches when the AC dosage is achieved with masses of AC higher than 1 mg, as shown in Figure 20. By weighing 2 mg of AC for a dosage of 0.05 g/L, PS-KOH-0.5:1-2batch removes 68 ± 4 % of CBZ from ultra-pure water solution, and analogously, the corresponding AC from the third batch removes 65 ± 13 %. Similar observations can be made for a dosage of 0.1 g/L in which 2 mg of AC was weighed, with PS-KOH-0.5:1-2batch and PS-KOH-0.5:1-3batch presenting comparable adsorptions of 82 ± 5 % and 92 ± 6 %, respectively. For PS-KOH-1:1 the adsorption percentages vary more pronouncedly between PS-KOH-1:1-2batch and PS-KOH-1:1-3batch, even when 2 mg of AC were weighed, whose results are not consistent with the S_{BET} values. As already mentioned, it would be expected to have similar CBZ removal percentages for the two batches of PS-KOH-1:1, with surface areas of 820 and 816 m²/g.

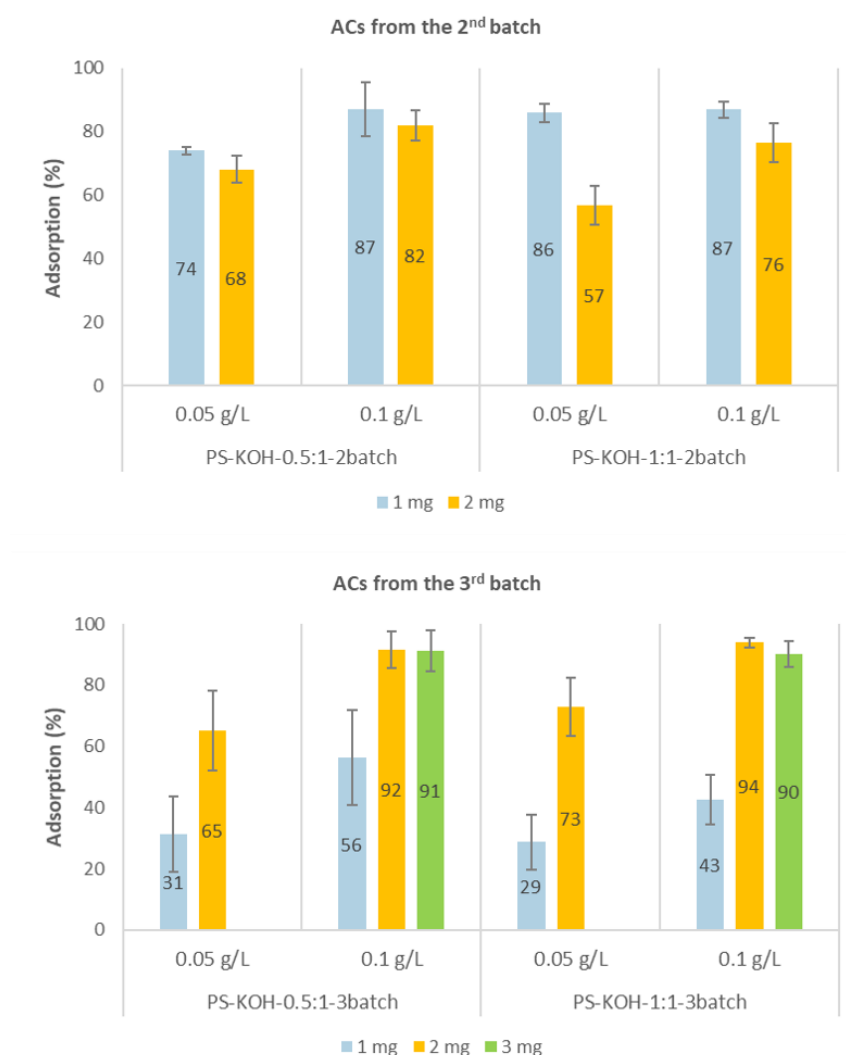


Figure 20. Evaluation of the effect of the mass of AC weighed on the CBZ adsorption percentages for a contact time of 24 h

It can be noted that for PS-KOH-0.5:1-2batch and PS-KOH-1:1-2batch, for both AC dosages of 0.05 and 0.1 g/L, the increase of the AC mass from 1 to 2 mg results in lower CBZ removal percentages. The opposite trend is observed for the two ACs from the third batch, for both AC dosages of 0.05 and 0.1 g/L, in which the increase of the AC mass from 1 to 2 mg results in higher percentages of CBZ removed. The experiments in which 3 mg of AC was weighed, demonstrate that the adsorption percentages do not vary significantly either by weighing 2 or 3 mg of AC, for a dosage of 0.1 g/L. With that being said, for a dosage of 0.1 g/L, PS-KOH-0.5:1-3batch is able to remove CBZ from aqueous solution with a percentage of $92 \pm 6 \%$ and $91 \pm 7 \%$, for a mass of AC of 2 and 3 mg, respectively.

Analogously, PS-KOH-1:1-3batch has removal percentages of $94 \pm 2 \%$ and $90 \pm 4 \%$, for an AC mass of 2 and 3 mg, respectively. With these results, one observes that the pharmaceutical uptake does not differ significantly for the same AC dosage obtained by weighing masses of 2 and 3 mg, which means that there should be homogeneity within ACs from the same batch. The amount of AC available did not allow the experiments with 3 mg of AC for PS-KOH-1:1-2batch, which would be helpful to demonstrate whether or not there was homogeneity between the two batches of PS-KOH-1:1 with similar textural properties.

Theoretically the same removal percentage should be achieved regardless of the mass of AC weighed for a specific dosage of AC in suspension, which in practice is not observed. It seems that increasing the amount of AC, for instance, by performing the experiments for AC dosages of 0.1 g/L, weighing masses of 2 or 3 mg, might increase the reliability of the obtained results, improving the repeatability of the experiments within the batches. Taking into account ACs produced by MW pyrolysis, available literature has shown that, overall, batch adsorption experiments are performed for AC dosages above 0.1 g/L. Nevertheless, the adsorbate concentrations are also significantly higher than the initial concentration considered in this work (5 mg/L). Some examples include Saucier *et al.* (2015) that used an AC dosage of 2.5 g/L, that is, 50 mg of adsorbent per 20 mL of 100 mg/L pharmaceutical solution. Also Ahmed and Theydan (2014a) performed tests to assess the effect of the AC dosage on the adsorption percentage. For a 20 mg/L stock solution of ciprofloxacin, the authors observed an increase of the removal rate, from 79.94 % to 96.12 % when the AC dosage was increased from 0.25 to 0.75 g/L (5 mg of AC per 20 mL of pharmaceutical solution and 15 mg of AC per 20 mL of pharmaceutical solution, respectively) (Ahmed & Theydan, 2014a). One observes that the adsorption experiments were performed with relatively high dosages of AC, implying the use of higher masses of AC when compared to the masses of adsorbent used in the present work, and therefore, if effects such as AC adhesion onto the walls of the vessels occurred, they would be imperceptible.

Overall, the obtained results also show that different production batches resulted in ACs with different properties and performances, that ideally should present identical

features since they were produced under the same conditions. As far as it is known, the repeatability of the production process of ACs by MW pyrolysis is not discussed in literature. This subject should gain more focus given that, generally, the production process is limited to small amounts of slurry (or dried impregnated precursor), as mentioned in Section 3.1., which in addition to relatively low product yields may restrict physico-chemical characterisation and adsorption experiments, including removal percentages, kinetic and equilibrium studies.

3.3.4. EVALUATION OF THE EFFECT OF CONTACT TIME

Beside the possible effect of the mass of AC used, it was also hypothesised if the contact time between adsorbent/pharmaceutical (24 h) was enough to guarantee that the adsorbate could access the micropores of the produced ACs. In order to complement the already obtained results for 24 h, tests were carried out for PS-KOH-0.5:1-2batch and PS-KOH-0.5:1-3batch for contact times of 49 and 72 h, by using 1 and 2 mg of AC for both AC dosages of 0.05 and 0.1 g/L. Results demonstrate that for both ACs, regardless of the adsorbent dosage, the percentage of CBZ adsorbed onto the AC decreased over time, as demonstrated in Figure 21 and Figure 22.

It would be expected to observe a behaviour similar to the one described in Figure 3 (Section 1.2.1.), in which the amount of CBZ adsorbed onto the AC would increase over time, until an equilibrium was attained. Even without reaching a plateau it was expected to observe an increase of the percentage of adsorption and not the other way around. Although the process of adsorption is an equilibrium between adsorbent and adsorbate in which there is, naturally, adsorption and desorption, the desorption of the pharmaceutical does not seem to explain the results obtained, at least not so pronouncedly.

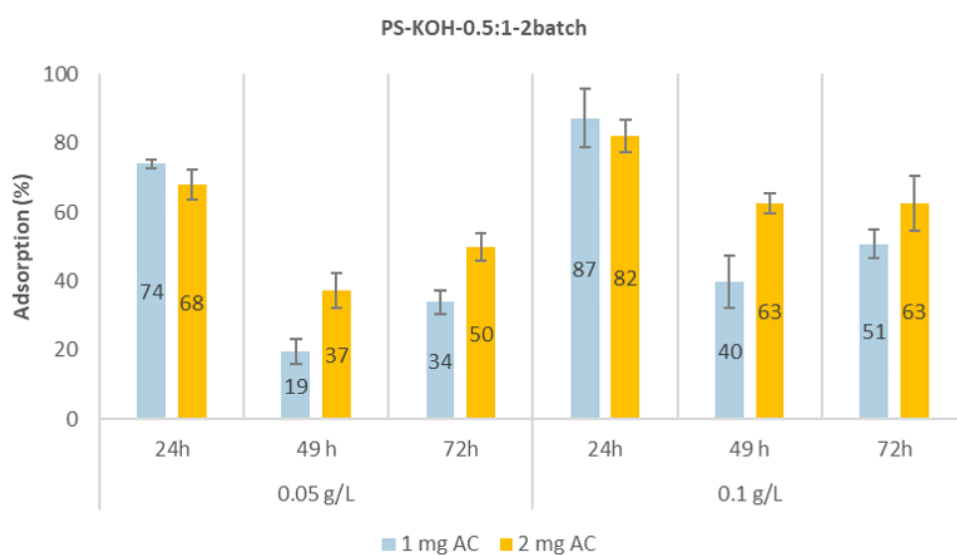


Figure 21. Evaluation of the effect of contact time between CBZ and AC on the adsorption percentages, for AC dosages of 0.05 g/L and 0.1 g/L

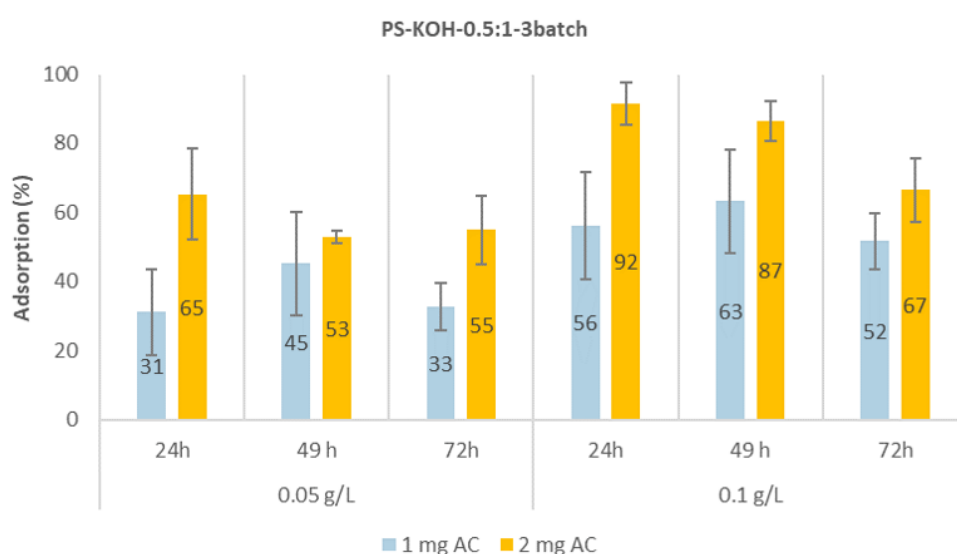


Figure 22. Evaluation of the effect of contact time between CBZ and AC on the adsorption percentages, for AC dosages of 0.05 g/L and 0.1 g/L

It seems that the increase of the contact time in addition to the possible effect of AC adhesion onto the walls/lids of the tubes (Figure 23), may be related to the decrease of the percentages of CBZ removed from aqueous solution. Probably, this effect may increase over time, resulting in the reduction of the amount of adsorbent available to retain CBZ.

With the tubes in constant shaking, it seems unlikely that some particles of AC could also be aggregate to each other, nevertheless it is a possibility that also need to be considered.

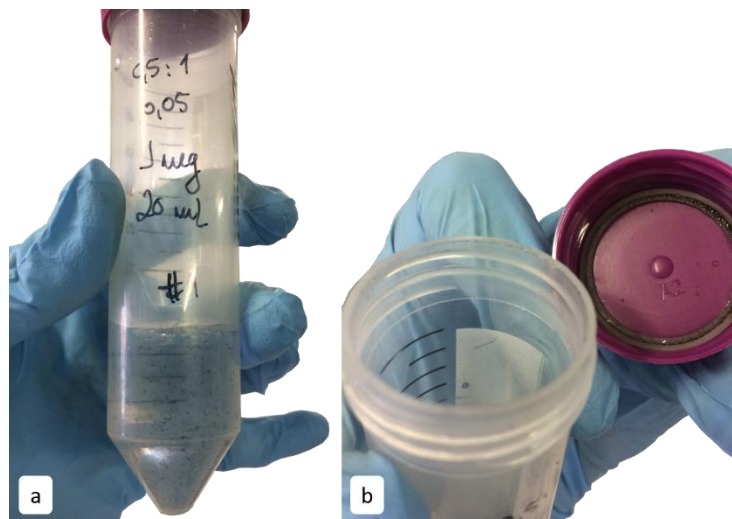


Figure 23. Conclusion of adsorption tests: (a) Appearance of a suspension after the experiment; (b) AC adhesion to the walls/lid of the tube

Figure 24 illustrates the appearance of the suspensions after 72 h shaking at controlled temperature for a) PS-KOH-0.5:1-2batch and b) PS-KOH-0.5:1-3batch. The difference in the appearance of the ACs suspensions reinforce that, regardless of the common production conditions, the two adsorbents present different characteristics.

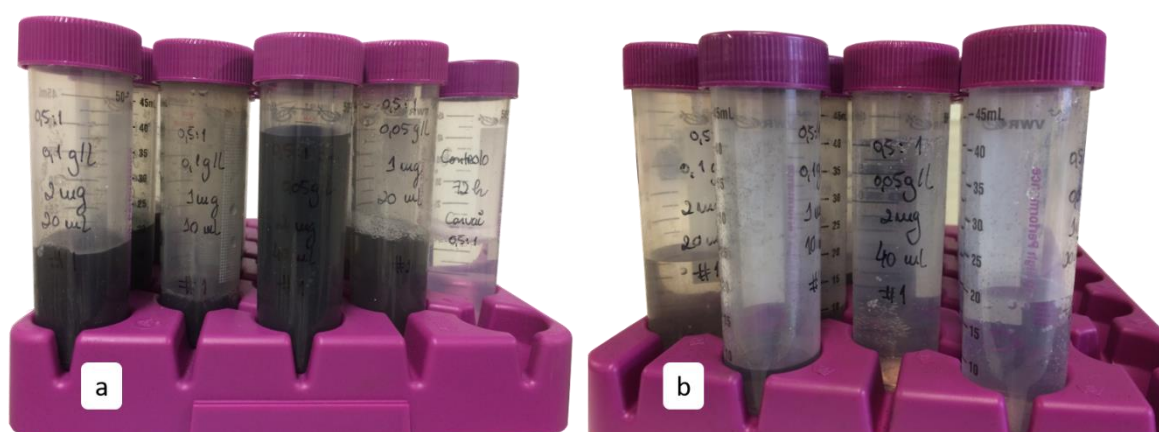


Figure 24. Adsorption tests after 72 h shaking for: (a) PS-KOH-0.5:1-2batch; (b) PS-KOH-0.5:1-3batch

Overall, the adsorption percentages are lower for the experiments in which 1 mg of AC was used instead of 2 mg, for the same final dosage. The removal percentages are also lower for the adsorbent dosage of 0.05 g/L when compared to 0.1 g/L, evidencing that the reduced pharmaceutical uptake could be linked to the reduction of the amount of AC and therefore, reduction of adsorption active sites. Moreover, one highlights that PS-KOH-0.5:1-3batch presents higher removal percentages than PS-KOH-0.5:1-2batch, which is in agreement with the better textural properties of the latter, with a S_{BET} and V_p of 875 m²/g and 0.68 cm³/g, respectively.

Studies found in literature, usually do not use contact times as long as 72 h, being commonly up to 24 h. Typically, several contact times are evaluated and the adsorption of pharmaceuticals onto the ACs tend to increase over time until the equilibrium is reached (Ahmed & Theydan, 2014a; Chayid & Ahmed, 2015; Huang et al., 2011). In order to understand the reason why the removal percentages of CBZ decreased over time, it would be relevant to test more contact times, which was not accomplished due to the insufficient amount of ACs.

CHAPTER 4: CONCLUSIONS AND FUTURE DEVELOPMENTS

This work aimed to produce ACs using solid wastes from paper mill industry, namely PS, through non-conventional pyrolysis. Three MW pyrolysed ACs were produced in triplicate by changing the activating agent:precursor IR, from which nine ACs resulted. The produced adsorbents were physico-chemically characterised by determining TOC, S_{BET} and V_p . In addition, the produced ACs were subjected to batch adsorption tests in order to assess their efficiency to remove CBZ from ultra-pure water solutions. The global appreciations were as follow:

- The experimental results have shown that within the same IR, the produced ACs presented different properties and removal performances, evidencing that the production process needed to be enhanced in order to make it repeatable. The lack of repeatability could be related to the poor levels of reaction control such as difficulty to guarantee the uniformity of MW radiation inside the modified domestic MW. Moreover, it could be related to an incomplete carbonisation, requiring the process optimisation by defining the optimal MW power, radiation time, chemical agent and IR. Considering the exploratory nature of this work and the limited timeline, the IR was the only production parameter tested.
- Overall, the ACs were characterised by a porous structure more developed than the commercial AC (PBFG4) used as reference. The ACs that presented better S_{BET} (on average 946 m²/g), were those with lower concentrations of activating agent, PS-KOH-0.5:1, being a satisfactory feature in the economic point of view.
- According to the removal percentages of CBZ from ultra-pure water solutions, it was shown that higher uptakes were achieved when the adsorption experiments were performed with PS-KOH-0.5:1, for an AC dosage of 0.1 g/L (weighing 2 or 3 mg of AC) and a contact time of 24 h. Under these experimental conditions, removal efficiencies above 80 % were observed.

The produced ACs had appreciable textural properties at an early and pioneering stage with regard to the type of precursor and heating methodology. Therefore, some future developments could include:

- In a first stage, studies should be made in order to guarantee the repeatability of the production process.
- Besides the effect of the IR, other operational parameters should be tested, including the effect that other activating agents such as K_2CO_3 and H_3PO_4 , MW power and radiation time could have on the final AC and how it would be reflected in the pharmaceutical removal efficiencies.
- Physico-chemical characterisation (beside TOC, S_{BET} and V_p), kinetic adsorption studies and adsorption equilibrium studies should be performed.
- Considering the difficulty to guarantee the homogeneous slurry packaging into the quartz reactor, experiments could be performed in parallel by using the dried impregnated precursor.
- Other classes and mixtures of pharmaceuticals could be assessed and tests could also be carried out for spiked WWTP effluents.

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