Ana Rita Pereira Almendra

Licenciada em Ciências da Engenharia Química e Bioquímica

THE EFFECT OF WATER INORGANIC MATRIX IN IBUPROFEN ADSORPTION ONTO ACTIVATED CARBON FOR WATER AND WASTEWATER TREATMENT

Dissertação para obtenção do Grau de Mestre em
Engenharia Química e Bioquímica

Presidente: Maria Madalena Alves Campos de Sousa Dionísio Andrade, Doutora, FCT/UNL
Arguente: Ana Sofia Dias Mestre Homem, Doutora, FCUL
Orientador: Rui Manuel Carvalho Viegas, Doutor, LNEC
Co-orientador: Isabel Maria de Figueiredo Ligeiro da Fonseca, Doutora, FCT/UNL

FACULDADE DE
CIÊNCIAS E TECNOLOGIA
UNIVERSIDADE NOVA DE LISBOA

Dezembro 2011

Ana Rita Pereira Almendra

Licenciada em Ciências da Engenharia Química e Bioquímica

THE EFFECT OF WATER INORGANIC MATRIX IN IBUPROFEN ADSORPTION ONTO ACTIVATED CARBON FOR WATER AND WASTEWATER TREATMENT

Dissertação apresentada à Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa para obtenção do Grau de Mestre em Engenharia Química e Bioquímica

Dezembro 2011

THE EFFECT OF WATER INORGANIC MATRIX IN IBUPROFEN ADSORPTION ONTO ACTIVATED CARBON FOR WATER AND WASTEWATER TREATMENT

AGRADECIMENTOS

Quero agradecer ao Laboratório Nacional de Engenharia Civil (LNEC), em especial ao Doutor Sérgio Coelho pela integração no NES (Núcleo de Engenharia Sanitária) e ao Doutor José Menaia pelo acolhimento no LABES (Laboratório de Engenharia Sanitária), pela simpatia e disponibilização dos meios necessários para que este trabalho se realizasse.

Um agradecimento também a todos os outros que de uma maneira ou de outra contribuíram para a realização desta tese.

À professora Isabel Fonseca, à Doutora Maria João Rosa e ao professor José Paulo Mota o meu mais sincero agradecimento por toda a ajuda.

Ao Doutor Rui Viegas pela orientação, disponibilidade e motivação prestadas, assim como pelos longos debates que tivemos.

Ao grupo do LABES pela amizade e apoio no laboratório, em especial ao Vítor pela paciência e ensinamentos muito úteis.

À Doutora Inês, ao Nuno e à Carla pela ajuda prestada e disponibilidade imediata na funcionalização e análise do carvão.

Aos meus amigos Marta, Jô, Joana, Alexandra e Joaquim por todos os momentos passados ao longo destes anos.

À minha Maria, sem ti, nada teria sido a mesma coisa. Obrigada por toda a amizade e carinho, por todos os momentos longo da tese e ao longo da vida, és fantástica!

Ao Tiago, por todo o amor e pela paciência inesgotável, obrigada também pela ajuda que foi muito necessária para seguir em frente nesta etapa não só da minha, mas também das nossas vidas. Amo-te muito. Conseguimos!

À minha família pela alegria, companhia e amor e em especial à minha mãë por ter sempre acreditado nas minhas capacidades e pelo esforço desenvolvido para me proporcionar as melhores condições para que este momento se concretizasse. Obrigada mãe adoro-te muito.

A todos um muito obrigada e um beijinho muito especial. Sem vocês certamente não teria conseguido.

ABSTRACT

In this thesis the ibuprofen adsorption onto activated carbon F400 was studied. Some of the chemical and physical properties of the carbon were studied, with two different particle sizes and one functionalized carbon. Through model solutions of natural and wastewaters, the influence of the pH and ionic strength was studied, varying also the ratio of monovalent and divalent ions.

The integrated analyses of the chemical and the textural characterization of the carbons as well as the kinetic and isotherm studies performed, using non-linear models for the parameters calculation and respective fittings of the experimental data allowed the following conclusions: i) the carbon particle size has a significant influence on the adsorption, being the limiting step the external mass transfer for the smaller granulometry, while for the larger granulometry the process was governed by the internal diffusion; ii) increasing the basicity of the carbon surface (functionalized carbon) it was possible to obtain better removal ratios, so the chemical surface is relevant in this process; iii) adsorption at acid pH is primarily governed by hydrophobic forces and the compound removal is favored; iv) when electrostatic forces govern the reaction (pH 6-8) the adsorption greatly depends on the ionic strength, being favored when the adsorbent/adsorbate interactions are repulsive and disfavored when the interactions are attactive; v) for saline waters with high pH it proved disadvantageous the use of carbon with higher basicity, possibly because the two effects cancel each other out the functionalization has only proven effective when the pH and the ionic strength varied inversely; vi) the ibuprofen adsorption did not varied when the only parameter changed was the type of ion, the ions used were the calcium (which confers hardness) and the potassium (conferring salinity). Therefore, only the ionic strength seems to influence the compound adsorption and not the nature of the ions.

Key-words: Activated carbon, F400, adsorption, ibuprofen, water inorganic matrix, water treatment.

RESUMO

Foi investigada nesta tese a adsorção de ibuprofeno em carvão activado F400. Algumas das propriedades físicas e químicas do carvão foram estudadas através da análise com duas granulometrias e uma funcionalização do carvão. Utilizaram-se várias soluções modelo de águas naturais e residuais para diferentes valores de pH e forças iónicas, fazendo variar também a razão entre iões monovalentes e divalentes.

A análise integrada da caracterização química e textural do carvão, assim como os estudos cinéticos e de isotérmicas realizados, com modelação expressa por modelos não-lineares para o cálculo dos parâmetros e ajuste dos resultados experimentais permitiu concluir que: i) a granulometria do carvão tem uma influência significativa na adsorção, sendo o passo limitante a transferência de massa externa para a menor granulometria (na maior granulometria o processo foi governado pela difusão interna); ii) aumentando a basicidade da superfície do carvão (carvão funcionalizado) conseguiram-se taxas de remoção efectivamente mais elevadas, pelo que a química de superfície é relevante; iii) a pH ácido a adsorção é maioritariamente governada por forças hidrofóbicas e a remoção do composto é favorecida; iv) quando as forças electrostáticas governam a adsorção (pH 6-8), a adsorção depende fortemente da força iónica, sendo favorecida quando as interacções adsorvente/adsorbato são repulsivas e desfavorecida quando estas são atractivas; v) para águas de elevado pH e salinidade não foi vantajosa a utilização de um carvão com maior basicidade, possivelmente porque os efeitos se anularam, a funcionalização só se mostrou vantajosa para casos em que pH e força iónica variaram inversamente; vi) a adsorção do ibuprofeno não sofreu qualquer alteração quando o único parâmetro a ser variado foi o tipo de iões, tendo sido usados iões cálcio (que conferem dureza) e potássio (salinidade), pelo que, apenas a força iónica em si é influente para estas condições e para este composto e não a sua natureza.

Palavras-chave: Carvão activado, F400, adsorção, ibuprofeno, matriz inorgânica da água, tratamento de água.

TABLE OF CONTENTS

INDEX OF FIGURES

INDEX OF TABLES

ABREVIATIONS

A_{BET}	Specific area calculated from BET model
AC	Activated carbon
BET	Brunauer, Emmet and Teller
COX	Cyclooxygenase (enzyme)
DFT	Density functional theory
DQA	Directive Quadro da Água
EC	Electrical conductivity, at 25ºC
EPA	Environmental Protection Agency
GAC	Granular activated carbon
IPWR	Indirect potable water reuse
IR	Infrared spectroscopy
IS	Ionic Strength
IUPAC	International Union of Pure and Applied Chemistry
MC	Microcystins
NOM	Natural organic matter
NSAIF	Non-steroidal anti-inflammatory
PAC	Powdered activated carbon
PhAC	Pharmaceuticals active compounds
pH_{PZC}	pH at the point of zero charge
Ppb	Part per billion
PPCP	Pharmaceuticals and personal care products
Ppm	Part per million
PSD	Pore size distribution
PSD	Pore size distribution
SPE	Solid phase extraction

TPD - Temperature programmed desorption

UF - Ultrafiltration

UPW - Ultrapure water

UV - Ultra violet

WHO - World Health Organization

WTP - Water treatment plant

WWTP - Wastewater treatment plant

XPS - X-ray photoelectron spectroscopy

SYMBOLS

b - Langmuir energy of adsorption parameter

Bt - Boyd values

$\mathbf{C_0}$ - Initial concentration in the solution at a specific time

$\mathbf{C_e}$ - Equilibrium aqueous concentration

$\mathbf{C_t}$ - Adsorbate concentration in the solution at a specific time

$\mathbf{C_t/C_0}$ - Normalised concentration

K - Freundlich unity-capacity parameter

$\mathbf{k_1}$ - Equilibrium rate constant

$\mathbf{k_i}$ - Intraparticle diffusion rate constant

n - Freundlich site-energy distribution parameter

$\mathbf{q_e}$ - Surface concentration at equilibrium

$\mathbf{q_{max}}$ - Langmuir maximum capacity parameter

$\mathbf{q_t}$ - Surface concentration at a specific time

1 INTRODUCTION

1.1 BACKGROUND

Water is an essential resource for life on Earth's ecosystems and since the first reports on pharmaceuticals in wastewater effluents and natural waters were published in the United States in the seventies, the scientific community became increasingly concerned about their potential impact in public health [1].

For society in our days is unthinkable to live without pharmaceuticals or personal care products (PPCPs). These compounds are known today as emergent pollutants. Prescription and non-prescription human and veterinary compounds are included.

Although the concentrations of pharmaceuticals found in the environment are vestigial, much lower than is believed to represent a measurable risk and not covered by law, their continue introduction in the environment may represent a long-term risk to both humans and other living beings.

It is crucial to assess the risks of these emerging contaminants, because although there are no acute toxic effects know, the constant introduction and bioaccumulation of these drugs in the water cycle could have chronic effects [2,3], in fact they are designed to cause a physiological response on humans and animals. Being biologically active and having persistence against biological degradation to retaining their chemical structure enough time to perform their therapeutic action, they can persist in the environment for long periods of time [4,5]. Besides it has to be considered that the contaminants co-exists in mixtures with other chemicals forming the so-called chemical "cocktails" [6].

Today, they are not routinely monitored by water treatment companies due to the lack of regulations, as standards do not exist for most of the compounds. Furthermore, there is an extreme cost involved for monitoring thousands of potential contaminants that are expected to be removed with the treatment.

In attempts to address the lack of water supply in areas with growing urban population, reuse of treated wastewater has been considered. This process is called by indirect potable water reuse (IPWR) and the presence of organic contaminants such as pharmaceuticals is a big challenge, at risk of increasing the presence in water to consumer, rising the chronic exposure [7].

So the implementation of efficient treatment systems becomes a matter of public interest in order to remove pharmaceutical compounds from water to avoid chronic effects caused by their presence.

In wastewater treatment plants (WWTP) the pharmaceuticals fraction removed are partially retained in the sludge, or metabolized to a more hydrophilic compound, but still a considerable fraction remain in the treated effluent waters. Other treatments have already been successfully applied on pharmaceuticals (including ibuprofen) removal, but due to high costs associated they have not been implemented [8]. So adsorption onto activated carbon (AC) presents as a good option because this technology is versatile, easily implemented and efficient [9]. Therefore it is important to understand the removal mechanisms involved, under different chemical conditions, as to be able to optimize and to study the best conditions for an efficient removal of the pharmaceutical active compound (PhAC) ibuprofen by this technology.

Some studies on the removal of ibuprofen from water by activated carbon adsorption have already been reported, but these investigations were performed with higher concentrations then those currently found in real waters [10,11].

1.2 OBJECTIVES

This thesis aimed at conducting a research approach to the adsorption of ibuprofen onto activated carbon, with lower concentrations then those that were studied and understand how the matrix of natural and wastewaters affects this process, through:

- Understand the adsorption behavior of ibuprofen at lower concentrations than those studied by other authors [10,11];
- Studying the impact of the chemical composition of the water (water inorganic matrix) by varying the:
    - Solution pH;
    - Ionic strength, with different ratios of monovalent (salinity, i.e. KCl) and divalent ions (hardness, i.e. $CaCl_2$) to understand if the nature of the charges can affect the adsorption, because it was proven in other papers that this kind of changes in the charges influence the adsorption of other compounds onto activated carbon, such as natural organic matter (NOM) and microcystins (MC) [12,13];
- Studying the effect of activated carbon particle size on ibuprofen adsorption;
- Studying how the functionalization of the activated carbon (F400) can affect the adsorption of ibuprofen;
- Application of integrated kinetic and isotherm models (non-linear forms).

1.3 STRUCTURE OF THE THESIS

1. Introduction
2. Literature review
3. Materials and methods
4. Results and discussion
5. Conclusions and future developments
6. References

Chapter 1 included the background, objectives and the structure of the thesis.

Chapter 2 presents the main aspects of ibuprofen: presence in the environment; toxicological issues; existing legislation and the actual treatment processes applied in water treatment of pharmaceuticals, focusing on activated carbon adsorption.

The materials and experimental methods applied are presented in the chapter 3.

Chapter 4 reports the results and discussion for all tests and was divided in two parts. The first part (4.1) includes the characterization results of the activated carbons studied (surface charge, functional groups and textural characterization). The second part (4.2) is composed by the isotherm and kinetic experiments to study the equilibrium time, and possible effects of the pH, the ionic strength, including the influence of the type of ions (monovalent and divalent), the functionalized AC and the activated carbon particle size effects on the adsorption of ibuprofen.

Main conclusions and proposals for future work developments are presented in chapter 5.

2 LITERATURE REVIEW

2.1 IBUPROFEN

2.1.1 General

Ibuprofen is the common name of 1-[4-(2-metylpropyl) phenyl] propionic acid and is a pharmaceutical active compound used in drugs. It is a non-steroidal anti-inflammatory (NSAIF) from the subgroup of propionic acid chemical derivatives. These drugs have in common the ability to fight inflammation, pain and fever. Like other anti-inflammatory drugs ibuprofen acts by inhibiting the activity of an enzyme called cyclooxygenase (COX). The COX enzyme converts certain fatty acids to prostaglandins production, chemicals produced by the body that cause inflammation and contribute to the perception of pain by the brain. Ibuprofen also reduces fever by blocking prostaglandin synthesis in the hypothalamus, a brain structure responsible for regulating body temperature and has also anticoagulant properties, decreasing the formation of blood clots. Prostaglandin synthase exists under two isoforms: COX - 1, which is expressed in most of tissues and COX - 2, induced by cytokines endoxins and responsible for imflammation. Only the COX - 2 is important in these processes but ibuprofen is not selective, acting also at the COX - 1 level (Figure 2.1) that inhibits the production of thromboxane avoiding platelet aggregation and therefore promotes the occurrence of thrombosis. However, a long exposure to the drug can cause adverse gastrointestinal effects [14].

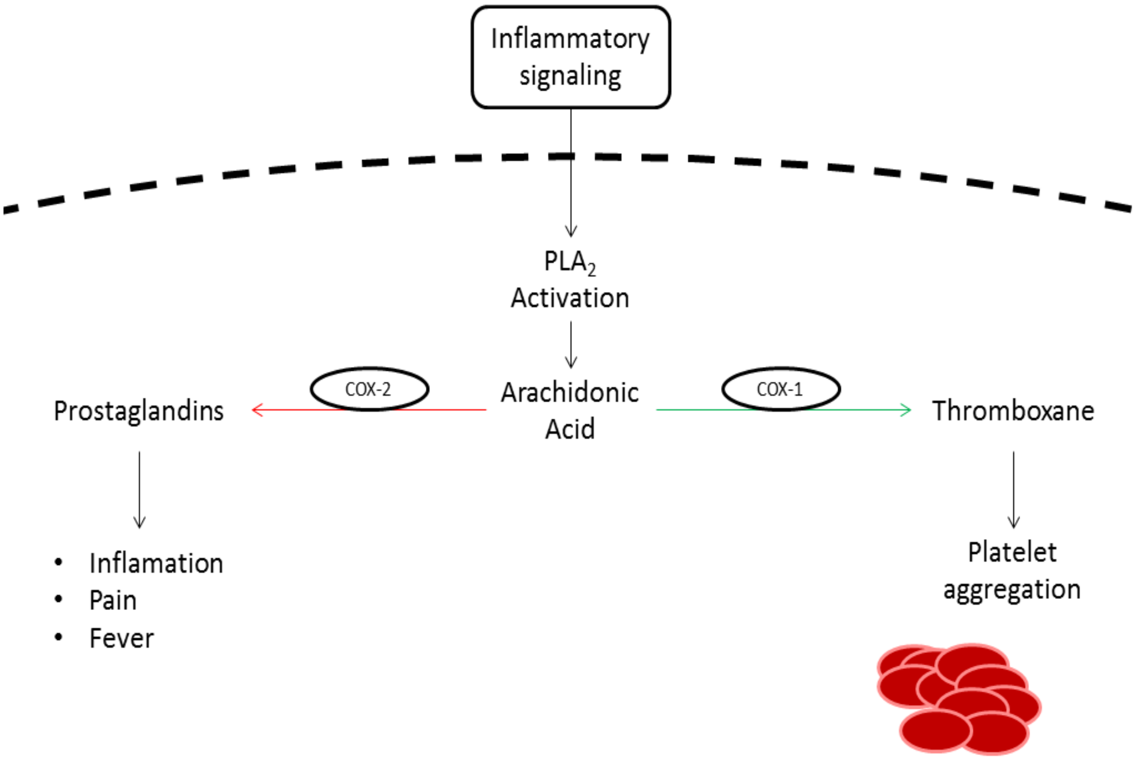


Figure 2.1. Non-steroidal anti-inflammatory (NSAIF) acting mode in the body (adapted from **[15]**).

Along with acetylsalicylic acid (the active ingredient of Aspirin and other drugs), and acetaminophen (the active ingredient of Ben-U-Ron and other drugs) ibuprofen is part of the list of essential drugs of the World Health Organization (WHO) and recognized with a huge global consumption rate.

It is notorious the increase in sales of drugs with the ibuprofen as PhAC in the last years in Portugal, passing from the 90th place in Infarmed ranking of 2003 to the 8th place in 2009 with about 2 million packages sold of which more than 1 million are Brufen the 5th most sold drug in Portugal [16].

The main characteristics of ibuprofen are presented in Table 2.1:

Table 2.1. Ibuprofen properties **[17-19]**.

IBUPROFEN ACID	
Molecular Formula	$C_{13}H_{18}O_2$
CAS number	15687-27-1
Molecular Mass	206.29 g/mol
Water solubility	21 mg/dm^3
pK$_a$	4.9
Log K$_{OW}$	3.97
Melting point	75 ºC – 78 ºC
Excretion	70% – 80% of therapeutic dosage (renal)
Metabolites	(+)-(S)-2-OHIbu, (−)-(R)-2-OHIbu, (2′S,2S)-COOHIbu, (2′R,2S)-COOHIbu, (2′S,2R)-COOHIbu, (2′R,2R)-COOHIbu
Synonyms	2-(4-isobutylphenyl)propionic Acid; Apsifen; Apsifen-F; Alpha-Methyl-4-(2-methylpropyl)benzeneacetic acid; Ibuprocin; para-Isobutylhydratropic acid; (+/-)-2-(p-Isobutyl phenyl)propionic acid; (+)-2-(4-Isobutyl phenyl)propionic acid; 4-Isobutyl- alpha-methylphenylacetic acid; Ibufen; Ibuprin; Alpha-methyl-4-(2-Methylpropyl)- Benzeneacetic Acid;

The octanol-water partition coefficient, K_{OW}, is an indicator of the tendency for compounds to bind to organic matter, and it is an important tool to help understand the fate of the compound in the environment. It is also a measure of the bioaccumulation which is the ability of the compounds to accumulate in the organisms, from direct exposure to water and food containing the substances [20].

As can be inferred in Table 2.2, ibuprofen has a high propensity to adsorb to AC (high efficiency removal) due to its high value of K_{OW} (3.97) but a high potential to bioaccumulate in aquatic organisms.

Table 2.2. Relation between K_{OW}, sorption potential and bioaccumulation potential **[20,21]**.

Log K_{OW}	Sorption potential	Log K_{OW}	Bioaccumulation potential
< 2.5	Low	< 3	No significant bioaccumulation potential
2.4 < K_{OW} < 4	Medium/high	≥ 3	Potential to bioaccumulate in aquatic organisms
> 4	High		

Ibuprofen molecular structure and dimensions are shown in Figure 2.2. It has **1.03 nm** (length) x **0.52 nm** (width) x **0.34 nm** (depth) [10].

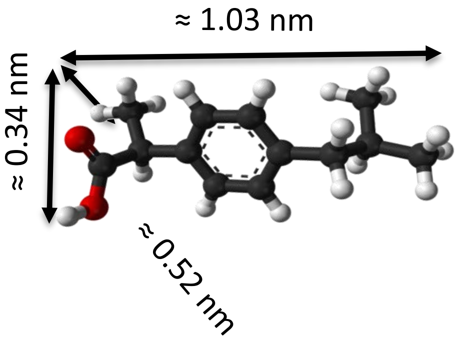


Figure 2.2. Molecular structure of ibuprofen (adapted from **[10]**).

The ibuprofen molecule contains one center (carboxylic group) that can be protonated or not, depending on the pH of the solution. Figure 2.4 shows the structure of the neutral form (HL) and of the anionic form (L^-) of ibuprofen. The pK_a is 4.9 (Table 2.1).

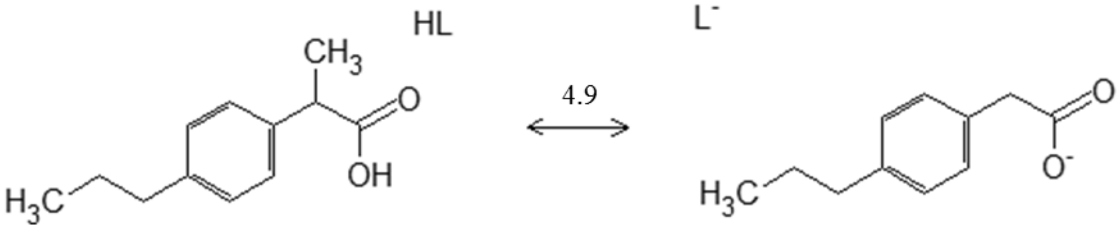


Figure 2.3. Ibuprofen protonation-deprotonation equilibrium.

The specification plot of ibuprofen is displayed in Figure 2.4. As it can be observed at the typical pH of water treatment (6 - 9) ibuprofen has always a negative net charge (L^-). Just for pH below 4.9 the net charge starts becoming neutral (HL). This compound is a weak electrolyte and so its ionization strongly depends on pH of the solution. For pH values below 3, the ibuprofen is almost 100% undissociated, while at pH 4.9 it is 50% in the dissociated form. At pH around 6 there are already about 90% of the molecules in dissociated form and 100% above pH 7.

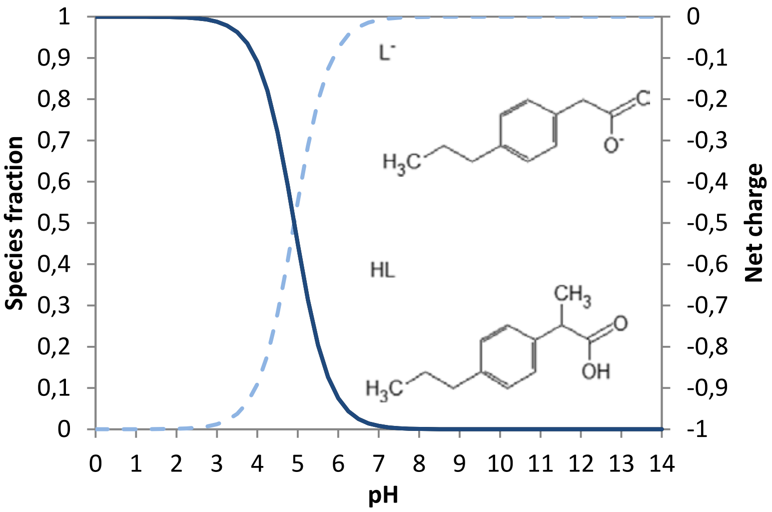


Figure 2.4. Ibuprofen species fraction and net charge.

2.1.2 Water contamination with ibuprofen

Pharmaceuticals are continually being disposed via wastewater in the environment from different sources. The major source of pharmaceuticals in the environment (water and soil) is the human and animal excretion (from medical care). Other sources have to be considered such as emission from production sites, manufacture, spill accidents, direct disposal in households, underground leakage from sewage infrastructures, hospitals, agriculture by animal manure and activated sludge (containing contaminants removed in WWTP) application [22].

Figure 2.5 shows possible routes of pharmaceutical compounds introduction in environment.

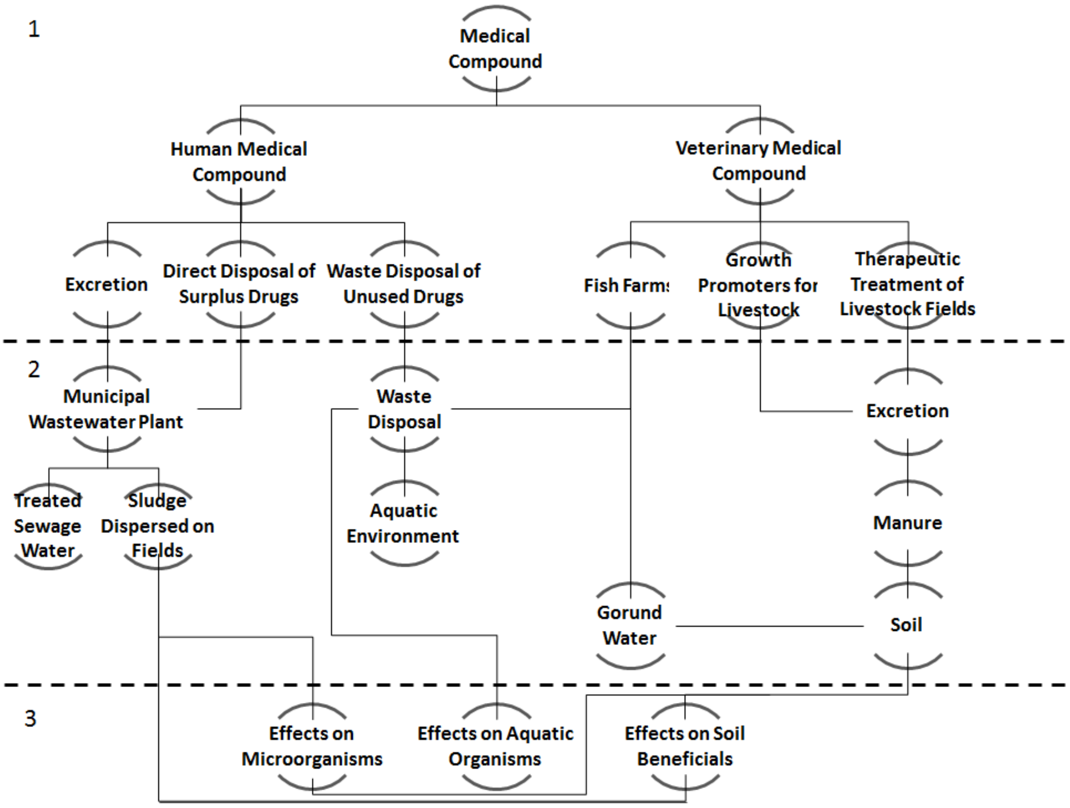


Figure 2.5. Routes of entry of pharmaceutical compounds in the environment (1 – exposure, 2 – fate and 3 – effects) (adapted from **[23]**).

Physico-chemical properties of ibuprofen referred above shows its mobility in the aquatic environment, making it possible to detect its presence in natural waters, wastewaters and even in drinking water.

Studies have shown the presence of significant amounts of pharmaceutical compounds, namely ibuprofen, in the order of magnitude of ppb and ppm in water, confirming the contamination of surface waters (rivers and lakes) and wastewaters, proving that although there is a partial removal in treatment plants a significant portion persists in the environment.

According to a European Commission report [24], *"the most prominent pharmaceuticals were non-steroidal anti-inflammatory drugs (NSAIDs) and analgesics in both influent and effluent water of the WWTPs. One of the most significant NSAIDs was ibuprofen*".

The following tables are compiled values referred by various authors on the occurrence of ibuprofen in surface, drinking waters and WWTP influents and effluents.

Table 2.3. Surface water (concentration of ibuprofen found).

7 ng/L	Germany [25]
2,7 µg/L	Netherlands [18]
0.2 µg/L	USA [26]

Table 2.4. Drinking water (concentration of ibuprofen found).

3 ng/L	Netherlands [18]
3 ng/L	Germany [25]

Table 2.5. WWTP influent (concentration of ibuprofen found).

3.7 µg/L – 12.13 µg/L	Spain [26,27]
54.2 µg/L	Brazil [26]
0.1 µg/L - **20 µg/L**	Norway [28]

Table 2.6. WWTP effluent (concentration of ibuprofen found).

3.4 µg/L	Germany [26]
85 µg/L	Netherlands [18]
3 µg/L - **27 µg/L**	England [29]
0.78 µg/L - **48.2 µg/L**	Spain [27]
48.4 µg/L	Brazil [26]

In Portugal few studies were performed addressing this issue. There is a recent study (of which only one poster has been published) featuring the quantification of pharmaceutical compounds in six water treatment plants (WTP) in Lisbon [30]. Several compounds were screened including the anti-inflammatories ketoprofen and ibuprofen.

Although the concentration values detected were low, their presence shows a persistence of the PhAC ibuprofen in the aquatic environment and confirms the difficulties of biodegradation.

2.1.3 Ibuprofen toxicity

The presence of pharmaceutical compounds in water represents a risk to aquatic ecosystems and even for human health, so their acute toxicity in some aquatic organisms has been studied, to clarify the chronic toxicity of those chemicals [2], which can affect the organisms physiology, metabolism, behavior and even their immunologic defense and cause some susceptibility to diseases [31,32].

Some ecotoxicological tests were developed to analyze the toxic effects of ibuprofen and reveal that at the concentrations that ibuprofen can be found in the environment only crustaceans are affected in their morphology [33]. However, toxicological bioassays focus on acute effects when, in fact, aquatic organisms are exposed to low concentrations continuously and therefore, the chronic effects are more probable [26]. The fact that the compounds are not alone in the environment as they are in laboratory tests and their potential combined toxicity can reveal that a significant ecotoxicological response is also important [34].

2.1.4 Legislation

The legislation to water treatment has been modified in order to make more stringent values of the contaminants already covered by law and also to add to the list new contaminants that arise (emerging contaminants).

In Portugal, the current legal framework on the water quality is established by *Decreto-Lei Nº 306/2007 (27 Agosto)* [35], that has complemented and tighten the values contained in *Decreto-Lei 236/98 (1 Agosto)* [36], setting standards, criteria and quality objectives in order to protect water resources and improve water quality in terms of its main uses.

The *Directiva Quadro da Água (DQA – Directive 2000/60/EC))* [37] aims to stipulate environmental quality standards to prevent, protect and improve water quality, as well as promote its rational and prudent use. It includes (annex X) a list of substances deemed to pose risks to the aquatic environment (called priority substances) and its aim is reducing the compounds to an eventual complete elimination in wastewater discharges, taking into account a risk assessment of ecotoxicity data in the aquatic system and humans with exposure pathways by water.

These Decree-Laws and directives do not yet include pharmaceutical compounds, which are not currently legislated by law. However it is clearly established in the same directive that substances discharge into the water should be controlled. This is the case of pharmaceuticals, which are able to reach surface waters even after its treatment in WWTPs, especially if they can cause adverse effects on the ecosystems.

Despite the permanent records and growing presence of pharmaceutical compounds in water, their concentrations and ecotoxicity do not seem to justify legal means to impose limits to its concentration in water. However the existing studies mainly address the acute toxicity of the compounds, having minor conclusions related to chronic toxicity. Thus, although the acute effects are recorded for concentrations above 1 μg/dm^3 (which do not often occur in the water) the organisms are continuously exposed to these contaminants promoting the possibility of chronic effects [26].

2.2 WATER TREATMENT OPTIONS FOR IBUPROFEN

In order to obtain the desired water quality, treatment processes are chosen taking into account several factors such as physical, chemical and microbiological water source. New technological developments for water treatment processes have been achieved through emerged support or replacing some conventional processes to treat contaminants already known and also to treat new contaminants (the so-called emerging). It is also important to refer that the laws concerning the allowed concentration of the compounds in the water are constantly changing, becoming more rigorous.

An example of a conventional WTP is represented in Figure 2.6.

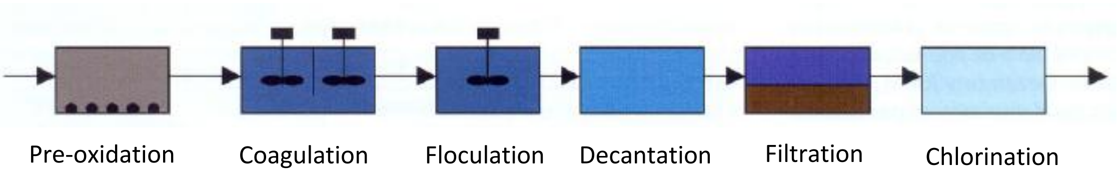


Figure 2.6. Representative scheme of conventional water treatment plant. (adapted from **[38]**).

Not all the treatment options are efficient for the removal of micropollutants (e.g. synthetic organic compounds).

The conventional system is ineffective to remove pharmaceutical compounds [39] and thus modifications to the conventional process have already been made in order to remove some pharmaceutical compounds, increasing the sludge retention times, or using membranes bioreactors and advanced oxidation processes [40,41]. Activated carbon is being explored as well.

The adsorption depends on the characteristics of pharmaceutical compounds, e.g., ionic structure and solubility, and on the properties of the adsorbent. Some values found in the literature for the removal of ibuprofen in WWTPs are relatively low, indicating that the process conditions need to be optimized, and show a high variability for the various types of water.

Membrane processes (reverse osmosis and nanofiltration) are reported to remove very efficiently ibuprofen; removing almost 100% of the contaminant and have the advantage of its rate removal being more independent of the conditions (pH, redox, potential, temperature and flow rate) than the others.

In the case of microcontaminants as ibuprofen, treatments most commonly applied are presented in Table 2.7.

Table 2.7. Most common technics applied for removal of pharmaceutical compounds in water treatment plants (adapted from **[42]**).

TREATMENT OPTIONS	**RELATIVE EFFICIENCY**	**OBSERVATIONS**
Physico-chemical treatments		Activated carbon adsorption is particularly good to remove non-polar compounds (log $pK_a>2$); PAC dose/GAC regeneration are important factors
- Coagulation/Floculation	Inefficient	
- Adsorption onto activated carbon	Very efficient for both PAC and GAC options	
Biological treatments		For ibuprofen, no significant differences in removal efficacy by CAS and MBR were detected (but for many other pollutants MBR is significantly better.
- Conventional activated sludge (CAS)	Very efficient	
- Membrane bioreactors (MBR)	Very efficient	
Reverse osmosis (RO)	Very efficient	Removals estimated to be greater than 90%, except for ketoprofen and diclorofnac (50 - 70%).
Ozonation and advanced oxidation processes (AOPs)	Promising technics for an efficient degradation of pharmaceuticals Low efficiency for ibuprofen	Incensement in the biodegradability of persistent substances; Ibuprofen is relatively resistant to ozonation; removal efficiency depends on many factors such as oxidant dose, concentration of pharmaceuticals, wastewater quality parameters and operation mode.
Nanofiltration (NF)	Efficient in general	Removal efficiency varies greatly according to : the characteristics of the compounds (molecular size, hydrophobicity, solubility, diffusivity, polarity and charge); membrane properties (permeability, pore size, hydrophobicity and surface charge); membrane operational conditions: flux, transmembrane pressure, rejections/recovery and water feed quality.

TREATMENT OPTIONS	RELATIVE EFFICIENCY	OBSERVATIONS
Disinfection	Inefficient	
Natural polishing treatment by constructed wetlands (CWs)	Efficient	Large number of promising techniques to pharmaceuticals elimination (photolysis, plant uptake, microbial degradation and sorption to the soil); Vertical and horizontal subsurface flow systems in the existence of anaerobic, aerobic and anoxic conditions; Ibuprofen is best reduced at aerobic conditions.

The presence of pharmaceutical compounds in water revealed a flaw in the current treatments that depends in large part to the treatment applied, but also to the physical and chemical properties of the compound, the origin and composition of the water as well as the operating parameters of the water treatment system. Although many of the techniques presented have good results for this compounds elimination, in many cases due to high associated costs they are not commonly applied [8].

2.3 COMPOSITION OF NATURAL WATERS

The water quality is a function of their nature and human activities.

Natural waters are composed of material within and aquatic matrix. This matrix is composed of two pairs of major states of chemical components from different sources [43]:

- soluble or insoluble;
- organic and inorganic matter.

Three of the states involved in biological transformations are identified in Figure 2.7 in white. Soluble inorganic material has either a chemical (e.g., dissolved from rocks) or a biological origin, while insoluble inorganic components are mainly mineral particulates. Soluble organic compounds are derived either as secretory (e.g., algal exudates) or breakdown products of aquatic biomass. These may be taken up by aquatic organisms (heterotrophic bacteria) or converted to soluble inorganic material in the process of mineralization. The different chemical components are derived either from biological interchange or from external sources [43].

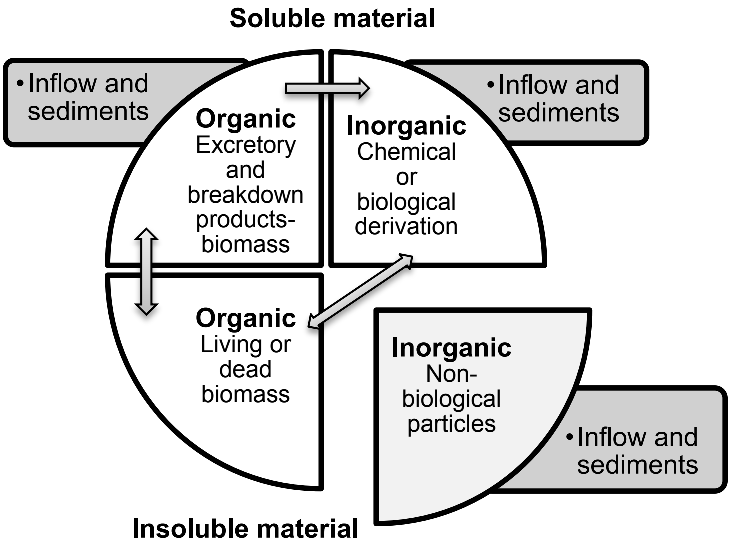


Figure 2.7. Representative scheme of the chemical composition of natural waters (adapted from **[43]**).

Water in the natural environment contains many dissolved substances and non-dissolved particulate matter. Dissolved salts and minerals are important for a good water quality because they keep the health and vitality of the organisms that rely on ecosystem.

Organic matter is important in the cycling of nutrients and can affect the biological availability of minerals and elements [43].

The focus of this study is the soluble inorganic matter in ionic forms and how it affects the adsorption of ibuprofen onto AC. Typical major ions present in natural waters include the cations Ca^{2+} and Mg^{2+} (divalent ions) and Na^{+} and K^{+} (monovalent ions), and the anions HCO_3^{-}.

Water **hardness** is a measurement of the amount of minerals present, being calcium and magnesium the most common. Hardness is usually reported as an equivalent quantity of calcium carbonate ($CaCO_3$) and is a water quality parameter very influenced by geology [44].

The values of alkalinity and hardness of water are directly related since the most common source of alkalinity is carbonate rocks (limestone). If the alkalinity is mainly based on the presence of this compound, alkalinity and hardness are almost equal and both expressed as $CaCO_3$.

Hard waters are rich in carbonates and metals so they have a high alkalinity (unless it is composed of sodium and/or potassium carbonate, which do not contribute to hardness). Correspondingly, soft waters have low alkalinity.

Usually the total hardness of a natural freshwater is around 35 mg/dm^3 in $CaCO_3$, although this value can be much higher. Even for high values (> 400 mg/dm^3) human health is not affected, however, the high hardness and high alkalinity of water are unpleasant to the taste and the association with high pH, and dissolved solid, in general, can be risky [44].

In Portugal calcium salts and their ions are abundant in the south of the country where the soils are mainly limestone. The northern granitic soils are the source of sweeter waters.

While there is no universally accepted classification for water hardness, in Table 2.8 it is presented a common classification used by the U.S. Environmental Protection Agency (EPA), and a relation of hardness, expressed in $CaCO_3$, to the water quality.

Table 2.8. Classification of water on the hardness ($CaCO_3$) and quality (adapted from **[44]**).

Hardness classification		**Hardness and quality classification**	
Type of water	**Hardness (mg/dm^3)**	**Type of water**	**Hardness (mg/dm^3)**
Soft water	0 - 75	Good quality	< 150
Moderately hard	75 - 150	Average quality	150 - 300
Hard	150 - 300	Acceptable quality	300 - 600
Very hard	> 300	Softening hard	> 600

The **pH** of the water is linked to biological productivity and a water pH in a range of $6 < pH < 8.5$ indicates a good water quality.

The **ionic strength** of a solution is a measure of the concentration of dissolved chemical constituents and can be estimated using the equation (2.1):

$$I = \frac{1}{2}\sum C_i \; Z_i^2 \tag{2.1}$$

where I (mol/dm^3) is the ionic strength, C_i (mol/dm^3) the concentration of the ith species and Z_i the valence number of ith species.

Electrical conductance is caused by substances that form ions when dissolved in water. Most substances dissolved in water dissociate into ions that can conduct an electrical current. Consequently, specific electrical conductance is an indicator of the amount of total dissolved solids (TDS) concentration in water. The higher the conductance, the more mineralized the water [45]. The classification adopted for water salinity is presented in Table 2.9.

Table 2.9. Classification of water salinity **[45]**.

Salinity	TDS (mg/L)
None	<500
Slight	500-1000
Moderate	1000-2000
Severe	>2000

2.4 ADSORPTION

Sorption processes involves adsorption and absorption. **Adsorption** is defined as the accumulation of ions and molecules in the external or internal surface of an adsorbent through adherence or bonds. Is a mass transfer operation in that a constituent in liquid phase (or gas) is transferred to the solid phase [46] and in most cases (like activated carbon) this process is reversible, the opposite of adsorption is called by **desorption**. **Absorption** involves the incorporation of one substance (gas or liquid) into another state (liquid or solid, respectively).

It is called ***adsorbate*** to the substance that is being removed from the liquid phase at the interface (e.g. pollutant) and ***adsorbent*** to the solid, liquid or gas phase onto which the adsorbate accumulates (e.g. activated carbon) [45].

Depending on the nature of the forces involved, adsorption can be called ***chemisorption***, which is a chemical reaction and involves transfer of electrons and where the adsorbate chemical composition has a crucial importance or physical adsorption, ***physisorption***, that is caused by Van Der Waals or hydrophobic forces (non-electrostatic forces), in which there are no chemical changes of adsorbed molecules and the adsorption heat is small. This type of adsorption can form overlapping layers with the molecules decreasing the strength of adsorption with the increase of layers number, unlike the chemisorption where the adsorption strength decreases because it forms a single adsorbed molecular layer (monolayer) and the surface begins to saturate [46].

There are a large number of factors that affect adsorption and which are presented in Table 2.10.

Table 2.10. Factors that affects adsorption (adapted from **[45]**).

Adsorbent	Surface area Pore size distribution Ash content Density Chemical surface	**Adsorbate**	Polarity Hydrophobicity Molecular size Solubility Acidity or alkalinity	**Operating conditions**	Temperature pH Solvent polarity Stirring speed of solid-liquid relationship Size of the particles Initial concentration (adsorbate and adsorbent) Presence of other species competing for adsorption sites

2.5 ACTIVATED CARBON

Adsorption can be used at the air-liquid interface in the flotation process [45], but only the adsorption at the liquid-solid interface has interest for this study, more specifically adsorption onto activated carbon. Activated carbon is a good adsorbent because it is very porous and possesses a very large surface area.

2.5.1 Activated carbon precursor materials and preparation

AC is an amorphous solid composed essentially of carbon and characterized by its physical structure, which includes surface area, pore volume and pore size distribution.

Chemically, its surface is composed of heteroatoms (oxygen, nitrogen, phosphorus and hydrogen) forming a complex surface which may play a decisive role in the interactions between the AC and the adsorbate, as they determine the basicity/acidity character of ACs [10]. The presence of these compounds depends on the precursor material and the activation method of the AC.

Practically all the organic material can be used as precursor for AC preparation: mineral like peat; bituminous and subbituminous coal or biomass-derived like wood or nutshells. These materials have high fixed carbon content and a low content of inorganic matter (ash) [47].

The process of manufacturing is identical for all the start materials and can be **physical** or **chemical** activation.

- Physical activation consists in two steps. The first step is the **carbonization** of the raw material that occurs at temperatures until 800 ºC in an inert atmosphere (nitrogen) to remove heteroatoms such as oxygen and hydrogen and to drive-off gases generated, enriching the carbon material and creating a porous structure still undeveloped. The other step is the **activation** with an oxidant gas such as steam, CO_2 or both (activated agents) at high temperatures to burn-off the decomposition products developing the porous structure. Evolution of microporosity is relatively similar for both activating agents and is a function of the contact time with the steam. Increasing the contact time increases the pore size of AC [48].
- Chemical activation is usually carried out if the raw material is wood or peat. The raw material is impregnated by a compound such as H_3PO_4 or $ZnCl_2$, and consists of a pyrolysis followed by washing to remove the activated agent [47].

According to the size, there are two most common forms of AC after activation, the **granular activated carbon** (GAC), that is the larger form, with particle size above 177 μm and is the type of AC used in packed bed contact basins of water treatment plants and the **powdered activated carbon** (PAC), in which the particle size is usually around 5 - 50 μm and is regularly added in water treatment plants in the rapid mixing coagulation/flocculation [49,50].

PAC processes are ideal for treatment plants when the adsorption technology is only infrequently (and for short periods of time) necessary, since no changes are needed to be made in the conventional treatment. Otherwise the increase of sludge volume (not regenerated) that has to be disposed of through land filling or other solids handling. In such cases the use of GAC is economically more viable. The factors that affect the choice of GAC, besides the possibility to remove organic and inorganic constituents at very low concentrations, are the easy handling and safe operation in both batch and continuous equipment, no sludge formation and the possibility of the adsorbent being regenerated and used again [51], however it should not be forgotten the fact that thermal regeneration requires a significant quantity of energy, which may lead indirectly to greater environmental risks. A cost benefit analysis must take these factors into account [42].

2.5.2 Activated carbon textural properties

Textural properties of AC included the **surface area**, **pore volume** and **pore size distribution**.

The classification recommended by the International Union of Pure and Applied Chemistry (IUPAC) for ACs pore structure is composed by ultramicropores (< 7 Ǻ diameter), supermicropores (7 - 20 Ǻ diameter), mesopores (20 - 500 Ǻ diameter) and macropores (> 500 Ǻ diameter) [52]. Micropores constitute the majority of the internal area of ACs, strongly contributing to the adsorption capacity, and the mechanism of adsorption is by superimposition of the adsorption potential of opposite walls. Mesopores allow the adsorbate to reach the micropores and the mechanism of adsorption is by capillary condensation of adsorbate. Lastly the macropores transport the adsorbate to the pore size below which fall within the AC, have a reduced surface area and cannot be filled by capillary condensation but may still influence the kinetics of the process. The adsorption of an adsorbate in a solution requires the presence of all pore types, requiring different reasons for different adsorbate types. Pore size distribution is dependent on the precursor material and the activation process [45].

In Figure 2.8 the AC structure is ilustrated.

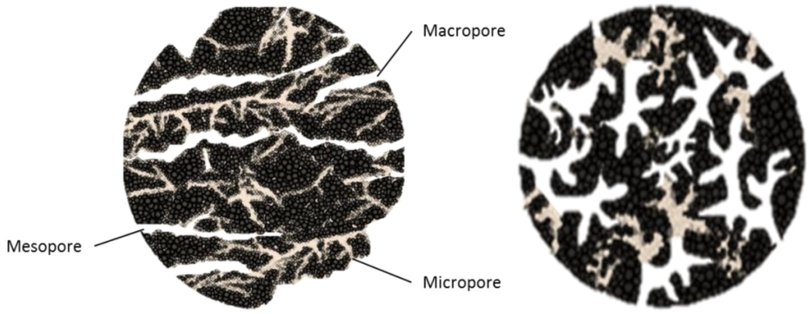


Figure 2.8. Schematic illustration of activated carbon porous surface (micropore, mesopore and macropore active sites) (adapted from **[53]**).

It is very important to know the **pore volume** of activated carbons because they strongly influence adsorption. All the porous sizes are important for a good adsorption but depending on the adsorbate size some are preferred. The adsorbent pore size can affect the adsorption in two different ways that needed to be considered:

- The adsorption strength increases with diminishing pore size, since the contact points between adsorbent surface and the adsorbate increases;
- It is also important to consider that if the pores are too small, size exclusion can occur, limiting the adsorption of adsorbate. There is a relation valid for aqua solutions that avoid this phenomenon saying that if the pore width is smaller than about 1.7 times the second dimension of the contaminants, size exclusion becomes relevant.

Pore size distribution (PSD) of the adsorbent usually involves the approximate solution of the generalized adsorption isotherm:

$$N(P) = \int f(w)\, v(w,P) dw \qquad \textbf{(2.2)}$$

where $N(P)$ is the number of moles adsorbed at pressure P, $f(w)$ is the pore size distribution and $v(w,P)$ is the molar density of nitrogen at pressure P in a pore of width w [54].

The density functional theory (DFT) is one of the most widely applied methods for the calculation of $v(w,P)$, as it describes the adsorption oven the entire range of carbon pore sizes [55].

AC surface area influences the adsorption, in the way that larger surfaces increase the adsorption process. The technique most applied and recommended by IUPAC for AC pore structure characterization is low temperature N_2 adsorption isotherm analysis (at 77 K) [56]. The Brunauer-Emmett-Taller (BET) equation can be applied to this adsorption isotherms, allowing the determination of specific surface area, called **BET surface area** (A_{BET}) through the determination of nitrogen amount required to form a complete monolayer of the nitrogen on activated carbon surface [46]. The porous volume is calculated through this technic either.

CO_2 adsorption isotherm analysis, at 273 K, is required for a detailed microporous analysis. The DR equation permits to obtain the ultramicroporous volume [48].

2.5.3 Activated carbon surface chemistry

AC **Chemical composition** essentially depends on heteroatoms content and exerts a strong influence in the adsorption process.

The **surface charge** and **hydrophobicity** are properties of each carbon type and determined by the surface groups, mainly oxygen and hydrogen content. They can be a property of the raw material but can be introduced either by the activation process or after preparation (by post-treatment).

Oxygen is present in functional groups such as: carboxyls, phenols, lactones, aldehydes, ketones, quinines, hydroquinones, anhydrides or ethers. The presence of these elements causes the heterogeneous **chemical surface** of the AC. In solution, the dissociation of surface groups causes a surface charge in AC. Some of the groups have an acidic character (carbonyl, carboxyl, phenolic hydroxyl and lactones) and other can contribute to the basicity of the structure (pyrones, chromene and quinones) [57].

The **Elemental analysis** is often applied to determine the chemical elementals (e.g., carbon, oxygen, nitrogen and sulfur) content of the AC. The element with the highest percentage is carbon, but the other elements (especially oxygen) give an indication about the acidity or alkalinity of the material.

Owing to the amphoteric character of the carbon surface (acid/basic functional groups) the surface properties may be influenced by the pH value of the coexisting liquid bulk phase, so the surface charge of ACs is a function of the solution pH. In Table 2.11 an explanatory scheme of how the pH can affect the AC surface is shown [58].

Table 2.11. Macroscopic representation of the pH effect on the AC surface groups (adapted from **[58]**).

Acid Medium	Carbon Surface	Basic Medium
$Ar_\pi - H_3O^+$	Ar_π	Ar_π
ArO^+	$Ar\mathrm{O}$	$Ar\mathrm{O}$
$Ar\mathrm{N}{H_3}^+$	$Ar\mathrm{N}H_2$	$Ar\mathrm{N}H_2$
$ArOH$	$ArOH$	ArO^-
$ArCOOH$	$ArCOOH$	$ArCOO^-$

The **point of zero charge** (pH_{PZC}) of ACs is the pH value at which net the surface charge is zero. For typical amphoteric carbons, the surface is positively charge at $pH < pH_{PZC}$ and negatively charge at $pH > pH_{PZC}$ [47,59].

The experimental techniques most often used to determine the pH_{PZC} are based on **surface titration** that includes:

- *Mass titration* [60,61].

To the persistent mineral matter (inorganic oxides) of carbon combustion is given the name of ash. Carbon **ash content** depends on the precursor material and on the treatments (impregnation/modification). The best AC for adsorption must have low ash content [62].

Other experimental techniques can be applied to study the AC properties:

- Temperature-programmed desorption (TPD) - used for the characterization of the solid surfaces. This technique is based on the fact that oxygenated functional groups decompose upon heating by releasing CO and CO_2 (inert atmosphere), producing distinct peaks [63];
- Infrared spectroscopy (IR) - for the determination of surface groups, namely by Fourier Transform IR (FTIR) [61];

2.5.4 Factors that control the adsorption onto activated carbon

As mentioned earlier, AC adsorption is a very suitable process for water treatment. However, the AC ability to adsorb contaminants depends of various important factors mentioned above, including the water inorganic matrix, e.g., the pH and ionic strength of the solution.

There is an extensive range of energies contributing to the free energy of adsorption that can be grouped into **non-electrostatic** and **electrostatic**. By electrostatic forces understands only columbic interactions, although at atomic level all ionic and molecular interactions can be "electric”.

Adsorption of non-ionized organic compounds does not depend of the surface charge of the AC when pH < pK_a. However, when pH > pK_a, those compounds are dissociated and the adsorption of their ionic form depends on the surface charge, **electrostatic** forces controls the adsorption process [47,59]. A negatively charged surface will repel negatively charged molecules and attract positive ones: a positively charge carbon will attract negative molecules to his surface and repel the positives. These interactions strongly depend on the charge densities for both carbon surface and the adsorbate molecules and on the ionic strength of the solution, as will be studied later [58].

The **non-electrostatic** interactions are always attractive, and include **van der Walls** forces, **hydrophobic** interactions and **hydrogen bonding** [58].

Another factor that has a significant role in adsorption is the affinity between the adsorbate and the solvent (e.g. solubility).

AC-adsorbate interactions are mainly of hydrophobic or electrostatic nature, being the ionic strength of the solution a very relevant factor in the last situation. Ionic strength exerts an adsorbent-solute **shielding effect** that is advantageous when the forces are repulsive and harmful when they are attractive.

2.5.5 Adsorption models

2.5.5.1 Adsorption isotherms, models

The adsorption isotherm relates the amount of adsorbed adsorbate per unit mass of adsorbent and solute concentration in equilibrium at a constant temperature. The amount adsorbed was calculated as follows:

$$\boldsymbol{q_t = \frac{(C_0 - C_t)V}{m_{AC}}} \qquad \textbf{(2.3)}$$

where q_t (mg/g) is the quantity adsorbed in the solid phase, C_0 and C_t (mg/dm^3) are, respectively, the initial adsorbate concentrations in the solution and at time t, V (dm^3) is the solution volume and m_{AC} (g) the adsorbent weight.

In this study the **Langmuir** and **Freundlich** models, the two most common models, are applied to describe the adsorption equilibrium being important to determine the AC adsorption capacity in single-solute solutions, especially for organic compounds at very low concentrations. The Langmuir equation applies to processes in which usually the adsorption occurs in monolayer while the Freundlich equation is used to analyze systems in which there is adsorption on surfaces without an uniform pore distribution [46,64].

The **Langmuir** model was developed to describe the gas-solid-phase adsorption onto activated carbon but it has been most widely used to describe the adsorption of a solute from a liquid solution. The isotherm is based on several basic assumptions [46]:

1. The sorption takes place at specific homogeneous sites within the adsorbent;
2. Once a molecule occupies a site, no further sorption takes place;
3. All sites are identical and energetically equivalent, i.e., the adsorbent is structurally homogenous;
4. The forces of interaction between adsorbed molecules are negligible.

With * representing the active sites and considering that each adsorbed molecule A occupies one of the site, the equilibrium adsorption/desorption can be represented by the equation (2.4) [46]:

$$A + * \leftrightarrow A * \qquad \textbf{(2.4)}$$

Although this model does not apply satisfactorily in some cases, having some real limited representation and interpretation, it is widely used given its simplicity and rationality.

The **Langmuir** equation is described as:

$$\boldsymbol{q_e = \frac{q_{max} b C_e}{1 + b C_e}} \qquad \textbf{(2.5)}$$

where q_e (mg/g) and C_e (mg/dm^3) are respectively, the solid-phase and the liquid-phase concentrations of adsorbate at equilibrium, the constant q_{max} (mg/g) is the maximum adsorption capacity (surface concentration at monolayer coverage), representing the maximum value of q_e that can be achieved as C_e is increased, and *b* (dm^3/mg) is the adsorption equilibrium constant, or Langmuir constant, which is related to the energy of adsorption, and which increases as the strength of the adsorption bond increases.

The **Freundlich** isotherm model adsorption is an empirical equation (2.6) applicable to non-ideal adsorption on heterogeneous surfaces and is expressed as follows:

$$\boldsymbol{q_e = K C_e^{1/n}} \qquad \textbf{(2.6)}$$

where q_e (mg/g) and C_e (mg/dm^3) are the equilibrium surface and solution concentrations, respectively. *K* (mg/g) (dm^3/g)$^{1/n}$ is the Freundlich constant related to sorption capacity, and *n is* the heterogeneity factor.

The parameter *K* is a measure of the capacity of the adsorbent for the adsorbate and the higher is this value, the higher is the adsorption capacity. On the other side, when *1/n* is small (higher values of *n*) the stronger is the adsorption. As *1/n* becomes higher (small n values), the adsorption capacity declines.

The Freundlich equation only applies until the activated carbon is saturated, i.e., when q_e increases with the increase of C_e. When q_e becomes independent of the C_e value the Freundlich model can no longer be applied.

Linear regression was the frequently used method to determine the best-fitted isotherm models and its parameters, due to the simplicity in estimation. However, according to other authors the non-linear form of the models is always better to the estimation of the parameters, as well as the correlation coefficients (between the experimental and modeled values), that in the case of linearization can lead to erroneous results [65,66].

2.5.5.2 Adsorption kinetic models

In adsorption processes in aqueous phase, three consecutive steps (**mechanistic steps of adsorption**) can be considered, according to Reichenberg [67]:

- **Film diffusion**, consisting in the travel of the material to adsorb towards the external surface of the adsorbent (external mass transfer);
- **Intraparticle diffusion**, which is the transport from the external surface of the adsorbent to the active adsorption sites (diffusional mass transfer within the pores of the adsorbent, excluding a small amount of adsorption that occurs on the exterior surface of the adsorbent);
- Physical or chemical **adsorption** of molecules on the surface of the internal pores of the adsorbent (adsorption stage).

The last stage (adsorption) is not to be considered as the rate limiting step as it is very fast.

If the internal transport is slower than external transport, the transport rate is governed by particle diffusion, if it is the opposite (the external transport is slower than the internal transport), the transport rate is governed by film diffusion [67].

Two kinetic models have been widely used: one developed by Lagergren , representing a first order reaction , another developed by Ho and co-workers, representing a second order reaction, and are, respectively, entitled as **pseudo-first** and **pseudo-second** order kinetic models [68].

The **pseudo-first order** model is expressed by the following equation [69]:

$$\frac{dq_t}{dt} = k_1\,(q_e - q_t) \qquad \textbf{(2.7)}$$

where q_e (mg/g) is the surface concentration at equilibrium, q_t (mg/g) is the average surface concentration at time t, and k_1 (min^{-1}) is the kinetic constant of pseudo first-order reaction.

The adjustments were made to the values of concentration in the aqueous phase (C_t), since this is the experimentally measured quantity, so it was necessary to change the variable q_t (solid-phase concentration) for the variable C_t (liquid-phase concentration) as following:

$$\frac{dq_t}{dt} = \frac{dC_t}{dt} \times \frac{dq_t}{dC_t} \tag{2.8}$$

The following equation (2.9) was obtained through a series of mathematical operations, as follows:

$$k_1\left(q_e - q_t\right) = \frac{dC_t}{dt} \times \frac{dq_t}{dC_t} \xRightarrow[(2.3)]{equation} k_1\left(q_e - \frac{(C_0 - C_t)\,V}{m_{AC}}\right) = \frac{dC_t}{dt} \times \frac{d\left(\frac{(C_0 - C_t)\,V}{m_{AC}}\right)}{dC_t}$$

thus resulting in:

$$\frac{dC_t}{dt} = \frac{-m_{AC} \times k_1\left(q_e - \frac{(C_0 - C_t)\,V}{m_{AC}}\right)}{V} \tag{2.9}$$

The **pseudo-second order model** can also describe the sorption kinetic. The reaction rate is dependent on the amount of solute adsorbed on the surface of the adsorbent and the amount adsorbed at equilibrium. The differential equation is the following [69,70]:

$$\frac{dq_t}{dt} = k_2\left(q_e - q_t\right)^2 \tag{2.10}$$

where q_e (mg/g) is the surface concentration at equilibrium, q_t (mg/g) is the average surface concentration at time *t* and k_2 (g/(mg.min)) is the pseudo second-order constant.

Considering equation (2.8)

$$k_2\left(q_e - q_t\right)^2 = \frac{dC_t}{dt} \times \frac{dq_t}{dC_t} \xRightarrow[(2.3)]{equation} k_2\left(q_e - \frac{(C_0 - C_t)\,V}{m_{AC}}\right)^2 = \frac{dC_t}{dt} \times \frac{d\left(\frac{(C_0 - C_t)\,V}{m_{AC}}\right)}{dC_t}$$

thus appearing:

$$\frac{dC_t}{dt} = \frac{-m_{AC} \times k_2\left(q_e - \frac{(C_0 - C_t)\,V}{m_{AC}}\right)^2}{V} \tag{2.11}$$

As for the isotherm adsorption, the non-linear kinetic equations are described as the method to the estimation of the parameters, as well as the correlation coefficients of adsorption [71-74].

In order to apply these models to the experimental data it is necessary to know the value of the equilibrium surface concentration (q_e) [75]. The value of q_e can be calculated using the value, given by the isotherm that better describes the equilibrium. Since the equilibrium equations are complex and non-linear it is not possible to calculate the value of q_e analytically, so it should be calculated numerically by a system of equations, composed by the equation describing the equilibrium, equation (2.5*)* or equation (2.6), with the equation obtained rearranging the equation (2.3):

$$C_e = C_0 - q_e \frac{m_{AC}}{V} \tag{2.12}$$

where q_e (mg/g) is the surface concentration at equilibrium, C_0 and C_e are, respectively, the initial and in equilibrium adsorbate concentrations in the solution (mg/dm^3), V (dm^3) is the solution volume and m_{AC} (g) the adsorbent weight.

The **Intraparticle diffusion model** is a mechanistic way to describe the sorption kinetic; this model allows identifying the controlling step, or the combination of steps, of the overall adsorption process: film or external diffusion, pore diffusion or surface diffusion.

According to Webber and Morris, the amount adsorbed at time *t*, can be expressed as [76]:

$$q_t = k_{id} t^{0.5} + A \tag{2.13}$$

Where q_t (mg/g) is the amount adsorbed at time t (min), k_{id} (mg/(g.min$^{0.5}$)) is the intraparticle diffusion constant, and *A* (mg/g) is a constant related to the thickness of the boundary layer.

If the result is a straight line passing through the origin ($A = 0$) suggests that the intraparticle diffusion is the only rate-limiting step. However, if the plot is linear but does not pass through the origin, the external mass transfer cannot be neglected and the larger is the value of A, the greater is the boundary layer effect. The data can also exhibit multi-linear plots, meaning that there is more than one step controlling the sorption process. Only in the first stage of adsorption external resistance to mass transfer can be significant, so this resistance is represented by the first sharper portion. The intraparticle diffusion controls the second stage of adsorption (represented by the second linear portion) [77].

The rate limiting step of adsorption process can be inferred by analyzing the kinetic data with a model developed by Boyd (1947) [78] and Reichenberg (1953) [79]. The expression developed by the model is the following:

$$F = \frac{q}{q_e} = 1 - \frac{6}{\pi^2} \times \sum_{n=1}^{\infty} \frac{1}{n^2} \times e^{-n^2 \times Bt} \tag{2.14}$$

where B (1/s, if t is in s) is given by:

$$B = \frac{\pi^2 \times D_i}{r^2} \quad \textbf{(2.15)}$$

D_i (cm^2/s) is the effective diffusion coefficient and r (cm) is the particle radius (assuming spherical particles).

The model is based in the following assumptions:

- F is a mathematical function of Bt and vice versa. Plotting data values of Bt against the values of t, a straight line passing through the origin should be obtained so long as the diffusion coefficient D_i does not vary with F over the range of values involved;
- F is independent of the concentration of solute ions (depends only on D_i/r^2);
- B is inversely proportional to the square of the particle radius; dF/dt and dq/dt are proportional to B for a given value of F.

According to Reichenberg, for values of F < 0.85, equation (2.14) can be simplified to:

$$Bt = 6.28318 - 3.2899\,F - 6.28318\,(1 - 1.0470\,F)^{0.5} \quad \textbf{(2.16)}$$

If the line passes through the origin, the intraparticle transport is the rate limiting step; if the line does not pass through the origin, external mass transfer is the rate limiting step.

Other important tool to determine the rate-limiting step(s) in adsorption is the **homogeneous surface diffusion model** (HSDM). In this model, the internal mass transfer is only due to surface diffusion. The diffusion of a molecule from the external surface of the adsorbent particle through the pore surface to the adsorption site is predicted under the following assumptions [80]:

- Internal mass transfer is only governed by surface diffusion;
- External mass transfer is governed by a linear driving force;
- At the solid/liquid interface, there is continuity between external mass transfer and internal diffusion;
- At the solid/liquid interface, the adsorbate concentration in the fluid is in equilibrium with the adsorbate load on the surface concentration;
- The particle of adsorbent is supposed to be spherical and homogeneous.

This model can be very useful to predict the AC doses needed for the removal of micropollutants.

3 MATERIALS AND EXPERIMENTAL PROCEDURE

3.1 RESEARCH STRATEGY

In order to propose the defined objectives, the research strategy developed for the study of ibuprofen adsorption onto activated carbon includes:

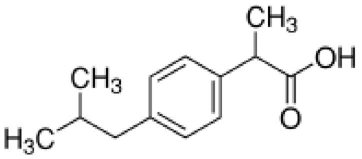
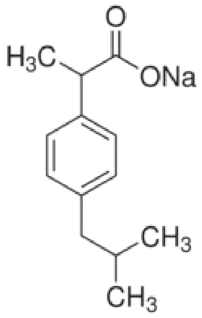
- **Activated carbon selection** (based on literature review);
- The choose of two **particle sizes** for the activated carbon;
- The **functionalization** of the activated carbon chosen to change the chemical composition and the textural structure;
- The **chemical** (elemental analysis and surface groups analyses and surface charge by carbon titration) and **textural characterization** (porous structure) of the selected activated carbon for both particle sizes and the functionalized;
- Isotherm and kinetic studies simulating natural and wastewaters to investigate the adsorption mechanisms and the impact of water inorganic matrix (pH and ionic strength) on adsorption capacity.

3.2 MATERIALS

3.2.1 Ibuprofen

Ibuprofen sodium salt was purchased from Sigma-Aldrich with a purity of approximately 98% and used as the single component adsorbate in this study. Physicochemical properties of both acid and salt form of ibuprofen are presented in Table 3.1.

Table 3.1. Main physicochemical differences between ibuprofen acid and sodium salt **[18,81,82]**.

	Ibuprofen acid	Ibuprofen sodium salt
Structure		
Molecular Formula	$C_{13}H_{18}O_2$	$C_{13}H_{17}NaO_2$
CAS number	15687-27-1	31121-93-4
Weigth (g/mol)	206.29	228.26
Water solubility (25 ºC)	(Low solubility) 21 mg/L	100 mg/mL

The concentrations of contaminant ibuprofen used were 100 μg/dm^3 at the first stage of the work and increased to 10 mg/dm^3 for the last experiments (these experiments were performed to support the results of the first stage and in order to answer some questions raised more promptly). The first values are closer to values found in wastewaters (influents or effluents) but also deviate somewhat from the values reported for natural waters. These concentrations were used to fit the available analysis methods and to guaranty that the experiments had acceptable errors associated with measurements.

A solution with a concentration of 20 mg/dm^3 of Ibuprofen was initially prepared for each model water study (for the different electrolytes) to serve as starting solutions to all other diluted solutions.

3.2.2 Activated carbon

In this study, a commercial activated carbon reference Filtrasorb 400 (F400) from Chemviron Carbon (European Operations of Calgon Carbon Corporation, USA) was used as adsorbent. This carbon was chosen based on literature review.

Choice of activated carbon

According to the manufactor, F400 is made from grades of bituminious coal and is physically (steam) activated, leading to a high adsorption capacity and a high number of transport pores. These characteristics make the carbon specially recommended for drinking water treatment, in which is necessary to remove organic micropollutants such as pharmaceuticals [83].

Considering what was referred in section 2.5, an AC to efficiently remove ibuprofen should be basic, have a high BET surface area and a large number of micropores, preferentially around 8.8 Å or greater, because according to the literature the pore width should be about 1.7 times the second largest dimension of the adsorbate. (suprermicropores range (7 - 20 Å diameter)).

Four activated carbons were screened (F400, F200, NOR 0.8 and NOR 1240) and F400 activated carbon was selected (the comparative table is presented in ANNEX VI). This carbon has a high micropore volume (special supermicroporous), an adequate pH_{PZC} (around 7.9) and a satisfactory A_{BET} as shown in Table 3.2.

Table 3.2. The structural properties of F400 AC found in literature (**[83-85]**).

Property			F400 AC
Material			Bituminous coal
Iodine number (mg/g) (min.)			1000
Moisture, weight % (max %)			2%
Average particle size (µm)			40
Methylene blue			260
Absolute density (g/cm^3)			2.19
Appearance density, ρ_{app} (g/cm^3)			0.818
pH_{PZC}			7.9
Surface areas (m^2/g)			
	A_{BET}		825
	A_{micro}		768
	A_{ext}		57
Pore volume (cm^3/g)			
	V_{micro}		0.387
		$V_{SUPERmicro}$	0.387
		$V_{ULTRAmicro}$	1.83E-24
	V_{ext}		0.104
	V_{total}		0.491

Elemental analysis is also a good indicator of the AC properties (decreasing the oxygen content will decrease the acidity of the AC surface). Some results found in the literature are presented in Table 3.3.

Table 3.3. Elemental analysis (wt %) for F400 AC found in literature **[84]**.

N (%)	C (%)	H (%)	S (%)	O (%)	Ash (%)
0.8	87.5	0.18	0.65	*10.879	6.6

For this study the F400 AC was used in two GAC particle sizes: 63 - 90 µm and 125 - 180 µm. Also at a functionalized form with 125 - 180 µm particle size was used.

3.2.3 Assayed waters

The experiments were performed using electrolyte solutions with different ionic strengths and different concentrations of monovalent and divalent cations and with different concentration ratios, adding the salts KCl and $CaCl_2$, respectively. The salts were added to Milli-Q® water obtained from a Millipore system with a resistivity of 18.2 MΩ.cm at 25 ºC and total organic carbon (TOC) not exceeding 10 ppb, ultrapure water (UPW).

A summary of the characteristics of the assayed waters are presented in Table 3.4 (ionic strength, ions composition, hardness, pH and electrical conductivity (EC)), and were intended to simulate typical natural and wastewaters.

For the ionic strength were used six values ranging between 2.5 mM and 9.35 mM.

Table 3.4. Characteristics of the electrolyte solutions used before ibuprofen addition.

IS (mM)	**Ions concentration (mg/dm^3)**		**Ca/K**	**Hardness (mg/dm^3)**	**Measured values (25 ºC)**		**Classification according to hardness**
	K^+	Ca^{2+}			pH	EC (µS/cm)	
2.5	39.10	20.00	0.50	50.00	5.71	271.00	Soft
2.5	39.10	20.00	0.50	50.00	8.00	273.00	Soft
3.5	78.20	20.00	0.25	50.00	5.67	390.00	Soft
4.25	66.50	34.10	0.50	85.00	5.67	448.00	Moderately hard
5.5	39.10	60.10	1.50	150.00	5.85	499.00	Hard
5.95	133.00	34.10	0.25	85.00	5.80	717.00	Moderately hard
9.35	66.50	102.00	1.50	255.00	5.92	820.00	Hard
9.35	146.23	74.80	0.50	187.00	8.00	827.00	Hard

3.3 EXPERIMENTAL PROCEDURE

3.3.1 Analytical methods

3.3.1.1 pH and conductivity

The pH meter and the electrical conductivity was measured at 20 ºC (±0.01 ºC) with a Consort C863 multiparameter analyzer (precision ± 0.001 μS/cm), using standard methods of analysis [86].

3.3.1.2 Solid phase extraction

In order to analyze the low concentration of ibuprofen in water it was necessary to carry out a solid phase extraction (SPE) of the aqueous samples. SPE was carried using C18 cartridges (1 g in a 6 ml reservoir, from Argonaut Technologies) and the method were adapted from IST Chemistry Data Sheet [87]. The apparatus used is presented in Figure 3.1. The cartridges were first conditioned with 10 mL of methanol 100%, followed by 10 mL of ultrapure water. After conditioned, ibuprofen solutions were passed through the cartridges at a flow rate of approximately 10 mL/min, without letting dry, cartridges were washed with ultrapure water (6mL).

Ibuprofen was recovered from the cartridges with 6 mL of methanol 100%, and after elution, methanol was evaporated by air sparging.

Figure 3.1. Picture of the solid phase extraction (SPE) apparatus.

3.3.1.3 UV-vis spectroscopy measurements

A UV-vis spectrophotometer (Jasco V-630 UV/Vis) was used for measure the absorbance of Ibuprofen.

An UV scan was performed to obtain the UV absorption spectrum of aqueous ibuprofen, shown in Figure 3.2, where it is possible to see the existence of two peaks, one characteristic of aromatic compounds in the 260 nm (UV_{260}) and other, more evident, in the 220 nm (UV_{220}). The last one was chosen for the detection of the compound.

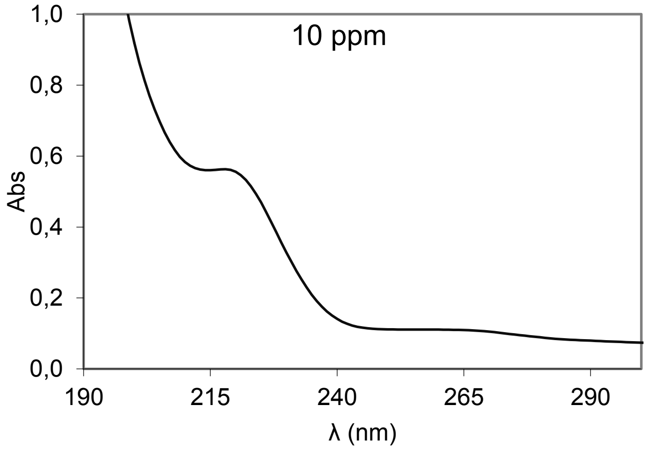


Figure 3.2. Adsorption spectrum of ibuprofen in the UV region (10 ppm).

A calibration curve of absorbance at 220 nm (UV_{220}) versus concentration was made, for the concentration range of 0.25 - 10 mg/dm^3 of ibuprofen. A good correlation was obtained (R^2 = 0.999) (presented in ANNEX IV).

3.3.2 Calculation methods

The software package Scientist^{TM}, from Micro-Math$^{®}$, was used to perform the non-linear fitting calculations of the kinetic and isotherm models used, calculating the parameters values and the associated errors for 95% confidence level.

3.3.3 Activated carbon preparation

The AC available was in the form of granules with dimensions exceeding those intended. To get an AC with the characteristics required for this study was necessary a prior treatment consisting of grinding, sifting and thereafter washing and drying. The procedure was performed in Chemistry Department of the Faculty of Sciences and Technology – New University of Lisbon (FCT/UNL).

<u>Grinding and sifting</u>

The effective particle size of GAC F400 was (D10) 0.55 – 0.7 mm. To obtain the desired dimensions (125 – 180 μm and 63 – 90 μm) homogeneously, the procedure was as following:

- The carbon was introduced in a ball mill (The Pascal Engineering CO.LTD.) and grinded for five minutes at a speed of 30 rpm (Figure 3.3 (a) and Figure 3.3 (b));

- After mincing the AC was sieved in sieves with calibrated MESH (80, 120 and 170) which corresponds to 180 μm, 125 μm, 90 μm (ASTM E-11) (Figure 3.3 (c));
- The fraction sifted through 180 μm and 125 μm sieves was subsequently washed, dried and stored. The sifted through 90 μm and 63 μm sieves was also obtained and was treated identically;
- Procedure was repeated for particles that were not yet in the desired size.

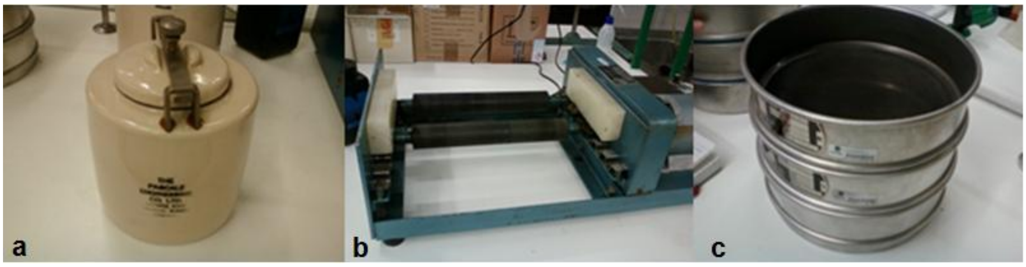


Figure 3.3. (a) and (b) ceramic ball mill, (c) sieves, used in the procedure to grind and sift AC (FCT/UNL).

Washing and drying

To remove fines and other impurities, the washing of activated carbons was carried out with Milli-Q water according to the procedure:

- The two fractions of activated carbon were placed in *erlenmeyer* flasks of 250 mL. The ratio of coal and water used was 4:1 (v/v). Solutions with 125-180 μm (36.37 g) and 63 - 90 μm (18.49 g) were prepared with 142 mL and 73 mL of water Milli-Q, respectively;
- Erlernmeyer flasks were manually stirred and left to stand until the coal was deposited;
- Then, the wash water was decanted and its conductivity was measured;
- The procedure was repeated until the conductivity values stabilized, meaning that all the impurities had been removed (ANNEX V);
- After washing, the carbons were dried in an oven (Memmert U30) at 103 °C for 24 h, and were stored in a desiccator in opaque flasks until use.

3.3.3.1 Functionalization

The procedure to functionalize F400 was performed in FCT/UNL in a tubular reactor (Figure 3.4).

Procedure:

For this procedure 3 g of F400 AC (125 - 180 μm) were placed on a perforated column, which was subsequently placed in an oven programed to heat to 800 ºC for 3 hours under a nitrogen flow rate of 160 mL/min.

Figure 3.4. Tubular oven used in the procedure to modify the AC (FCT/UNL).

3.3.4 Chemical and textural characterization of the activated carbons

3.3.4.1 Surface charge characterization by direct pH measurement

The determination of F400, 63 - 90 µm, 125 - 180 µm and functionalized surface charge were performed by using a direct pH measurement method [61].

The procedure was: 1 g of AC was weighted and placed in a glass flask; 10 mL of ultrapure water was added. This suspension was purged of dissolved CO_2 with nitrogen and was magnetically stirred for 48 h, after which the stirring was stopped and the pH of the solution was measured at 20 ºC. The value obtained was taken as the pH of the point of zero charge, pH_{PZC}. The procedure was repeated three times, to obtain an average value.

3.3.4.2 Characterization of the surface functional groups by elemental analysis

Elemental analysis (C, H, N and S) was carried out on a CHNS Analyser (Thermofinnigan Flash, EA, 1112 SERIES).

The oxygen content was estimated by difference between the total (100%) and the sum of the other compounds (wt %) (equation 3.1).

$$O\ (\%) = \{100 - [N\ (\%) + C(\ \%) + H\ (\%) + S\ (\%)]\} \qquad \textbf{(3.1)}$$

3.3.4.3 Ash content

The procedure to determine the ash content of F400 AC was conducted in FCT/UNL with the residue obtained after combustion of the samples to air according to the procedure adapted from the Spanish Standard UNE 32 111 October 1995. The determination of the mass loss of the samples was performed on an analytical scale (ae Adam equipment WP 250, 0.001 g) and it muffle furnace (Leton Thermal Designs Ltd.) was used for the carbonization of the samples.

Procedure:

The AC was firstly dried in an oven at 100°C for 24 h. After cooling, 1 g of AC was put into a crucible and introduced into the muffle furnace for complete combustion of the carbonaceous matrix. The heating method used was as follows: at the first 10 minutes the temperature increased up to 500 ºC and was maintained for the next 30 minutes; then it was again increased to 800 ºC for 15 minutes and maintained for 2.5 h. After this treatment, furnace was cooled to a temperature around 150 ºC.

A scheme resuming the heating protocol used is represented on Figure 3.5.

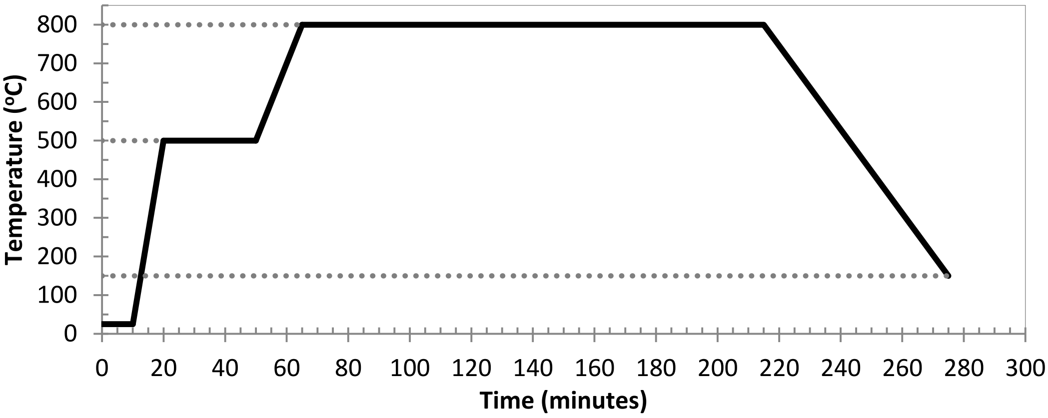


Figure 3.5. Heating treatment used to obtain the AC ash content.

After cooling, the samples were removed from the muffle furnace and stored in a desiccator, allowed to cool to room temperature and then was weighed again. The ash content was determined according to equation (3.2).

$$\% \, ashes = \frac{m_{residue}}{m_{dry}} \times 100 \qquad \textbf{(3.2)}$$

3.3.4.4 Textural characterization by N_2 adsorption isotherms, 77 K

The analytical determination of the AC porous structure was performed by Professor Isabel Fonseca's research group from the Chemistry Department of FCT/UNL.

The physical characteristics of the activated carbons, which included the specific surface area, the micropore area, the total pore volume, the micropore volume and the pore size distribution, were measured by N_2 adsorption in a ASAP 2010 Pore Structure Analyser, Micromeritrics, USA, at 77 K with liquid N_2.

3.4 Adsorption studies

Kinetic and isotherm adsorption studies were performed. The conditions are presented in Table 3.5.

Table 3.5. Tests carried out in laboratory for kinetic and isotherm adsorptions.

pH	IS (mM)	Ca/K	F400 particle size (µm)	
5.6 - 6	2.5	0.5	125 - 180	**C_0 = 100 µg/dm^3**
	3.5	0.25		
	4.25	0.5		
	5.5	1.5		
	5.95	0.25		
	9.35	1.5		
4.5	2.5	0.5		
8	2.5	0.5		
5.6 - 6	2.5	0.5	63 - 90	
8	2.5	0.5	125 - 180	**C_0 = 10 mg/dm^3**
	9.35	0.5		
	9.35	1.5		
	2.5	0.5	63 - 90	
	2.5	0.5	Functionalized	
	9.35	0.5	125 - 180	

3.4.1 General procedure

Kinetic and isotherm experiments were performed with electrolyte solutions described in section 3.1.3. F400 AC with two particle sizes (125 - 180 µm and 63 - 90 µm) and functionalized F400 were used.

The AC previously weighted was added to glass flasks (with capacities for 300 or 60 mL) and ibuprofen electrolyte solutions were added. The flasks were closed and placed in an incubator (Hucoa-Erloss) under stirring (170 rpm) at a controlled temperature of 23 ºC. For the kinetic experiments the contact time was varied. After the contact, the solutions were collected and filtered through a Whatmana-GF/C filter and the filtrate was passed through a SPE cartridge to extract and concentrate the ibuprofen, for analysis by UV-VIS spectrophotometer.

Duplicate flasks were always performed and a flask treated like the others but without AC were analyzed (blank) for better process control.

3.4.2 Kinetic studies – General procedure

These studies were divided in two sets:

In the first set of experiments, 250 mL of electrolyte solution spiked with ibuprofen (100 µg/dm^3) were added to glass flasks with 2.5 mg of AC previously weighted, without pH adjustment to prevent introduction of any new electrolyte into the system (except for experiments to study the pH effect, for which the pH of the samples was adjusted to 4.5 and 8). The contact varied between 2 h and 24 h.

Table 3.6. Conditions used in the first set of kinetic experiments.

	C_0 ibuprofen (µg/dm^3)	**V_{ESol} (mL)**	**m_{AC} (mg)**	**C_{AC} (mg/dm$^{3)}$**
• F400 125 - 180 µm • F400 63 - 90 µm	100	250	2.5	10

For the second set, 40 mL of ibuprofen electrolyte solutions were added to flasks containing 8 mg of AC previously weighted. The pH was adjusted to 8 and the SPE procedure was not necessary as in this set the samples concentration range could be read directly in the spectrophotometer. The contact times varied between 1 and 120 minutes.

Table 3.7. Conditions used in the second set of kinetic experiments.

	C_0 ibuprofen (mg/dm$^{3)}$	**V_{ESol} (mL)**	**m_{AC} (mg)**	**C_{AC} (mg/dm^3)**
• F400 125 - 180 µm • F400 63 - 90 µm • F400 Functionalized	10	40	8	200

3.4.3 Determination of equilibrium time

Preliminary kinetic experiments were performed to know the necessary equilibrium adsorption time, for the first set (with 100 µg/dm^3 of ibuprofen) and for the second set (with 10 mg/dm^3 of ibuprofen) of the studies.

For the first set, 250 mL of electrolyte solution with 2.5 mM of ionic strength and 100 µg/dm^3 of ibuprofen were added to flasks with the F400 AC (125 -180 µm) previously weighed, without pH adjustment (~6). The AC dosage used was 4 mg/dm^3 (1 mg/250 mL) in all experiments. The procedure described above for the kinetic studies was followed, varying the contact time among the AC and the solution between 2 and 120 hours.

For the second set, with the concentration of 10 mg/dm^3 of ibuprofen, 40 mL of ibuprofen electrolyte solution with 2.5 mM of ionic strength were used, and the pH was adjusted to 8 with NaOH. F400 AC (125 - 180 µm) was previously weighed and the concentration used was 200 mg/dm^3 (8 mg/40 mL). The contact time varied between 3 minutes to 24 hours. The samples were collected, filtered and analyzed directly in the spectrophotometer.

3.4.4 Isotherm studies – General procedure

These studies were also divided in two sets:

In the first set of experiments, the isotherms were determined by varying the AC concentration between 4 mg/dm^3 and 20 mg/dm^3, keeping the ibuprofen concentration (100 µg/dm^3) in the electrolyte solution (250 mL) constant (except for the first point, which concentration used was 150 µg/dm^3). All the flasks were maintained in the incubator for 7 days (160 hours) and the experiments were performed without pH adjustment except for the experiments in which the pH effect in adsorption was studied.

The conditions used are presented in Table 3.8.

Table 3.8. Conditions used in the first set of isotherm experiments.

	C_0 ibuprofen (µg/dm^3)	**V_{ESol} (mL)**	**m_{AC} (mg)**	**C_{AC} (mg/dm^3)**
• F400 125 - 180 µm • F400 63 - 90 µm	150	250	1	4
	100	250	1	4
	100	250	2.5	10
	100	250	4	16
	100	250	5	20

In the second set of experiments, 40 mL of electrolyte solution with 10 mg/dm^3 of ibuprofen were added to flasks with AC concentrations from 25 to 1250 mg/dm^3 and the samples were filtered and read directly in spectrophotometer, without SPE procedure.

The conditions used are presented in Table 3.9.

Table 3.9. Conditions used in the second set of isotherm experiments.

	C_0 ibuprofen (mg/dm^3)	V_{ESol} (mL)	m_{AC} (mg)	C_{AC} (mg/dm^3)
• F400 125 - 180 µm • F400 63 - 90 µm • F400 Functionalized	10	40	1	25
	10	40	2	50
	10	40	3	75
	10	40	4	100
	10	40	6	150
	10	40	8	200
	10	40	16	400
	10	40	28	700
	10	40	40	1000
	10	40	50	1250

4 RESULTS AND DISCUSSION

4.1 CHARACTERIZATION OF THE ACTIVATED CARBON

4.1.1 Surface charge

The pH_{PZC} of the carbons was determined following the direct pH measurement method reported elsewhere [61] and explained in section 3.2.3. The obtained values are presented in Table 4.1.

Table 4.1. Point of zero charge of the studied forms of F400 AC.

	pH_{PZC}	
F400 125 - 180 µm	**F400 63 - 90 µm**	**F400 Functionalized**
7.25	7.28	8.90

Obtained values for AC pH_{PZC} in crescent order were: F400 (125 - 180 µm) ≈ F400 (63 - 90 µm) < F400 (Functionalized).

Analyzing the charge of the carbons used in the pH range of the experiments knowing their pH_{PZC} is crucial to understand electrostatic and hydrophobic interactions between the carbons and ibuprofen: positive carbons attract negative molecules in solution and negative charge repels negative molecules.

For pH of 6 all the carbons were positively charged ($pH < pH_{PZC}$) but increasing pH to 8, the non-functionalized F400 carbon will become negatively charged. For functionalized F400 at pH 8, the $pH < pH_{PZC}$ and the AC will maintain the negative charge. Ibuprofen is mainly deprotonated (COO^-) for pH > 4.9 ($pH > pK_a$).

At pH 4.5, all the ACs studied will be positively charged but ibuprofen will be mainly protonated (COOH) so, hydrophobic interactions might become relevant.

Functionalizing F400 increases significantly its pH_{PZC} from 7.3 to 8.9 (Table 4.1). This difference is very important when the pH of the solution is 8, because the nature of electrostatic interactions will change.

A scheme representing the variations in process, as AC charge and ibuprofen protonation/deprotonation with the different pH values used, are presented in Figure 4.1.

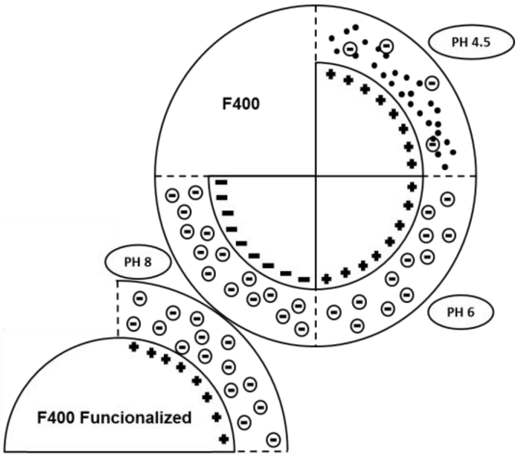


Figure 4.1. Representative scheme of the charges of ibuprofen and activated carbon F400 — "virgin" and functionalized at the different pH values used in this studi.

4.1.2 Functional groups

Elemental analysis and **ash content** for the three forms of F400 AC studied were performed as described in section 3.3.4 and the results are present in Table 4.2:

Table 4.2. Elemental analysis (wt %) of the studied activated carbons.

	N (%)	C (%)	H (%)	S (%)	O (%)	Ash (%)
F400 125 - 180 µm	0.50	80.69	0.00	0.37	*18.44	7.30%
F400 63 - 90 µm	0.27	82.06	0.00	0.54	*18.21	-
F400 Functionalized	0.28	86.18	0.00	0.60	*14.15	-

* obtained from subtraction of total C, N, H, S.

Comparing with the values found in literature, these samples have more oxygen and less of the other compounds [84], although the differences are not very significant.

Typically, the higher is the oxygen content of an AC surface, the stronger is its acidic character (although there are basic groups with oxygen) [88]. The differences in oxygen content between F400 functionalized and without functionalization are consistent with the pH_{PZC} of the samples. Through F400 functionalization apparently the oxygen-containing surface groups mainly from the acid nature were removed, which increased the basicity of the material, as it was expected.

The variations in chemical surface given by elemental analysis of the two different particles sizes of F400 AC 125 - 180 µm and 63 - 90 µm were not substantial, because the changes were only physicals, through a mechanical milling.

4.1.3 Textural characterization

A textural characterization of F400 125 - 180 µm, 63 - 90 µm, and functionalized samples were performed by N_2 adsorption isotherms at 77 K, as described in section 3.3.4. The **pore size distribution**, **apparent surface area**, **total microporous volume**, **specific external area**, **total volume of pores**, **specific microporous surface area** and **volume of macro and mesopores** were obtained.

The pore size distribution was determined by the Density Functional Theory already explained in section 2.5.2. (data presented in ANNEX I) represented in Figure 4.2.

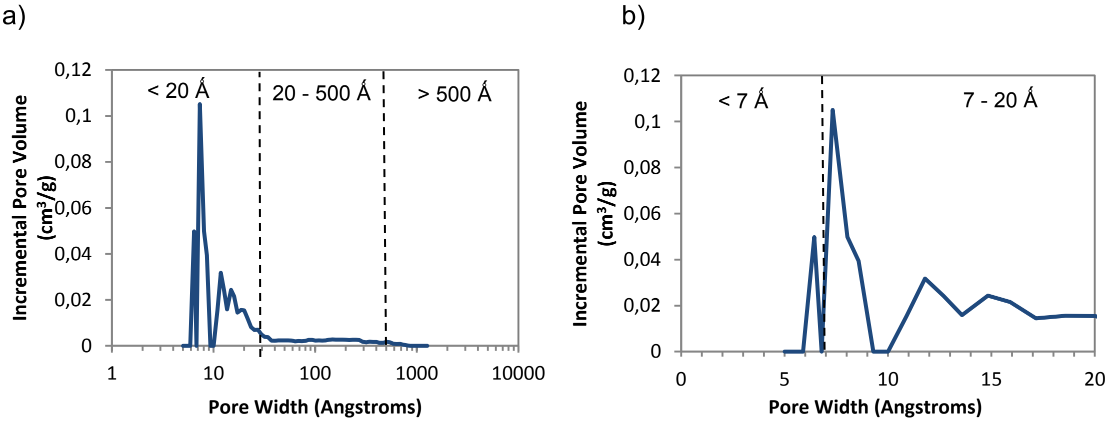


Figure 4.2. Pore size distribution of F400 activated carbon 125 - 180 µm obtained from PSD equation applied to the N_2 adsorption isotherm at 77K. a) full range pore size distribution and b) microporous size distribution.

These results are consistent when compared to the characterization presented in other publications [89]. The range of ultramicropores is higher than the expected based on literature review [85,89]. As it was mentioned before, size exclusion effects can occur for pores below 8.8 Å other studies performed the adsorption of ibuprofen in different activated carbons and refer that size exclusion strongly affects the adsorption capacity [11], which may have hindered the adsorption, however, to improve the confidence in the micropores distribution, a CO_2 isotherm adsorption should have been performed.

The apparent surface area ($A_{BET\ app}$) was determined by the BET method. The t - plot was used to estimate the external area (A_{ext}) and the total microporous volume (V_{micro}). The results are presented in table Table 4.3 (the plots and calculus were performed and are presented in ANNEX I. II and III). The results are according to what was expected based on literature review (section 3.2.2) [83,84,85].

Table 4.3. Textural properties of F400 activated carbon.

Property	Method	F400 125 - 180 μm	F400 63 - 90 μm	F400 Functionalized
Apparent surface area ($A_{BET\ app.}$) (m^2/g)	BET	1174	1242	1242
External area (mesopores) (A_{ext}) (m^2/g)	t - plot	413	425	410
Microporous surface area (m^2/g)	A_{BETapp} - A_{ext}	761	817	832
Total microporous volume (V_{micro}) (cm^3/g)	t - plot	0.37	0.41	0.41
Volume of macropores and mesopores (cm^3/g)	BJH	0.35	0.36	0.35
Total volume of pores (cm^3/g)	Gurvitsch rule	0.72	0.77	0.76

Through the analysis of the N_2 adsorption isotherm of the samples with the methods mentioned above (t - plot, BJH and Gurvisch) (ANNEX II) and by the plot of PSD presented in Figure 4.2 these three different forms of activated carbons are micro/mesoporous as it was expected.

Through the analysis of the results seems that grinding the AC increased not only the transport pores (macro and mesopores) as it was expected but also the volume of micropores shown an increase of about 10%.

Heating the AC (functionalization) leads to an increase in the specific surface area (A_{BET}) caused mainly by an increase of the microporous area (about 6.6%).

The textural characterization of both F400 63 - 90 μm and functionalized is very similar. But a more detailed analysis to study the percentage of super an ultramicropores would be interesting. Since it was not held, the revalence of supermicropores for F400 AC, described in the literature (section 3.1.2), will be assumed. This range is the most effective taking into account the dimensions of ibuprofen.

4.2 ISOTHERMS AND KINETICS OF IBUPROFEN ADSORPTION ONTO F400 ACTIVATED CARBON

4.2.1 Equilibrium time

Equilibrium time was determined for both concentrations used in this work (100 µg/dm^3 and 10 mg/dm^3). Experiments were carried out in the conditions described in section 3.4.3 and the results are presented in Figure 4.3 and Figure 4.4, respectively. The pH used was 6 for the first case and 8 for the second, to be consistent with most of the tests for these same concentrations.

a) b)

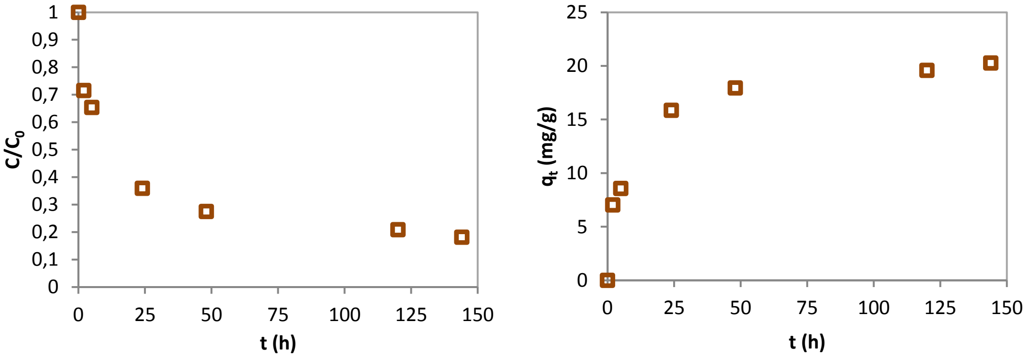


Figure 4.3. Adsorption kinetic tests for equilibrium time determination for the smallest concentration used. a) adsorption uptake and b) adsorption capacity. (C_0 = 100 µg/dm^3; F400 125 - 180 µm; C_{AC} = 4 mg/dm^3, pH = 6).

After 144 hours (6 days), the removal percentage increased only 3.4%, is then expected that the equilibrium has been reached.

a) b)

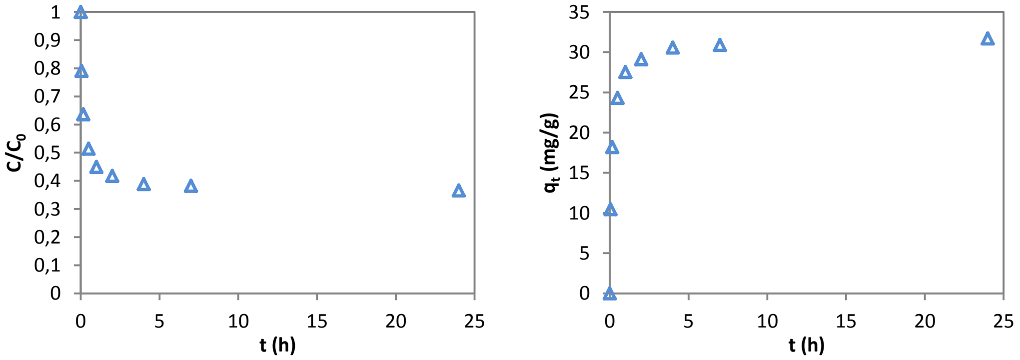


Figure 4.4. Adsorption kinetic tests for equilibrium time determination for the highest concentration used. a) adsorption uptake and b) adsorption capacity (C_0 = 10 mg/dm^3, F400 125 - 180 µm; C_{AC} = 200 mg/dm^3, pH = 8).

Equilibrium time was reached after 24h, with a removal percentage increase of just 2.5% in the last 17 hours.

In both cases one more day was used in adsorption isotherms to guarantee the equilibrium.

4.2.2 The effect of pH in the adsorption of ibuprofen onto activated carbon

Above was explained the importance of the solution pH in adsorption. This influence is enhanced when the solute is a weak electrolyte such as ibuprofen that can easily ionized (pK_a 4.9), but strongly depends on the nature of the adsorbent as mentioned in other studied [11].

Isotherms were performed with 100 µg/dm^3 of ibuprofen for an ionic strength of 2.5 mM in F400 AC with a particle size of 125 - 180 µm, for seven days (experimental procedure described in section 3.3.2).

To cover wide range of pH conditions, three cases were studied: pH 4.5, 6 and 8. For pH 4.5, the scenario is improbable being studied for academic interest only, pH 8 is the most interesting for water treatment because it is the most common.

Langmuir and Freundlich isotherm models were applied to fit the adsorption isotherms and the parameter values were calculated using the non-linearized equations of both models. The results are shown on Figure 4.5 and Table 4.4.

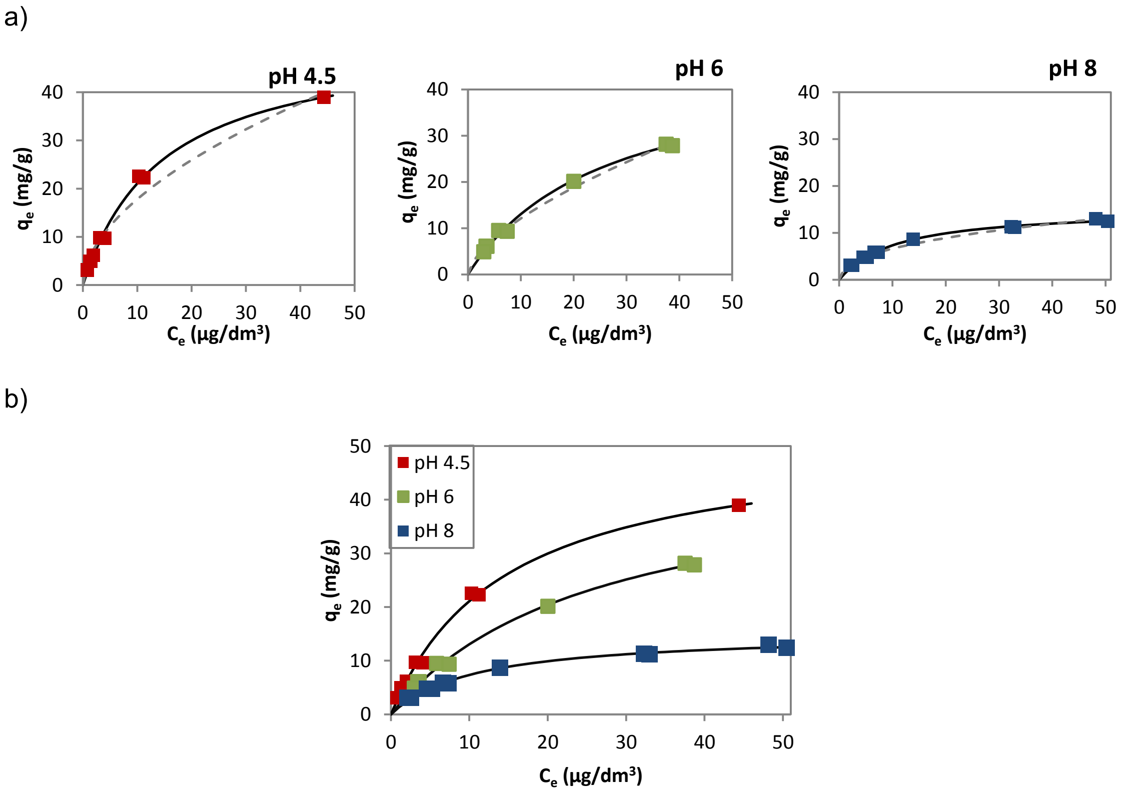


Figure 4.5. Adsorption isotherms of ibuprofen onto AC: a) non-linear fittings of Langmuir and Freundlich models, b) comparison of the best fit representation for the three pH studied. (—— Langmuir model**,** – – Freundlich model) (IS = 2.5 mM, Ca/K = 0.5, C_0 = 100 µg/dm^3, F400 125 - 180 µm).

The Langmuir model seems to have a better fitting of experimental data than the Freundlich model for all studied pHs, with better correlation coefficients (Table 4.4).

For the three cases, seems that saturation was not achieved, making it possible to adjust also the Freundlich model (section.2.5.6).

Table 4.4. Parameter values of Langmuir and Freundlich adsorption models observed in experimental conditions: IS = 2.5mM, Ca/K = 0.5, C_0 = 100 μg/dm^3, F400 125 - 180 μm.

pH	Langmuir model					Freundlich model				
	b (dm^3/μg)	*Error	q_{max} (mg/g)	*Error	R^2	K (mg/g)/(μg/dm^3)$^{1/n}$	*Error	1/n	*Error	R^2
4.5	0.0689	23%	51.7	10%	0.997	5.13	40%	0.541	24%	0.977
6	0.0387	20%	46.8	22%	0.996	2.82	35%	0.633	18%	0.994
8	0.0935	27%	15.2	15%	0.993	2.51	29%	0.423	21%	0.983

* Associated error for 95% confidence level.

It is notorious by the observation of adsorption isotherms that the adsorption capacity is much influenced by the adsorptive solution pH. Crescent when solution pH decreases.

In decreasing order of adsorption capacity we have: pH 4.5 > pH 6 > pH 8. In fact, by Langmuir model analysis when pH increases q_{max} value becomes smaller. This parameter value is a measure of adsorption capacity. With Freundlich model the same conclusion can be drawn, because 1/n value are similar for pH 4.5 and 6 and K (Freundlich constant, measure of the adsorption capacity of the adsorbent) is higher for the lower pH.

Such as mentioned before, pH influence is exercised both in activated carbon surface charge and in ibuprofen ionization degree.

For pH 6 and 8, ibuprofen is in deprotonated form (COO^-), 92% and 100%, respectively, and electrostatic interactions predominate between the AC and the ibuprofen. Electrostatic forces can be attractive or repulsive, depending on the AC being positively or negatively charged.

For pH 6, adsorbate-adsorbent electrostatic interactions are attractive, which means that activated carbon attracts ibuprofen anions (that represents 92 %) to its surface.

At pH 8, 100 % of ibuprofen is in anionic form, but the F400 surface is already negatively charged (pH > pH_{PZC}), so electrostatic interactions will be repulsive and the carbon will repel ibuprofen molecules, decreasing adsorption rate, as observed in other paper for higher initial concentrations of ibuprofen (between 20 and 60 mg/dm^3) [10].

For pH 4.5 (pH < pH_{PZC}), F400 is positively charged but ibuprofen, according to the dissociation constant (pK_a ~4.9) is adsorbed mostly in the neutral form (72% of the molecules are neutral). For this pH, the adsorption is higher. In these operational conditions, seems that non-electrostatic interactions governed adsorption of ibuprofen.

These results give an indication that probably van der Waals, hydrophobic interactions and /or hydrogen bonding dominates this process. This phenomenon of hydrophobicity is widely reported in literature for compounds with an aromatic ring such as ibuprofen. In these conditions ibuprofen carboxylic group is in protonated form being hydrophobic and adsorbing better to the carbon [10,11,89,90].

Adsorption kinetic studies were performed in order to better understand the adsorption process. The procedure is described in section 3.4.2.

Pseudo-first order and pseudo-second order models were applied as shown in Figure 4.6. Pseudo-second order model presented better fits of the experimental data, and it is observed that the pseudo-first order model does not adequately fits the experimental data, as shown in Figure 4.6a. The parameter values are presented in Table 4.5.

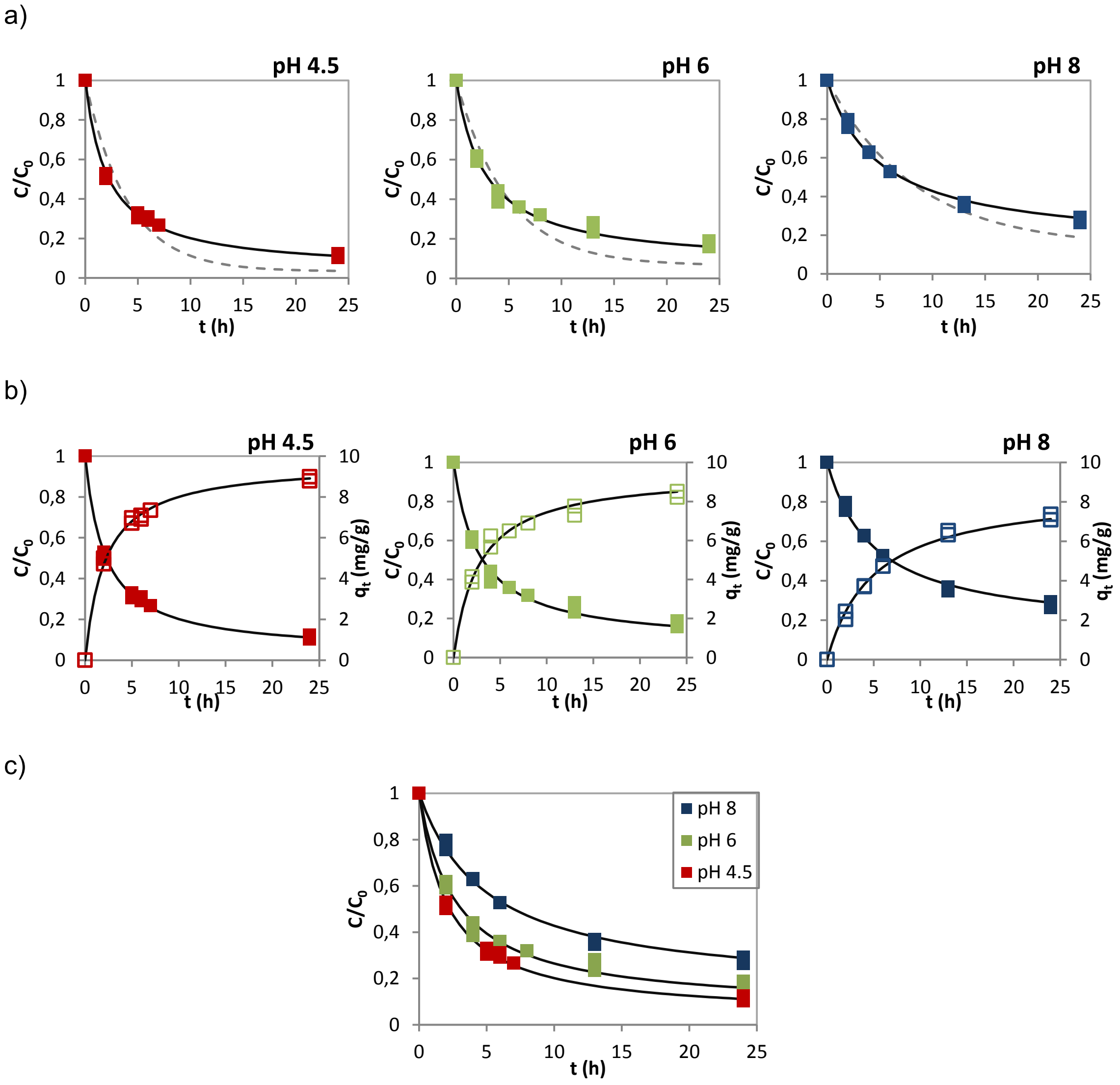


Figure 4.6. Adsorption kinetics of ibuprofen onto AC, a) non-linear fittings of pseudo-first and pseudo-second order models, b) best fit representation and c) comparison of the best fit representation for the three pH studied. (‒ ‒ pseudo-first order model, —— pseudo-second order model) (IS = 2.5 mM, Ca/K = 0.5, C_0 = 100 μg/dm^3, F400 125 - 180 μm).

Table 4.5. Parameter values for pseudo-first and pseudo-second order kinetic adsorption models (IS = 2.5 mM, Ca/K = 0.5, C_0 = 100 μg/dm^3, F400 125 - 180 μm).

pH	Pseudo 1st order model				Pseudo 2nd order model		
	q_e_calc (mg/g)	k_1 (1/h)	*Error	R^2	k_2 (g/(mg.h))	*Error	R^2
4.5	9.69	0.251	22%	0.730	0.0490	8%	0.987
6	9.47	0.207	29%	0.624	0.0388	13%	0.965
8	8.62	0.120	22%	0.913	0.0230	11%	0.989

* Associated error for 95% confidence level.

Pseudo-second order rate constant, k_2, is higher for pH 4.5 as shown in Table 4.5, although to the k_2 value for pH 6 at pH 8 the reaction is slower.

It is possible to verify through the analysis of the data that the pseudo-second order model produces a good fit. The fact that the isotherm follows the Langmuir model can provide the information that the chemisorption possibly be the adsorption mechanism.

The removal percentage after 24 hours for the three pH values studies are presented in

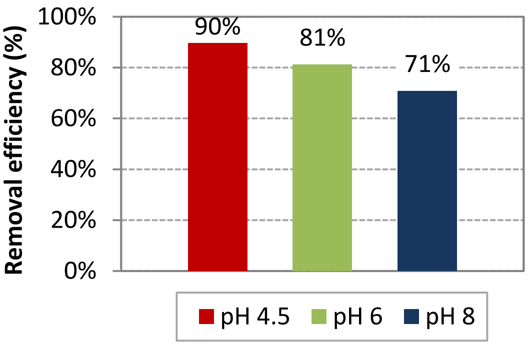


Figure 4.7. Removal efficiency of ibuprofen for the three pH values studied.

The differences in removal efficiency show that the adsorption capacity after 24 hours differs around 10% for each pH value.

As the experimental conditions using these very low concentrations of ibuprofen were very difficult to handle, leading to higher errors associated with the experimental procedure, it was decided to use from this point on higher concentrations of ibuprofen.

4.2.3 The effect of initial concentration in the adsorption of ibuprofen onto activated carbon

To trace a bond between the two scenarios, adsorption isotherms, in the same conditions to the previous presented, but with higher ibuprofen concentration (10 mg/dm^3), were performed. The results are presented in Figure 4.8.

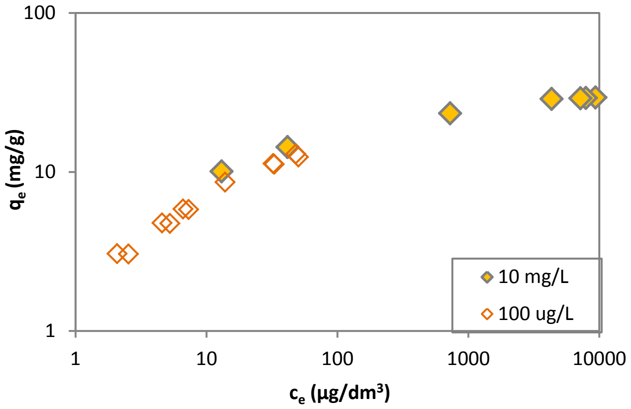


Figure 4.8 Adsorption isotherms of ibuprofen in 100 µg/dm^3 and 10 mg/dm^3. (IS = 2.5 mM, Ca/K = 0.5, F400 125 - 180 µm, pH = 8).

By the analysis of the plot depicted for the two initial concentrations of ibuprofen it is possible to verify that the lower concentration points describes well the first part of the isotherm, which justifies the fact that both models of Freundlich and Langmuir apply could be applied. The points corresponding to the maximum concentration of ibuprofen are used to correctly describe the final phase of the adsorption isotherm.

It seems to be possible to bridge the gap between the concentrations without major errors with regard to the nature of adsorption.

This conclusion important for the analysis of the following results.

4.2.4 The effect of the ionic strength in the adsorption of ibuprofen onto activated carbon

To study the effect of the ionic strength in ibuprofen adsorption, isotherms were performed, with an initial concentration of ibuprofen of 100 µg/dm^3, as it was described in section 3.3, for six ionic strengths with three different Ca/K ratios and without any pH adjustment (pH ~6).

Maintaining the relation between the ions in water (Ca/K ratios used: 0.25; 0.5 and 1.5), the ionic strength was changed in order to understand its effect in the adsorption. Isotherms were performed and **Freundlich** and **Langmuir** non-linear models were applied (Figures 4.9 - 4.11).

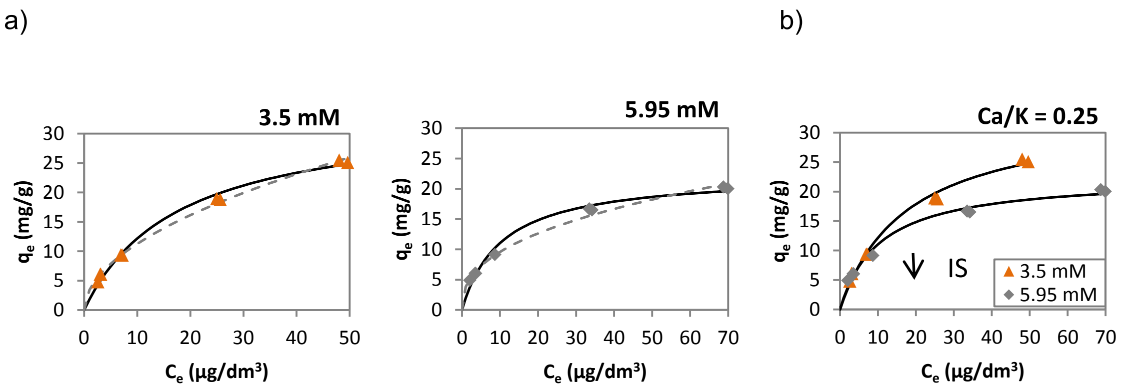


Figure 4.9. Adsorption isotherms of ibuprofen onto AC: a) non-linear fittings of Langmuir and Freundlich models, b) comparison of the best fit representation for the two ionic strengths. (— Langmuir model, - - Freundlich model) (Ca/K = 0.5, C_0 = 100 µg/dm^3, F400 125 - 180 µm, pH = 6).

Table 4.6. Parameter values for Langmuir and Freundlich adsorption models. (Ca/K = 0.25, C_0 = 100 µg/dm^3, F400 125 - 180 µm, pH = 6).

IS (mM)	**Langmuir model**					**Freundlich model**				
	b (dm^3/µg)	Error (%)*	q_{max} (mg/g)	Error (%)*	R^2	K (mg/g)/(µg/dm^3)$^{1/n}$	Error (%)	1/n	Error (%)*	R^2
3.5	0.0566	44%	33.6	21%	0.998	3.41	23%	0.519	13%	0.996
5.95	0.0960	44%	22.5	15%	0.987	3.81	29%	0.400	20%	0.990

* Associated error for 95% confidence level.

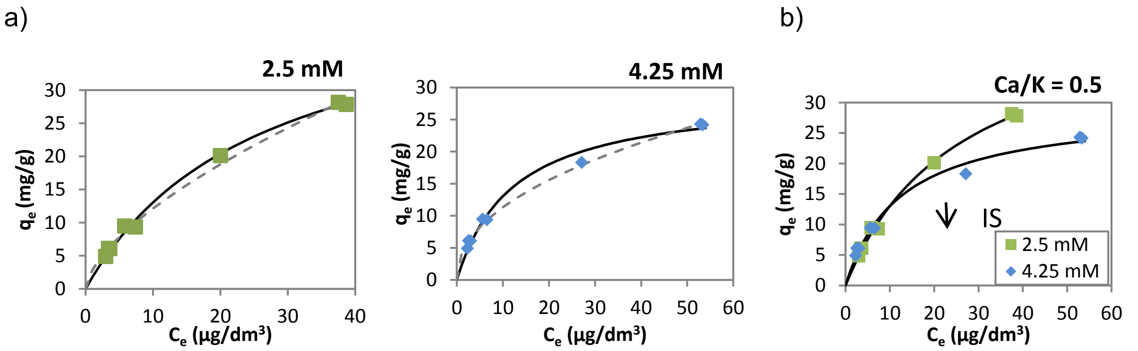


Figure 4.10. Adsorption isotherms of ibuprofen onto AC: a) non-linear fittings of Langmuir and Freundlich models, b) comparison of the best fit representation for the two ionic strengths. (— Langmuir model, - - Freundlich model) (Ca/K = 0.25, C_0 = 100 µg/dm^3, F400 125 - 180 µm, pH = 6).

Table 4.7. Parameter values for Langmuir and Freundlich adsorption models. (Ca/K = 0.5, C_0 = 100 µg/dm^3, F400 125 - 180 µm, pH = 6).

IS (mM)	Langmuir model					Freundlich model				
	b (dm^3/µg)	*Error	q_{max} (mg/g)	*Error	R^2	K (mg/g)/(µg/dm^3)$^{1/n}$	*Error	1/n	*Error	R^2
2.5	0.0387	20%	46.8	22%	0.996	2.82	35%	0.633	18%	0.994
4.5	0.0814	48%	29.1	20%	0.987	3.93	23%	0.459	14%	0.996

* Associated error for 95% confidence level.

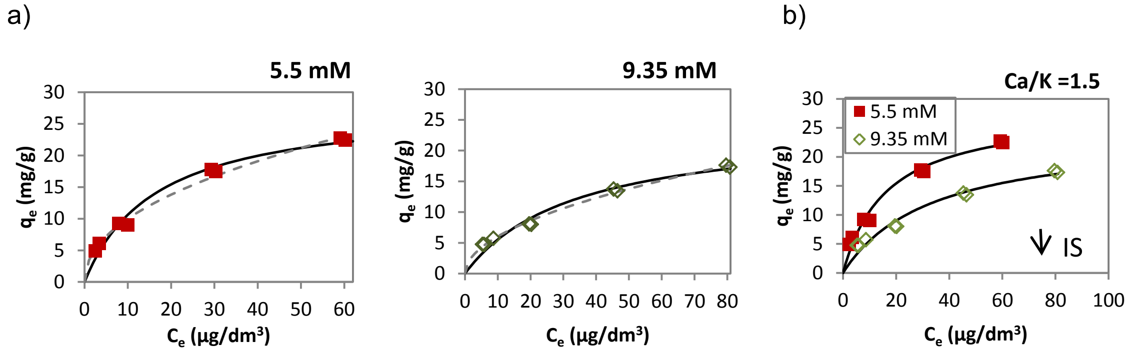


Figure 4.11. Adsorption isotherms of ibuprofen onto AC: a) non-linear fittings of Langmuir and Freundlich models, b) comparison of the best fit representation for the two ionic strengths. (—— Langmuir model, – – Freundlich model) (Ca/K = 1.5, C_0 = 100 µg/dm^3, F400 125 - 180 µm, pH = 6).

Table 4.8. Parameter values for Langmuir and Freundlich adsorption models. (Ca/K = 1.5, C_0 = 100 µg/dm^3, F400 125 - 180 µm, pH = 6).

IS (mM)	Langmuir model					Freundlich model				
	b (dm^3/µg)	*Error	q_{max} (mg/g)	*Error	R^2	K (mg/g)/(µg/dm^3)$^{1/n}$	*Error	1/n	Error	R^2
5.5	0.0604	53%	28.2	24%	0.981	3.40	30%	0.467	19%	0.992
9.35	0.0297	64%	24.2	24%	0.970	1.86	30%	0.512	16%	0.994

* Associated error for 95% confidence level.

The difference between the models does not allow to firmly concluding about the model that best fits the experimental data and consequently about the mechanism of adsorption, there is a lack of experimental points in the phase of saturation of the adsorption curves.

For every ratio, Ca/K, when the ionic strength increases, there is a decrease in the adsorption capacity.

Furthermore, the highest ionic strength (9.35 mM) showed the lowest adsorption and the lowest ionic strength (2.5 mM) the highest. Figure 4.12 shows the comparison of the adsorption isotherms, and it can be observed that there is a decrease in the order: 2.5 mM > 3.5 mM ≈ 4.25 mM > 5.5 mM ≈ 5.95 mM > 9.35 mM.

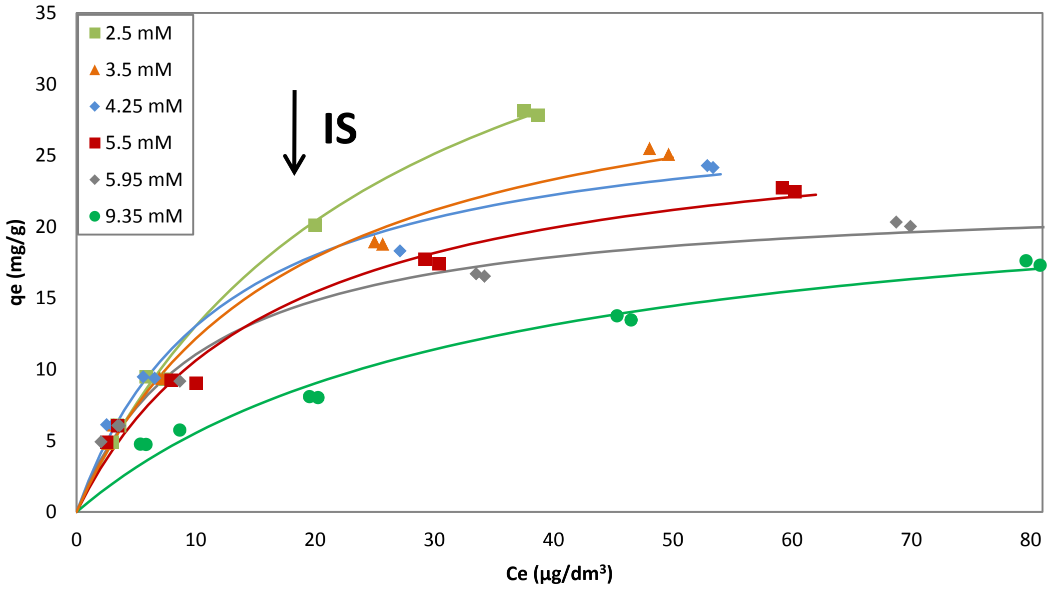


Figure 4.12. Adsorption isotherms for all the solutions performed for different ionic strengths. (C_0 = 100 µg/dm^3, F400 125 - 180 µm, pH = 6).

At the pH of the solution (~6) the AC was positive charged (pH < pH_{PZC}) and ibuprofen was mainly deprotonated (COO^-) charged, consequently, electrostatic interactions play an important role. It is notorious the adsorbent-solute shielding effect, that affects negatively the attraction between the AC and ibuprofen. This effect is reported in literature for this compound [12,13], and for other microcontaminants (including other anti-inflammatory drugs such as ketorpofen and naproxen) [91] proving that electrostatic forces are probably the most responsible for the adsorption in this conditions.

Kinetic experiments were then performed in similar conditions to those used for the isotherm adsorption tests, for an initial ibuprofen concentration of 100 µg/dm^3, for six ionic strengths with three different Ca/K ratios and without any pH adjustment. Pseudo-first and pseudo-second models were applied in their non-linear forms and the results are presented in Figure 4.13.

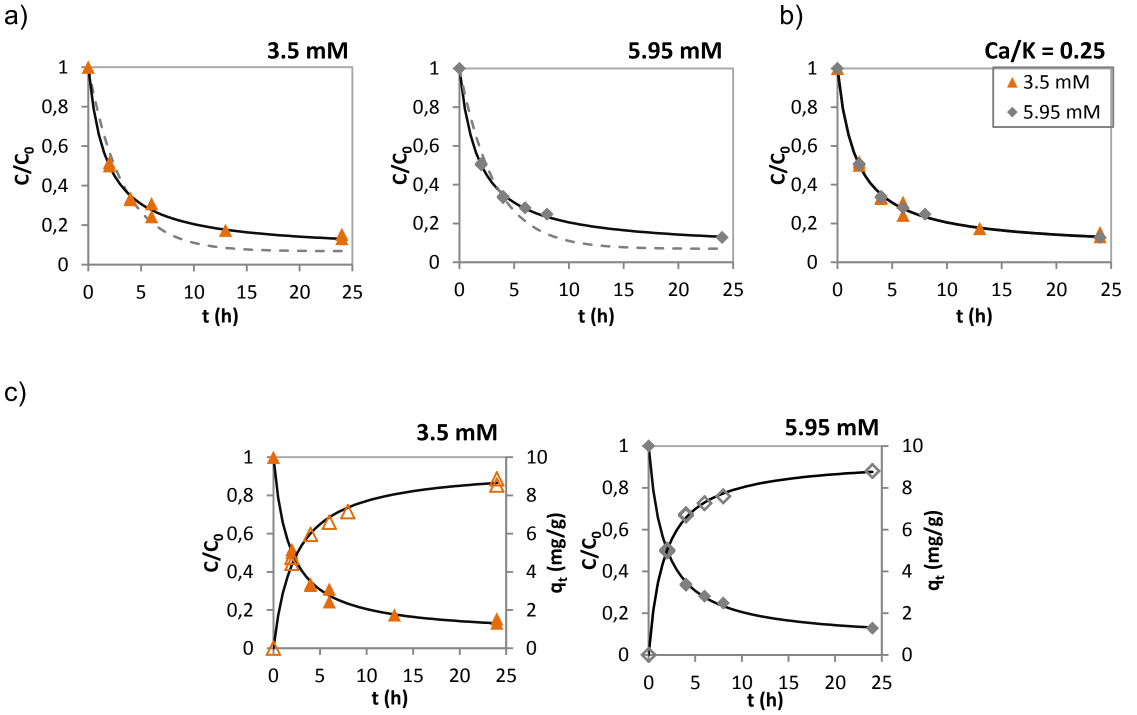


Figure 4.13. Adsorption kinetics of ibuprofen onto AC, a) non-linear fittings of pseudo-first and pseudo-second order models, b) comparison of the best fit representation for the two ionic strengths and c) best fit representation. (– – pseudo-first order model, —— pseudo-second order model) (Ca/K = 0.25, C_0 = 100 µg/dm^3, F400 125 - 180 µm, pH = 6).

Table 4.9. Parameter values for pseudo-first and pseudo-second order kinetic adsorption models. (Ca/K = 0.25, C_0=100 µg/dm^3, F400 125-180 µm, pH = 6).

IS (mM)	**Pseudo 1st order model**				**Pseudo 2nd order model**		
	q_e_calc (mg/g)	k_1 (1/h)	*Error	R^2	k_2 (g/(mg.h))	*Error	R^2
3.5	9.41	0.309	23%	0.769	0.0616	11%	0.978
5.95	9.40	0.312	23%	0.762	0.0618	6%	0.994

* Associated error for 95% confidence level.

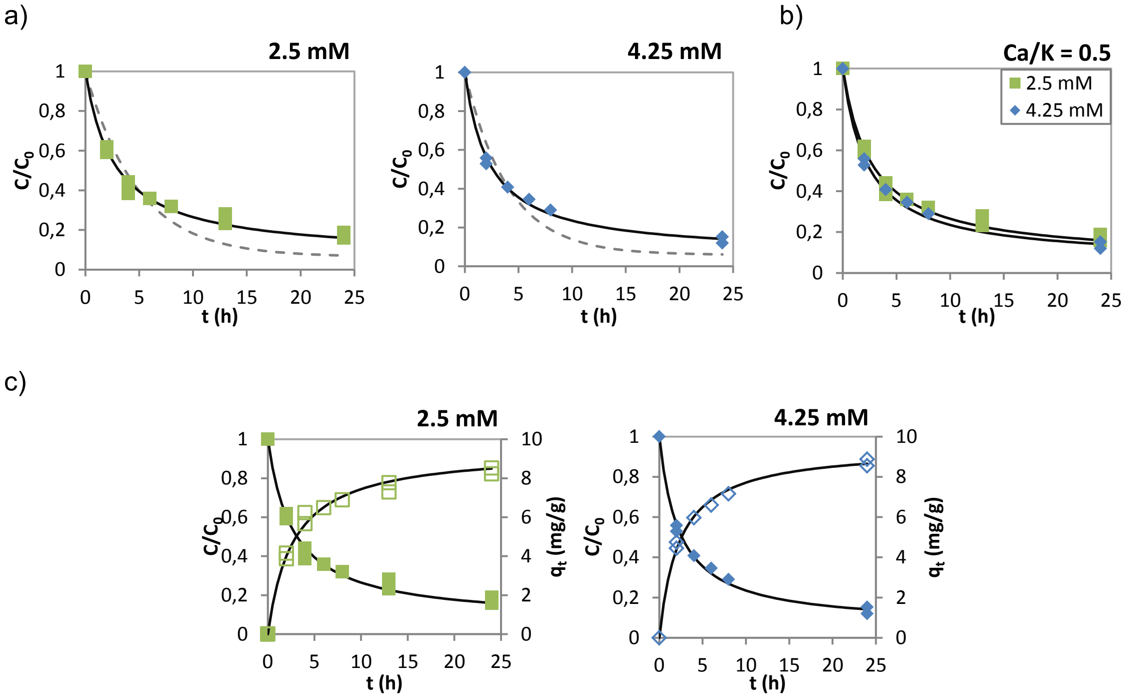


Figure 4.14. Adsorption kinetics of ibuprofen onto AC, a) non-linear fittings of pseudo-first and pseudo-second order models, b) comparison of the best fit representation for the two ionic strengths and c) best fit representation. (_ _ pseudo-first order model, —— pseudo-second order model) (Ca/K = 0.5, C_0 = 100 µg/dm^3, F400 125 - 180 µm, pH = 6).

Table 4.10. Parameter values for pseudo-first and pseudo-second order kinetic adsorption models. (Ca/K = 0.5, C_0=100 µg/dm^3, F400 125-180 µm, pH = 6).

IS (mM)	Pseudo 1st order model				Pseudo 2nd order model		
	q_e_calc (mg/g)	k_1 (1/h)	*Error	R^2	k_2 (g/(mg.h))	*Error	R^2
2.5	9.47	0.207	29%	0.624	0.0388	13%	0.965
4.25	9.48	0.247	30%	0.749	0.0459	12%	0.997

* Associated error for 95% confidence level.

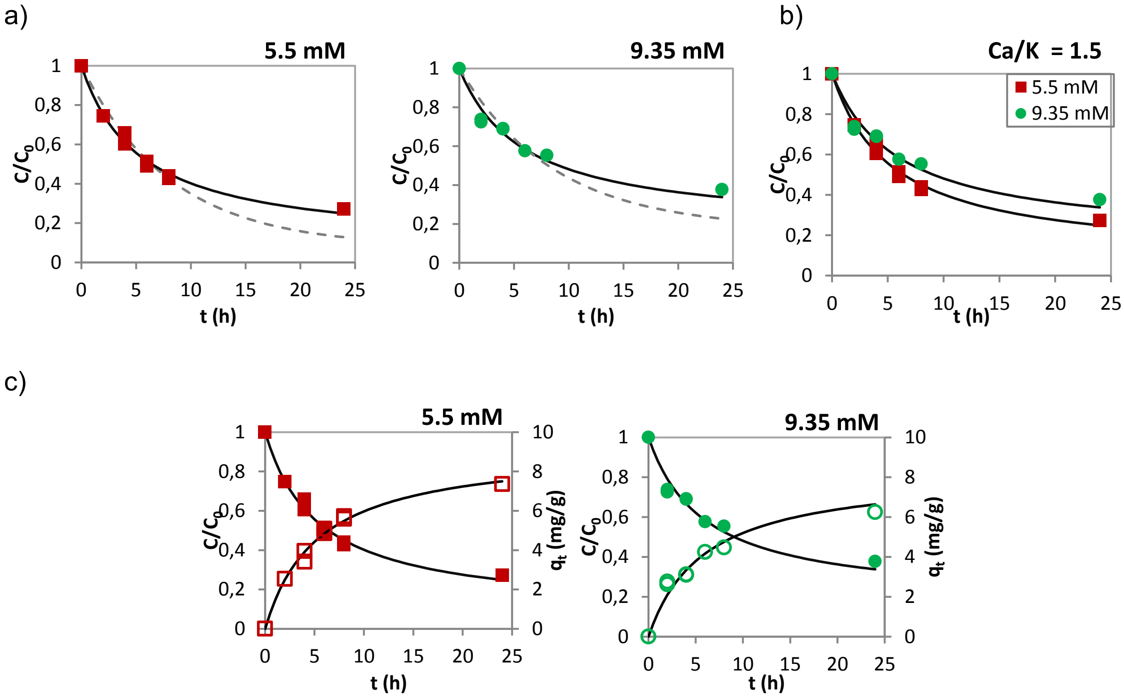


Figure 4.15. Adsorption kinetics of ibuprofen onto AC, a) non-linear fittings of pseudo-first and pseudo-second order models, b) comparison of the best fit representation for the two ionic strengths and c) best fit representation. (-- pseudo-first order model, —— pseudo-second order model) (Ca/K = 1.5, C_0 = 100 µg/dm^3, F400 125 - 180 µm, pH = 6).

The parameter values were calculated for the models but only pseudo-second order model seems to apply to the experimental data, as shown in Figure 4.11.

Table 4.11. Parameter values for pseudo-first and pseudo-second order kinetic adsorption models. (Ca/K = 1.5, pH = 6, C $_0$= 100 µg/dm^3, F400 125 - 180 µm).

IS (mM)	**Pseudo 1st order model**				**Pseudo 2nd order model**		
	q_e_calc (mg/g)	k_1 (1/h)	*Error	R^2	k_2 (g/(mg.h))	*Error	R^2
5.5	9.18	0.123	20%	0.851	0.0202	11%	0.974
9.35	8.27	0.115	34%	0.555	0.0205	22%	0.894

* Associated error for 95% confidence level.

These experimental results show that the ionic strength does not seem to affect the kinetic of adsorption of ibuprofen onto F400 activated carbon. No significant differences can be observed in pseudo-second order rate constant, k_2, for these conditions.

To better understand the effect of ionic strength on ibuprofen adsorption, especially at a pH more commonly found in natural waters and wastewaters, new adsorption isotherms were performed varying the ionic strength from 2.5 mM to 9.35 mM. These isotherms were performed with F400 125 - 180 µm at pH 8 and the ratio of ions divalent and monovalent were kept constant (Ca/K=0.5). The initial concentration of ibuprofen was 10 mg/dm^3.

The Langmuir and Freundlich isotherms were applied to fit the experimental results (Figure 4.16) and as can be observed from the correlation coefficients (R^2) and the errors associated to the parameters obtained for the models, presented in Table 4.12, the Langmuir model fits better the experimental data than the Freundlich model, which gives an indication of the formation of a complete monolayer.

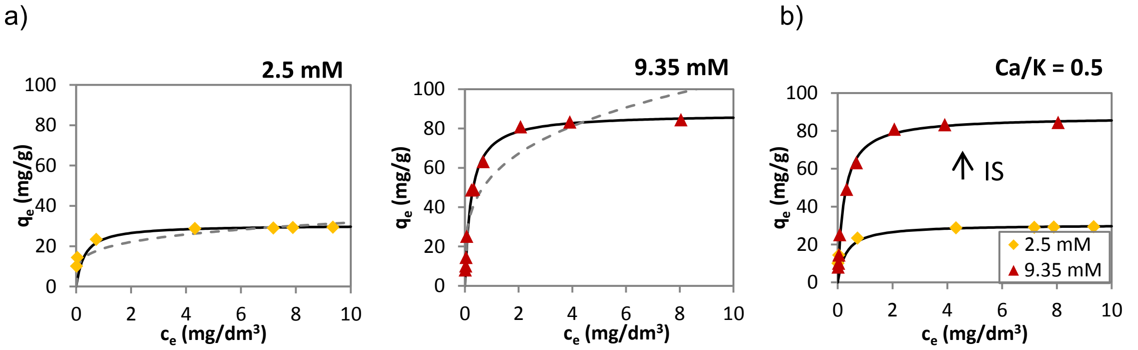


Figure 4.16. Adsorption isotherms of ibuprofen onto AC: a) non-linear fittings of Langmuir and Freundlich models, b) comparison of the best fit representation for the two ionic strengths studied. (— Langmuir model, -- Freundlich model) (Ca/K = 0.5, C_0 = 10 mg/dm^3, F400 125 - 180 µm, pH = 8).

Table 4.12. Parameter values for Langmuir and Freundlich adsorption models (Ca/K = 0.5, C_0 = 10 mg/dm^3, F400 125 - 180 µm, pH = 8).

IS (mM)	**Langmuir model**					**Freundlich model**				
	b (dm^3/µg)	*Error	q_{max} (mg/g)	*Error	R^2	K (mg/g)/(µg/dm^3)$^{1/n}$	*Error	1/n	Error	R^2
2.5	3.32	50%	30.5	13%	0.979	19.9	30%	0.221	29%	0.888
9.35	4.36	32%	87.5	8%	0.996	55.6	32%	0.273	58%	0.889

* Associated error for 95% confidence level.

For pH = 8 the reverse situation is observed than for pH = 6. F400 activated carbon is negatively charged (pH > pH_{PZC} and ibuprofen is negative as well (pH >> pK_a). So, in this case repulsive electrostatic interactions are significant and the adsorption process is favorable for higher ionic strengths. The minimization of repulsive effects is notorious. This result is in agreement with other studies reported in literature, referring that the shielding effect exerted in adsorbent-solute electrostatic interactions by the ionic strength can support adsorption process if the interactions between the activated carbon and the adsorbate are repulsive and harm if they are attractive [91,58].

This effect is evident in Langmuir parameters showed in Table 4.12: q_{max} is much higher for the highest ionic strength, indicating that adsorption is probably very favored by ionic strength, for a pH of 8.

Kinetic adsorption studies were then performed. Pseudo-first order, pseudo-second order and intraparticle diffusion models were tested to fit the experimental data.

The pseudo-first order model cannot be applied in the full range of contact time of the experimental data. On the other side, the pseudo-second order model provides very good fittings of the experimental data (Figure 4.17 and Table 4.13).

These results are consistent with the results obtained in the adsorption isotherms. The adsorption is described by pseudo-second order model which means that chemisorption has been occurs, and therefor was well described by the Langmuir model.

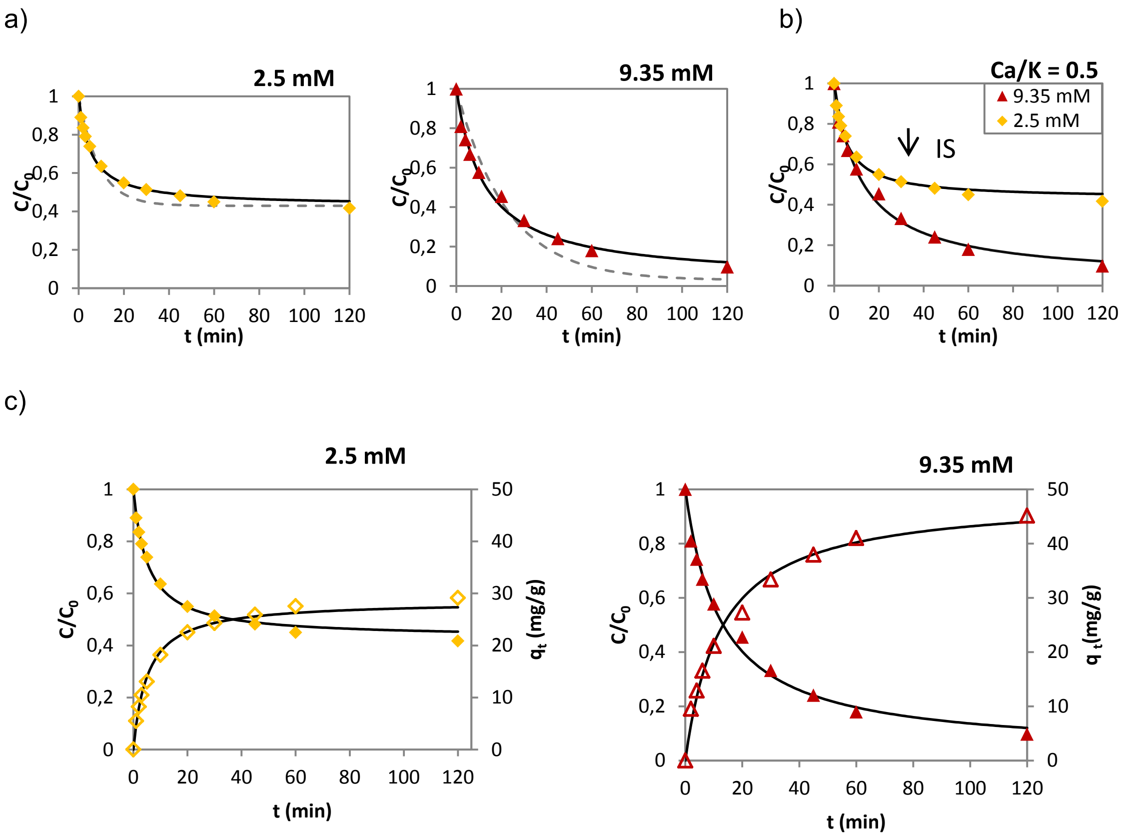


Figure 4.17. Adsorption kinetics of ibuprofen onto AC, a) non-linear fittings of pseudo-first and pseudo-second order models, b) comparison of the best fit representation for the two ionic strengths and c) best fit representation. (- - pseudo-first order model, ── pseudo-second order model) (Ca/K = 0.5, C_0 = 10 mg/dm^3, F400 125 -180 µm, pH = 8).

Table 4.13. Parameter values for pseudo-first and pseudo-second order kinetic adsorption models. (Ca/K = 0.5, C_0 = 10 mg/dm^3, F400 125 - 180 µm, pH=8).

IS (mM)	**Pseudo 1st order model**				**Pseudo 2nd order model**		
	q_{e_calc} (mg/g)	k_1 (1/h)	*Error	R^2	k_2 (g/(mg.h))	*Error	R^2
2.5	28.5	0.112	29%	0.953	6.74E-3	15%	0.990
9.35	48.6	0.0445	29%	0.491	1.65E-3	15%	0.990

* Associated error for 95% confidence level.

It can be observed that considering the rate of overall adsorption process for these experimental conditions such as pH 8, lower ionic strength values achieved faster kinetic (pseudo-second order constant, k_2 is higher).

Intraparticle diffusion model was then applied to complement the studies above and the results are illustrated in Figure 4.18. In fact, many studies reported that in many cases the external mass transfer (film diffusion) or intraparticle diffusion (particle diffusion) are often the rate-limiting steps of adsorption and both affect the plot traced by the intraparticle diffusion model. These models describe well the kinetic adsorption with acceptable correlation coefficients as shown in Table 4.14. Boyd kinetic expression (described in section 2.5.6) was applied to get a deeper perception of the step that controls the adsorption process and to determine the diffusion coefficients. The results are presented on Figure 4.18 and Table 4.14.

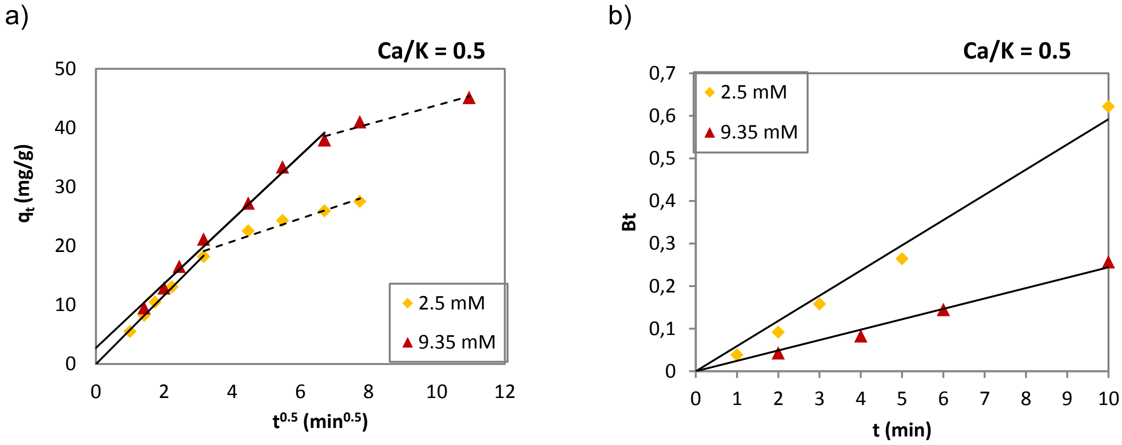


Figure 4.18. a) Intraparticle diffusion model and b) Boyd plot (diffusion coefficient) for ibuprofen adsorption. (Ca/K=0.5, C_0=10 mg/dm^3, F400 125-180 μm, pH=8).

Table 4.14. Parameter values for intraparticle diffusion model and Boyd plot (diffusion coefficient) for ibuprofen adsorption. (Ca/K = 0.5, C_0 = 10 mg/dm^3, F400 125 - 180 μm, pH = 8).

IS (mM)	**Intraparticle diffusion model**			**Boyd model**		
	K_p (mg/(g.min$^{0.5}$))	A (mg/g)	R^2	Equation	D_i (cm^2/s)	R^2
2.5	5.82	-2.51E-2	0.997	Bt =0.06 t	5.81E-7	0.984
9.35	5.43	2.74	0.992	Bt =0.02 t	2.20E-7	0.997

Is possible to identify two linear sections when the ionic strength is 2.5 mM and two linear sections when is 9.35 mM. According to the literature, if the data exhibit multi-linear plots, it means that two or more steps influence the adsorption process [77]. If three linear sections were presented, the external resistance is represented by the first linar section (adsorption in macro and mesopores), the second represents the internal diffusion (adsorption in micropores) and the last is relative to the equilibrium, but in this case, the first section of the plot does not exist.

In both cases pore diffusion seems to be the rate-controlling step of adsorption. The point where interpolation intercepts the y-axis gives a measure of the boundary layer thickness represented by the value of A on the Table 4.14. The larger is the boundary layer thickness, the greater effect of the external resistance (film diffusion) on the adsorption kinetics, which in these cases seems to have a negligible contribution.

4.2.5 The effect of monovalent and divalent ions on ibuprofen adsorption onto activated carbon

To understand the impact of the monovalent and divalent ions in ibuprofen adsorption, tests were performed with the same ionic strength but different ratios of divalent/monovalent ions. The initial concentration of ibuprofen used was 10 mg/dm^3 at pH 8 for the activated carbon F400 125 - 180 µm. Ionic strength 9.35 mM was used, as it had shown the better adsorption results. The ratios of Ca/K used were 0.5 and 1.5.

Adsorption isotherms were performed and Langmuir and Freundlich models were applied to fit the experimental data. For both, Langmuir model gave a good fit but Freundlich model does not fit well the experimental data. The results are shown on Figure 4.19 and the non-linear fitting for Ca/K=0.5 was performed in the section above to study the effect of ionic strength and is presented on Figure 4.16a.

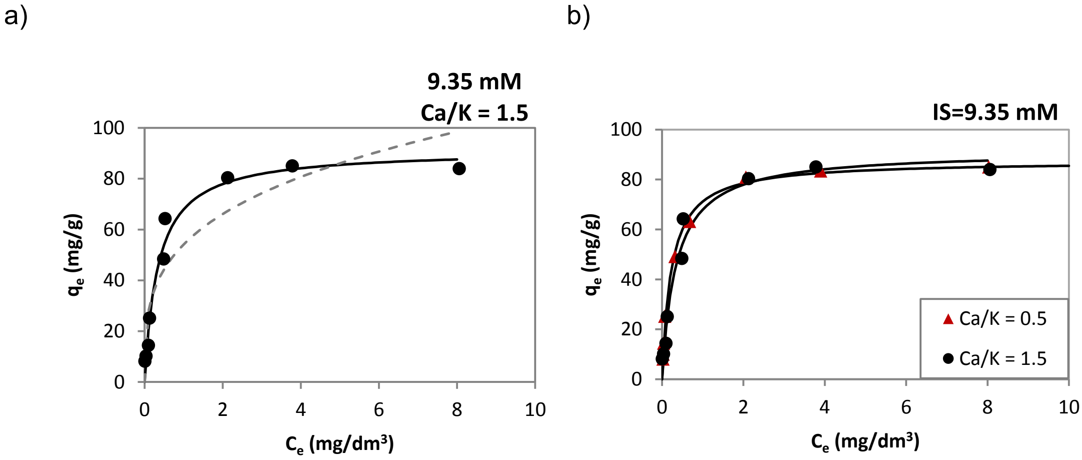


Figure 4.19. Adsorption isotherms of ibuprofen onto AC: a) non-linear fittings of Langmuir and Freundlich models, b) comparison of the best fit representation for the two ratios of ions studied. (— Langmuir model, -- Freundlich model). (— Langmuir, -- Freundlich) (IS = 9.35 mM, C_0 = 10 mg/dm^3, F400 125 - 180 µm, pH= 8).

The parameter values of the models are presented in Table 4.15, with correlation coefficients and the errors associated with the parameters.

Table 4.15. Parameter values for Langmuir and Freundlich adsorption models. (IS = 9.35 mM, C_0 = 10 mg/dm^3, F400 125 - 180 µm, pH = 8).

Ca/K	Langmuir model					Freundlich model				
	b (dm^3/mg)	*Error	q_{max} (mg/g)	*Error	R^2	K (mg/g)/(mg/dm^3)$^{1/n}$	*Error	1/n	*Error	R^2
0.5	4.36	32%	87.5	8%	0.996	55.6	32%	0.273	58%	0.889
1.5	2.89	58%	91.4	19%	0.978	54.1	36%	0.288	63%	0.860

* Associated error for 95% confidence level.

It is notorious that the type of ions present in the solution does not appear to affect the adsorption. The parameter values of the models were very similar. This fact indicates that maintaining the ionic strength, the adsorption will remain the same no matter which ions contribute for that (monovalent or divalent).

Once more the Langmuir model describes better the adsorption process, with lower error of the parameters and better correlation coefficient (R^2).

Adsorption kinetic studies were also performed to investigate the effect of the type of ions. Pseudo first order, pseudo-second order and intraparticle diffusion models were applied to experimental points, in order to understand the influence of monovalent and divalent ions in kinetic adsorption rate. The non-linear fittings of pseudo-first order and pseudo-second order models for Ca/K = 0.5 is presented in Figure 4.17 and the other results are displayed in Figure 4.20.

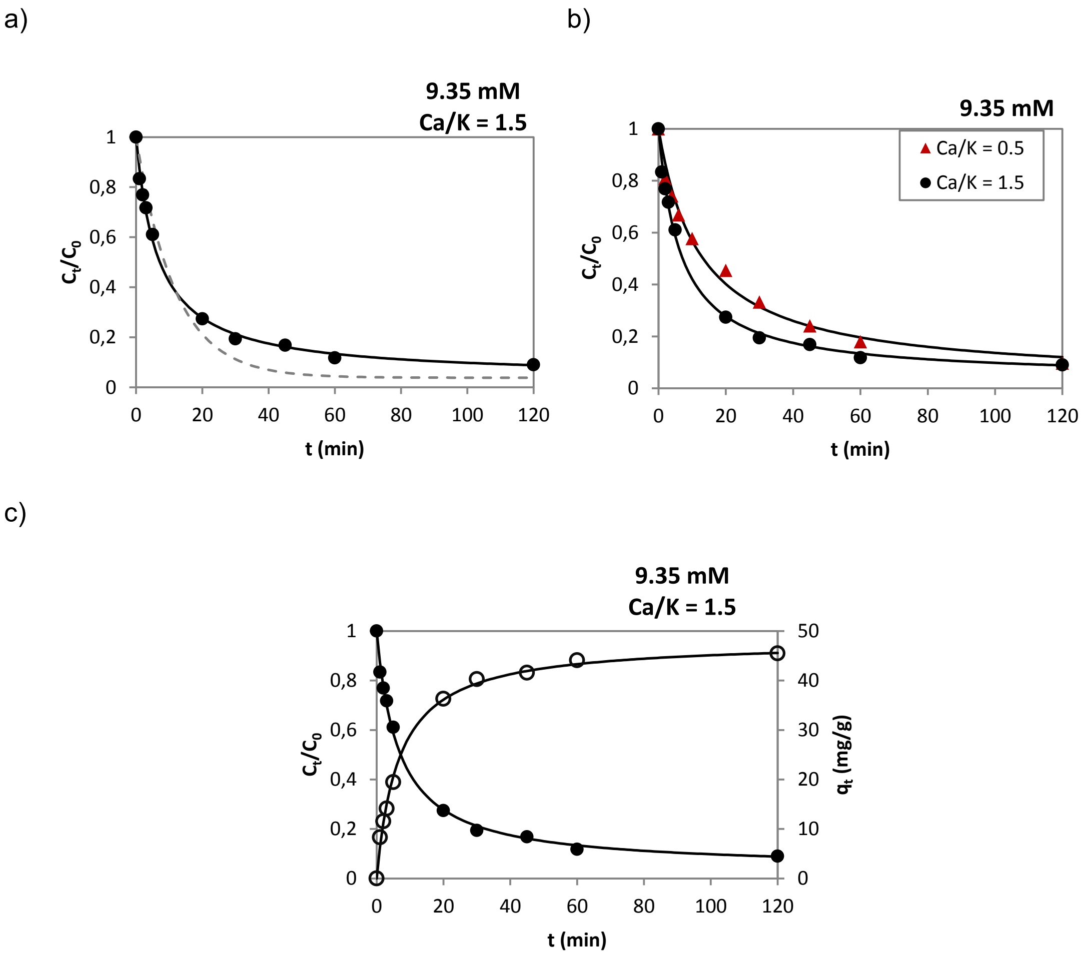


Figure 4.20. Adsorption kinetics of ibuprofen onto AC, a) non-linear fittings of pseudo-first and pseudo-second order models, b) comparison of the best fit representation for the two ratios of ions studied and c) best fit representation. (– – pseudo-first order model, —— pseudo-second order model) (IS = 9.35 mM, C_0 = 10 mg/dm^3, F400 125 - 180 μm, pH = 8).

Once again the pseudo-first order model cannot be applied in the full range of. Pseudo-second order presented a good adjust to all experimental points (R^2 > 0.99 and low errors in parameters) Table 4.16.

Table 4.16. Parameter values for pseudo-first and pseudo-second order kinetic adsorption models. (IS = 9.35 mM, C_0 = 10 mg/dm^3, F400 125 - 180 μm, pH = 8).

Ca/K	**Pseudo 1st order model**				**Pseudo 2nd order model**		
	q_e_calc (mg/g)	k_1 (1/h)	*Error	R^2	k_2 (g/(mg.h))	*Error	R^2
0.5	48.6	0.0445	29%	0.491	1.65E-3	15%	0.990
1.5	48.1	0.0855	35%	0.914	3.14E-3	11%	0.997

* Associated error for 95% confidence level.

It can be observed that, when the divalent ions prevail, kinetic adsorption seems to be faster, being slightly affected by the type of salts that are presented in the solution.

The intraparticle diffusion model was then applied. The results are presented in Figure 4.21.

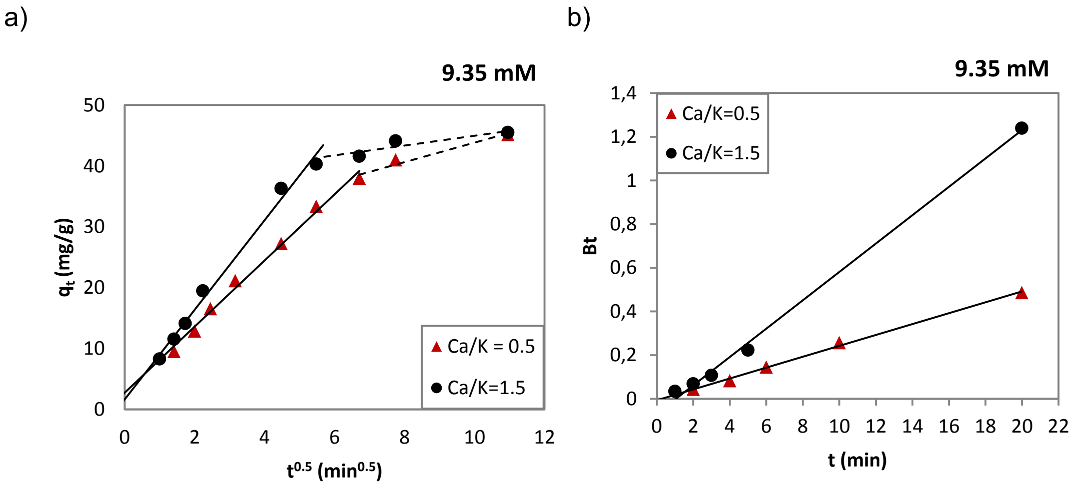


Figure 4.21. a) Intraparticle diffusion model and b) Boyd plot (diffusion coefficient) for ibuprofen adsorption. (IS = 9.35 mM, Ca/K = 0.5, C_0 = 10 mg/dm^3, F400 125 - 180 µm, pH = 8).

Table 4.17. Parameter values for intraparticle diffusion model and Boyd plot (diffusion coefficient) for ibuprofen adsorption. (IS = 9.35 mM, C_0 = 10 mg/dm^3, F400 125 - 180 µm, pH = 8).

Ca/K	**Intraparticle Diffusion model**			**Boyd model**		
	K_p (mg/(g.min$^{0.5}$))	A (mg/g)	R^2	Equation	D_i (cm^2/s)	R^2
0.5	5.43	2.74	0.992	Bt =0.02 t	2.20E-7	0.997
1.5	8.09	0.392	0.998	Bt = 0.06 t	5.90E-7	0.985

The value of *A* can be disregarded and the adsorption seems to be controlled by intraparticle diffusion. Apparently, when there are more calcium ions than potassium, the diffusion coefficient (D_i) is higher (5.9E-7).

Other studies refer that the presence of monovalent, divalent and a mixture of both in different concentrations can affect the adsorption [12,13], but they also refer that this effect depends on the molecular size of the contaminant. Only high molecular size contaminants present significant differences. Probably, as ibuprofen is a relatively small molecule this effect is not observed.

4.2.6 The influence of functionalize the activated carbon F400 in the adsorption of ibuprofen onto activated carbon

Functionalized activated carbon was tested in the same conditions to compare with F400 without functionalization. Both have the same sizes (125 - 180 µm). The pH used was 8, the ionic strength was 2.5 mM and Ca/K value 0.5.

Langmuir and Freundlich models were tested for the experimental data and results are presented in Figure 4.22.

Langmuir model can be applied, presenting good correlation coefficient and low associated errors, while the Freundlich model does not fit the experimental data. The results are presented in Table 4.18.

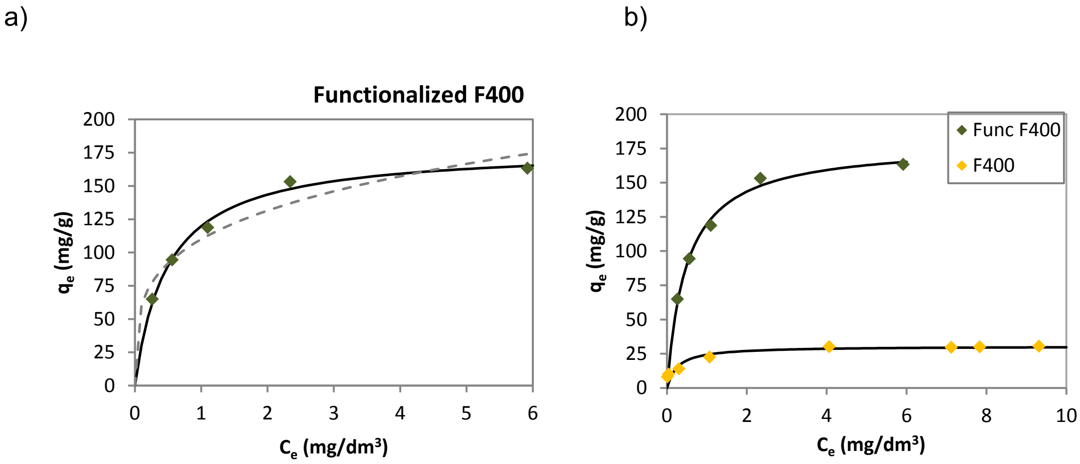


Figure 4.22. Adsorption isotherms of ibuprofen onto AC: a) non-linear fittings of Langmuir and Freundlich models, b) comparison of the best fit representation for the two ACs studied. (—— Langmuir model, – – Freundlich model) (IS = 2.5 mM, Ca/K = 0.5, C_0 = 10 mg/dm^3, pH = 8).

Table 4.18. Parameter values for Langmuir and Freundlich adsorption models. (IS = 2.5 mM, Ca/K = 0.5, C_0 = 10 mg/dm^3 , pH = 8).

Activated Carbon	**Langmuir model**					**Freundlich model**				
	b (dm^3/mg)	*Error	q_{max} (mg/g)	*Error	R^2	K (mg/g)/(mg/dm^3)$^{1/n}$	*Error	1/n	*Error	R^2
F400	3.32	50%	30.5	13%	0.979	19.9	30%	0.221	29%	0.888
Func F400	2.03	25%	179	17%	0.990	110	33%	0.258	76%	0.912

* Associated error for 95% confidence level.

There is a major difference between the carbons, with the functionalized AC showing a very high adsorption capacity (q_{max} = 179 mg/g).

The functionalized AC is positively charged (pH < pH_{PZC}), while the non-functionalized is negatively charged (pH > pH_{PZC}). Since almost all ibuprofen is negatively charged, in the first case attractive electrostatic interactions dominates the process but for non-functionalized AC the repulsive forces are dominant, how it was referred before when it was studied how the pH of the solution can affect the adsorption process. This situation is similar to pH 6 with non-functionalized AC, where the attractive forces are also predominant.

The functionalization of activated carbon F400 would then seem to have accomplished the desired effect of promoting adsorption. This may be caused by changes in surface chemistry due to an increase in the basicity of the carbon but also an increase of micropores observed in the functionalized carbon, as discussed earlier, functionalized F400 activated carbon has suffered a slight increase of micropores structure, although the most importante factor seems to be the chemical changes in the surface.

Kinetic studies were performed and the pseudo-first and pseudo-second order models were applied to fit the experimental data and the parameters values were calculated (Figure 4.23 and Table 4.19).

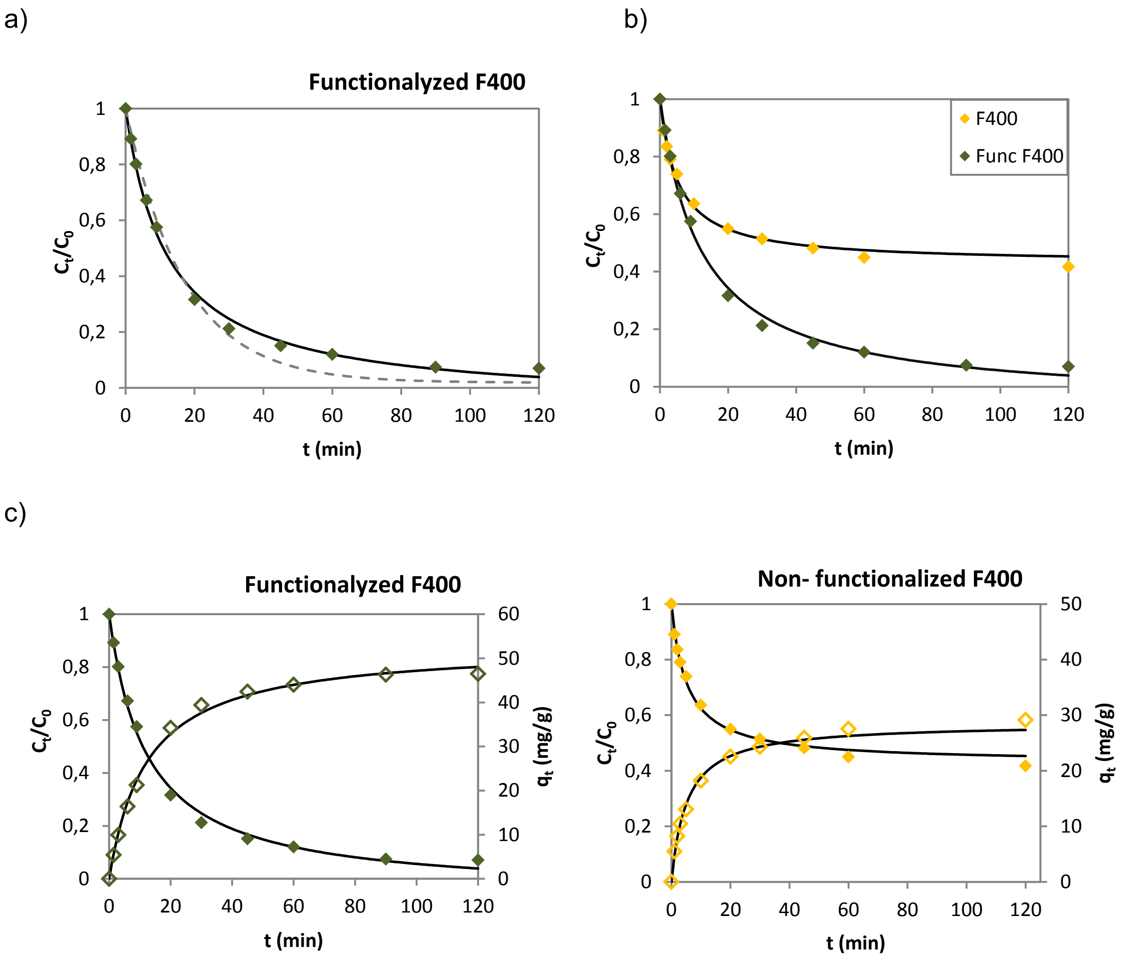


Figure 4.23. Adsorption kinetics of ibuprofen onto AC, a) non-linear fittings of pseudo-first and pseudo-second order models, b) comparison of the best fit representation for the two ACs studied and c) best fit representation. (– – pseudo-first order model, —— pseudo-second order model) (IS = 2.5 mM, Ca/K = 0.5, C_0 = 10 mg/dm^3, pH = 8).

The best results were achieved with pseudo-second order model, with higher correlation coefficient (R^2=0.996) and lower parameter errors.

Table 4.19. Parameter values for pseudo-first and pseudo-second order kinetic adsorption models. (IS = 2.5 mM, Ca/K = 0.5, C_0 = 10 mg/dm^3, pH = 8).

Activated Carbon	q_e_calc (mg/g)	Pseudo 1st order model			Pseudo 2nd order model		
		k_1 (1/h)	*Error	R^2	k_2 (g/(mg.h))	*Error	R^2
F400	28.5	0.112	29%	0.953	6.74E-3	15%	0.990
Func F400	49.1	0.0583	17%	0.984	1.54E-3	21%	0.996

* Associated error for 95% confidence level.

Functionalization of the activated carbon F400 seems to affect the adsorption kinetic. It is possible to observe by the values presented in Table 4.19 for the pseudo-second order rate constant, k_2, that the F400 functionalized AC has a slower adsorption kinetic constant, although the adsorption capacity is much higher as it can be observed in Figure 4.23c.

Kinetic follows the pseudo-second order model in complement with adsorption isotherm being of Langmuir type, characterized by a steep initial rise and approaching a plateau attributed to the formation of a complete monolayer.

The intraparticle diffusion model was also applied to identify the limiting adsorption step and the diffusion/transport mechanisms during ibuprofen adsorption as it is shown Figure 4.24.

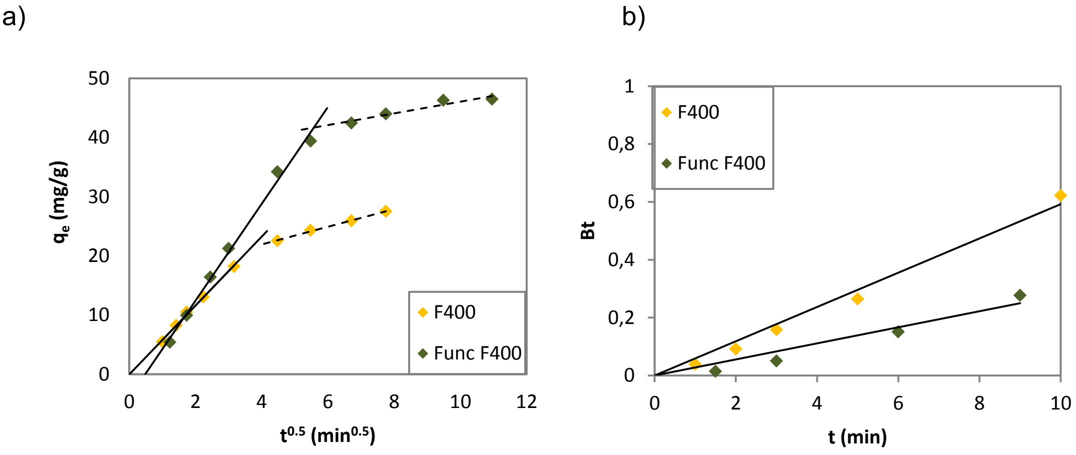


Figure 4.24. a) Intraparticle diffusion model and b) Boyd plot (diffusion coefficient) for ibuprofen adsorption in experimental conditions: (IS = 2.5 mM, Ca/K = 0.5, C_0 = 10 mg/dm^3, pH = 8).

The calculated parameter values are presented in Table 4.20.

Table 4.20. Parameter values for intraparticle diffusion model and Boyd plot (diffusion coefficient) for ibuprofen adsorption. (IS = 2.5 mM, Ca/K = 0.5, C_0 = 10 mg/dm^3, pH = 8).

AC	Intraparticle diffusion model			Boyd model		
	K_p (mg/(g.min$^{0.5}$))	A (mg/g)	R^2	Equation	Di (cm^2/s)	R^2
F400	5.82	-2.51E-2	0.997	Bt =0.06 t	5.81E-7	0.984
Func. F400	8.18	-3.95	0.994	Bt = 0.03 t	2.73E-7	0.931

The constant related to the boundary layer thickness (A) was near to zero and this low value indicates a small film resistance to mass transfer surrounding the adsorbent particle.

The ionic strength effect already studied for F400 activated carbon without any functionalization was studied at this point to understand the effect in functionalized F400 AC as well.

Adsorption isotherm was performed for the functionalized F400 AC but with an ionic strength of the solution of 9.35 mM and keeping Ca/K = 0.5. The pH was adjusted for 8 like before, with NaOH, and the Langmuir and Freundlich models were applied. The results are presented in Figure 4.25.

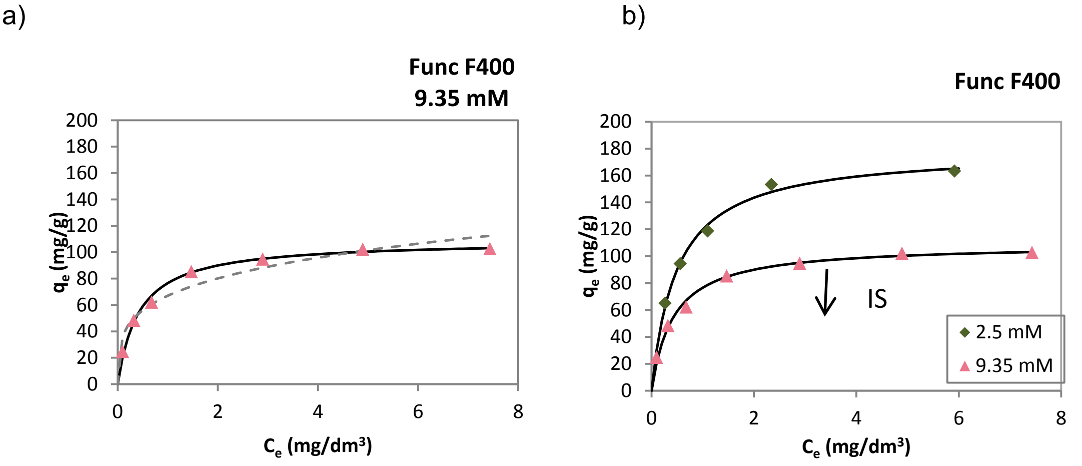


Figure 4.25. Adsorption isotherms of ibuprofen onto AC: a) non-linear fittings of Langmuir and Freundlich models, b) comparison of the best fit representation for the two ionic strengths studied. (—— Langmuir model, - - Freundlich model) (Ca/K = 0.5, C_0 = 10 mg/dm^3, F400 Functionalized, pH = 8).

Only the Langmuir model fits the experimental data as can be observed in Figure 4.25a.

The parameter values were calculated and are presented in Table 4.21.

Table 4.21. Parameter values for Langmuir and Freundlich adsorption models. (Ca/K = 0.5, C_0 = 10 mg/dm^3, F400 Functionalized, pH = 8).

IS (mM)	**Langmuir model**					**Freundlich model**				
	b (dm^3/mg)	*Error	q_{max} (mg/g)	*Error	R^2	K (mg/g)/(mg/dm^3)$^{1/n}$	*Error	1/n	*Error	R^2
2.5	2.03	25%	179	17%	0.990	110	33%	0.258	76%	0.912
9.35	2.37	40%	109	11%	0.991	67.0	27%	0.258	57%	0.922

* Associated error for 95% confidence level.

As it was expected, an increase in the ionic strength will affect the adsorption, lowering the q_{max} parameter from 179 mg/g to 109 mg/g.

This can be explained because the activated carbon is still positively charged at this pH value ($pH < pH_{PZC}$) and the ionic strength, as it was said before, may exert an adsorbent-solute shielding effect that decreases both, attractive and repulsive electrostatic interactions, that in this case are attractive (the activated carbon was positively charged and ibuprofen negative).

The evolution of the concentration of ibuprofen and the carbon uptake as a function of time, plotted as C_t/C_0 and q_t over time, is shown in Figure 4.26. Pseudo-first and pseudo-second order models were applied, with only the pseudo-second order model fitting all the experimental data.

As it can be observed in Figure 4.26a, pseudo-first order model only fits the experimental data for the first 10 minutes, being very far from the experimental points in the subsequent contact times. For this reason, just the pseudo-second order model is considered for this analysis.

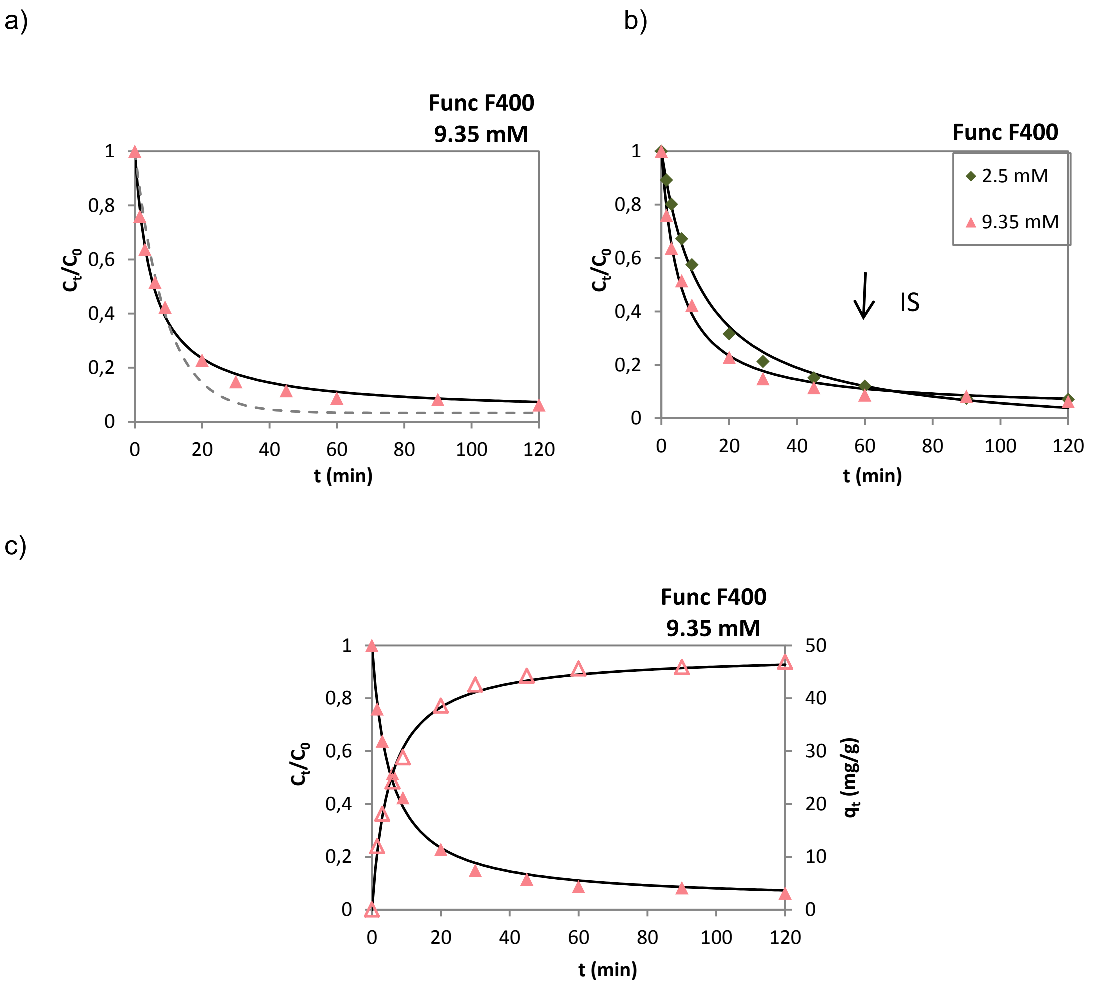


Figure 4.26. Adsorption kinetics of ibuprofen onto AC, a) non-linear fittings of pseudo-first and pseudo-second order models, b) comparison of the best fit representation for the two ionic strengths and c) best fit representation. (– – pseudo-first order model, —— pseudo-second order model) (Ca/K = 0.5, C_0 = 10 mg/dm^3, F400 Functionalized AC, pH = 8).

The calculated parameter values are presented in Table 4.22.

Table 4.22. Parameter values for pseudo-first and pseudo-second order kinetic adsorption models. (Ca/K = 0.5, C_0 = 10 mg/dm^3, F400 Functionalized AC, pH = 8).

IS (mM)	**Pseudo 1st order model**				**Pseudo 2nd order model**		
	q_{e}_calc (mg/g)	k_1 (1/h)	*Error	R^2	k_2 (g/(mg.h))	*Error	R^2
2.5	49.1	0.0583	17%	0.984	1.54E-3	21%	0.996
9.35	48.4	0.108	27%	0.957	3.92E-3	12%	0.995

* Associated error for 95% confidence level.

The kinetic seems to increase when the ionic strength increase from 2.5 mM to 9.35 mM (as it shows the value of k_2 in Table 4.22)

To better understand the controlling step, the data was analyzed by the intraparticle diffusion model and the Boyd expression, as shown in Figure 4.27.

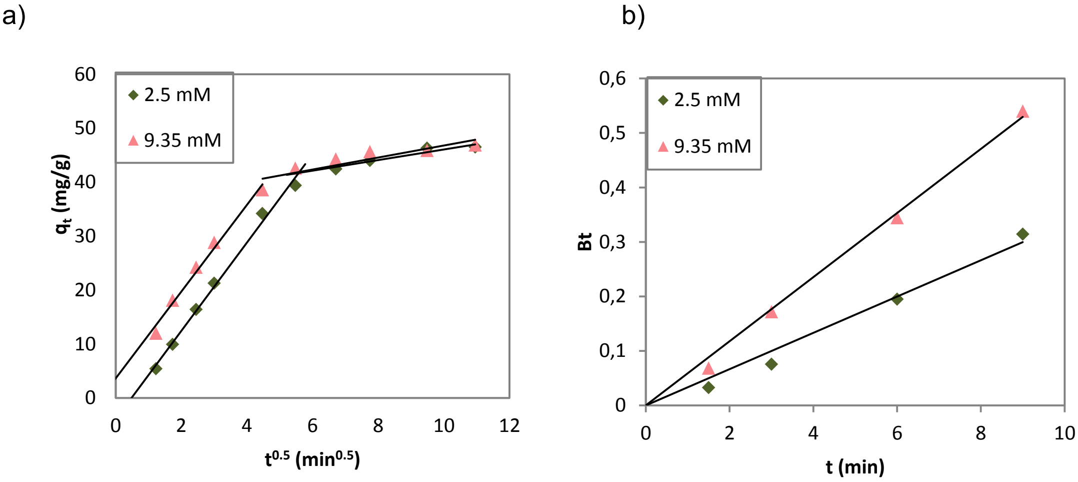


Figure 4.27. a) Intraparticle diffusion model and b) Boyd plot (diffusion coefficient) for ibuprofen adsorption. (pH = 8, Ca/K = 0.5, C_0 = 10 mg/dm^3, F400 Functionalized AC).

The parameter values are presented in Table 4.23.

Table 4.23. Parameter values for intraparticle diffusion model and Boyd plot (diffusion coefficient) for ibuprofen adsorption. (Ca/K = 0.5, C_0 = 10 mg/dm^3, pH = 8).

IS (mM)	Intraparticle diffusion model			Boyd model		
	K_p (mg/(g.min$^{0.5}$))	A (mg/g)	R^2	Equation	D_i (cm^2/s)	R^2
2.5	7.50	-0.544	0.995	Bt = 0.03 t	3.27E-7	0.977
9.35	8.04	3.65	0.987	Bt =0.06 t	5.77E-7	0.996

In the case of ionic strength of 9.35 mM, the boundary layer thickness (A = 3.65 mg/g) seems to be significant (Table 4.23), which means that the external mass diffusion can be relevant in the kinetic.

The values of Bt were plotted against time (t), as shown in Figure 4.27b. The linearity of this plot is used to distinguish if the external transport or the intraparticle transport controls the adsorption rate. The plot is linear and passes through the origin, which helps to understand the plot of q_t versus $t^{0.5}$ and conclude that possibly the intraparticle diffusion is the rate controlling step of adsorption.

The major differences between the F400 and the functionalized F400 AC are presented for 2.5 mM seems to be suppressed when the ionic strength increases to 9.35 mM as it can be observed in Figure 4.28. The F400 virgin, for this ionic strength will increase the adsorption because the repulsive electrostatic forces between the activated carbon and the ibuprofen prevailed. For the case of F400 functionalized this ionic strength cause the opposite and prejudice the adsorption that is favored because activated carbon and ibuprofen are presented with opposite charges.

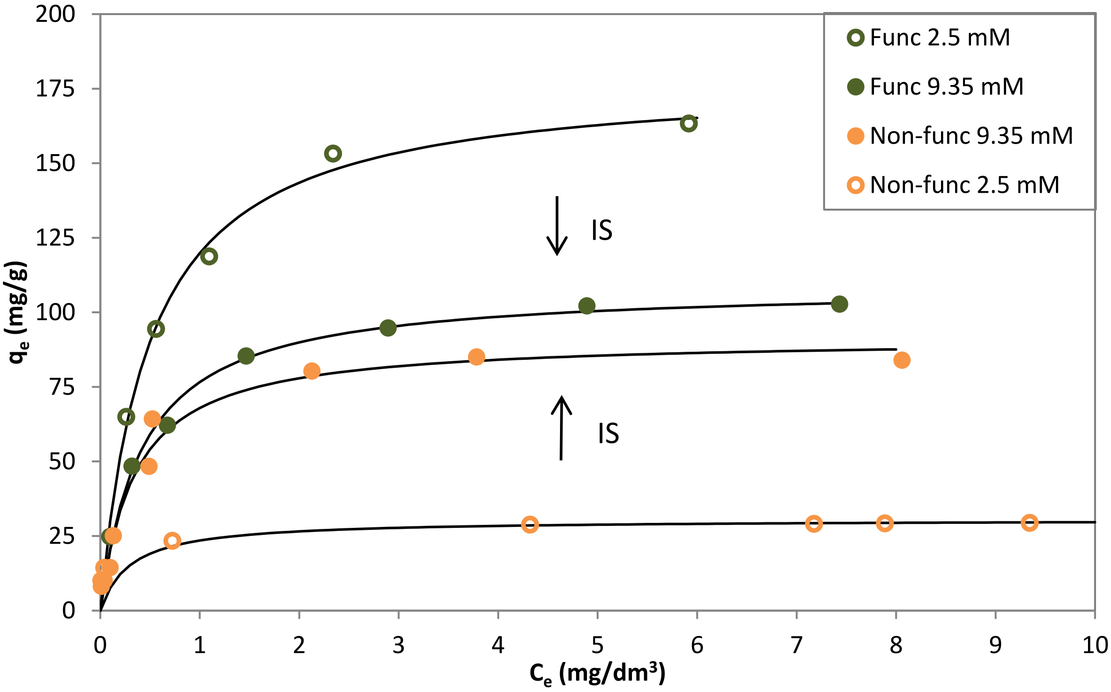


Figure 4.28. Adsorption isotherms of ibuprofen onto AC, comparison of the best fit representation (Ca/K = 0.5, C_0 = 10 mg/dm^3, pH = 8).

For water treatment plants with high values of ionic strength (> 9.35 mM), and high values of pH (~8) (normally founded in wastewater treatment), functionalization of the AC ceases to be advantageous.

4.2.7 The effect of activated carbon F400 particle size in the adsorption of ibuprofen onto activated carbon

Decreasing the grain of F400 activated carbon will expose more external surface to the bulk solution and the diffusion path for adsorbate migration onto active sites decreases, which could lead the adsorption process to an equilibrium plateau quickly [85].

The plot of ibuprofen adsorption onto the two different particle sizes of F400 activated carbon (125 - 180 μm and 63 - 90 μm) are presented in Figure 4.29 with the Langmuir and Freundlich models curves.

Langmuir model fits well the adsorption results for the conditions studied (Figure 4.29).

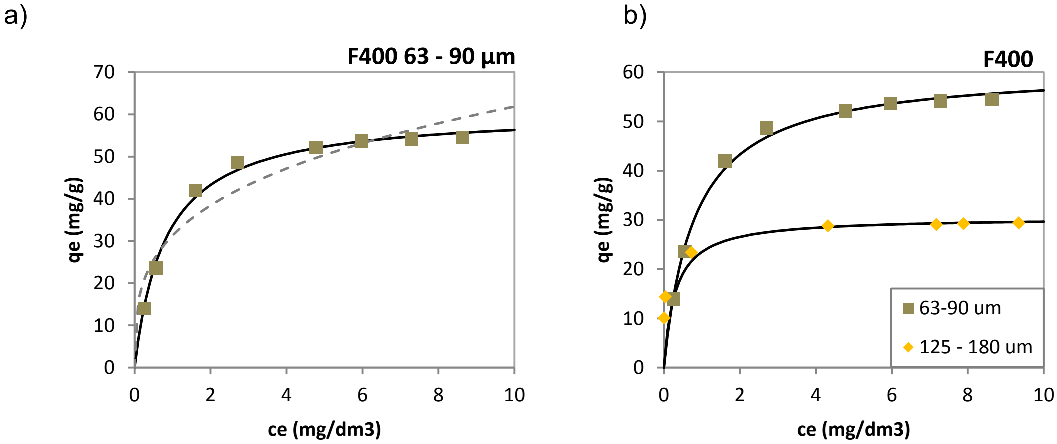


Figure 4.29. Adsorption isotherms of ibuprofen onto AC: a) non-linear fittings of Langmuir and Freundlich models, b) comparison of the best fit representation for the two particle sizes of AC studied. (── Langmuir model, – – Freundlich model) (IS = 2.5 mM, Ca/K = 0.5, C_0 = 10 mg/dm^3, pH = 8).

Table 4.24. Parameter values for Langmuir and Freundlich adsorption models. (IS = 2.5 mM, Ca/K = 0.5, C_0 = 10 mg/dm^3, pH = 8).

AC particle size (µm)	**Langmuir model**					**Freundlich model**				
	b (dm^3/mg)	*Error	q_{max} (mg/g)	*Error	R^2	K (mg/g)/(mg/dm^3)$^{1/n}$	*Error	1/n	*Error	R^2
125-180	3.32	50%	30.5	13%	0.979	19.9	30%	0.221	29%	0.888
63-90	1.23	32%	60.9	8%	0.994	31.3	35%	0.296	60%	0.899

* Associated error for 95% confidence level.

The adsorption seems to be favored by decreasing the size of F400 activated carbon particles, with a significant increase in q_{max} parameter for 63 - 90 µm.

Kinetic adsorption was studied for the two different activated carbon F400 particle sizes. The models applied were the pseudo-first order, pseudo-second order and intraparticle diffusion models. The pseudo-first order model does not seem to fit these experimental results. Pseudo-second order model presented good results as it can be observed in Figure 4.30 and in Table 4.25.

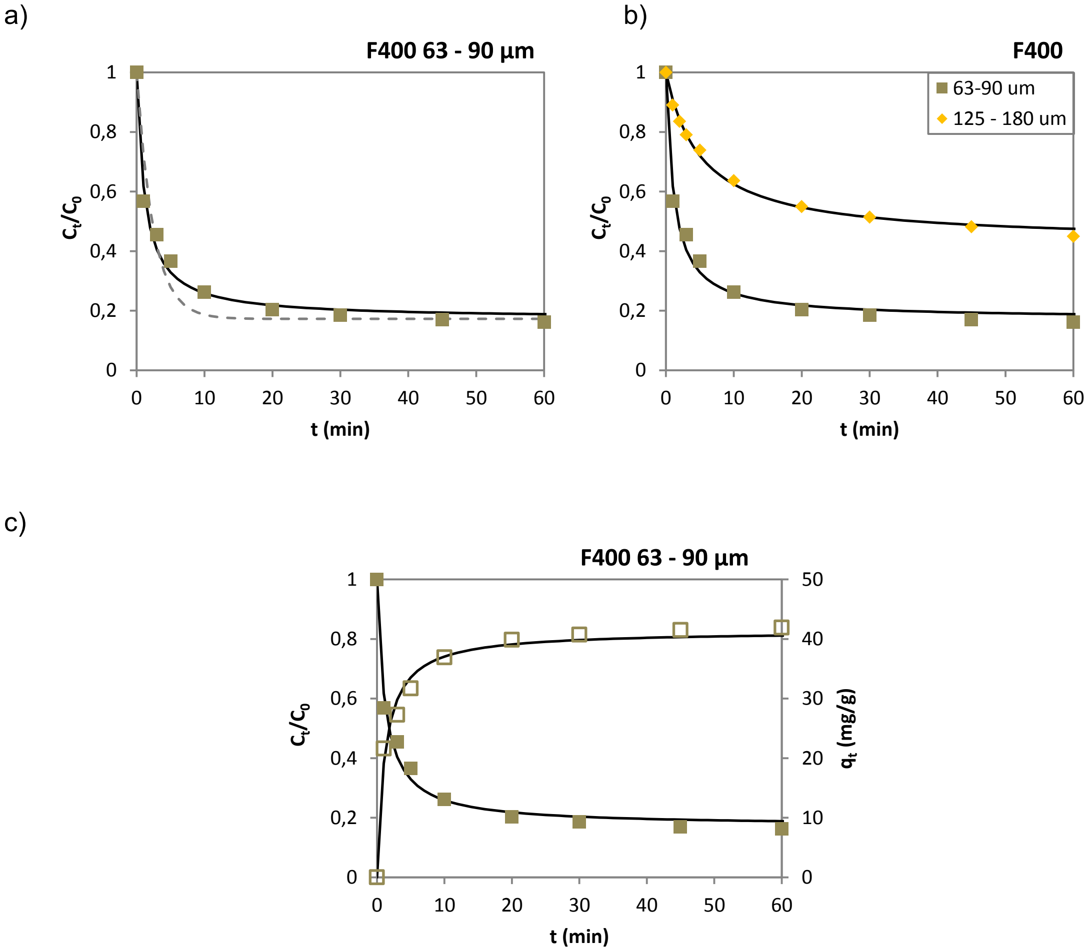


Figure 4.30. Adsorption kinetics of ibuprofen onto AC, a) non-linear fittings of pseudo-first and pseudo-second order models, b) comparison of the best fit representation for the two particle sizes of AC studied and c) best fit representation. (_ _ pseudo-first order model, —— pseudo-second order model) (IS = 2.5 mM, Ca/K = 0.5, C_0 = 10 mg/dm^3, pH = 8).

Pseudo-second order model presented the best adjustment to these experimental results.

Table 4.25. Parameter values for pseudo-first and pseudo-second order kinetic adsorption models. (IS = 2.5 mM, Ca/K = 0.5, C_0 = 10 mg/dm^3, pH = 8).

AC particle size (µm)	q_e_calc (mg/g)	**Pseudo 1st order model**			**Pseudo 2nd order model**		
		k_1 (1/h)	*Error	R^2	k_2 (g/(mg.h))	*Error	R^2
125-180	28.5	0.112	29%	0.953	6.74E-3	29%	0.990
63-90	41.4	0.409	35%	0.940	2.07E-2	27%	0.984

* Associated error for 95% confidence level.

Observing the pseudo-second order rate constant, k_2, an increase with increasing the particle size was obtained as it was expected.

The intraparticle diffusion model is plotted in Figure 4.31 for the two particle sizes of F400 AC studied.

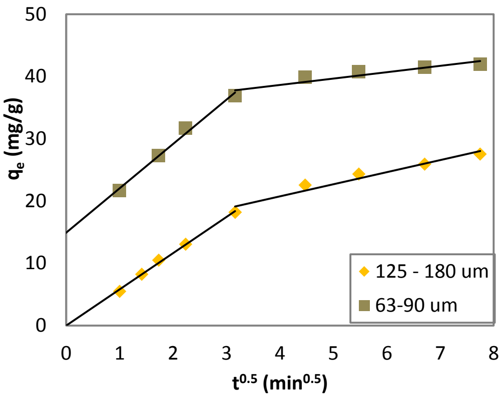


Figure 4.31. Intraparticle diffusion model for ibuprofen adsorption. (IS = 2.5 mM, Ca/K = 0.5, C_0 = 10 mg/dm^3, pH = 8).

Table 4.26. Parameter values for intraparticle diffusion model and Boyd plot (diffusion coefficient) for ibuprofen adsorption. (IS = 2.5 mM, Ca/K = 0.5, C_0 = 10 mg/dm^3, pH = 8).

F400 AC particle size (µm)	**Intraparticle diffusion model**		
	k_p (mg/(g.min$^{0.5}$))	A (mg/g)	R^2
125 - 180	5.82	-2.51E-02	0.997
63 - 90	7.12	14.9	0.991

The intraparticle diffusion model plots seem to be very influenced by the change in activated carbon particle size. The increase in the value of parameter A (related to the boundary layer thickness), from near to zero to almost 14 mg/g, suggests that for the smaller grain, the adsorption is controlled by the external mass transfer (film diffusion). The intraparticle diffusion rate constant (k_p) is higher as well This result explained the fact that the adsorption capacity increases for the smaller grain of F400, which occurs because the intraparticle diffusion ceases to control the adsorption process for this experimental conditions. Activated carbon particle diameter seems to be advantageous for fast adsorption kinetics. This result was obtained in the studies of other compounds [12,13].

This effect was studied for lower concentrations (100 µg/dm^3) at pH 6 and the results are presented in Figure 4.32.

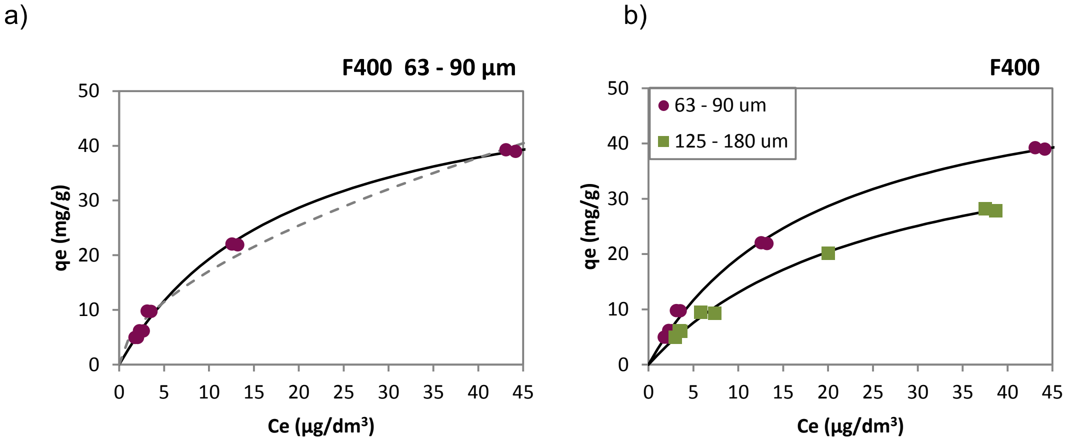


Figure 4.32. Adsorption isotherms of ibuprofen onto AC: a) non-linear fittings of Langmuir and Freundlich models, b) comparison of the best fit representation for the two particle sizes of AC studied. (— Langmuir model, -- Freundlich model) (IS = 2.5 mM, Ca/K = 0.5, C_0 = 100 µg/dm^3, pH = 6).

Parameter values calculated by the non-linear equations of the models are presented in Table 4.27 for both sizes of activated carbon.

Table 4.27. Parameter values for Langmuir and Freundlich adsorption models. (IS = 2.5 mM, Ca/K = 0.5, C_0 = 100 µg/dm^3, pH = 6).

F400 AC particle size (µm)	**Langmuir model**					**Freundlich model**				
	b (dm^3/µg)	*Error	q_{max} (mg/g)	*Error	R^2	K (mg/g)/(µg/dm^3)$^{1/n}$	*Error	1/n	*Error	R^2
125-180	0.0387	20%	46.8	22%	0.996	2.82	35%	0.633	18%	0.994
63-90	0.0529	31%	55.8	15%	0.996	4.56	38%	0.574	22%	0.986

* Associated error for 95% confidence level.

The results show that either for the experimental conditions used, the smaller particle size favors the adsorption of ibuprofen onto F400 AC, presenting a higher value of q_{max}.

The results show that the Langmuir model fits better the experimental data.

Pseudo-first order and pseudo-second order models were performed and adjusted with non-linear equations. The plots with the respective adjustments are presented in Figure 4.24.

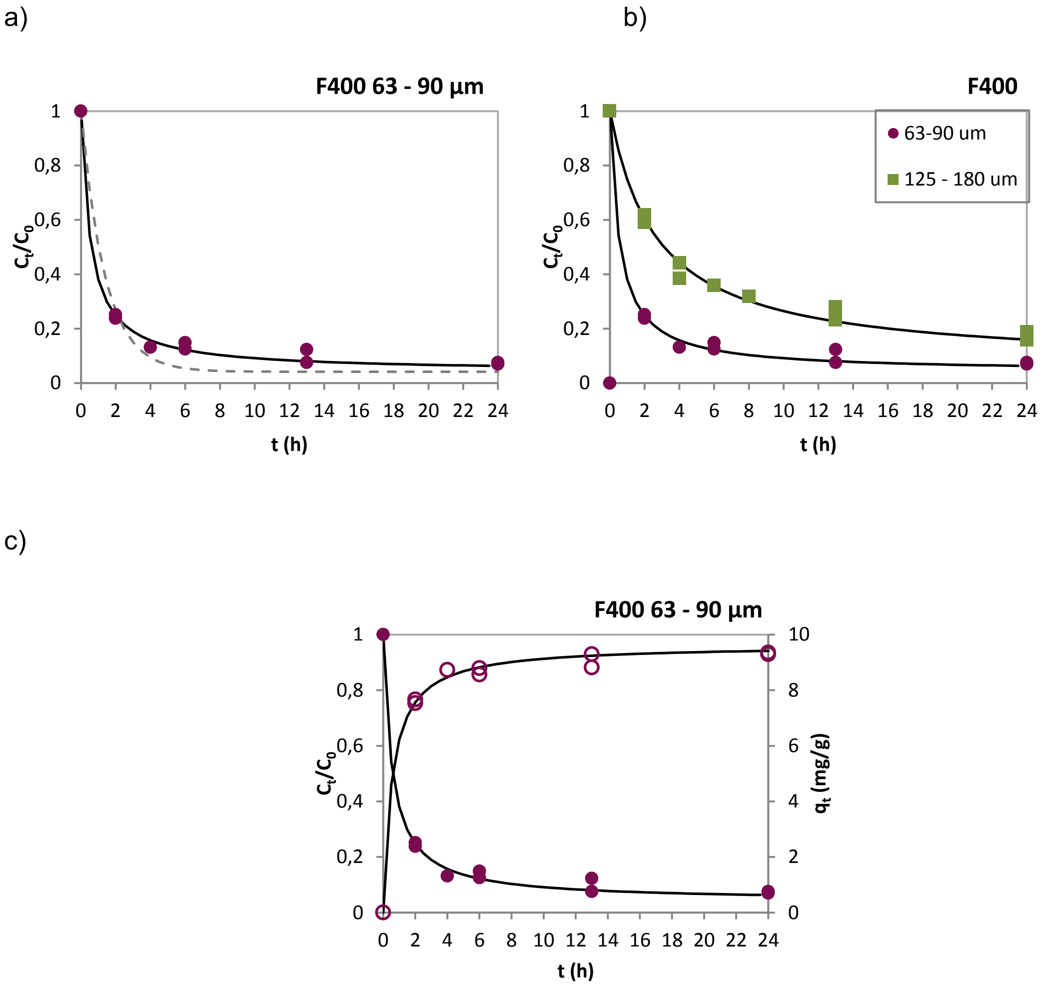


Table 4.28. Adsorption kinetics of ibuprofen onto AC, a) non-linear fittings of pseudo-first and pseudo-second order models, b) comparison of the best fit representation for the two particle sizes of AC studied and c) best fit representation. (- - pseudo-first order model, —— pseudo-second order model) (IS = 2.5 mM, Ca/K = 0.5, C_0 = 100 µg/dm^3, pH = 6).

The parameter values calculated for the kinetic models are presented in Table 4.29.

Table 4.29. Parameter values for pseudo-first and pseudo-second order kinetic adsorption models. (IS = 2.5 mM, Ca/K = 0.5, C_0 = 100 µg/dm^3, pH = 6).

AC particle size (µm)		**Pseudo 1st order model**			**Pseudo 2nd order model**		
	q_e_calc (mg/g)	k_1 (1/h)	*Error	R^2	k_2 (g/(mg.h))	*Error	R^2
125 - 180	9.47	0.207	29%	0.624	0.0388	13%	0.965
63 - 90	9.63	0.726	27%	0.963	0.189	9%	0.995

* Associated error for 95% confidence level.

The kinetic is much faster for the smaller particle size, as it shows the value of k_2, confirming the previous results obtained for bigger concentrations.

5 CONCLUSIONS AND FUTURE DEVELOPMENTS

5.1 CONCLUSIONS

The contamination of natural waters or wastewaters by pharmaceuticals, namely by the anti-inflammatory widely used in Portugal, ibuprofen, has gradually become a cause of concern. Although there is still no specific legislation for this type of compounds, many studies have been developed to find effective solutions for their removal, since the conventional techniques implemented in the treatment plants have reveled low efficiency on the removal of these organic microcontaminants.

The adsorption onto activated carbon has proved to be a good alternative, having the advantages of being a low cost technology and given its ease of implementation in water treatment plants (in powdered or granular forms). Nevertheless, the removal rates are strongly dependent on several factors, such as:

- The type of activated carbon;
- The carbon surface chemical properties and the type of structure;
- The impact of water inorganic matrix (pH, ionic strength and inclusive the type of ions present in solution, monovalent or divalent).

This research work aimed to understand these factors, their influence in adsorption of ibuprofen onto activated carbon and the best conditions to its removal. To achieve these goals, a methodology was developed and included:

- Activated carbon selection based on literature review;
- Selection of two particle sizes for the activated carbon;
- Functionalization of the activated carbon selected, in order to change the chemical composition and the textural structure;
- Chemical and textural characterization of the selected activated carbons (both particle sizes and functionalized);
- Isotherm and kinetic studies, with different inorganic matrices, simulating natural and wastewaters, to investigate the adsorption mechanisms and the impact of water inorganic matrix (pH and ionic strength) on adsorption capacity.

Activated carbon selection

The activated carbon selection was based on literature review and since there were not many studies available on the adsorption of the compound ibuprofen with commercial activated carbons, the selection took into account the physical and chemical properties of the ACs and the characteristics of ibuprofen.

The literature indicates that F400 activated carbon is widely used in water treatment processes with good removal capacities of organic microcontaminants (such as phenol and ketoprofen). Factors such as the pH_{PZC} and the microporous volume were the most relevant to this choice.

The high adsorption capacities (q_{max} Langmuir parameter) obtained, proved that this choice was adequate.

Chemical and textural characterization of the selected activated carbon

The textural characterization performed for the activated carbon, for both particle sizes (125 - 180 µm and 63 - 90 µm), revealed a high surface area and a high microporous volume. The results also showed that the grinding of the AC increases the total volume of pores (including macro, meso and micropores). The functionalization increased essentially the microporous volume, but the textural differences between the different AC forms did not seem to be very significant. The pore size distribution performed for the F400 AC (125 - 180 µm) showed that a large portion of the pores are micropores (< 20 Å diameter), namely supermicropores (7 - 20 Å diameter), although a straight analysis of CO_2 isotherm should have been performed to certificate this results. This pore size range is the most favorable, considering that the molecular size of ibuprofen is 1.03 nm (length) x 0.52 nm (width) x 0.43 nm (depth) and that the pore width that maximizes the interactions should be about 1.7 times the second largest dimension of the adsorbate.

The chemical characterization revealed some differences between the functionalized F400 AC and the F400 without treatment: at a pH of 4.5 and 6 the F400 AC has an alkaline character; at a pH of 8, the AC F400 has an acidic character while in case of functionalization it possesses a basic character. In crescent order of pH_{PZC}: F400 125 - 180 µm (7.25) ≈ F400 63 - 90 µm (7.28) < Functionalized F400 (8.9).

The surface chemistry of the activated carbons largely depends on their surface oxygen content, so, the heteroatom content was also analyzed. The elemental analyses showed that the Functionalized F400 contained the lowest percentage of oxygen (~14% against ~18%) The differences in oxygen content between the ACs are consistent with the pH_{PZC} results, and revealed a great importance when the various types of aqueous matrices were analyzed.

The impact of water inorganic matrix (pH and ionic strength), F400 AC particle size and functionalization on ibuprofen adsorption

The impact of the water background matrix, in terms of pH, ionic strength and the type of ions (monovalent and divalent) was evaluated through kinetic and isotherm studies with different natural and wastewater model solutions.

The adsorption was studied through an integrated analysis of isotherm, based on non-linear Langmuir and Freundlich plots and constants, and kinetic studies, applying three different models, non - linear pseudo-first order, pseudo-second order and intraparticle diffusion models.

In all the studies, the adsorption of ibuprofen onto the carbons showed that the equilibrium data presented a better fitting to the Langmuir model and followed a pseudo-second order kinetic which means that the chemisorption can be the main adsorption mechanism, although other interactions, namely electrostatic, must be involved. The intraparticle diffusion model could also be applied.

The effect of the solution pH was studied for F400 (125 - 180 µm). The results showed that this parameter remarkably influences the removal of ibuprofen. An increase of the pH to above the pH_{PZC} of the adsorbent (7.2) leads to the presence of net negative charge on its surface, which revealed to be the worst case scenario, as the contaminant has the same charge, causing repulsive electrostatic interactions and decreasing the adsorption capacity.

In the case of pH below the pH_{PZC}, two different cases were observed. One, for pH values above the pK_a and other for values below the pK_a of ibuprofen (4.9). The best adsorption rates were observed for pH of 4.5, which indicates that an increase of the hydrophobic interactions and decrease in the electrostatic interactions improved the removal of ibuprofen, so the hydrophobic interactions seemed to be more relevant in this case.

The ionic strength effect on ibuprofen adsorption onto F400 AC was studied with different ions concentrations and for different pH values and the kinetic and isotherm studies showed that it also affects the adsorption process.

When the electrostatic interactions between the AC and the ibuprofen are attractive, an increase of ionic strength will decrease the adsorption rate, probably due to the shielding effect, which weakens these interactions.

This effect was notorious for pH 6 using the F400 AC and for pH 8 using the functionalized F400, where the AC was positively charged and the adsorbate negatively charged.

The opposite is valid, when the electrostatic forces between the AC and the ibuprofen are repulsive, the increase of ionic strength will improve the adsorption. That was observed for pH 8 using the F400 activated carbon without functionalization, when the ionic strength increases from 2.5 mM to 9.35 mM, the adsorption rate increases.

The results show that even without functionalization, the activated carbon has effective removal ratios, seeing as usually the increase of the water pH is followed by an increase of the ionic strength and the inverse is valid as well, the decrease of water pH means a decrease of the ionic strength. The best results were obtained for a pH of 6, with low ionic strength (2.5 mM); and for pH 8 with high ionic strength (9.35 mM). This water balance favors the adsorption of ibuprofen onto the activated carbon.

For extreme conditions, in which the pH is above the pH_{PZC} of the AC and the ionic strength shielding effect is not sufficient, the use of an activated carbon with a higher pH_{PZC} is recommended. When both the pH and the ionic strength are high, it is no longer useful to use an AC with higher basicity. This conclusion is particularly useful, for the treatment of waters of the south of Portugal, which are hard waters, with high ion concentration and high pH.

The possible influence of the type of ions was studied, using monovalent (K^+) and divalent (Ca^{2+}) ions and maintaining constant the ionic strength. The results revealed that this factor was not significant on the adsorption of ibuprofen, possibly because is a small molecule comparing with the other compounds used in other studies in which the adsorption kinetics and the adsorption capacity presented significant differences when the electrolyte solutions had monovalent, divalent or a combination of both ions.

The Boyd plot can be applied to the 125 - 180 µm particle size but not for the smaller particle size, 63 - 90 µm. This means that the smaller the particle, the greater is the relevance of the external mass transfer over intraparticle diffusion, being the external mass transfer the rate limiting step for 63 - 90 µm F400 particle size. This difference lead not only to faster kinetic values but also to larger amounts of the compound adsorbed than the other particle size (125 - 180 µm), which proves the advantageous of ACs with small particle sizes in a water treatment plant, since it minimized the internal diffusional limitation, allowing the contaminant easier access to the pores of the AC where they will be adsorbed.

Considering the results obtained, it is believed that this work contributed to a better understanding of the best conditions to remove ibuprofen (and other similar organic contaminants) from natural and wastewaters with activated carbon (powdered).

5.2 FUTURE DEVELOPMENTS

The research of this work contributed to a better understanding of the best conditions to remove ibuprofen with adsorption onto activated carbon from natural and wastewaters; however there are still some aspects that can be studied in further research.

- Study more potential activated carbons, to better understand the effect of the textural and chemical composition of AC on ibuprofen adsorption;
- Investigate the influence of the presence of the natural organic matter (NOM), also in combination with the water background inorganic matrix, on ibuprofen adsorption onto activated carbon, including the NOM competition and carbon preloading;
- Apply the homogeneous surface diffusion model (HSDM) to analyze the kinetic results, which will allow to build a more predictive model of the adsorption process;
- Determine the design data (isotherm constants and Rapid Small Scale Column Tests data) for full-scale GAC systems;
- Study a PAC/UF hybrid process for the removal of ibuprofen from water, including the study of water background matrix.

6 REFERENCES

[1] S. Kim, J. Cho, I. Kim, B. Vanderford, and S. Snyder, "Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters.," *Water research*, vol. 41, pp. 1013 – 1021, 2006.

[2] K. Fent, A. Weston, and D. Caminada, "Ecotoxicology of human pharmaceuticals," *Aquatic Toxicology*, vol. 76, pp. 122-159, 2006.

[3] Robert A. Boyd and Edward T. Furlong, "Human-Health Pharmaceutical Compounds in Lake Mead, Nevada and Arizona, and Las Vegas Wash, Nevada," U.S. GEOLOGICAL SURVEY, Carson City, Nevada, 2002.

[4] A. Chatzitakis et al., "Photocatalytic degradation and drug activity reduction of Chloramphenicol," *Water Research*, vol. 42, pp. 386 – 394, 2008.

[5] Fabiola Méndez-Arriaga, Santiago Esplugas, and Jaime Giménez, "Photocatalytic degradation of non-steroidal anti-inflammatory drugs with TiO2 and simulated drugs with TiO2 and simulated," *Water Research*, vol. 42, pp. 585 – 594, 2008.

[6] Maria Klavarioti, Dionissios Mantzavinos, and Despo Kassinos, "Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes," *Environment International*, vol. 35, pp. 402–417, 2009.

[7] Paul E. Stackelberg et al., "Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water-treatment plant," *Science of the Total Environment*, vol. 329, pp. 99–113, 2004.

[8] Ana V. Dordio, Cátia Duarte, Margarida Barreiros, A.J. Palace Carvalho, and A.P. Pinto, "Toxicity and removal efficiency of pharmaceutical metabolite clofibric acid by Typha spp. – Potential use for phytoremediation?," *Bioresource Technology*, vol. 100, pp. 1156–1161, 2009.

[9] EPA, U.S. Enviroment Protection Agency. (2010) Treating Contaminants of Emerging Concern. [Online]. http://www.clu-in.org/download/citizens/activatedcarbon.pdf

[10] A. S. Mestre, J. Pires, J.M. F. Nogueira, and A. P. Carvalho, "Activated carbons for the adsorption of ibuprofen," *Carbon*, vol. 45, pp. 1979-1988, 2007.

[11] Ana S. Mestre et al., "Waste-derived activated carbons for removal of ibuprofen from solution: Role of surface chemistry and pore structure," *Bioresource Technology*, vol. 100, pp. 1720–1726, 2009.

[12] Margarida Campinas and Maria João Rosa, "The ionic strength effect on microcystin and natural organic matter surrogate adsorption onto PAC," *Journal of Colloid and Interface Scienc*, vol. 299, pp. 520-529, 2006.

[13] Helena Cristina Reis Costa, "Activated carbon adsorption of cyanotoxins from natural waters," Faculdade de Ciências e Tecnologia - Universidade do Algarve, Faro, Doutoramento em Ciências e Tecnologias do Ambiente, Especialidade de Tecnologias do Ambiente 2010.

[14] Alexey Goltsov et al., "Kinetic modelling of NSAID action on COX-1: Focus on in vitro/in vivo aspects and drug combinations," *European Journal of Pharmaceutical Science*, vol. 36, pp. 122-136, 2009.

[15] Arrault Alban, Aurélien Monge, Christophe Marot, and Luc Morin-Allory, "Computer-aided design of original COX2-inhibitors: docking protocols and virtual screening under pharmacophoric constraints," Institut de Chimie Organique et Analytique, Laboratoire de Modélisation Moléculaire, France,.

[16] Infarmed. (2009) Estatística do Medicamento 2009 - Infarmed. [Online]. http://www.infarmed.pt/portal/page/portal/INFARMED/PUBLICACOES/TEMATICOS/ESTATISTICA_MEDICAMENTO/EstMed-2009.pdf

[17] Shane A. Snyder et al., "Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals," *Desalination*, vol. 202, pp. 156–181, 2006.

[18] Victor Quintanilla, "Rejection of emerging organic contaminants by nanofiltration and reverse osmosis membranes: effects of fouling, odelling and water reuse," Netherlands, pHD 2010.

[19] Ralph Linstadt, Traugott Scheytt, Ralph Lindstadt, and Thomas Heberer, "1-octanol/water partition coefficients of 5 pharmaceuticals from human medical care: carbamazepine, clofibric acid, diclofenac, ibuprofen, and propyphenazone," *Water, Air, and Soil Pollution*, vol. 165, pp. 3-11, 2005.

[20] Theres Söderberg, "Powdered Activated Carbon used as adsorbent of Active Pharmaceutical Ingredients and Estrogensin the Biological Treatment of Wastewater," Lund university, Denmark, Master Thesis in Environmental Science 2008.

[21] O. Jones, N. Voulvoulis, and J. Lester, "Potential ecological and human health risks associated with the presence of pharmaceutically active compouds in the aquatic environment," *Critical reviews in toxixology*, vol. 34, pp. 335-350, 2004.

[22] Asu Ziylan and Nilsun H. Ince, "The occurrence and fate of anti-inflammatory and analgesic pharmaceuticals in sewage and fresh water: Treatability by conventional and non-conventional processes - Review," *Journal of Hazardous Materials*, vol. 187, pp. 24–36, 2011.

[23] B. Halling Sorensen et al., "Occurrence, fate and effects of pharmaceutical substances in the environment- a review," *Chemosphere*, vol. 36, pp. 357-393, 1998.

[24] European commission - DG Environment News Alert Service. (2010, February) How well do wastewater treatment plants remove pharmaceuticals? Science for environment policy. [Online]. http://ec.europa.eu/environment/integration/research/newsalert/pdf/183na4.pdf

[25] S. Webb, Simon Webb, Thomas Temes, Michel Gibert, and Klaus Olejniczak, "Indirect human exposure to pharmaceuticals via drinking water," *Toxicology Letters*, vol. 142, pp. 157-167, 2008.

[26] Silene Santos Melo, Alam Gustavo Trovó, Ivonete Rossi Baututz, and Raquel Fernandes Nogueira, "Degradação de fármacos residuais por processos oxidativos avançados," *Quim. Nova*, vol. 32, pp. 188-197, 2009.

[27] J. Santos, I. Aparício, and E. Alonso, "Occurrence and risk assessment of pharmaceutically active compounds in wastewater treatment plants. A case study: Seville city (Spain)," *Environment International*, vol. 33, pp. 596–601, 2007.

[28] S. Weigel et al., "Determination of selected pharmaceuticals and caffeine in sewage and seawater from Tromsø/Norway with emphasis on ibuprofen and its metabolites," *Chemosphere*, vol. 56, pp. 583–592, 2004.

[29] Martin Hilton and Kevin Thomas, "Determination of selected human pharmaceutical compounds in effluent and surface water samples by high-performance liquid chromatography–electrospray tandem mass spectrometry," *Journal of Chromatography A*, vol. 1015, pp. 129–141, 2003.

[30] R. Salgado et al., Occurrence and fate of pharmaceutical active compounds, musks and steroids in waste water treatment plants in Lisbon, Portugal, 2007, Faculdade de Ciencias e Tecnologia da Universidade Nova de Lisboa; Escola Superior de Tecnologia do Instituto Politécnico de Setúbal. (Poster).

[31] R. Filho, J. Barreiro, E. Vieira, and Q. Cass, "Pharmaceuticals drugs, WWTP and hydric bodies," *Ambiente e Água - An Interdisciplinary Journal of Applied Science*, vol. 2, pp. 54-61., 2007.

[32] Daniel R. Dietrich, Simon F. Webb, and Thomas Petry, "Hot spot pollutants: pharmaceuticals in the environment," *Toxicology Letters*, vol. 131, pp. 1–3, 2002.

[33] H. Lange, W. Noordovem, A. Murk, M. Lurling, and E. Peeters, "Behavioural responses of G. pulex to low concentrations of pharmaceuticals," *Aquat. Toxicol.*, vol. 78, pp. 227-216., 2006.

[34] R. Brain et al., "Effects of 25 pharmaceutical compounds to Lemna gibba using a seven-day static-renewal test," *Environmental Toxicology and Chemistry*, vol. 23 (2), pp. 371-382., 2004.

[35] Diário da República, Ministério do Ambiente. (2007, 27 de Agosto) Decreto-Lei n.º 306/2007. [Online]. http://dre.pt/pdf1s/2007/08/16400/0574705765.pdf

[36] Diário da República, Ministério do Ambiente. (1998, 1 de Agosto) Decreto-Lei nº 236/98. [Online]. http://www.povt.qren.pt/tempfiles/20080213150349moptc.pdf

[37] Parlamento Europeu e Conselho da União Europeia, "Directiva 2000/60/CE do parlamento europeu e do conselho de 23 de outubro de 2000, que establece um quadro de acção comunitária no domínio da política da água ," *Jornal Oficial das Comunidades Europeias*, vol. L 327, pp. 1-72, Dec. 2000.

[38] Maria João Rosa and Margarida Campinas, "Alterações tecnológicas a implementar na linha de tratamento para cumprimento da nova legislação relativa à qualidade da água para consumo humano," *Tecnologia da água*, vol. II, pp. 18-31, 2007.

[39] Shane A. Snyder, Paul Westerhoff, Yeomin Yoon, and David L. Sedlak, "Pharmaceuticals, personal care products and endocrine disruptors in water: implications for water industry," *Environmental Engineering Science*, vol. 20(5), pp. 449-469, 2003.

[40] Tove A. Larsen, Judit Lienert, Adriano Joss, and Hansruedi Siegrist, "How to avoid pharmaceuticals in the aquatic environment," *Journal of Biotechnology*, vol. 113, pp. 295–304, 2004.

[41] Taro Urase, Chie Kagawa, and Tomoya Kikuta, "Factors affecting removal of pharmaceutical substances and estrogens in membrane separation bioreactors," *Desalination*, vol. 178, pp. 107-113, 2005.

[42] P. Verlicchi, A. Galletti, M. Petrovic, and D. Barceló, "Hospital effluents as a source of emerging pollutants: An overview of micropollutants and sustainable treatment options - Review Paper," *Journal of Hydrology*, vol. 389, pp. 416–428, 2010.

[43] David C. Siegee, *Freshwater microbiology*. England: Wiley, 2005.

[44] Fred L. Troise, David Keith Todd, and Frits Van Der Leeden, *The water encyclopedia*, 2nd ed. United States of America: Lewis Publishers, 1990.

[45] Metcalf and Eddy, *Wastwater Engineering: Treatment and Reuse*, 4th ed.: McGraw-Hill, 2003.

[46] J. L. Figueiredo and F. R. Ribeiro, *Catálise Heterogénea*, 2nd ed.: Fundação Calouste Gulbenkian, 2007.

[47] A. Dabrowski, P. Podkoscielny, Z. Hubicki, and M. Barczak, "Adsorption of phenolic compounds by activated carbon—a critical review," *Chemosphere*, vol. 58, pp. 1049–1070, 2005.

[48] F. Rodriguez-Reinoso, M. Molina-Sabio, and M. T. Gonzáçez, "The use of steam and CO2 as activating agents in the preparation of activated carbons," *Carbon*, vol. 33, pp. 15-23, 1995.

[49] T. Cecílio, E. Mesquita, H. Costa, and M.J. Rosa, "Processos avançados de tratamento de água para consumo humano," *Águas & Resíduos*, vol. 3, pp. 4-17, Janeiro a Abril 2007.

[50] ASTM - American Society fot Testing Materials, ASTM D2652-05a Standard Terminology Relating to Activated Carbon, 2005.

[51] K. Mohanty, D. Das, and M. Biswas, "Preparation and characterization of activated carbons from Sterculia alata nutshell by chemical activation with zinc chloride to remove phenol from wastewater," *Adsorption*, vol. 12, pp. 119–132, 2006.

[52] Christian Lastoskie, Keith E. Gubbins, and Nicholas Quirke, "Pore Size Heterogeneity and the Carbon Slit Pore: A Density Functional Theory Model," *Langmuir*, vol. 9, pp. 2693-2702, 1993.

[53] LeCarbone.com. Activated carbon. [Online]. http://lecarbone.com/uk/article.php3?id_article=13

[54] Tengyan Zhang, Walter P. Walawender, and L.T. Fan, "Preparation of carbon molecular sieves by carbon deposition from methane," *Bioresource Technology*, vol. 96, pp. 1929–1935, 2005.

[55] R. J. Dombrowski, D. R. Hyduke, and C. M. Lastoskie, "Pore size snalysis of sctivated carbons from argon and nitrogen porosimetry using density fFunctional theory," *Langmuir*, vol. 16 (11), pp. 5041 -5050, 2000.

[56] P. A. Gauden, E. Szmechting-Gauden, G. Rychlicki, S. Duber, and J. K. Garbacz, "Changes of the porous structure of activated carbons applied in a filter bed pilot operation," *Journal of Colloid and Interface Science*, vol. 295, pp. 327–347, 2005.

[57] A. Dabrowski, P. Podkoscielny, Z. Hubicki, and M. Barczaki, "Adsorption of phenolic compounds by activated carbon—a critical review," *Chemosphere*, vol. 58, pp. 1049–1070, 2005.

[58] Carlos Moreno-Castilla, "Adsorption of organic molecules from aqueous solutions on carbon materials," *Carbon*, vol. 42, pp. 83–94, 2004.

[59] P. Podkoscielny, K. Nieszporek, and P. Szabelsk, "Adsorption from aqueous phenol solutions on heterogeneous surfaces of activated carbons—Comparison of experimental data and simulations," *Colloids and Surfaces A*, vol. 277, pp. 52–58, 2006.

[60] Mick Bjelopavlic, Gayle Newcombe, and Rob Hayes, "Adsorption of NOM onto activated carbon: effect of surface charge, ionic strength, and pore volume," *Journal of Colloid and Interface Science*, vol. 210, pp. 271 – 280, 1999.

[61] C. Moreno-Castilla, M.V Lopez-Ramon, and F. Carrasco-Marın, "Changes in surface chemistry of activated carbons by wet oxidation," *Carbon*, vol. 38, pp. 1995–2001, 2000.

[62] Ramin Azargohar, "Production Of Activated Carbon And Its Catalytic Application For Oxidation Of Hydrogen Sulphide," University of Saskatchewan, Saskatoon, Saskatchewan, PhD 2009.

[63] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, and J.J.M. Órfão, "Modification of the surface chemistry of activated carbons," *Carbon*, vol. 37 (9), pp. 1379-1389, 1999.

[64] Shamik Chowdhury, Rahul Misra, Praveen Kushwaha, and Papita Das, "Optimum sorption isotherm by linear and nonlinear methods for safranin onto alkali-treated rice husk," *Bioremediation Journal*, vol. 15:2, pp. 77-89, 2011.

[65] B. Subramanyam and A. Das, "Linearized and non-linearized isotherm models comparative study on adsorption of aqueous phenol solution in soil," *Int. J. Environ. Sci. Tech*, vol. 6 (4), pp. 633-640, 2009.

[66] Mohammad Mehdi Salarirad and Ali Behnamfard, "Modeling of equilibrium data for free cyanide adsorption onto activated carbon by linear and non-linear regression methods," *International Conference on Environment and Industrial Innovation*, vol. 12, pp. 79-84, 2011.

[67] Alok Mittal, Vibh Gajbe, and Jyoti Mittal, "Removal and recovery of hazardous triphenylmethane dye, Methy Violet through adsorption over granulated waste materials," *Journal of Hazardous Materials*, vol. 150, pp. 364–375, 2008.

[68] Y. S. HO and G. McKAY, "A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents," *Trans IChemE*, vol. 76, Part B, pp. 332-340, 1998.

[69] Y.S. Ho and G. McKay, "Pseudo-second order model for sorption processes," *Process Biochemistry*, vol. 34, pp. 451–465, 1999.

[70] Y. S. HO and G. Mckay, "The kinetics of sorption of divalent metal ions onto sphargnum moss peat," *Wat. Res.*, vol. 34, pp. 735-742, 1999.

[71] Yuh-Shan Ho, "Second-order kinetic model for the sorption of cadmium onto tree fern: A comparison of linear and non-linear methods," *Water Research*, vol. 40, pp. 119 – 125, 2006.

[72] Junxiong LIN and Lan WANG, "Comparison between linear and non-linear forms of pseudo first-order and pseudo-second-order adsorption kinetic models for the removal of methylene blue by activated carbon," *Front. Environ. Sci. Engin*, vol. 3(3), pp. 320–324, 2009.

[73] Shamik Chowdhury and Papita Saha, "Pseudo-second-order kinetic model for sorption of malachite green onto sea shell: comparison of linear and non-linear methods," *IIOAB Journal*, vol. 1, no. 2010, pp. 3-5, 2010.

[74] J. X. Lin, S. L. Zhan, M. H. Fang, and X. Q. Qian, "The adsorption of dyes from aqueous solution using diatomite," *J Porous Mater*, vol. 14, pp. 449–455, 2007.

[75] Y.S. Ho and G. McKay, "A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents," *Trans IChemE*, vol. 76, Part B, pp. 332-340, 1998.

[76] A. Selatnia et al., "Biosorption of Ni2+ from aqueous solution by a NaOH-treated bacterial dead Streptomyces rimosus biomass," *Minerals Engineering*, vol. 17, pp. 903–911, 2004.

[77] V. Fierro, V. Torné-Fernández, D. Montané, and A. Celzard, "Adsorption of phenol onto activated carbons having different textural and surface properties," *Microporous and Mesoporous Materials*, vol. 111, pp. 276–284, 2008.

[78] Adamson Boyd and A. Myers, "The exchange adsorption of ions from aqueous solutions by organic zeolites. II Kinetics," *Journal of American Chemical Society*, vol. 69, pp. 2836–2844, 1947.

[79] D. Reichenberg, "Properties of ion-exchange resins in relation to their structure. III. Kinetics of exchange," *Journal of American Chemical Society*, vol. 75, pp. 589–597, 1953.

[80] S. Baup, C. Jaffre, D. Wolbert, and A. Laplanche, "Adsorption of Pesticides onto Granular Activated Carbon: Determination of Surface Diffusivities Using Simple Batch Experiments," *Adsorption*, vol. 6, pp. 219–228, 2000.

[81] Sigmaaldrich. http://www.sigmaaldrich.com. [Online]. http://www.sigmaaldrich.com/catalog/ProductDetail.do?D7=0&N5=SEARCH_CONCAT_PNO|BRAND_KEY&N4=I1892|FLUKA&N25=0&QS=ON&F=SPEC

[82] Hyun-Hee Cho, Haiou Huang, and Kellogg Schwab, "Effects of Solution Chemistry on the Adsorption of Ibuprofen and Triclosan onto Carbon Nanotubes," *Langmuir*, vol. 27, pp. 12960–12967, 2011.

[83] Calgon Corporation. chemviron. [Online]. http://www.zwicky.dk/ny/datablade/W-2060%20-%20Filtrasorb%20300%20and%20400%20-%2002.04.03.pdf

[84] J. Riviera-Utrilla and M. Sánchez-Polo, "Ozonation of 1,3,6-naphthalenetrisulphonic acid catalysed by activated carbon in aqueous phase," *Applied Catalysis B: Environmental*, vol. 39, pp. 319–329, 2002.

[85] G. McKay and M. F.F. Sze, "An adorption diffusion model for removal of para-chlorophenol by activated carbon derived from bituminous coal," *Environmental Pollution*, vol. 158, pp. 1669–167, 2009.

[86] American Public, Ed., *Standard Methods for the Examination of Water and Wastewater*, 21st ed. Washington: Standard Methods for the Examination of Water and Health Association, American Water Works Association, Water Environmental Federation, 2005.

[87] IST - Biotage. [Online]. http://www.weber.hu/PDFs/SPE/TN136_Evolute_envir.pdf

[88] Lei Li, Patricia A. Quinlivan, and Detlef R.U. Knappe, "Effects of activated carbon surface chemistry and pore structure on the adsorption of organic contaminants from aqueous solution," *Carbon*, vol. 40, pp. 2085–2100, 2002.

[89] Catherine Morlay, Etienne Quivet, Michaela Pilshofer, René Faure, and Jean-Pierre Joly, "Adsorption of Imazamox herbicide onto Filtrasorb 400 activated carbon," 2011.

[90] Oualid Hamdaoui and Emmanuel Naffrechoux, "Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon. Part II. Models with more than two parameters," *Journal of Hazardous Materials*, vol. 147, pp. 401–411, 2007.

[91] Eduardo M. Cuerda-Correa and Joaquín Domínguez-Vargas, "On the use of carbon blacks as potential low-cost adsorbents for the removal of non-steroidal anti-inflammatory drugs from river water," *Journal of Hazardous Materials*, vol. 177, pp. 1046-1053, 2010.

[92] P.C.C. Faria, J.J.M. Órfão, and M.F.R. Pereira, "Adsorption of anionic and cationic dyes on activated carbons with different surface chemistries," *Water Research*, vol. 38 (8), pp. 2043-2052, 2004.

[93] Svetlana B. Lyubchik, Andrej I. Lyubchik, and Elena S. Lygina, "Simultaneous removal of 3d transition metals from multi-component solutions by activated carbons from co-mingled wastes," *Separation and Purification Technology*, vol. 60, pp. 264–271, 2008.

[94] Rafael Rodriguez-Fuentes, Brian A. Hilts, and Bruce I. Dvorak, "Disinfection By-Product Precursor Adsorption as Function of GAC Properties: Case Study," *Journal of Environmental Engineering*, vol. 131, pp. 1462-1465, 2005.

ANNEXES

ANNEX I. PORE SIZE DISTRIBUTION OF ACTIVATED CARBONS

F400 (125 180 µm)

Volume in Pores	<	5.00 Å	:	0.00000 cm³/g
Total Volume in Pores	<=	1265.80 Å	:	0.55208 cm³/g
Area in Pores	>	1265.80 Å	:	22.729 m²/g
Total Area in Pores	>=	5.00 Å	:	985.077 m²/g

Pore size Table

F400 (125 180 µm)

Pore Width (Angstroms)	Incremental Pore Volume (cm³/g)
5.003867552	0
5.36128664	0
5.897415219	0
6.433544011	0.049764
6.790962992	0
7.327091571	0.105076
8.04192996	0.049837
8.578058539	0.039382
9.292896928	0
10.00773489	0
10.90128266	0.015464
11.79483044	0.031785
12.68837821	0.024163
13.58192598	0.015849
14.83289338	0.024321
15.90515054	0.021548
17.15611708	0.014427
18.585793	0.015588
20.01546978	0.015452
21.6238568	0.011966
23.41095234	0.008153
25.19804789	0.006887
27.34256221	0.006994
29.48707652	0.005002
31.81030107	0.003887
34.31223586	0.003762
36.99287918	0.002294
40.03093956	0.002253
43.24771359	0.00239
46.64319445	0.002374

Pore size Table (cont.)

F400 (125 180 µm)

Pore Width (Angstroms)	Incremental Pore Volume (cm³/g)
50.39609578	0.002344
54.32770394	0.00233
58.79544281	0.002258
63.44189191	0.001968
68.44575808	0.002089
73.98575836	0.002026
79.8831723	0.002146
86.31671354	0.00258
93.10767526	0.002547
100.6134779	0.002325
108.6554079	0.00238
117.2334651	0.002302
126.5263702	0.002336
136.7128093	0.002641
147.6140894	0.002761
159.4089173	0.002686
172.0973066	0.002674
185.8579369	0.002732
200.6908354	0.00261
216.5959748	0.002523
233.9307962	0.002633
252.5166062	0.002634
272.7107913	0.002495
294.5133516	0.001714
317.9242869	0.001495
343.3010654	0.001783
370.6436055	0.00167
400.3094025	0.001694
432.2984018	0.001311
466.7893786	0.001323
503.9609442	0.001725
544.170594	0.001506
587.5969939	0.00092
634.4189191	0.00073
684.9937012	0.000819
739.6788359	0.000512
798.6529889	0.000236
862.4523218	0
931.2554458	0
1005.598686	0
1085.660545	0
1172.334679	0
1265.799754	0

ANNEX II. TEXTURAL PROPERTIES OF THE ACTIVATED CARBONS

AII.1 Volume adsorbed obtained in the t-plot report for activated carbons

F400 (125 - 180 μm)		F400 (63 - 90 μm)		Func F400	
P/P_0	Volume adsorbed (cm^3/g)	P/P_0	Volume adsorbed (cm^3/g)	P/P_0	Volume adsorbed (cm^3/g)
4.64E-06	20.20	4.98E-06	20.20	5.30E-06	20.20
6.24E-06	40.40	5.88E-06	40.41	7.09E-06	40.40
7.98E-06	60.60	6.90E-06	60.61	8.64E-06	60.60
1.12E-05	80.81	9.28E-06	80.81	1.13E-05	80.80
1.83E-05	101.01	1.48E-05	101.01	1.77E-05	101.00
3.22E-05	121.21	2.59E-05	121.21	2.94E-05	121.19
5.83E-05	141.40	4.47E-05	141.40	5.04E-05	141.38
1.08E-04	161.59	7.81E-05	161.60	8.83E-05	161.57
2.12E-04	181.75	1.42E-04	181.78	1.62E-04	181.74
4.58E-04	201.85	2.76E-04	201.94	3.18E-04	201.89
1.09E-03	221.79	5.81E-04	222.05	6.84E-04	221.96
2.72E-03	241.36	1.32E-03	241.96	1.58E-03	241.84
6.40E-03	260.10	3.09E-03	261.53	3.68E-03	261.31
1.33E-02	277.64	6.90E-03	280.43	7.95E-03	279.85
2.38E-02	293.54	1.37E-02	298.43	1.54E-02	297.58
3.81E-02	307.80	2.40E-02	315.03	2.64E-02	313.91
5.18E-02	317.81	3.79E-02	330.18	4.84E-02	334.54
8.01E-02	332.35	5.15E-02	341.12	1.06E-01	362.49
1.02E-01	340.30	1.07E-01	367.60	1.60E-01	375.61
1.30E-01	347.72	1.62E-01	381.53	2.11E-01	384.07
1.57E-01	353.25	2.18E-01	391.09	2.68E-01	391.25
1.84E-01	357.83	2.74E-01	398.30	3.14E-01	396.01
2.08E-01	361.19	3.17E-01	402.94	4.00E-01	403.40
2.31E-01	364.18	4.00E-01	410.44	5.00E-01	410.77
2.54E-01	366.81	5.00E-01	418.11	5.99E-01	417.67
2.78E-01	369.39	5.99E-01	425.24	6.99E-01	425.19
3.03E-01	371.75	6.99E-01	433.09	7.98E-01	434.75
3.94E-01	379.41	7.98E-01	443.11	8.60E-01	443.38
5.00E-01	386.78	8.60E-01	451.78	9.01E-01	451.86
5.98E-01	393.26	9.00E-01	459.96	9.26E-01	459.43
6.98E-01	400.48	9.26E-01	467.13	9.50E-01	469.02
7.98E-01	409.69	9.50E-01	476.00	9.75E-01	482.28
8.59E-01	418.05	9.74E-01	488.56	9.91E-01	494.25
9.00E-01	426.30	9.91E-01	500.31		
9.25E-01	433.53				
9.49E-01	442.64				
9.74E-01	455.51				
9.90E-01	467.41				

AII.2. Determination of A_{BET}, A_{ext}, V_{micro} and single point total point volume for F400 AC

Determination of specific area using BET method

In this method, the monolayer capacity is obtained from the physical adsorption isotherm of nitrogen at 77 K, experimentally determined. A type II or type IV isotherm is usually obtained and the BET equation (I.1) is applied.

$$\frac{\frac{P}{P_0}}{V_{ads}\left(1-\frac{P}{P_0}\right)}=\frac{1}{n_m^a\,c}+\frac{c-1}{n_m^a\,c}\times\frac{P}{P_0} \qquad \textbf{(II.1)}$$

where, P and P_0 are respectively the equilibrium pressure and the pressure of saturation (at the temperature used). V_{ads} is the amount adsorbed at pressure p, n_m^a (mol/g) the amount adsorbed on the monolayer and *c* the is BET constant.

Plotting the BET equation, number of moles adsorbed in the monolayer (n_m^a) and the BET constant (c), through values of the slop and origin interception.

BET area (m^2/g) was determined from the following equation:

$$A_{BET}=N\times n_m^a\times a_m \qquad \textbf{(II.2)}$$

where *N* is the Avogadro number ($6{,}02\text{x}10^{23}$ mol^{-1}) and a_m is the area occupied by one molecule of the adsorbate (for N_2 is $16{,}2\text{x}10^{-20}$ m^2).

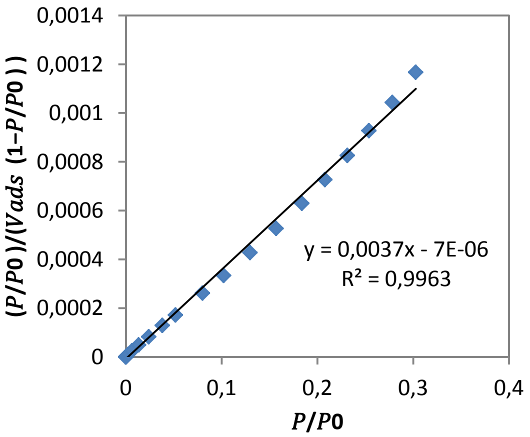


Figure AII.1. BET plot representation for F400 (125 - 180 µm).

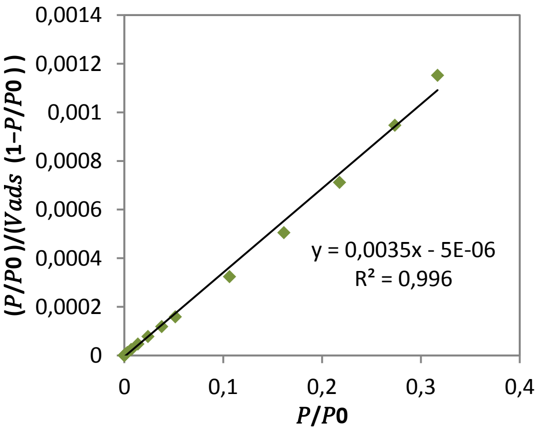


Figure AII.2. BET plot representation for F400 (63 - 90 µm).

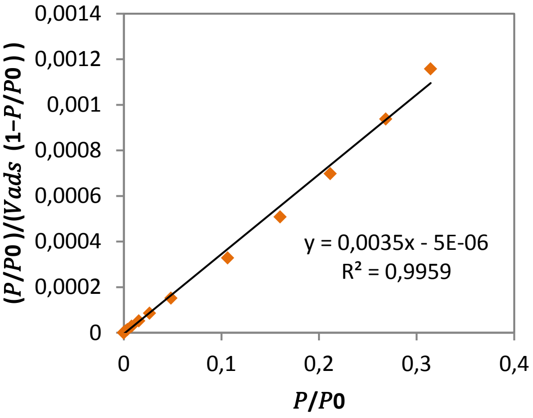


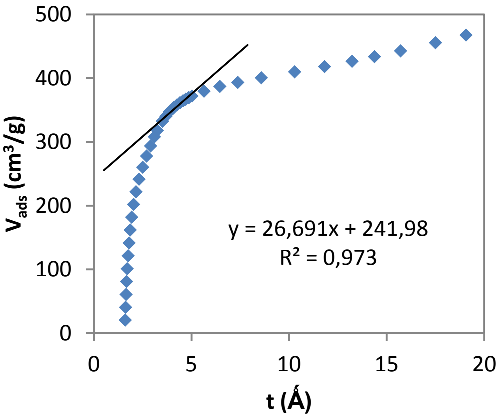
Figure AII.3. BET plot representation for F400 (Functionalized).

Table AII.1. BET equation parameters.

	c (BET)	n_m^a (cm^3/g)	n_m^a (mol/g)	A_{BET} (m^2/g)
F400 (125 180 µm)	-530	270	0.012	1174
F400 (63 - 90 µm)	-700	285	0.013	1242
F400 (Functionalized)	-701	285	0.013	1242

Determination of microporous volume (V_{micro}) and external area (A_{ext})

T-plot method was used to calculate the microporous volume and the external area of the AC, by protting V_{ads} vs t. The intercept will give the V_{micro} and the slop the value of A_{ext}, just needing a conversion with the density factor (that for N_2 is 0.001547 = 34.7 cm^3/mol/22.4*10^3 mol.cm^3/mol).



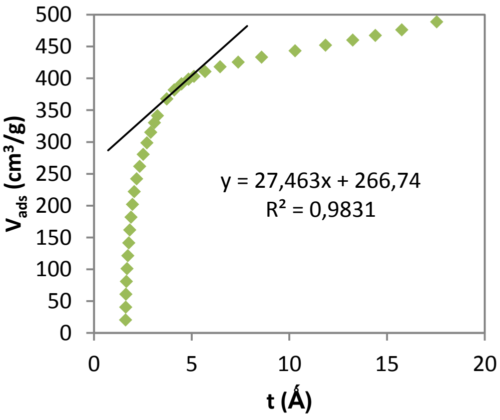


Figure AII.4. T-plot adjusted with standard adsorption carbon isotherm for F400 (125 - 180 µm).

Figure AII.5. T-plot adjusted with standard adsorption carbon isotherm for F400 (63 - 90 µm).

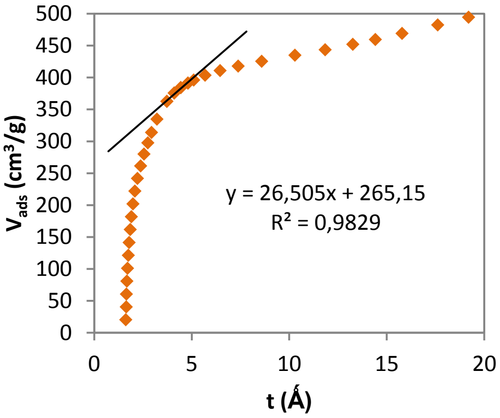


Figure AII.6. T-plot adjusted with standard adsorption carbon isotherm for F400 (Functionalized).

Table AII2. Parameters values calculated by T-plot method.

	V_{micro} (cm^3/g)	A_{EXT} (m^2/g)
F400 (125 180 µm)	0.374	413
F400 (63 - 90 µm)	0.413	425
F400 (Functionalized)	0.410	410

Determination of the single point total pore volume

The Gurvitsch rule was used to calculate total volume of pores as follows:

$$V_p = n_{sat}^a \times V_M^t \qquad \textbf{(II.3)}$$

where n_{sat}^a (mol/g) is the adsorbed amount at saturation and V_M^t (cm^3/mol) is the molar volume adsorbed in the liquid stage. For N_2 is 35 cm^3/mol (28 (g/mol)/0.8 (g/cm^3)).

Table AII3. Parameters values calculated by Gurvitsch method.

	P/P_0	n_m^a (cm^3/g)	n_{sat}^a (mol/g)	V_M^t (cm^3/mol)
F400 (125 180 µm)	0.989	467	0.021	0.723
F400 (63 - 90 µm)	0.991	500	0.022	0.774
F400 (Functionalized)	0.991	494	0.410	0.764

ANNEX III. ADSORPTION/DESSOPTION ISOTHERM PLOTS

F400 (125 - 180 µm)

Analysis adsorptive: N_2

Analysis Bath: 77.35 K

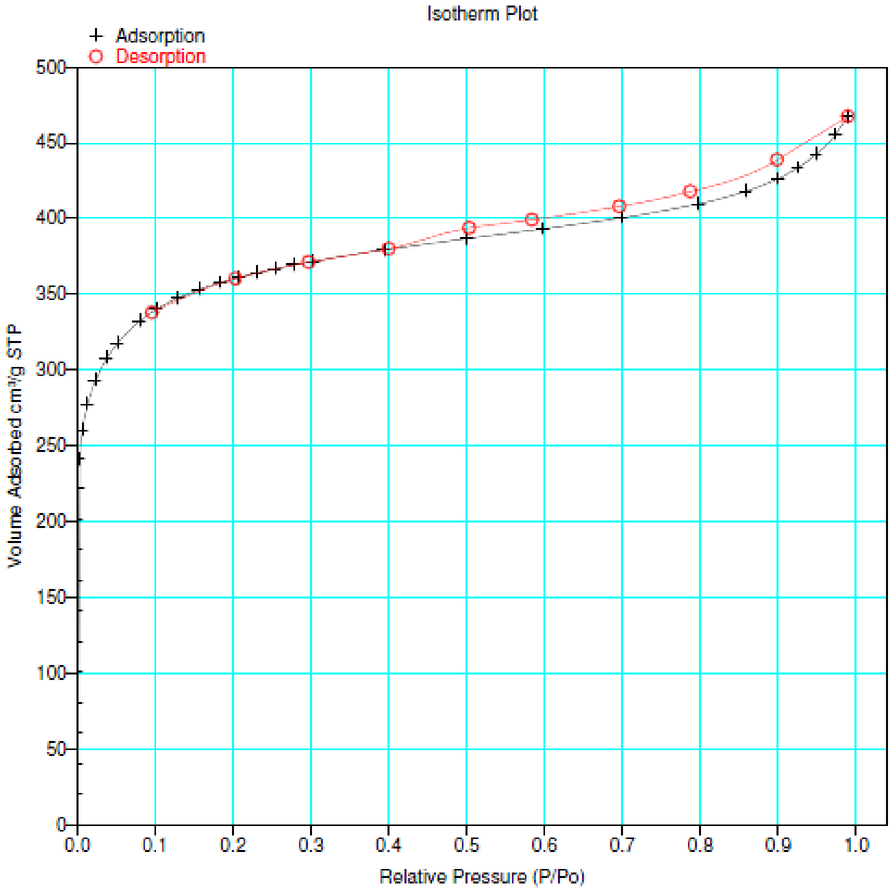


Figure AIII.1. Adsorption/desorption isotherm plots for F400 (125 - 180 µm).

F400 (63 - 90 µm)

Analysis adsorptive: N_2

Analysis Bath: 77.35 K

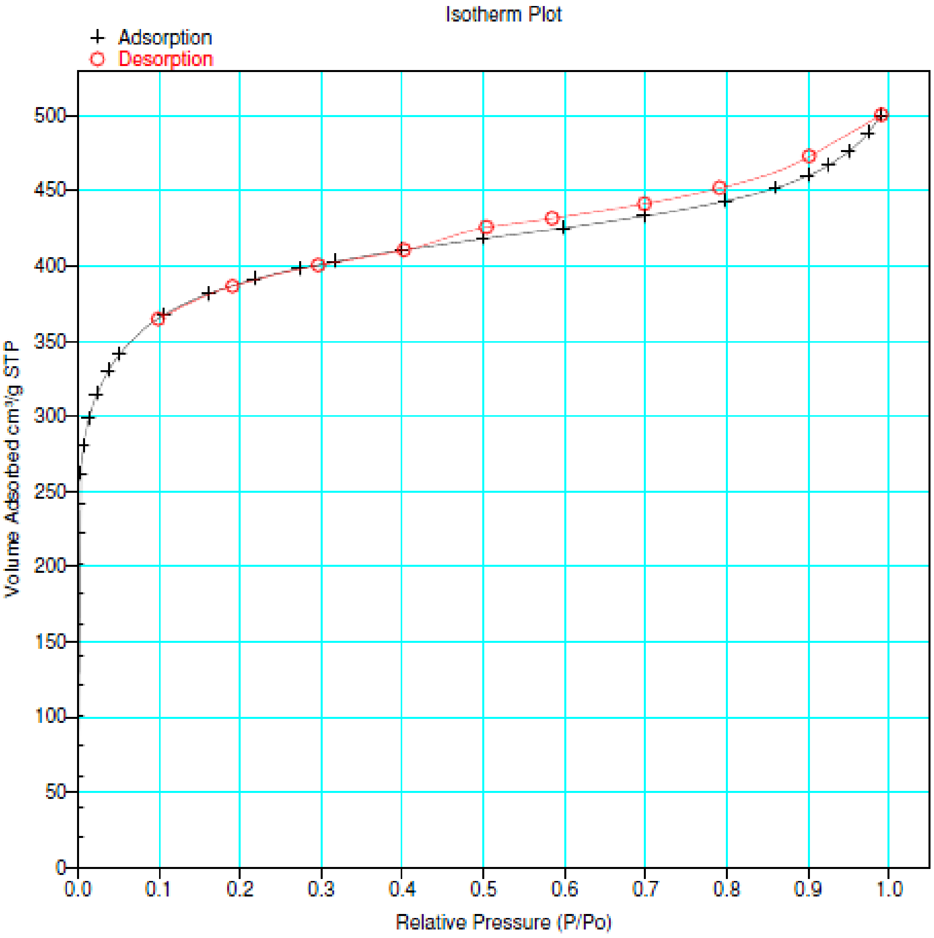


Figure AIII.2. Adsorption/desorption isotherm plots for F400 (63 - 90 µm).

F400 (Functionalized)

Analysis adsorptive: N_2

Analysis Bath: 77.35 K

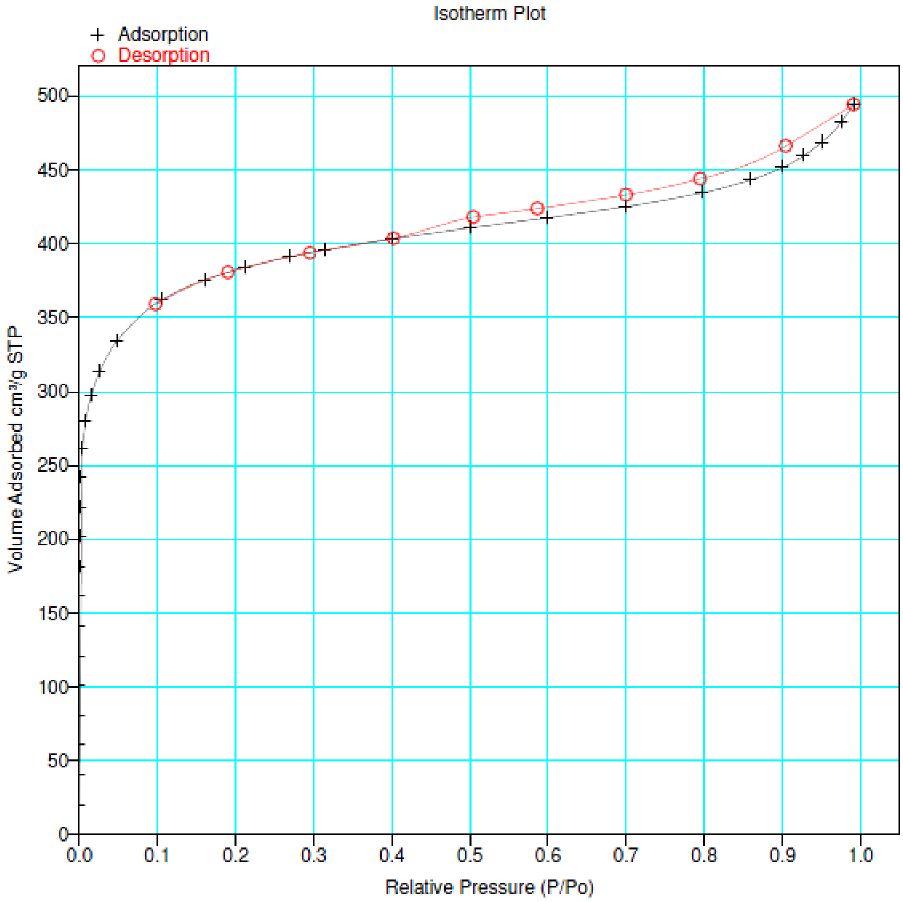
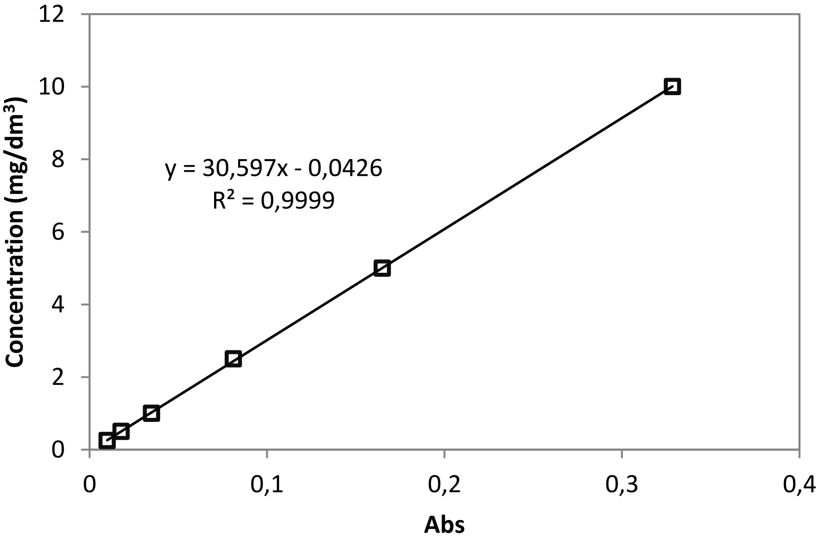


Figure AIII.3. Adsorption/desorption isotherm plots for F400 (Functionalized).

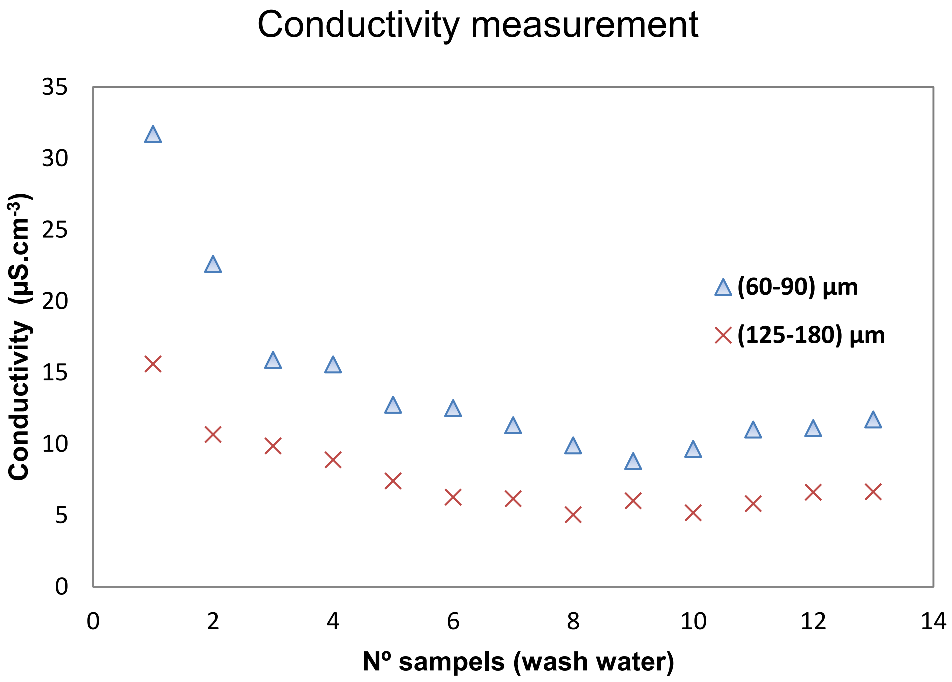
ANNEX IV. CALIBRATION CURVE

Calibration curve of ibuprofen at λ = 220 nm.



ANNEX V. WASH WATER CONDUCTIVITY.

Wash water	**Activated carbon particle size**	
	(63 -90) µm	**(125 -180) µm**
	Conductivity (µS/cm^3) 25ºC	
1	31.7	15.6
2	22.6	10.65
3	15.88	9.86
4	15.56	8.88
5	12.74	7.4
6	12.5	6.26
7	11.3	6.16
8	9.89	5.04
9	8.79	6.01
10	9.64	5.17
11	11	5.81
12	11.1	6.61
13	11.71	6.64



ANNEX VI. SELECTION OF ACTIVATED CARBON

Literature review - properties of the ACs studied

	FILTRASORB F400 [83,84,85]	***FILTRASORB F200*** [13]	***NORIT 0.8 SUPRA*** [13,61]	***NORIT GAC 1240*** [92,93,94]
Material	Bituminous coal	Bituminous coal	Extruded-peat	Bituminous coal
TEXTURAL CHARACTERIZATION				
Surface areas (m^2/g)				
BET surface area (**A_{BET}**)	825	714	900	871
External area (mesopores and macropores) (A_{ext})	57	83	153	83
Microporous surface area ($A_{BET} – A_{ext}$)	768	631	747	788
Pore volume (cm^3/g)				
Total microporous volume (V_{micro})	0.346	0.32	0.38	0.38
External volume (mesopores and macropores)	0.104	0.14	0.25	0.25
Total volume of pores (V_P)	0.491	0.48	0.66	0.40
POINT OF ZERO CHARGE				
pH_{PZC}	7.9	7.1	9.5	6.92
ELEMENTAL ANALYSIS (wt%)				
N (%)	0.8	0.4	0.5	0.2
C (%)	87.5	84.6	87.2	94.9
H (%)	0.18	0.2	0.4	0.3
S (%)	0.65	0.4	0.5	1
O (%)	10.87	14.4	11.5	3.6
Ash (%)	6.6	5.6	6.0	5.5