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Activated carbon production from agricultural wastes for micropollutants elimination

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INTRODUCTION	21
CHAPTER 1	
STATE OF THE ART	
1.1 GENERAL PRESENTATION OF ACTIVATED CARBON PRODUCTION	24
1.1.1 Conventional wastes - from agriculture and wood industry	29
1.1.2 Non-conventional wastes	30
1.1.3 Methods for activated carbon production from agricultural wastes	31
<i>1.1.3.1 Pyrolysis or Carbonization</i>	31
<i>1.1.3.2 Activation</i>	33
<i>1.1.3.2.1 Physical activation</i>	34
<i>1.1.3.2.2 Chemical activation</i>	35
<i>1.1.3.2.3 Steam pyrolysis/activation</i>	36
<i>1.1.3.2.4 Example of activated carbon production</i>	37
1.1.4 Applications and uses of agricultural based active carbons	40
<i>1.1.4.1 Adsorption of heavy metals by agricultural based active carbons</i>	40
<i>1.1.4.2 Adsorption of organic pollutants by agricultural based active carbons</i>	41
<i>1.1.4.3 Sugar Beet Pulp for water treatment</i>	43
<i>1.1.4.4 Peanut Hulls for water treatment</i>	44
1.1.5 Adsorption on activated carbon	45
<i>1.1.5.1 Porous structure of activated carbons</i>	45
1.1.6 Kinetic sorption models	47
<i>1.1.6.1 Pseudo-first order kinetic model</i>	47

1.1.6.2 Pseudo-second order kinetic model	48
1.1.7 Diffusion models	49
1.1.7.1 Intraparticle diffusion	50
1.1.8 Sorption models and sorption capacity	50
1.1.8.1 Adsorption on a solid surface	50
1.1.8.2 Adsorption isotherm equations	51
1.1.8.3 Langmuir isotherm equation	52
1.1.8.4 Freundlich adsorption isotherm	53
1.2 ARSENIC CONTAMINATION AND TREATMENT PROCESS	54
1.2.1 Arsenic – Chemical Characteristics	54
1.2.2 Arsenic in the environment	57
1.2.3 Pollution sources	61
1.2.4 Toxicity	62
1.2.5 International legislation for arsenic concentration in water	64
1.2.6 Main arsenic removal technologies	65
1.2.7 Arsenic remediation by adsorption	67
1.2.7.1 Biosorption	68
1.2.7.2 Activated carbons for arsenic removal	69
1.2.7.2.1 Commercial activated carbons	69
1.2.7.2.2 Activated carbons from wastes and chars	70
1.2.8 Arsenic elimination by metal loaded activated carbons	71
1.3 TETRACYCLINE CONTAMINATION AND TREATMENT PROCESS	73
1.3.1 Chemical characteristics	74

1.3.2 Pharmaceuticals substances in the environment	76
1.3.3 Tetracycline environmental pollution sources	78
1.3.4 Toxicity	80
1.3.5 International legislation for TC concentration in water	81
1.3.6 Main tetracycline removal technologies	81
<i>1.3.6.1 Tetracycline elimination by sorption</i>	82
<i>1.3.6.2 Tetracycline elimination by oxidation</i>	84
CHAPTER 2	
MATERIALS AND EXPERIMENTAL METHODS	
2.1 ACTIVATED CARBONS FABRICATION	88
2.2 CHARACTERIZATION OF CARBONACEOUS MATERIALS	89
2.2.1 Physical characterization – BET surface analysis	89
2.2.2 Elemental analysis and total ash content	92
2.2.3 Iron content measurement	94
2.2.4 Zeta potential measurement	94
2.2.5 pH_{ZC} determination	100
2.2.6 Scanning electron microscopy (SEM)	100
2.3 ARSENIC MEASUREMENTS	102
2.4 EXPERIMENTAL PROCEDURES FOR ARSENIC REMOVAL WITH CARBONACEOUS MATERIALS AND GAC1	107
2.4.1 Sorption kinetic	107
2.4.2 pH effect on As (V) sorption	107

2.4.3 Adsorption isotherms	108
2.4.4 Adsorption study in natural water spiked with As(V)	108
2.5 TETRACYCLINE MEASUREMENTS	109
2.6 EXPERIMENTAL PROCEDURES FOR TETRACYCLINE REMOVAL WITH CARBONACEOUS MATERIALS AND ACTIVATED CARBONS	111
2.6.1 Sorption kinetic	111
2.6.2 pH effect on TC sorption	111
2.6.3 Adsorption isotherms	112
2.6.4 Adsorption study in natural water spiked with tetracycline	112
2.7 CONCLUSION	113

CHAPTER 3

CARBONACEOUS MATERIALS CHARACTERIZATION

3.1 PRODUCTION OF CARBONACEOUS MATERIALS	115
3.1.1 Char and activated carbons	115
3.1.2 Modified activated carbons	118
3.2 POROUS STRUCTURE OF THE MATERIALS	119
3.2.1 BET surface analysis	119
3.2.2 Porous volumes and median diameters	122
3.2.3 Scanning electron microscopy	123
3.3 CHEMICAL CHARACTERIZATION OF THE ACTIVATED CARBONS	128
3.3.1 Elemental analysis and total ash content	128

3.3.2 Zeta potential measurement	129
3.3.3 pH_{PZC} determination	132
3.4 CONCLUSIONS	135
CHAPTER 4	
APPLICATIONS OF ACTIVATED CARBONS FOR ADSORPTION OF INORGANIC AND ORGANIC MICROPOLLUTANTS	
4.1 ADSORPTION STUDY OF ARSENATE IONS	141
4.1.1 Kinetic study of arsenate adsorption	141
<i>4.1.1.1 Contact time experiments</i>	141
<i>4.1.1.1.1 Kinetic decay curves obtained with the raw material and char</i>	141
<i>4.1.1.1.2 Kinetic decay curves obtained with BP-H_2O, BP-H_2O-Fe, PH-H_2O, PH-H_2O-Fe and GAC1</i>	142
<i>4.1.1.1.3 Conclusion about contact time experiments</i>	145
<i>4.1.1.2 Kinetic modeling</i>	147
<i>4.1.1.2.1 Diffusion modeling</i>	147
<i>4.1.1.2.2 Chemisorption model</i>	149
<i>4.1.1.3 pH effect</i>	152
4.1.2 Adsorption isotherms	154
<i>4.1.2.1 Langmuir and Freundlich isotherms</i>	154
<i>4.1.2.2 Adsorption in natural waters spiked with arsenic</i>	160
4.1.3 Sorption mechanism approach and conclusion	162
4.2 ADSORPTION STUDY OF TETRACYCLINE	164
4.2.1 Kinetic study of tetracycline adsorption	166

4.2.1.1	Contact time experiments	166
4.2.1.1.1	Kinetic decay curves obtained with activated and modified carbonaceous materials	166
4.2.1.1.2	Kinetic decay curves obtained with BP-H ₂ O, BP-H ₂ O-Fe, GAC1 and GAC2	168
4.2.1.1.3	Conclusion about contact time experiments	170
4.2.1.2	Kinetic modeling	171
4.2.1.3	pH effect	177
4.2.2	Adsorption isotherms	178
4.2.2.1	Langmuir and Freundlich isotherms	179
4.2.2.2	Adsorption in natural water spiked with tetracycline	182
4.2.3	Sorption mechanism approach	184
4.2.4	Conclusion	186
GENERAL CONCLUSION AND PERSPECTIVES		189
RESUME EN FRANCAIS		193
REFERENCES		233

CHAPTER 1

Figure 1.1 Schematic representation of the pore network of a carbon adsorbent.	25
Figure 1.2 World production of activated carbon per region and per precursor, production is given in kton/year	27
Figure 1.3 World production capacity by leading country	28
Figure 1.4. Carbonization reaction scheme of a carbonaceous material	32
Figure 1.5. General scheme for the production of thermal activated carbons	33
Figure 1.6 Eh-pH diagram for aqueous As species in the system As–O ₂ –H ₂ O at 25 °C and 1bar total pressure	56
Figure 1.7 (a) Arsenite and (b) arsenate speciation as a function of pH (ionic strength of about 0.01M). Redox conditions have been chosen such that the indicated oxidation state dominates the speciation in both cases	57
Figure 1.8 Distribution of documented world problems with As in groundwater in major aquifers as well as water and environmental problems related to mining and geothermal sources. Areas in blue are lakes	60
Figure 1.9 Molecular structure of TC on a planar view.	75
Figure 1.10 Tetracycline forms at different pH values.	75
Figure 1.11 Origin and routes of pharmaceutical substances	77
Figure 1.12 Transformation pathways of PPs (PC: parent compound, M: Metabolite(s), TP: Transformation Product(s), WWTP: Waste Water Treatment Plant; DWT: Drinking Water Treatments)	78

CHAPTER 2

Figure 2.1 Classification of gas adsorption isotherms	90
Figure 2.2 Sorption isotherm of N ₂ adsorption on GAC1 for surface BET determination.	91
Figure 2.3 Surface BET analyzer components.	92
Figure 2.4 Scheme of CHNS/O analysis process.	93

Figure 2.5. Triple layer model. The Helmholtz internal plane is located at the distance x_i of the surface and the Helmholtz external plane is located at the distance d .	96
Figure 2.6. Schema of SEM technique	101
Figure 2.7. Absorption of light through an optical filter in AAS technique.	103
Figure 2.8. Light absorption by a sample.	104
Figure 2.9 Absorption spectra of the TC at pH 4.5	110
Figure 2.10 Absorption spectra of the TC at pH 9.5	110

CHAPTER 3

Figure 3.1 Evolution of the pH during the washing procedure of BP-H ₂ O and PH-H ₂ O	118
Figure 3.2. SEM micrograph of Raw-BP	124
Figure 3.3. SEM micrograph of BP-H ₂ O	124
Figure 3.4. SEM micrograph of BP-H ₂ O-Fe	124
Figure 3.5. SEM micrograph of Raw-PH	125
Figure 3.6. SEM micrograph of PH-H ₂ O	125
Figure 3.7. SEM micrograph of PH-H ₂ O-Fe (Fe non-detectable)	125
Figure 3.8. SEM micrograph of GAC1	126
Figure 3.9 EDX spectrum of BP-H ₂ O	126
Figure 3.10 EDX spectrum of BP-H ₂ O-Fe	127
Figure 3.11 EDX spectrum of PH-H ₂ O	127
Figure 3.12 EDX spectrum of PH-H ₂ O-Fe	127
Figure 3.13 ζ potential for BP-H ₂ O	130
Figure 3.14 ζ potential for BP-H ₂ O-Fe	130
Figure 3.15 ζ potential for PH-H ₂ O	130

Figure 3.16 ζ potential for PH-H ₂ O-Fe	131
Figure 3.17 ζ potential for GAC1	131
Figure 3.18 Determination of pH _{PZC} for BP-H ₂ O.	132
Figure 3.19 Determination of pH _{PZC} for BP-H ₂ O-Fe.	133
Figure 3.20 Determination of pH _{PZC} for PH-H ₂ O.	133
Figure 3.21 Determination of pH _{PZC} for PH-H ₂ O-Fe.	133
Figure 3.22 Determination of pH _{PZC} for GAC1	134
Figure 3.23 Determination of pH _{PZC} for GAC2	134

CHAPTER 4

Figure 4.1 Kinetic decay curves for removal of As (V) as a function of time and initial concentration of 100, 500 and 1000 $\mu\text{g.L}^{-1}$ for BP-C and 500 $\mu\text{g.L}^{-1}$ for BP.	142
Figure 4.2 Kinetic decay curve for removal of As(V) by BP-H ₂ O (particle size 0.5-1 mm) and BP-H ₂ O-Fe (>1 mm) as a function of time and initial concentration of 100, 500 and 1000 $\mu\text{g.L}^{-1}$.	143
Figure 4.3 Kinetic decay curve for removal of As(V) by PH-H ₂ O (particle size 0.5-1 mm) and PH-H ₂ O-Fe as a function of time and initial concentration of 100, 500 and 1000 $\mu\text{g.L}^{-1}$ (particle size > 1 mm).	144
Figure 4.4 Kinetic decay curve for removal of As (V) as a function of time and initial concentration of 500, 1000 and 2000 $\mu\text{g.L}^{-1}$ for GAC1 (particle size 0.5-1 mm).	145
Figure 4.5 Kinetic decay curve for removal of As (V) as a function of time and initial concentration of 1000 $\mu\text{g.L}^{-1}$ for BP-H ₂ O, PH-H ₂ O and GAC1.	146
Figure 4.6 Kinetic decay curve for removal of As (V) as a function of time and initial concentration of 1000 $\mu\text{g.L}^{-1}$ for BP H ₂ O-Fe, PH-H ₂ O-Fe and GAC1.	146
Figure 4.7 Intraparticle diffusion modeling for A) BP-H ₂ O, BP-H ₂ O-Fe and GAC1 and B) PH-H ₂ O, PH-H ₂ O-Fe and GAC1 (particle size < 0.5 mm).	148
Figure 4.8 Arsenic adsorption by BP-H ₂ O, BP-H ₂ O-Fe and GAC1 fitted with pseudo-second order kinetic model (linear).	150

Figure 4.9 Arsenic adsorption by PH-H ₂ O, PH-H ₂ O-Fe and GAC1 fitted with pseudo-second order kinetic model (linear).	151
Figure 4.10 Kinetic decay curves of As(V) adsorption onto BP-H ₂ O at 2 different initial concentrations (500 and 1000 µg.L ⁻¹) and different pH values (3.5, ≈7 and 12).	152
Figure 4.11 Experimental adsorption isotherms of As (V) and modelled results using the Langmuir equation	155
Figure 4.12 Experimental adsorption isotherms of As(V) and modelled results using the Freundlich equation	155
Figure 4.13 A) Freundlich constant (K_F) and B) n constant in function of microporous volume (V_{micro}) fitted to a linear equation	159
Figure 4.14 A) Sorption isotherm of arsenic(V) onto: A) PH-H ₂ O-Fe and B) PH-H ₂ O in deionized water (DW) and spring water with high (HMC) and low (LMC) mineral	161
Figure 4.15 Sorption isotherm of arsenic(V) onto PH-H ₂ O and PH-H ₂ O-Fe in deionized water (DW) and spring water with high mineral content (HMC)	162
Figure 4.16 As(V) sorption phenomena on AC and iron impregnated AC	163
Figure 4.17 a) Structure and (b) pH-dependent speciation of tetracycline (TC)	165
Figure 4.18 Kinetic decay curves for removal of TC as a function of time and initial concentration of 50 mg.L ⁻¹ for BP-H ₂ O, BP-H ₂ O-Fe, PH-H ₂ O, PH-H ₂ O-Fe	168
Figure 4.19 Kinetic decay curves for removal of TC as a function of time and initial concentration of 100 mg.L ⁻¹ for BP-H ₂ O, BP-H ₂ O-Fe and GAC1	169
Figure 4.20 Kinetic decay curve for removal of TC as a function of time and initial concentration of 300 mg.L ⁻¹ for GAC2	169
Figure 4.21 Tetracycline adsorption by BP-H ₂ O fitted with pseudo-second order kinetic model (linear) [TC]=50 mg.L ⁻¹	172
Figure 4.22 Tetracycline adsorption by BP-H ₂ O-Fe fitted with pseudo-second order kinetic model (linear) [TC]=50 mg.L ⁻¹	173
Figure 4.23 Tetracycline adsorption by PH-H ₂ O fitted with pseudo-second order kinetic model (linear) [TC]=50 mg.L ⁻¹	173
Figure 4.24 Tetracycline adsorption by PH-H ₂ O-Fe fitted with pseudo-second order kinetic model (linear) [TC]=50 mg.L ⁻¹	174

Figure 4.25 Tetracycline adsorption by BP-H ₂ O fitted with pseudo-second order kinetic model (linear) [TC]=100 mg.L ⁻¹	174
Figure 4.26 Tetracycline adsorption by BP-H ₂ O-Fe fitted with pseudo-second order kinetic model (linear) [TC]=100 mg.L ⁻¹ .	175
Figure 4.27 Tetracycline adsorption by GAC1 fitted with pseudo-second order kinetic model (linear) [TC]=100 mg.L ⁻¹ .	175
Figure 4.28 Tetracycline adsorption by GAC2 fitted with pseudo-second order kinetic model (linear) [TC]=300 mg.L ⁻¹ .	176
Figure 4.29 Tetracycline removal by BP-H ₂ O and GAC2, contact time of 5 days, initial concentration of 200 mg.L ⁻¹ and pH _i = 4, 8 and 11.	177
Figure 4.30 Experimental adsorption isotherms of Tetracycline and modelled results using the Langmuir equation.	180
Figure 4.31 Experimental adsorption isotherms of Tetracycline and modelled results using the Freundlich equation.	181
Figure 4.32 Sorption isotherm of Tetracycline onto BP-H ₂ O and GAC2 in deionized water (DW) (light symbols) and natural water (HMC) (plain symbols and fitted to Freundlich model).	183
Figure 4.33 V_{mesp} vs Freundlich constant (K_F) fitted to an exponential equation	185

CHAPTER 1

Table 1.1 Some activation conditions agricultural residues to obtain low-cost activated carbons reported in literature	38
Table 1.2 Oxyacids conjugate anions of As (V) and P (V)	55
Table 1.3 Arsenic Concentrations in Environmental Media (U.S. EPA)	58
Table 1.4 Occurring As concentrations in waters around the world	59
Table 1.5 Comparison of main arsenic removal technologies	66
Table 1.6 Activated carbons from agricultural wastes for arsenic removal	71
Table 1.7 Some characteristics of Tetracycline hydrochloride	74
Table 1.8 Sorption of Tetracycline by adsorbent materials	85

CHAPTER 2

Table 2.1 Zeta measurement conditions	99
Table 2.2. Optimized graphite furnace parameters	105
Table 2.3 Limit of detection (LD) and Limit of Quantification (LQ) for As(V)	106
Table 2.4. Mineral content of natural water utilized in this work	109
Table 2.5 Limit of detection (LD) and Limit of Quantification (LQ) for TC	111

CHAPTER 3

Table 3.1 Yield and particle size distribution of carbonaceous materials obtained from raw agricultural by-products (%)	116
Table 3.2 Textural parameters of produced activated carbons and GACs	120
Table 3.3 Studies of porosity of activated carbon obtained from agricultural by-products	121

Table 3.4 Total ash content and elemental analysis (wt.%) of carbonaceous materials	128
Table 3.5 pH_{pzc} of the prepared activated carbons and commercial GACs	135
Table 3.6 Summary of carbonaceous materials from agricultural wastes and commercial GACs characterization	137

CHAPTER 4

Table 4.1 Intraparticle diffusion values for As(V) sorption on the different the activated carbons	149
Table 4.2 Kinetic parameters for arsenic(V) adsorption fitted by the pseudo-second order model	151
Table 4.3 Different forms of As(V) determined from the speciation for an initial concentration of $1000 \mu\text{g.L}^{-1}$	153
Table 4.4 Adsorption constants for Langmuir and Freundlich models isotherms	156
Table 4.5 Iron impregnated carbons reported in literature and adsorption capacity	157
Table 4.6 Mineral content of spring water utilized for As(V) adsorption	160
Table 4.7 Different forms of tetracycline determined from the speciation for the adsorbent materials at pH_i and pH_f in kinetic tests	170
Table 4.8 Kinetic parameters for TC adsorption fitted by pseudo-second order model	176
Table 4.9 Adsorption constants for Langmuir and Freundlich models isotherms	182

GENERAL INTRODUCTION

In water treatment, activated carbons are among the most widely used adsorbents because of their excellent adsorption performance for organic pollutants. The high adsorption capacities of activated carbons are usually related to their specific surface area, pore volume or surface chemistry. They have been manufactured from a variety of materials and their characteristics depend on the nature of the raw precursor, and the carbonization/activation technique used in their production. Agricultural wastes are low-cost materials potentially used to produce activated carbons. They have been widely used as adsorbents in environmental applications to remove a wide range of dangerous pollutants in aqueous media.

Nowadays micropollutants water contamination is one of the most challenging environmental problems. Millions of people are exposed worldwide to arsenic contaminated waters that are used as their only source of drinking water. Moreover, another kind of micropollutants contamination is confirmed by the frequent detection of organic compounds such as antibiotics (*i.e.* tetracycline) in surface, ground and wastewaters. But treatment processes are always under investigation. Only few studies have determined the possibility of using activated carbons prepared from agricultural wastes for arsenic removal. And none results have been reported for tetracycline removal from aqueous solutions by this type of low-cost adsorbent materials.

Therefore, the present work evaluate the preparation and the use of activated carbons from sugar beet pulp and peanut hulls as alternate adsorbents for arsenic(V) and tetracycline removal from aqueous solutions. By this way, the objective is to find alternative solutions to two important environmental problems: the disposal of wastes and the presence of organic and inorganic micropollutants in water.

The research study is divided in four principal chapters; the first chapter proposes a state of the art. It describes the preparation of activated carbons from waste materials including the physical and chemical activation, applications and uses of different agricultural

based activated carbons. A focus on the use of two specific agricultural wastes: sugar beet pulp and peanut hulls is also presented. Kinetic and isotherms models related to the sorption are given. Finally, a panorama about arsenic and tetracycline problem around the world is proposed. Toxicological data and remediation technologies like adsorption processes are described.

The second chapter presents a description of the methods employed for the preparation of the activated carbons from sugar beet pulp and peanut hulls, the different techniques for the characterization of the materials and the analytical methods that were utilized for arsenic(V) and tetracycline determination.

The third chapter deals with the production of carbonaceous materials from the two selected agricultural wastes, their chemical modification as well as the physical chemical characterization. These results are compared with two commercial granular activated carbons (GACs).

Finally, the last chapter of this work is divided into two main parts, corresponding firstly to arsenic(V) sorption and then to tetracycline one. For both cases the presented results are based on experiments conducted in batch reactor, with synthetic solution of As(V) and tetracycline and the experimental data are compared in each case with commercial GAC. Sorption results consist in a kinetic study including the test of kinetic models and adsorption isotherms conducted in different experimental conditions. A tentative of correlation between the properties of the AC and their adsorption performances for a sorption mechanism approach is finally presented.

All the reported results confirms the interest in the use of activated carbons obtained from agricultural wastes in the treatment of water containing arsenic(V) or tetracycline as micropollutants.

CHAPTER 1

STATE OF THE ART

Nowadays there are many researches about the elimination of inorganic and organic pollutants from water using different techniques for water treatment; these scientific reports include technologies that have traditionally been used such as oxidation, precipitation, coagulation, membrane separation and adsorbent materials application. Most of the valuable and available literature has been reviewed on arsenic and tetracycline remediation by using adsorbent materials.

The aim of the first chapter is to present a literature review about the preparation of activated carbon from waste materials including the physical and chemical activation, applications and uses of different agricultural based activated carbons to remove arsenic and tetracycline. A description of their toxic characteristics as micropollutants in the environment is also proposed.

In the first part of this chapter there are a general view about the activated carbon production and their applications in organic and inorganic pollutants removal. Moreover, a focus on two specific agricultural wastes (sugar beet pulp and peanut hulls) is presented. Finally a description of kinetic and isotherms models employed to describe the sorption of the pollutants on the adsorbents materials.

The second part presents a brief study about arsenic occurrence, toxicology, and distribution in the environment, chemical characteristics and the main arsenic removal technologies including the adsorption process with activated carbons.

Finally, the third part of the chapter 1 gives a panorama about antibiotics problem around the world and focuses on tetracycline. Toxicological data and technologies like adsorption processes onto activated carbons, that have been used to eliminate this emerging pollutant from contaminated water are described.

1.1 GENERAL PRESENTATION OF ACTIVATED CARBON PRODUCTION

Activated carbon in its broadest sense is a term that includes a wide range of amorphous carbonaceous materials that exhibit a high degree of porosity and an extended surface area. They are obtained by pyrolysis and activation of a variety of carbonaceous substances. Activated carbons have been obtained first in granular and powdered forms. But they are now also being prepared in spherical, fibrous, and cloth forms for some special applications. The granular form has a large internal surface area and small pores, and the powdered form is associated with larger pore diameters and a smaller internal surface area. Carbon cloth and fibrous activated carbons (activated carbon fibers) have a large surface area and contain a comparatively higher percentage of larger pores (Bansal and Goyal, 2005).

Carbon is the major constituent of active carbons and is present to the extent of 85 to 95%. In addition, active carbons contain other elements such as hydrogen, nitrogen, sulfur, and oxygen. These heteroatoms are derived from the source raw material or become associated with the carbon during activation and other preparation procedures. The elemental composition of a typical active carbon is found to be around of 88% C, 0.5% H, 0.5% N, 1% S, and 6 to 7% O, with the balance representing inorganic ash constituents. The oxygen content of the active carbon, however, may vary between 1 and 20%, depending upon the source raw material and the history of preparation, which includes activation and subsequent treatments. The most widely used activated carbon adsorbents have a specific surface area on the order of 800 to 1500 m² /g and a pore volume on the order of 0.20 to 0.60 cm³ g⁻¹. The surface area in active carbons is predominantly contained in micropores that have effective diameters smaller than 2 nm and mesopores between 2 and 50 nm (Figure 1.1).

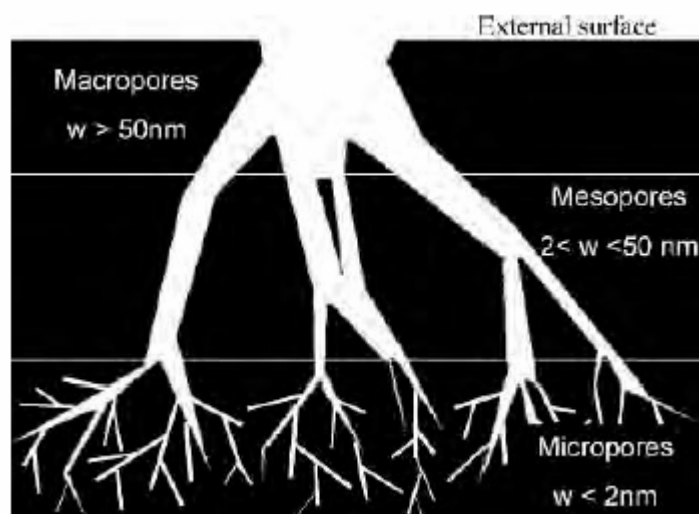


Figure 1.1 - Schematic representation of the pore network of a carbon adsorbent (Menéndez-Díaz and Martín Gullón, 2006).

Active carbons are mainly and almost exclusively prepared by thermal treatment of carbonaceous raw material at temperatures lower than $1000\text{ }^{\circ}\text{C}$. The preparation involves two main steps: carbonization of the raw material at temperatures below $800\text{ }^{\circ}\text{C}$ in an inert atmosphere also called pyrolysis, and activation of the carbonized product between 800 and $1000\text{ }^{\circ}\text{C}$. Thus, all carbonaceous materials can be converted into active carbons, although the properties of the final product will be different, depending upon the nature of the raw material used, the nature of the activating agent, and the conditions of the activation process. During carbonization most of the noncarbon elements such as oxygen, hydrogen, nitrogen, and sulfur are eliminated as volatile gaseous products by the pyrolytic decomposition of the source raw material. The residual elementary carbon atoms group themselves into stacks of aromatic sheets cross-linked in a random manner. The mutual arrangement of these aromatic sheets is irregular and, therefore, leaves free interstices between the sheets, which may become filled with the tarry matter or the products of decomposition or at least blocked partially by disorganized carbon. These interstices give rise to pores that make active carbons excellent adsorbents. The char produced after carbonization does not have a high adsorption capacity because of its less developed pore structure. This pore structure is further enhanced during the activation process when the spaces between the aromatic sheets are cleared of various carbonaceous compounds and disorganized carbon. The activation process converts the carbonized char into a form that contains the largest possible number of randomly distributed

pores of various shapes and sizes, giving rise to a product with an extended and extremely high surface area (Bansal and Goyal, 2005).

Activated carbons were the first adsorbents to be developed and they are produced from a solid carbonaceous based material, which is non-graphitic and non-graphitizable, and has an initial isotropic structure. The precursor is transformed or 'activated' by means of medium to high temperature treatments, which remove solid mass, and at the same time, create pores where the removed mass was previously located. The common properties of activated carbons and other kinds of carbon adsorbents is their well developed pore network, and the similar ways in which they are produced.

Since an activated carbon is structurally a non-graphitic carbonaceous material, almost any carbonaceous solid material can be converted into activated carbon. There are, therefore, plenty of possible raw materials such as wood, lignocellulosic biomass, peat, lignite and coals that can be used to make activated carbon. However, there are some limitations. Since activated carbon is disordered and isotropic, the raw material must not be allowed to pass through a fluid or pseudofluid state due to the fact that the solid structure tends to transform into an ordered structure. Consequently, coking coals are not an appropriate raw material, unless they are first treated with anti-coking processes (e.g. low-temperature preoxidation). Similarly, thermoplastic wastes are not a suitable raw material because they melt with increasing temperature, losing their initial shape and particle size (Banosz, 2006).

In practice, wood, coconut shells, fruit stones, coals, lignites, petroleum coke, etc. are all inexpensive materials with high carbon content and a low inorganic content, and consequently, are suitable for use as an activated carbon precursor. The resulting properties of the product are dependent on the precursor, and consequently, the carbons can be tailored for selected applications. Furthermore, the resulting activated carbon properties are also influenced to a great extent by the activation treatment. Selection of the appropriate raw material is based on the following criteria:

- Possibility of yielding a good activated carbon in terms of adsorption capacity, high density and hardness.
- Low content in inorganic matter. The adsorption capacity is measured per mass unit, and since inorganic materials are non-porous, their presence reduces the adsorption capacity.

- **Availability and cost.** As with any other product, the price of the raw material affects the final cost, so a high availability is important to ensure stable prices. It should also be taken into account that there is a considerable mass loss in all the activation treatments, if exists a lower product yield, it's higher the cost. The product yields may vary considerably, and can be as low as 5-10% for wood-based carbons. Moreover, raw material availability obviously depends on the part of the world in which the plant is located (Bandosz, 2006).

Figure 1.2 shows the estimated world production of activated carbon per region and per precursor in 1993. Total production exceeded 350000 tones/year: coconut shells (34%), coal (31%) and wood (24%) these being the most important precursors. However, the raw materials used per world region shows a very different picture. In Europe, the raw material most used was peat (36000 ton/year, 36% of total European production), whereas the production of coconut shell based carbon occupied fourth place with only 12% of the share. On the other hand, coconut based carbons led in Asia with over 60% of the share, North America occupying a position between Asia and Europe, with nearly the same production of coal, coconut and wood based activated carbons.

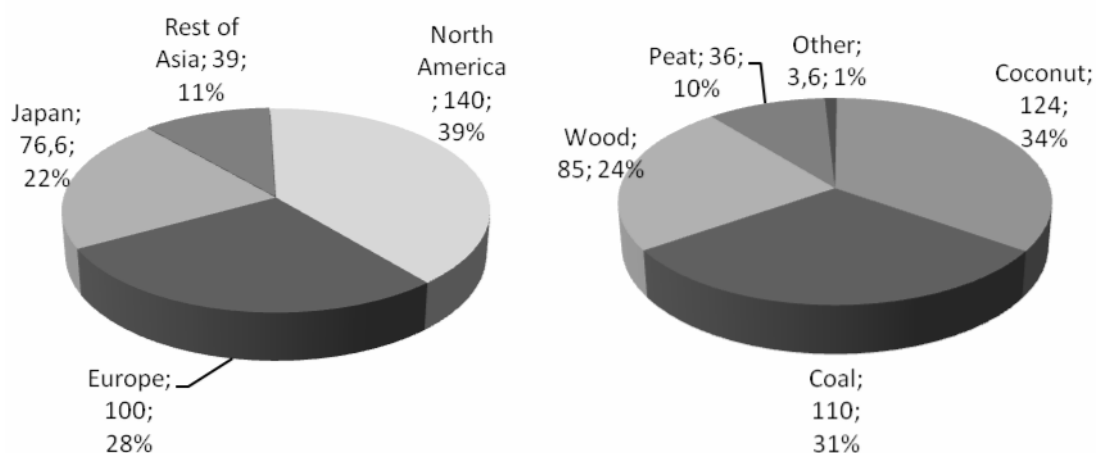


Figure 1.2 - World production of activated carbon per region and per precursor, production is given in kton/year (Menéndez-Díaz and Martín Gullón, 2006).

In 2002 the total production of activated carbon was estimated to be 750000 ton/year , which represents a rise of two times the level of production in less than 10 years. This change comes at a time when the production capacity is shifting from western industrialized countries to China and South-East Asia, where raw material, energy and labor costs are lower. By world

regions, Asia is leading world production with 54% of the total share, followed by America with 32% and Europe with only 14%. By countries, Figure 1.3 shows the current world producers, where it can be seen that China manufactures 23% of the world production (Bandosz, 2006).

Currently, there are many studies on the development of low-cost adsorbents, namely by using waste materials for that purpose. Crini, *et al.* (2006) have been reported a review about low-cost adsorbents for dye removal; Chuah *et al.* (2005) have been utilized rice husk as a potential low cost adsorbent for heavy metals and dyes removal, and Babel and Kurniawan (2003) and Wang *et al.* (2003) reported the uptake of heavy metals using low cost adsorbents.

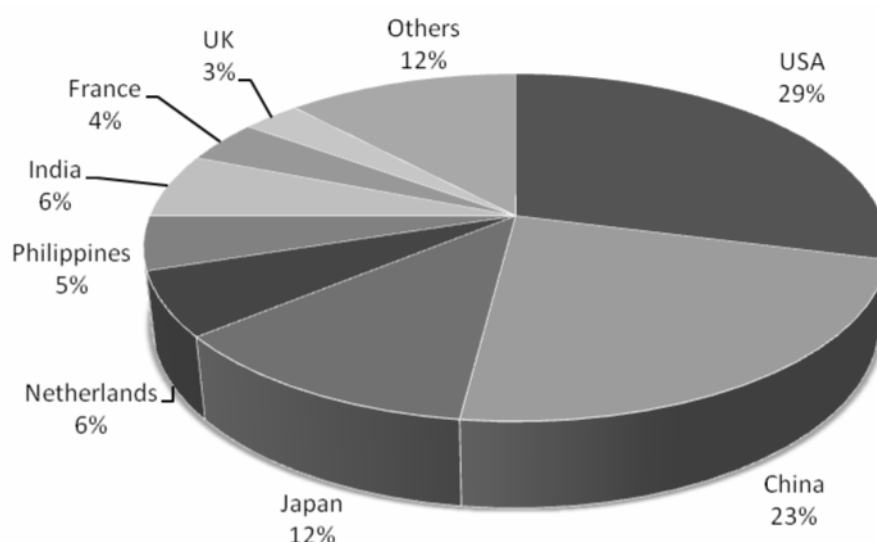


Figure 1.3 – World production capacity by leading country (Menéndez-Díaz and Martín Gullón, 2006).

A review reporting the use of waste materials for the production of activated carbons such as agricultural residues as precursors for activated carbon production has been proposed by Ioannidou and Zabaniotou (2007). Pollard *et al.* (1992) propose a review about low-cost alternatives to activated carbon for waste and wastewater treatment and an examination of the selection criteria and activation methods for the preparation of active carbon followed by a critical assessment of low-cost adsorbents prepared from carbonaceous industrial wastes, agricultural by-products and mineral-derived sources. Mohan and Pittman (2006a) have studied and compared low cost adsorbents for remediation of Cr. Mohan *et al.* (2000)

presented results for the adsorption of mercury with activated carbon obtained from fertilizer waste. However, such studies are restricted to either type of waste, preparation procedures, or specific aqueous-phase applications but not on relation between precursor material, activation and adsorption capacities (Dias *et al.*, 2007).

Most of the studies for activated carbon preparation make a focus on the use of waste materials of considerable rigidity, such as the shells and stones of fruits like nuts, peanuts, olives, dates, almonds, apricots and cherries; however, wastes resulting from the production of cereals such as rice, soybean, maize and corn as well as olive cakes, coffee pulp, sugar cane bagasse, sugar beet pulp, coirpith, oil-palm shell (from oil-palm processing mills) and various seed wastes were already used. The preparation of activated carbon from these materials has been made using both physical and chemical activation.

1.1.1 Conventional wastes - from agriculture and wood industry

The most common feedstock for the commercial production of activated carbons are anthracite and bituminous coal, lignite, peat, and the lignocellulosic materials, wood and coconut shells (Pollard *et al.*, 1992). Plentiful agricultural by-products such as sugarcane bagasse, rice straw, soybean hulls, rice hulls, and nutshells are lignocellulosic wastes that may offer an inexpensive and renewable additional source of activated carbons that may have the potential to replace existing commercial carbons, especially coal-based carbons used in many industrial applications like the removal of color and odor compounds in aqueous systems (e.g., raw sugar decolorization) (Ahmedna *et al.*, 2000).

The type of agricultural by-product is important to determine its suitability for activated carbon production. Agricultural by-products used as precursors in carbon production can be classified into two groups. Group 1: materials consist of soft compressible waste products of low density, such as sugarcane bagasse, rice straw, soybean hulls, peanut shells, and rice hulls. To make a good precursor for production of activated carbons, group 1 materials must be mixed with suitable binder and compressed into briquettes or pellets to increase the density of the original product. Johns *et al.* (1998) characterized and evaluated granular activated carbons (GACs), made from these feedstocks, as effective removers of organics and metals from water. The by-products included soft lignocellulosics such as rice straw, soybean hull,

sugarcane bagasse, peanut shell, and harder materials such as pecan and walnut shells. The precursors were CO₂ or steam-activated, and subsequent treatments included oxidation to enhance metal adsorption. Many of the GACs had acceptable physical GAC attributes, such as durability, for commercial usage. In contrast, group 2 materials, such as nutshells from pecan and walnut, are hard, dense and not easily compressed. Group 2 by-products are also suitable as GAC precursors without binder or briquette formation.

1.1.2 Non-conventional wastes

The economical activities in the modern society gradually created a pattern of mass production, mass consumption as well as mass deposition (Gao *et al.*, 2005). Several industrial and post-consumer waste products, which are difficult or poorly effective to be regenerated into other materials and were more currently end up in incineration plants or landfills, could be also serve as activated carbon precursors. Due to the more restricted environmental standards, limitations on the application of such alternatives are remarkably increasing.

The use of such non-conventional wastes as carbon source for the production of activated carbon might be an efficient alternative for both, adoption of effective waste management practices, and production of low-cost activated carbon.

There are studies dedicated to the valorization of such wastes, namely for the production of activated carbon. Plastic wastes, such as polyethylene terephthalate (PET) and polyvinyl chloride (PVC) (Hayashi *et al.*, 2005), various industrial wastes like pitch, and polymeric residues from factories as well as other wastes such as tyres and sewage sludge have been used as raw material for activated carbon production.

Also a waste commercial ion-exchange resin might be used to prepare activated carbon with values of specific surface area and pore volume suggesting its application in different purposes that might include aqueous-phase treatments (Gun'ko *et al.*, 2005). At present some studies focused on the application of activated carbon prepared from non-conventional waste materials for the removal of pollutants from aqueous phase (Gupta *et al.*, 2006).

Other studies have reported the production of chars and activated carbons from tyres, the potential of these products as possible adsorbents for various pollutants has been assessed and found to be very successful (Mui *et al.*, 2004).

1.1.3 Methods for activated carbon production from agricultural wastes

There are many ways of producing activated carbon, and thousands of patents have been registered worldwide, but the most used methods are listed below:

1.1.3.1 Pyrolysis or Carbonization

The terms pyrolysis or carbonization are often used without distinction, and both processes are almost identical. However, there are differences in the objectives of each process. Both pyrolysis and carbonization refer to the thermal degradation of a carbonaceous material (coal, lignite, wood, polymer, etc) in an inert atmosphere, where the total or partial devolatilization of the raw material takes place. The difference is that, in pyrolysis, it is the gaseous and volatiles compounds production from the solid which are the main objective of the process, and all process conditions (temperature, residence time, etc.) are focused on producing gaseous compounds (e.g. pyrolysis conditions to favor the light olefin fraction), regardless of the final char residue. On the other hand, in a carbonization process, thermal treatment focuses on the final properties of the char (e.g. porous texture, hardness, density, etc), regardless of the volatile compounds evolved.

There are many carbonization conditions for the production of the activated carbons from agricultural residues depending the characteristics of the raw materials, reported in the literature (Haykiri-Acma *et al.*, 2006; Lanzetta and Di Blasi, 1998; Minkova *et al.*, 2001, 2000; Cetin *et. al.*, 2004; Ahmedna *et. al.*, 2004; Aygun *et al.*, 2003). For more details see Table 1.1.

A scheme of the carbonization (or pyrolysis) of a carbonaceous material is shown in Figure 1.4. The starting material, based on an organic macromolecular structure, decomposes during the thermal treatment to yield:

- A gaseous fraction, rich in hydrogen, light hydrocarbons and tar.
- A solid fraction, rich in carbon, called char.

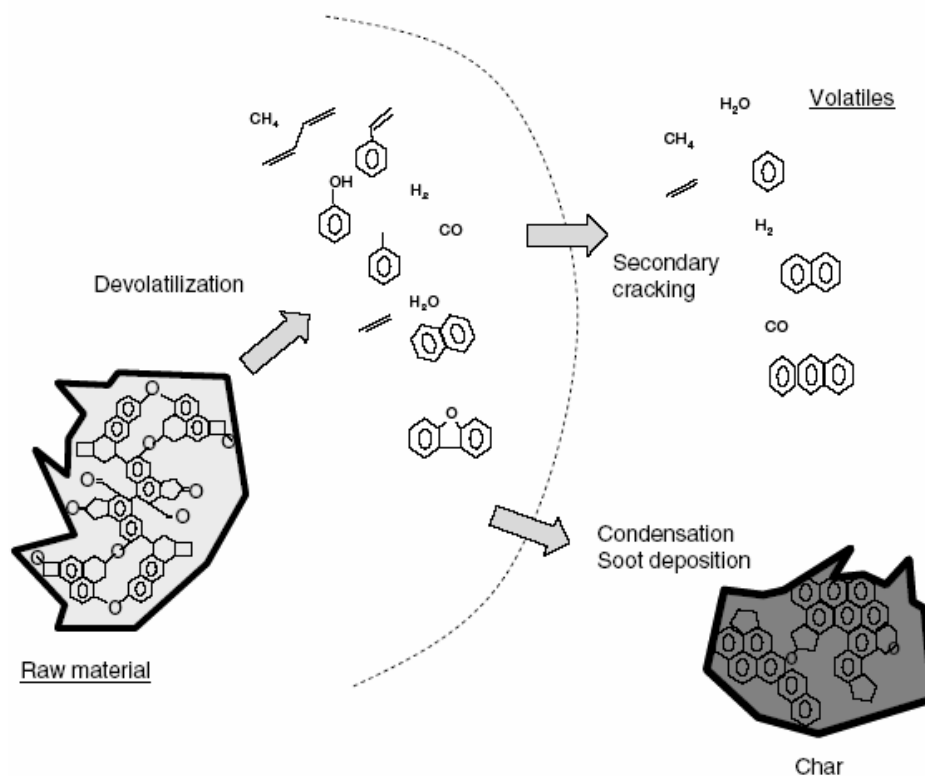


Figure 1.4. Carbonization reaction scheme of a carbonaceous material (from M  nendez-D  az and Mart  n-Gull  n, 2006).

The gases and vapours that first produce from the solid are primary products. These vapours come directly from fragments of the carbonaceous structure, so there are many radical species. Once this fraction is in gas phase, these species may react among themselves, depending on the treatment temperature and residence time, to yield secondary (cracking) products. At medium temperatures (500   C), there are few secondary reactions, and the gas phase consists mainly of stabilized primary products. Consequently, the gas composition is highly dependent on the precursor used under mild conditions. As the temperature is increased, the secondary reactions become more important, yielding at extreme conditions (above 1000   C) methane, hydrogen and soot. If the temperature is between 800-900   C, intermediates of soot formation (stabilized polyaromatics) can appear, together with olefins, methane, hydrogen, water and carbon oxides. If the heat treatment is carried out at high heating rates, cracking reactions are so quick that soot may be deposited over the char

particles. A knowledge of what is happening, in terms of chemical reactions, during the carbonization is important for an understanding of the final properties of the final char (Ménendez-Díaz and Martín-Gullón, 2006).

1.1.3.2 Activation

Basically, there are two main steps for the preparation and manufacture of activated carbon: the carbonization of the carbonaceous raw material below 800 °C, in the absence of oxygen, and the activation of the carbonized product (char), which is either physical or chemical that are described below. The main scheme for activation production is shown in Figure. 1.5.

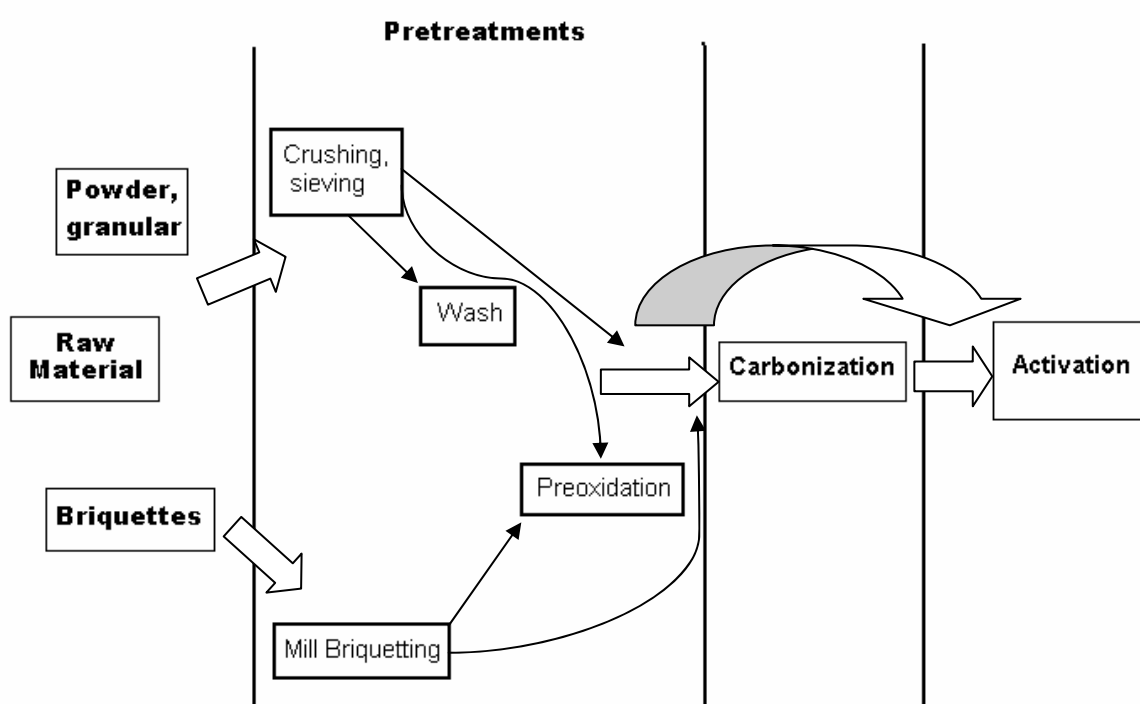


Figure 1.5. General scheme for the production of thermal activated carbons.

1.1.3.2.1 Physical activation

Physical activation is a two-step process. It involves carbonization of a carbonaceous material followed by the activation of the resulting char at elevated temperature in the presence of suitable oxidizing gases such as carbon dioxide, steam, air or their mixtures (Haykiri-Acma *et al.*, 2006; Ahmedna *et al.*, 2000; Marcilla *et al.*, 2000). Generally the physical activation temperature range between 600 and 900 °C.

In thermal activation, the char is partially oxidized with steam, carbon dioxide or air. These gases react with the carbon atoms and remove some of the mass of the internal surface of the solid, in the incipient micropores, creating a well developed microporous material. In addition, some internally blocked micropores may also become accessible due to tap burn-out. The activation rate is conditioned by the characteristics of the precursor and the activating agent. When the activation step is realized with oxygen, yields simultaneously carbon monoxide and dioxide, due to the high enthalpy, the temperature of the reaction is extremely difficult to control, and often a reaction runaway (self ignition or uncontrolled temperature) takes place so that the reaction is governed by diffusion control burning the carbon only on the surface of the particle and not in the inner surface. Consequently oxygen activation is scarcely applied.

For the carbon dioxide activation, the heterogeneous reaction between carbon and carbon dioxide yields carbon monoxide:



Depending on the partial pressures of the reagents and products, the temperature where the transition takes place is around 900 °C (or even lower), when the reaction rate is not very high. Under chemical control, the porosity development attained is as high as that obtained with steam (Rodríguez-Reinoso *et al.*, 1994).

1.1.3.2.2 Chemical activation

Another step for activation of carbons is the chemical activation that involves a reaction between the carbon precursor and a chemical reagent. At temperatures in the range of 400 to 900 °C the porosity of the material can be developed at the same time as the transformations that occur during heat treatment in an inert atmosphere. In the chemical activation process the two steps are carried out simultaneously, with the precursor being mixed with chemical activating agents, as dehydrating agents and oxidants (Tsai *et al.*, 1997; 1998; Zhang *et al.*, 2004). Chemical activation offers several advantages since it is carried out in a single step, combining carbonization and activation, performed at lower temperatures and therefore resulting in the development of a better porous structure. Although the environmental concerns of using chemical agents for activation could be discussed this way use less energy.

The reagents that have been most used by industry are zinc chloride, phosphoric acid and potassium hydroxide. Each reagent produces a very different pore development in the carbon precursor. The feasibility of chemical activation processes is strongly dependent upon the recovery efficiently of the reagent for recycling. This involves subsequent leaching stage, followed by an additional operation consisting of drying the washed carbon. Other low-volume processes utilize various Lewis acids such as aluminum chloride and ferric chloride with fibrous materials such as rayon (a product of cellulose) to produce activated cloths or fibers (Ménendez-Díaz and Martín-Gullón, 2006).

The chemical agents help to develop the porosity of activated carbons by means of dehydration and degradation; the mixture of the chemical and the carbon is then heated at a maximum of around 750 °C. The use of a lower temperature, compared to physical activation, is compensated by the interaction between the chemicals and the carbon skeleton. Major advantages of chemical activation are the higher yield, lower temperature of activation (less energy costs), less activation time and, generally, higher development of porosity; among the disadvantages are the activating agents costs and the need to perform an additional washing stage to remove the chemical agent (Maciá-Agulló *et al.*, 2004). Activated carbons characteristics (namely its surface area) strongly depend on both the raw material and the activation procedure. Consequently, it is not possible to preview which is the activation procedure that yields a product with the highest surface area.

1.1.3.2.3 Steam pyrolysis/activation

The raw residue is either heated at moderate temperatures (500–700 °C) under a flow of pure steam, or heated at 700–800 °C under a flow of just steam. (Fan *et al.*, 2004; Savova *et al.*, 2001; Minkova *et al.*, 2001; El-Hendawy *et al.*, 2001; Marcilla *et al.*, 2000).

The steam gasification reaction also "burns out" carbon (like the combustion reaction) but follows an endothermic pattern (Menéndez-Díaz and Martín-Gullón, 2006).



This reaction has been extensively studied, not only for activating carbons, but also because it is the main reaction of water shift. Because this reaction is endothermic, the reaction runaway does not take place. In addition to the heterogeneous reaction, gaseous products may react among themselves in gas phase, yielding:



Nevertheless, the kinetics of the two latter reactions is very low and they hardly take place.

In order to produce activated carbons, it is necessary that the steam gasification progresses are under chemical control to allow internal porosity to develop inside the char particles. Otherwise the reaction would only take place on the outside part of the particle. Due to the specific nature of steam gasification, chemical control is achieved at relatively high temperatures. Consequently, steam can be considered as a good activating agent. In most situations, chemical control can be maintained at temperatures up to 900 °C. Internal porosity (in terms of the BET specific surface area or the micropore volume) increases with the conversion degree, although the micropore sizes also increase, which indicates that activation is taking place throughout the porosity. The way in which porosity develops is similar for all chars but it is not exactly the same for several reasons. First, each char has a different origin and chemical structure, so the active sites are not the same. Second, most of the precursors

have a mineral content, which is able to catalyse the steam gasification. This catalysis may affect slightly the way in which porosity develops (Menéndez-Díaz and Martín-Gullón, 2006).

Steam activation is the most widely used method for producing activated carbons in the world. It is the cheapest activating agent and in terms of adsorption capacity, it easily reaches specific surface areas of $1000 \text{ m}^2\text{g}^{-1}$ at 50% of activation conversion degree (regardless of carbonization yield), when an acceptable raw material with an initial ash content below 10% is used. Basically, steam activated carbons are microporous materials, with a micropore size that increases with the activation degree, but with no mesopore development (Menéndez-Díaz and Martín-Gullón, 2006).

1.1.3.2.4 Example of activated carbon production

Like it was explained before, different precursors can be used to produce activated carbons and the type of porosity developed depending on the type of activation method applied. Generally phosphoric acid activation yields a carbon with a higher adsorption capacity than thermal activation and a wider micropore size distribution (even in the low mesopore range), whereas KOH yields extremely narrow microporous carbons. These characteristics, however, cannot be used to say which raw material or which activation method produces the best carbons in absolute terms. In fact, each type of carbon is suited to a particular application. In addition, the economic aspects of the process (including the cost of the raw material) also play an important role in the selection of the most suitable carbon for a specific application, the Table 1.1 shown different agricultural by-products like low cost precursors for activated carbon preparation and also the activation conditions utilized for each carbonaceous material.

Table 1.1 – Some activation conditions agricultural residues to obtain low-cost activated carbons reported in literature.

Raw Material	Activation Temperature/Time	Activating agent	Reference
Pecan shell	450°C/1h(Carbonization) 800°C/6h(Activation)	CO ₂	Ahmedna <i>et al.</i> , 2000.
Cassava peel	750°C(Carbonization)	KOH	Sudaryanto <i>et al.</i> , 2006.
<i>Moringa Oleifera</i>	750°C/2h(Carbonization) 800°C/1h minutes	Steam	Warhurst <i>et al.</i> , 1997.
<i>Ceiba pentandra</i> hulls	750°C/2h(Carbonization) 800°C/1h minutes	Steam	Madhava Rao <i>et al.</i> , 2008.
Olive pit	--	KOH	Martínez <i>et al.</i> , 2006.
Olive stones	900°C/12h 850°C/	CO ₂ CaCl ₂	Juárez-Galán <i>et al.</i> , 2009.
Wheat	127-375 °C	--	Lanzetta and Di Blasi, 1998.
Corn straw	127-375 °C	--	Lanzetta and Di Blasi, 1998.
Olive	750 °C/2h	Steam/CO ₂	Minkova <i>et al.</i> , 2001.
Radiata pine	950 °C	--	Cetin <i>et al.</i> , 2004.

Table 1.1 (*Continued*) – Some activation conditions agricultural residues to obtain low-cost activated carbons reported in literature.

Raw Material	Activation Temperature/Time	Activating agent	Reference
Sugarcane bagasse	950 °C	--	Cetin <i>et al.</i> , 2004.
Almond shells	800 °C/1h	Steam	Ahmedna <i>et al.</i> , 2004.
Apricot stones	800°C	Chemical (ZnCl ₂)	Aygun <i>et al.</i> , 2003.
Almond shells	400°C(Carbonization) 800°C(Activation)	Physical	Marcilla <i>et al.</i> , 2000.
Straw/Char	550°C(Fluidized bed)	--	Jensen <i>et al.</i> , 2001.
Oak	700 °C	--	Zhang <i>et al.</i> , 2004.
Peanut hulls	500°C(Carbonization) 700-900°C(Activation)	Physical	Girgis <i>et al.</i> , 2002.
Pistachio-nut shells	500°C(Carbonization) 900 °C/0.5h (Activation)	Physical/CO ₂	Lua <i>et al.</i> , 2004.
Macadamia nutshells	500°C	Chemical (ZnCl ₂)	Ahmadroup and Do, 1997.
Corn cob	500°C/0.5h	Chemical (ZnCl ₂)	Tsai <i>et al.</i> , 1998.
Rice husk	400°C/1h(Carbonization) 600°C/1h(Activation)	Steam	Malik, 2003.
Rice husk	600°C/3h	ZnCl ₂ /CO ₂	Yalcin and Sevinc, 2000.

1.1.4 Applications and uses of agricultural based active carbons

1.1.4.1 Adsorption of heavy metals by agricultural based active carbons

Heavy metals are considered to be one of the most hazardous water contaminants. According to the World Health Organization (WHO, 2006), among the most toxic metals are cadmium, chromium, copper, lead, mercury, and nickel.

Industrial activities (e.g. mining, painting, car manufacturing, metal plating, and tanneries) and agricultural activities (when fertilizers and fungicidal sprays are intensively used) are the main sources of wastes containing heavy metals. Activated carbons utilization concern many industries as diverse as food processing, pharmaceuticals, chemical, petroleum, mining, nuclear, automobile and vacuum manufacturing, because of their adsorptive properties. Up to date, many studies report that the removal of heavy metals by activated carbon is economically favorable and technically easy (Khezami and Capart, 2005); therefore, activated carbon are used to treat waters contaminated with heavy metals. Additional information regarding the adsorption of heavy metals such as cadmium, chromium, mercury, iron, and copper can be found in a review by Huang (1978).

Lignite, peat chars (Allen *et al.*, 1997; Mohan and Chander, 2006) bone-char (Sneddon *et al.*, 2005) and biochar (Mohan *et al.*, 2007) use in wastewater treatment has received increasing attention too. Being good substitutes for activated carbons, they are plentiful, inexpensive and locally available. Biochar by-products from fast wood/bark pyrolysis, were investigated as adsorbents for the removal of the As^{3+} , Cd^{2+} , and Pb^{2+} from water. Oak bark, pine bark, oakwood, and pinewood chars were obtained from fast pyrolysis at 400 and 450°C in an augerfed reactor and characterized. Sorption studies were performed at different temperatures, pHs and solid to liquid ratios in the batch mode. Maximum adsorption occurred over a pH range of 3–4 for arsenic and 4–5 for lead and cadmium. This study showed that by-product chars from bio-oil production might be used as abundant inexpensive adsorbents for arsenic remediation at a value above their pure fuel value (Mohan *et al.*, 2007).

Nowadays the use of agricultural based activated carbons is an alternative for treatment for water contaminated by different kind of pollutants. Other compounds like metalloids and others anions also can be removed by low-cost adsorbents like agricultural by-products and they have been shown a great efficiency in the removal of this kind of water pollutants

(Aworn *et al.*, 2008). Adsorption involves the use of granular adsorptive media for the selective removal of arsenic from water with or without pH adjustment and with or without spent media regeneration. For example, agricultural waste/by-products such as rice husks has been used for arsenic removal from water.

Adsorptive media that have been most widely used are activated alumina, ion exchange resin, elemental iron or iron compounds, organic polymers, chars, coal, red mud, blast furnace slag (BFS), kaolin clay and silica sand, etc. Sometimes a combination of the media mentioned above is used together to maximize the adsorption of arsenic compounds for example. Activated carbons may also be used in combination with oxidants such as manganese compounds to pre-oxidize any arsenites present to arsenates which are more efficiently adsorbed from the contaminated water. Pre-filtration of the contaminated water may also be required in order to remove particulate matter that can deactivate the adsorption media and/or physically plug the adsorption bed. The effectiveness of adsorption for arsenic treatment is more efficient than precipitation processes which can be affected by the effluent characteristics and contaminants other than arsenic. Small capacity systems using these technologies tend to have lower operating and maintenance costs and require less operator expertise. Adsorption and ion exchange therefore tend to be used more often when arsenic is the only contaminant to be treated, for relatively smaller systems, and as an auxiliary process for treating effluent from larger systems (Malik, 2009).

1.1.4.2 Adsorption of organic pollutants by agricultural based active carbons

The discharge of industrial wastes (generated in chemical industry activities) and the leaching from agricultural and forest land (when the application of chemical fertilizers and pesticides is made) are the main sources of organic pollution in several water streams (Dias *et al.*, 2007).

The adsorption process of organic solutes from water is an important application of activated carbons. This covers a wide spectrum of systems such as drinking water and waste water treatments, and applications in the food, beverage, pharmaceutical and chemical industries (Newcombe *et al.*, 1993). Activated carbon adsorption has been cited by the US Environmental Protection Agency as one of the best available environmental control

technologies. In spite of the large market for activated carbon, the specific mechanisms by which the adsorption of many compounds, especially organic compounds, takes place on this adsorbent are still ambiguous. This is because liquid-phase adsorption is a more complicated process than gas or vapour-phase adsorption. Literature shows an important amount of studies on the adsorption of organic compounds by activated carbon as compared with the inorganic ones (Moreno-Castilla, 2004).

In technologies that exist for water and air treatment, the processes that involves mass transfer phenomena and interactions of a molecule present in liquid or gaseous phase with a solid surface are widely used. These processes are used both in water and air purification. Activated carbons are recognized many times ago as effective materials for removing a large number of different organic substances present in air. However, the purification of water using these kinds of adsorbents has a shorter history (LeCloirec and Faur, 2006).

Now, the applications of adsorption in water and wastewater treatments, especially using activated carbon powder and granules, are increasing in order to remove a large variety of organic chemicals and some inorganic compounds that represent a health hazard.

In air treatment, activated carbon has been well known for a long time. Massive industrial production of this porous material was due to its significant utilization during wars for the protection of the individual against toxic gas. Now, filters are commonly employed to remove a large number of hazardous molecules and especially volatile organic compounds (VOC), odorous molecules or dioxins and furans present in industrial emissions. The applications are possible for a high concentration of pollutant (g m^{-3}) to diluted air (some mg or $\mu\text{g m}^{-3}$). These adsorption processes are carried out for the treatment of both industrial emissions and the domestic atmosphere. The installation design can account for an airflow between some $\text{m}^3 \text{h}^{-1}$ to $100,000 \text{ m}^3 \text{h}^{-1}$ (LeCloirec and Faur, 2006).

The most important characteristics of activated carbons in the adsorption of organic compounds are pore size distribution, surface chemistry (functionality), and mineral matter content. The adsorption capacity depends on the accessibility of the organic molecules to the microporosity which generally depends on their size (Dias *et al.*, 2007).

1.1.4.3 Sugar Beet Pulp for water treatment

In Europe, the sugar mainly comes from the sugar-beet. Its extraction leads to the production of beet pulp which is one of the main by-products of the food industry. Its production reached 33.2 millions of tons of dry matter in 2007 in the France (FOA, 2007). Its main use is incorporation in animal feeds, for which it is sold at a price around 70 €/Ton and 170 €/Ton when it is dehydrated (Chambre d'Agriculture de Champagne-Ardenne, 2008). Many studies have been carried out to find alternative uses for sugar beet pulp in order to increase its value.

During the sugar production, sugar beet pulp is left as a by-product after the extraction of sugar from beet. Because it is produced in large amount at low-cost in a reliable and constant supply, besides being utilized as animal feed, sugar beet pulp could be assumed as a peerless raw material for several purposes. An addition to its potential uses, sugar beet pulp has been evaluated as a natural sorbent and tested to remove heavy metal ions from aqueous solutions (Altundogan, 2005). Furthermore, sugar beet pulp has been investigated for making active carbon to eliminate organic compounds from aqueous media (Dursun *et al.*, 2005; Mudoga *et al.*, 2008) and ion exchanger to improve its sorption capacity.

The elemental content of sugar beet pulp is 42.6% of C, 48.4% of O and 6.3% of H and the ash content is 3.9% (Reddad, 2002). Pectic substances account for more than 40% of the dry matter of the beet pulp and are known to bind metal cations in solution because of the carboxyl function of their main component, galacturonic acid (GalA). In spite of that, few studies have been carried out on the potential use of sugar-beet pulp to entrap metals in aqueous solutions (Reddad *et al.*, 2002a; 2002b; 2003). The use of beet pulp as natural sorbent for the decontamination of industrial effluents contaminated with toxic metals may be a way to enhance its value. However, although the charge parameter in terms of dry matter may be similar to that of some synthetic resins or other natural sorbents, the hydration of beet pulp is too great to allow its direct use. (Dronnet *et al.*, 1998).

Some cellulosic agricultural waste materials may serve as cost-effective sorbents for the eliminating toxic heavy metals from industrial wastewaters. While their sorption capacity is usually less than those of synthetic sorbents, these materials could provide an inexpensive substitute for the wastewater treatment. To enhance the sorption capacity, these materials are converted into ion exchangers by modifying them with various organic compounds.

Alternatively, they could be converted into active carbons by a suitable carbonization and activation route like is the case of this work.

1.1.4.4 Peanut Hulls for water treatment

Peanut hulls are an abundant agricultural by-product in the south-eastern United States and the north of Mexico. They are plentiful, inexpensive, and a renewable resource. Previously thought of as a waste product, peanut hulls are gaining status as a useful commodity. Recently developed applications include their use in agriculture as a carrier for soil conditioning chemicals and pesticides and as filler in chicken feed. Over 70 000 tons of peanuts are produced annually in Mexico (USDA, 2008). The vast majority (over 95%) of this crop is originated in the north of the country. Peanut hulls are a waste product of this agribusiness and high quantities of hulls are produced annually.

Peanut hulls are locally available in large quantities at low price in most tropical and sub-tropical countries and have interesting physical and chemical characteristics: large specific surface area, neutral pH, large water holding capacity, nutrients for microbial growth and limited pressure drops when packed into a biofilter (Ramirez-Lopez *et al.*, 2010)

There have been some reports that peanut shells can be converted into activated carbon and used to absorb various metal ions and organic compounds using sulfuric acid as the activant (Periasamy *et al.*, 1993; Namasivayam and Periasamy, 1993); Periasamy and Namasivayam (1994, 1995a,b, 1996) reported that granular activated carbons produced from agricultural by-products, including peanut shells, by a combination of carbon dioxide or steam activation followed by air oxidation was considered an excellent adsorbent for both organic and metal pollutants. The authors found that a granular activated carbon made from peanut shells adsorbed Cd, Cu, Ni, Pb, and Zn ions to a greater extent than comparable commercial carbons.

The uptake of Cu^{2+} , Cd^{2+} , Zn^{2+} , and Pb^{2+} by peanut hulls, hull pellets, and a commercial grade ion exchange resin was investigated by Brown *et al.*, (2000) under steady state and transient rate batch conditions, in that study they found that raw peanut hulls and peanut hull pellets are effective adsorbents for metal ion removal. Though their capacity is lower than that

of the commercial grade ion-exchange resin tested, their low cost makes them an attractive option for the treatment of low-strength metal ion waste streams.

1.1.5 Adsorption on activated carbon

Adsorption arises as a result of the unsaturated and unbalanced molecular forces that are present on every solid surface. Thus, when a solid surface is brought into contact with a liquid or gas, there is an interaction between the fields of forces of the surface and that of the liquid or the gas. The solid surface tends to satisfy these residual forces by attracting and retaining on its surface the molecules, atoms, or ions of the gas or liquid. This results in a greater concentration of the gas or liquid in the near vicinity of the solid surface than in the bulk gas or vapor phase. The process by which this surface excess is caused is called adsorption. The adsorption involves two types of forces: physical forces that may be dipole moments, polarization forces, dispersive forces, or short-range repulsive interactions and chemical forces that are valency forces arising out of the redistribution of electrons between the solid surface and the adsorbed atoms (Bansal and Goyal, 2005).

Depending upon the nature of the forces involved, the adsorption is of two types: physical adsorption and chemisorption. In the case of physical adsorption, the adsorbate is bound to the surface by relatively weak van der Waals forces, which are similar to the molecular forces of cohesion and are involved in the condensation of vapors into liquids. Chemisorption, on the other hand, involves exchange or sharing of electrons between the adsorbate molecules and the surface of the adsorbent resulting in a chemical reaction. The bond formed between the adsorbate and the adsorbent is essentially a chemical bond and is thus much stronger than in the physisorption (Bansal and Goyal, 2005).

1.1.5.1 Porous structure of activated carbons

The activated carbon surface has a porous structure which generally determines its adsorption capacity, it has a chemical structure which influences the interaction with polar and nonpolar molecules, it has active sites in the form of edges, dislocations and discontinuities which determine the chemical reactions with other atoms. Thus, the adsorption

behavior of an activated carbon can not be interpreted on the basis of surface area and pore size distribution alone. Activated carbons that sometimes have a similar surface area but prepared by different methods or with different activation treatments could present different adsorption properties.

Active carbons with a random arrangement of microcrystallites and with a strong cross-linking between them have a well-developed porous structure. They have relatively low density (less than 2 gm/cm^3) and a low degree of graphitization. This porous structure formed during the carbonization process is developed further during the activation process, when the spaces between the elementary crystallites are cleared of tar and other carbonaceous material. The activation process enhances the volume and enlarges the diameters of the pores. The structure of the pores and their pore size distribution are largely determined by the nature of the raw material and the history of its carbonization. The activation also removes disorganized carbon, exposing the crystallites to the action of the activating agent and leads to the development of a microporous structure. In the latter phase of the reaction, the widening of existing pores and the formation of large pores by burnout of the walls between the adjacent pores also takes place. This causes an increase in the transitional porosity and macroporosity, resulting in a decrease in the micropore volume (Bansal and Goyal, 2005).

Micropores have molecular dimensions, the effective radii being less than 2 nm. The adsorption in these pores occurs through volume filling, and there is no capillary condensation taking place. The adsorption energy in these pores is much larger compared to larger mesopores or to the nonporous surface because of the overlapping of adsorption forces from the opposite walls of the micropores. They generally have a pore volume of 0.15 to $0.70 \text{ cm}^3 \text{ g}^{-1}$. Their specific surface area constitutes about 95% of the total surface area of the active carbon. Dubinin (1979) further suggested that for some active carbons, the microporous structure can be subdivided into two overlapping microporous structures involving specific micropores with effective pore radii smaller than 0.6 to 0.7 nm and the super micropores showing radii of 0.7 to 1.6 nm. The micropore structure of active carbons is largely characterized by the adsorption of gases and vapors and, to a smaller extent, by small-angle x-ray scattering technique.

Mesopores, also called *transitional pores*, have effective dimensions in the 2 to 50 nm range, and their volume usually varies between 0.1 and $0.2 \text{ cm}^3 \text{ g}^{-1}$. The surface area of these

pores does not exceed 5% of the total surface area of the carbon. However, by using special methods, it is possible to prepare activated carbons that have an enhanced mesoporosity. In this case the mesopores volume could attain from 0.2 to 0.65 cm³g⁻¹ and their surface area reaching as high as 200 cm²g. These pores are characterized by capillary condensation of the adsorbent with the formation of a meniscus of the liquefied adsorbate (Bansal and Goyal, 2005).

The adsorbent properties of activated carbons are essentially attributed to their large interparticulate surface area, universal adsorption effect, high adsorption capacity, a high degree of surface reactivity and a favorable pore size which makes the internal surface accessible and enhances the adsorption rate. Most of the adsorption on active carbons takes place in micropores and only small amount in mesopores. The macropores (more than 50 nm) acts only as conduits for the passage of the adsorbate into the interior mesopores and the micropore surface. The pore size distribution in a given carbon depends on the type of the raw material and the method and conditions under which the carbon has been prepared.

1.1.6 Kinetic sorption models

Several steps can be used to express the mechanism of solute sorption onto a sorbent. In order to investigate the mechanism of sorption, the constants of sorption and intraparticle diffusion of pollutants were determined using equations of Lagergren or pseudo-first order (1898), a pseudo-second order (Ho and McKay, 1998a; 1998b) and diffusion models.

1.1.6.1 Pseudo-first order kinetic model

The sorption kinetics may be described by a pseudo-first order (Lagergren, 1898). The differential equation is the following (McKay *et al.*, 1999):

$$\frac{dq_t}{dt} = k_1(q_1 - q_t) \quad (1.1)$$

Integrating equation (1.1) for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, gives:

$$\ln \left[\frac{q_e - q_t}{q_e} \right] = -k_1 t \quad (1.2)$$

which is the integrated rate law for a pseudo-first order reaction, where:

q_e is the amount of dye sorbed at equilibrium, mg g^{-1} ;

q_t is the amount of dye sorbed at time t , mg g^{-1} ;

k_1 is the equilibrium rate constant of pseudo-first sorption, min^{-1} .

In order to obtain the rate constants, the straight line plots of $\ln(q_e - q_t)$ against t for different contaminants and different carbonaceous materials have been analyzed. The rate constant, k_1 , and correlation coefficients, R^2 , values of the adsorbates under different conditions were calculated from these plots.

1.1.6.2 Pseudo-second order kinetic model

The sorption kinetics may be described by a pseudo-second order model. The differential equation is the following:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (1.3)$$

Integrating equation (1.3) for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \quad (1.4)$$

which is the integrated rate law for a pseudo-second order reaction, where:

q_e is the amount of dyes sorbed at equilibrium, mg g^{-1} ;

k is the equilibrium rate constant of pseudo-second order sorption, $\text{g mg}^{-1} \text{min}^{-1}$.

Equation (1.4) can be rearranged to obtain a linear form:

$$\frac{1}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t \quad (1.5)$$

and

$$h = kq_e^2 \quad (1.6)$$

where:

h is the initial sorption rate, $\text{mg g}^{-1}\text{min}^{-1}$.

The straight line plots of t/q_t against t have also been tested to obtain rate parameters. The k , q_2 and correlation coefficients, R^2 , values of adsorbates under different conditions were calculated from these plots (Ho and McKay, 1998a).

1.1.7 Diffusion models

In aqueous solution, interactions between organic compounds and hydrophobic surfaces are dominated by relatively weak dispersion forces (Franz *et al.*, 2000; Li *et al.*, 2002), and the adsorption can be considered reversible. In contrast, arsenate interactions with iron oxides are dominated by the formation of strong inner-sphere complexes and to a lesser extent by weaker ion exchange reactions (Goldberg and Johnston, 2001). However, mass transport processes may be similar for porous metal oxides and activated carbons. Therefore, it is proposed that arsenate adsorption on granular porous metal oxides involves a sequential progression through four steps: diffusion through the bulk liquid, film diffusion, intraparticle diffusion, and adsorption on the solid surface. Generally, the bulk liquid diffusion and adsorption steps are rapid and thus not rate-limiting. Contaminant flux through the stagnant film surrounding the adsorbent particle is directly proportional to the linear concentration gradient across the film and the film mass transfer coefficient (k_f). The magnitude of k_f is affected by the packed-bed hydraulics and the adsorbent particle size. Intraparticle diffusion may be within the pore space (i.e., pore diffusion) or along the adsorbent surface within the pores (i.e., surface diffusion) (Badruzzaman *et al.*, 2004).

1.1.7.1 Intraparticle diffusion

Regarding intraparticle diffusion, studies evaluating the adsorption of organic compounds by activated carbon showed that surface diffusion typically dominates over pore diffusion. The adsorption of metal cations by amorphous iron oxide has also been described with a surface diffusion model (Axe and Trivedi, 2002).

Theoretical treatments of intraparticle diffusion yield rather complex mathematical relationships which differ in form as functions of the geometry of the sorbent particle. A functional relationship common to most treatments of intraparticle diffusion is that uptake varies almost proportionately with the half power of time, $t^{0.5}$, rather than t ; nearly linear variation of the quantity sorbed with $t^{0.5}$ is predicted for a large initial fraction of reactions controlled by rates of intraparticle diffusion. Good linearization of the data is observed for the initial phase of the reaction in accordance with expected behavior if intraparticle diffusion is the rate-limiting step (Ho and Mc Kay, 1998a).

The intraparticle diffusion equation is the following (Morris and Weber, 1962):

$$q_t = k_i t^{0.5} \quad (1.7)$$

where:

k_i is the intraparticle diffusion rate constant, $\text{mg g}^{-1}\text{min}^{-0.5}$.

The k_i values for different materials can be calculated from the slopes of the straight line portions of the respective plots.

1.1.8 Sorption models and sorption capacity

1.1.8.1 Adsorption on a solid surface

The most common difference between the two kinds of adsorption (physical or chemical) is in the magnitude of the heat of adsorption. In the case of physical adsorption, the heat of adsorption is of the same order as the heat of condensation and does not usually

exceed 10 to 20 kJ per mole. By other in chemisorption the heat of adsorption is usually 40 to 400 kJ per mole. It may, however, be mentioned that in some cases the heat of chemisorption does not differ substantially from the heat of physical adsorption. Physisorption does not require any activation energy so that the rate of adsorption is very high, even at low temperatures. The chemisorption, on the other hand, requires activation energy; the rate of adsorption is low and depends upon the temperature. However, when the surface of the adsorbent is very reactive, as in the case of ultraclean carbon surfaces, the rate of chemisorption can be very high, even at low temperatures. Similarly, physisorption in microporous adsorbents may be very much retarded by the slow diffusion of the adsorbate into the fine pores and may require activation energy. Physical adsorption is nonspecific and occurs between any adsorbate-adsorbent system, while chemisorption is specific (Bansal and Goyal, 2005).

1.1.8.2 Adsorption isotherm equations

The adsorption isotherm is the most extensively employed method for representing the equilibrium states of an adsorption system. It can give useful information regarding the adsorbate, the adsorbent, and the adsorption process. It helps in the determination of the surface area of the adsorbent, the volume of the pores, and their size distribution, the heat of adsorption, and the relative absorbability of a gas or a vapor on a given adsorbent. Several adsorption isotherm equations have been derived. The more important adsorption isotherms are the Langmuir, the Freundlich, the Temkin, the Brunauer-Emmett-Teller (BET), and the Dubinin equations. The first three isotherm equations are very important for chemisorption, although the Langmuir and Freundlich isotherms are equally important for physisorption. The BET equation and Dubinin equations are most important for analysis of the physical adsorption of gases and vapors on porous carbons (Bansal and Goyal, 2005).

The isotherm equation can be obtained by equating this ratio to the corresponding ratio of concentrations; this approach has the advantage that it gives numerical value to the constants that cannot be evaluated by the kinetic approach. The equilibrium can also be approached thermodynamically, using either the conditions that the work done in transferring an infinitesimal amount of gas from the gas phase to the surface at constant temperature (Bansal and Goyal, 2005).

1.1.8.3 Langmuir isotherm equation

The Langmuir isotherm equation is the first theoretically developed adsorption isotherm. Many of the equations proposed later and which fit the experimental results over a wide range are either based on this equation, or these equations have been developed using the Langmuir concept. Thus, the Langmuir equation still retains an important position in physisorption as well as chemisorption theories. The equation has also been derived using thermodynamic and statistical approaches but we shall discuss the commonly used kinetic approach for its derivation. The American scientist I. Langmuir (1918) derived this equation based on certain assumptions. More important of these assumptions are:

- The adsorbed entities (atoms or molecules or ions) are attached to the surface at definite localized sites.
- Each site accommodates one and only one adsorbed entity.
- The energy state of each adsorbed entity is the same at all sites on the surface independent of the presence or absence of other adsorbed entities at neighboring sites. Thus, the Langmuir model (also called localized model) assumes that the surface is perfectly smooth and homogenous and that the lateral interactions between the adsorbed entities are negligible (Bansal and Goyal, 2005).

The Langmuir equation is represented by:

$$q_e = \frac{q_m b_L C_e}{1 + b_L C_e} \quad (1.8)$$

were:

q_e = amount of sorbate per unit mass of adsorbent ($\mu\text{g g}^{-1}$),

C_e = equilibrium solute concentration in solution ($\mu\text{g L}^{-1}$),

b_L = Langmuir constant ($\text{L } \mu\text{g}^{-1}$),

In Langmuir model, monolayer coverage represents maximum coverage, adsorption is reversible, no local movement of adsorbed species, and adsorption energy is independent of surface coverage (Ahuja, 2009).

1.1.8.4 Freundlich adsorption isotherm

The Freundlich isotherm is a limiting form of the Langmuir isotherm, and is applicable only in the middle ranges of vapor pressures.

In the middle ranges of pressure, the heterogeneity factor is represented by the reciprocal of n , which will tend to vary between zero and unity, the more the surface is heterogeneous, the closer to zero value of $1/n$ is (Ahuja, 2009). This can be expressed by a general form of the adsorption equation.

$$q_e = K_F C_e^n \quad (1.9)$$

This is known as the *Freundlich equation*, which is followed only at medium pressures. The equation is of greater significance for chemisorption although some physical adsorption have also been explained using this equation.

where C_e is the equilibrium concentration and q_e is the amount adsorbed per unit mass of the adsorbent. The constant n is the Freundlich equation constant that represents the parameter characterizing quasi-Gaussian energetic heterogeneity of the adsorption surface. (Bansal and Goyal, 2005).

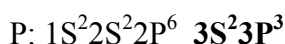
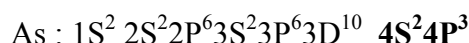
Freundlich is an empirical model and it does not predict sorption maximum. Single K_F indicates adsorption energy is independent of surface coverage (Freundlich, 1906). Multiple slopes should not be over-interpreted. n can represent also the adsorption equilibrium constant whose reciprocal ($1/n$) is the indicative of adsorption intensity. Sorption is non linear if n is significantly lower or higher than one. If n is less than one, sorption decreases with increasing aqueous concentration, and if n is greater than one, sorption increases with increasing aqueous concentration (Ter Laak *et al.*, 2006).

1.2 ARSENIC CONTAMINATION AND TREATMENT PROCESS

Arsenic's history in science, medicine and technology has been overshadowed by its notoriety as a poison. Arsenic is viewed as being synonymous with toxicity. Dangerous arsenic concentrations in natural waters are now a worldwide problem and often referred to as a 20th–21st century calamity. High arsenic concentrations have been reported recently from the USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, Japan and India (Mohan and Pittman, 2007).

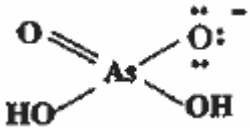
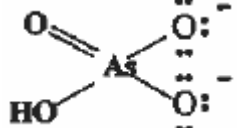
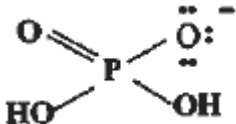
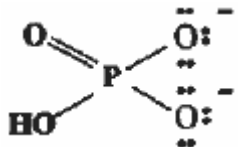
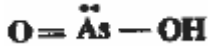
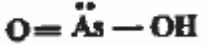
1.2.1 Arsenic – Chemical Characteristics

Arsenic is a semimetal or metalloid that is stable in several oxidation states (-III, 0, +III, +V). It is a natural constituent of Earth's crust and ranks 20th in abundance in relation to the other elements. It is located in Group VB (or new 15) of the periodic table along with nitrogen, phosphorous, antimony and bismuth. Unlike phosphorous, which is an essential nutrient for all living creatures, arsenic has attained notoriety primarily as a highly toxic and poisonous element. Nevertheless their chemistries characteristics are similar in several ways. The electronic configurations of As and P are as follows:



Identical outer electronic configurations (numbers in bold) result in similar chemical behaviors for many As and P compounds, especially in the +V oxidation states. The Table 1.2 summarizes a few such similarities between As (V) and P (V) oxyacids and the ligand properties of their conjugate oxyanions. For comparison, As (III) oxyacid is also included in the same table. Due to their near-identical ligand properties, phosphate solutions are often used to displace arsenates sorbed onto hydrous oxydes (Manning and Goldberg, 1997; Manning *et al.*, 1998).

Table 1.2 Oxyacids conjugate anions of As (V) and P (V).

Parent Oxyacid	pK_a Values	Predominant dissolved species at pH 5.5	Predominant dissolved species at pH 8.5
As(V) : H_3AsO_4	$pK_{a1} = 2.2$ $pK_{a2} = 6.98$ $pK_{a3} = 11.6$	 Monovalent monodentate ligand	 Divalent bidentate ligand
P(V) : H_3PO_4	$pK_{a1} = 2.12$ $pK_{a2} = 7.21$ $pK_{a3} = 12.70$	 Monovalent monodentate ligand	 Divalent bidentate ligand
As(III) : $HAsO_2$	$pK_{a1} = 9.2$	 Nonionized monodentated ligand	 Nonionized monodentated ligand

Redox potential (Eh) and pH are the most important factors controlling As speciation. Under oxidizing conditions, $H_2AsO_4^-$ is dominant at low pH (less than about pH 6.9), whilst at higher pH, $HAsO_4^{2-}$ becomes dominant (H_3AsO_4 and AsO_4^{3-} may be present in extremely acidic and alkaline conditions respectively). Under reducing conditions at pH less than about pH 9.2, the uncharged arsenite species H_3AsO_3 will predominate (Figure 1.6; Smedley and Kinniburgh, 2002).

The distributions of the species in solution as a function of pH are given in Figure 1.7 In practice, most studies in the literature report speciation data without consideration of the degree of protonation. In the presence of extremely high concentrations of reduced Sulphur, dissolved As-sulphide species can be significant. Reducing, acidic conditions favour precipitation of orpiment (As_2S_3), realgar (AsS) or other sulphide minerals containing

coprecipitated arsenic. Therefore high-arsenic concentrations in waters are not expected where there is a high concentration of free sulphide.

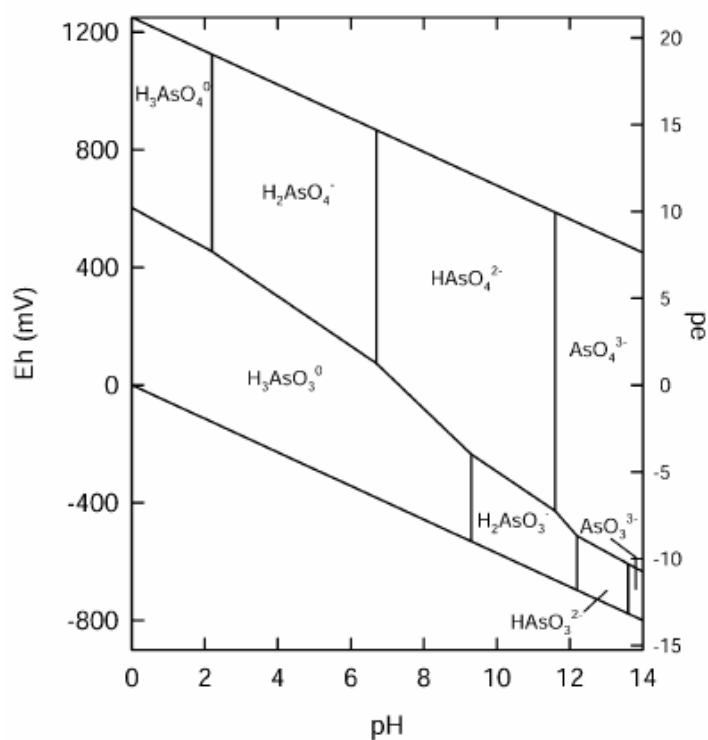
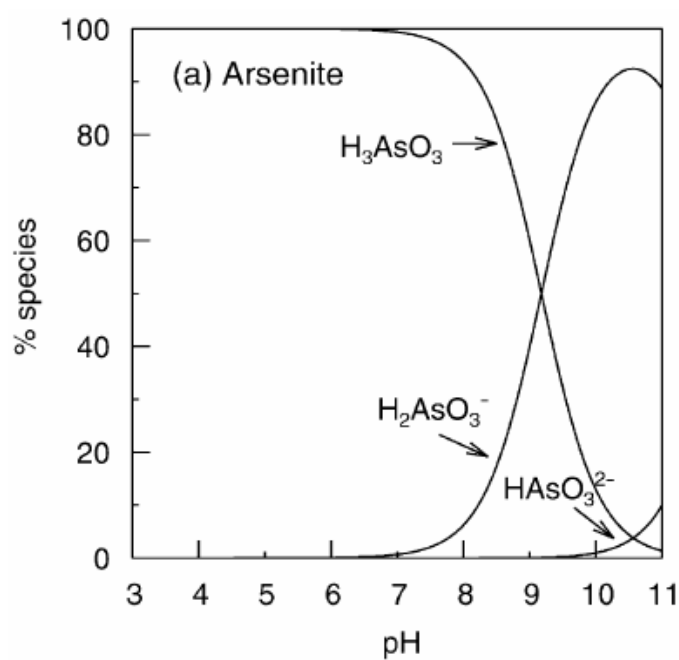


Figure 1.6 - Eh-pH diagram for aqueous As species in the system As–O₂–H₂O at 25 °C and 1 bar total pressure (Smedley and Kinniburgh, 2002).



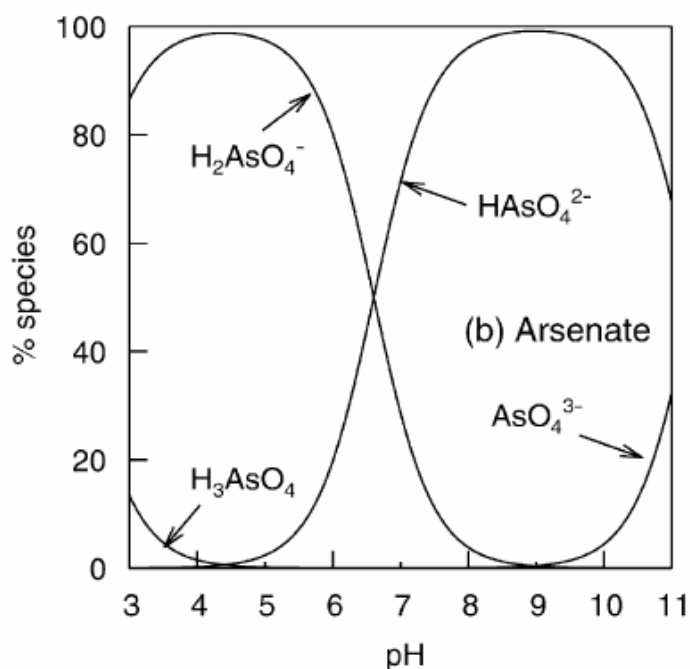


Figure 1.7. (a) Arsenite and (b) arsenate speciation as a function of pH (ionic strength of about 0.01M). Redox conditions have been chosen such that the indicated oxidation state dominates the speciation in both cases (Smedley and Kinniburgh, 2002).

1.2.2 Arsenic in the environment

Table 1.3 shows arsenic concentrations in various environmental media. It should be noted that the +III and +V states are most common in natural systems. Arsine(-III), a compound with extremely high toxicity, can be formed under high reducing conditions, but its occurrence in gases emanating from anaerobic environments in nature is relatively rare (Ahuja, 2009).

Concentrations of arsenic in fresh water vary by more than four orders of magnitude depending on the source of arsenic, the amount available and the local geochemical environment. Under natural conditions, the greatest range and the highest concentrations of arsenic are found in groundwater as a result of the strong influence of water-rock interactions and the greater tendency in aquifers for the physical and geochemical conditions to be favorable for arsenic mobilization and accumulation. The range of concentrations for many water bodies is large and hence ‘typical’ values are difficult to derive. Many studies of arsenic reported in the literature have also preferentially targeted known problem areas and hence

reported ranges are often extreme and unrepresentative of natural waters as a whole (Mohan and Pittman, 2007).

Table 1.3 Arsenic Concentrations in Environmental Media (U.S. EPA) (Ahuja, 2009).

Environmental Media	Range of Arsenic Concentrations
Air (ng/m ³)	1.5–53
Rain from unpolluted ocean air (µg/L) (ppb)	0.019
Rain from terrestrial air (mg/L)	0.46
Rivers (µg/L)	0.20–264
Lakes (µg/L)	0.38–1,000
Groundwater (well) (µg/L)	1.0–1,000
Seawater (µg/L)	0.15–6.0
Soil (mg/kg)	0.1–1,000
Stream/river sediment (mg/kg)	5.0–4,000
Lake sediment (mg/kg)	2.0–300
Igneous rock (mg/kg)	0.3–113
Metamorphic rock (mg/kg)	0.0–143
Sedimentary rock (mg/kg)	0.1–490

A number of large aquifers in various parts of the world have been identified with problems from arsenic occurring at concentrations above 50 µg.L⁻¹ (Table 1.4). The most noteworthy occurrences are in parts of Argentina, Bangladesh, Chile, China, Hungary, India (West Bengal), Mexico, Romania, Taiwan, Vietnam and many parts of the USA (Fig. 1.8). Recent reconnaissance surveys of groundwater quality in other areas such as parts of Nepal, Myanmar and Cambodia have also revealed concentrations of arsenic in some sources exceeding 50 µg.L⁻¹, although documentation of the affected aquifers is so far limited.

Table 1.4 Occurring As concentrations in waters around the world (from Smedley and Kinniburgh, 2002).

Country/Region	Concentration ($\mu\text{g.L}^{-1}$)	Aquifer type
Bangladesh	< 0.5–2500	Holocene alluvial/deltaic sediments.
Taiwan	10–1820	Sediments, including black shale.
Mongolia	< 1–2400	Holocene alluvial and lacustrine sediments.
Hungary, Romania	< 2–176	Quaternary alluvial plain.
Argentina	< 1–5300	Holocene and earlier loess with rhyolitic volcanic ash.
Chile	100–1000	Quaternary volcanogenic sediment.
USA	up to 2600	Holocene mixed aeolian, alluvial, lacustrine sediments, some thin volcanic ash bands.
Mexico	8–620	Volcanic sediments.
Greece	up to 10000	Mine tailings.
Germany	< 10–150	Triassic Keuper Sandstone with mineralisation.

Arsenic associated with geothermal waters has also been reported in several areas, including hot springs from parts of Argentina, Japan, New Zealand, Chile, Kamchatka, Iceland, France, Dominica and the USA. Localized groundwater arsenic problems are now being reported from an increasing number of countries and many new cases are likely to be discovered. Until recently, arsenic was not traditionally on the list of elements routinely tested by water-quality testing laboratories and so many high-arsenic water sources may have been missed. Revision of drinking-water regulations and guidelines for arsenic has prompted a reassessment of the situation in many countries. The recent discovery of arsenic enrichment

on a large scale in Bangladesh has highlighted the need for a rapid assessment of the situation in alluvial aquifers worldwide.

As described above, arsenic problems also occur in some areas where sulphide mining activity is prevalent, the arsenic being released from sulphide minerals as they are oxidized as a result of mining operations. In mining areas, arsenic problems can be severe with concentrations, in affected waters, sometimes being in the mg.L^{-1} range. However, unlike arsenic occurrences in major aquifers, the problems in these areas are typically localized, rather than of widespread occurrence. Mining related arsenic problems in water have been identified in many parts of the world, including Ghana, Greece, Thailand and the USA (Figure 1.8). While high-arsenic groundwater (with arsenic above drinking- water standards) are not uncommon, they are by no means typical of most aquifers and only exist under special circumstances. These relate to both the geochemical environment and to the past and present hydrogeology (Smedley and Kinniburgh, 2002).



Figure 1.8 - Distribution of documented world problems with As in groundwater in major aquifers as well as water and environmental problems related to mining and geothermal sources. Areas in blue are lakes (Smedley and Kinniburgh, 2002).

1.2.3 Pollution sources

Until recently, it was generally believed that arsenic is released in the soil as a result of weathering of the arsenopyrite or other primary sulfide minerals.

Important factors controlling the oxidation–reduction phenomenon of arsenopyrite weathering are listed as follows:

- Moisture (hydrolysis)
- pH
- Temperature
- Solubility
- Redox characteristics of the species
- Reactivity of the species with CO₂/H₂O

It has been reported that weathering of arsenopyrite in the presence of oxygen and water involves oxidation of S to SO₄²⁻ and As(III) to As(V):



Although there are both natural and anthropogenic inputs of arsenic to the environment, elevated arsenic concentrations in groundwater are often due to naturally occurring arsenic deposits. While the average abundance of arsenic in Earth's crust is between 2 and 5 mg kg⁻¹, enrichment in igneous and sedimentary rocks, such as shale and coal deposits, is not uncommon. Arsenic-containing pyrite (FeS) is probably the most common mineral source of arsenic, although it is often found associated with more weathered phases. Mine tailings can contain substantial amounts of arsenic, and the weathering of these deposits can liberate arsenic into the surface water or groundwater, where numerous chemical and biological transformations can take place. Arsenic may also be directly released into the aquatic environment through geothermal water such as hot springs. Anthropogenic sources of arsenic include pesticide application, coal fly ash, smelting slag, feed additives, semiconductor chips, and arsenic-treated wood, which can cause local water contamination (Ahujan, 2009).

1.2.4 Toxicity

Arsenic contamination in natural water is a worldwide problem and has become an important issue and challenge for the world engineers, scientists and even the policy makers. For example, chronic arsenic toxicity due to drinking arsenic-contaminated water has been one of the worst environmental health hazards affecting many water sources around the world.

Arsenic is a well-known poison, with a lethal dose in humans at about $1\text{--}3\text{ mg kg}^{-1}\text{ d}^{-1}$ (Kim *et al.*, 2004). Most of the ingested arsenic is excreted from the body through urine, stools, skin, hair, nails, and breath. In cases of excessive intake, some arsenic is deposited in tissues, causing the inhibition of cellular enzyme activities. In addition to consumption through drinking water, arsenic may also be taken up via the food chain. Direct consumption of rice irrigated with arsenic-rich waters is a significant source of arsenic exposure in areas such as Bangladesh and other countries where rice is the staple food and provides the main caloric intake (Ahuja, 2009).

The relative toxicity of arsenic depends mainly on its chemical form and is dictated in part by the valence state. Trivalent arsenic has a high affinity for thiol groups, as it readily forms kinetically stable bonds to sulfur. Hence, reaction with As(III) induces enzyme inactivation, as thiol groups are important to the functions of many enzymes. Arsenic affects the respiratory system by binding to the vicinal thiols in pyruvate dehydrogenase and 2-oxoglutarate dehydrogenase, and it has also been found to affect the function of glucocorticoid receptors. Pentavalent arsenic has a poor affinity toward thiol groups, resulting in more rapid excretion from the body. However, it is a molecular analog of phosphate and can uncouple mitochondrial oxidative phosphorylation, resulting in failure of the energy metabolism system. The effects of the oxidation state on chronic toxicity are confounded by the redox conversion of As(III) and As(V) within human cells and tissues. Methylated arsenicals such as monomethylarsenic acid (MMAA) and dimethylarsenic acid (DMAA) are less harmful than inorganic arsenic compounds (Ahuja, 2009).

Jain and Ali (2000) reported comprehensively on the occurrence and toxicity of arsenic. The toxicology of arsenic is a complex phenomenon and generally classified into acute and sub-acute types. The acute arsenic poisoning requiring prompt medical attention usually occurs through ingestion of contaminated food or drink. The major early manifestation due to

acute arsenic poisoning includes burning and dryness of the mouth and throat, dysphasia, colicky abdominal pain, projectile vomiting, profuse diarrhea, and hematuria. The muscular cramps, facial edema and cardiac abnormalities, shock can develop rapidly as a result of dehydration. Clinical symptoms of arsenicosis may take about 6–24 months or more to appear, depending on the quantity of arsenic ingested and also on the nutritional status and immunity level of the individual. Untreated arsenic poisoning results in several stages; for example, various effects on the skin with melanosis and keratosis; dark spots on the chest, back, limbs, and gums; enlargement of the liver, kidneys, and spleen. Later on, patients may develop nephropathy, hepatopathy, gangrene, or cancers of the skin, lung, or bladder.

Choong *et al.* (2007), have been reported that in general, there are four recognized stages of arsenicosis, or chronic arsenic poisoning:

Preclinical: the patient shows no symptoms, but arsenic can be detected in urine or body tissue samples.

Clinical: various effects can be seen on the skin at this stage. Darkening of the skin (melanosis) is the most common symptom, often observed on the palms. Dark spots on the chest, back, limbs or gums have also been reported. Oedema (swelling of hands and feet) is often seen. A more serious symptom is keratosis, or hardening of skin into nodules, often on palms and soles. WHO estimates that this stage requires 5–10 years of exposure to arsenic.

Complications: clinical symptoms become more pronounced and internal organ are affected. Enlargement of liver, kidneys and spleen have been reported. Some research indicates that conjunctivitis (pinkeye), bronchitis and diabetes may be linked to arsenic exposure at this stage.

Malignancy: tumors or cancers (carcinoma) affect skin or other organs. The affected person may develop gangrene or skin, lung or bladder cancer.

Choong *et al.* (2007) has been realized an overview about arsenic toxicity and health hazards and shown that the results of clinical findings for arsenic poisoning from drinking arsenic contaminated water show the presence of almost all the stages of arsenic clinical manifestation. Diseases caused by arsenic poisoning are no longer news but reported worldwide.

Arsenic toxicity has no known effective treatment, but drinking of arsenic free water can help the arsenic-affected people who are at the preliminary stage of their illness alleviate the symptoms of arsenic toxicity. Hence, provision of arsenic-free water is urgently needed for the mitigation of arsenic toxicity and the protection of the health and well-being of people living in the areas of these countries where the arsenic problem is acute (Ahuja, 2009).

1.2.5 International legislation for arsenic concentration in water

Following the accumulation of evidence for the chronic toxicological effects of arsenic in drinking water, recommended and regulatory limits of many authorities are being reduced. The WHO guideline value for As in drinking water was provisionally reduced in 1993 from 50 to 10 $\mu\text{g L}^{-1}$. The new recommended value was based on the increasing awareness of the toxicity of arsenic, particularly its carcinogenicity, and on the ability to measure it quantitatively (WHO, 1993). If the standard basis for risk assessment applied to industrial chemicals were applied to arsenic, the maximum permissible concentration would be lower still. The maximum admissible concentration (MAC) for arsenic in drinking water has been reduced to 10 $\mu\text{g.L}^{-1}$. The Japanese, Canadian and European limit for drinking water is also 10 $\mu\text{g L}^{-1}$ while the interim maximum acceptable concentration for Mexican (NOM, 2000) drinking water is 25 $\mu\text{g.L}^{-1}$. The US-EPA limit was also reduced from 50 to 10 $\mu\text{g.L}^{-1}$ in January 2001 following prolonged debate over the most appropriate limit. However, this rule is now (September 2001) being reconsidered given the high cost implications to the US water industry, estimated at \$200 million per year. Whilst many national authorities are seeking to reduce their limits in line with the WHO guideline value, many countries and indeed all affected developing countries, still operate at present to the 50 $\mu\text{g.L}^{-1}$ standard, in part because of lack of adequate testing facilities for lower concentrations. Until recently, arsenic was often not on the list of constituents in drinking water routinely analyzed by national laboratories, water utilities and non-governmental organizations (NGOs) and so, the body of information about the distribution of arsenic in drinking water is not as well known as for many other drinking-water constituents. In recent years, it has become apparent that both the WHO guideline value and current national standards are quite frequently exceeded in drinking water sources, and often unexpectedly so. Indeed, As and F are now recognized as the most serious inorganic contaminants in drinking water on a worldwide basis. In areas of high arsenic

concentrations, drinking water provides a potentially major source of arsenic in the diet and so its early detection is of considerable importance (Smedley and Kinniburgh, 2002).

By other, in France between the year 2007 and 2013 the maximum acceptable concentration of arsenic in water will be reduced in 30% according to the national plan of health and environment that establishes the reduction in the emissions of six priorities aqueous and atmospheric substances: benzene, APH, PCB, dioxins, arsenic, mercury and chloride solvents. (Grenelle Environnement, 2009).

1.2.6 Main arsenic removal technologies

A large number of approaches have been investigated for removing arsenic from drinking water. Several useful reviews of the techniques for removing arsenic from water supplies have been published (Bissen and Frimmel, 2003a,b; Ng *et al.*, 2004; Daus *et al.*, 2004; Thirunavukkarasu *et al.*, 2003). Various existing nowadays arsenic removal technologies are listed below:

- Coagulation with ferric chloride, alum, or natural products
- Sorption on activated alumina
- Sorption on iron oxide-coated sand particles
- Granulated iron oxide particles
- Polymeric ligand exchange
- Nanomagnetite particles
- Sand with zero valent iron
- Hybrid cation-exchange resins
- Hybrid anion-exchange resins
- Polymeric anion exchange
- Reverse osmosis

Arsenic removal technologies were also reviewed by Mohan and Pittman (2007) and they made a comparison between the major arsenic removal technologies (Table 1.5).

Most remediation methods discussed are more effectively for removing arsenic from water containing high initial arsenic concentrations (usually >100 mg/L). But residual arsenic concentrations exceed the 0.05 mg/L water quality standard used in most countries. In villages in India and Bangladesh, a highly successful technology may not succeed in rural areas unless it fits into the rural circumstances and is well accepted by the masses. Technology development is only possible when a partnership exists involving proper village level participation. Arsenic removal technologies all suffer from one or more drawbacks, limitations and scope of application (Mohan and Pittman 2007, Table 1.5).

Table 1.5. Comparison of main arsenic removal technologies (Adapted from Mohan and Pittman, 2007).

Arsenic removal technologies	Advantages	Disadvantages
<i>Oxidation/precipitation:</i>		
Air oxidation	Relatively simple, low-cost but slow process; <i>in situ</i> arsenic removal; also oxidizes other inorganic and organic constituents in water	Mainly removes arsenic(V) and accelerate the oxidation process
Chemical oxidation	Oxidizes other impurities and kills microbes; relatively simple and rapid process; minimum residual mass	Efficient control of the pH and oxidation step is needed
<i>Coagulation/electrocoagulation/coprecipitation:</i>		
Alum coagulation	Durable powder chemicals are available; relatively low capital cost and simple in operation; effective over a wider range of pH	Produces toxic sludges; low removal of arsenic; pre-oxidation may be required
Iron coagulation	Common chemicals are available; more efficient than alum coagulation on weigh basis	Medium removal of As(III); sedimentation and filtration needed
Lime softening	Chemicals are available commercially	Readjustment of pH is required

Table 1.5 (*Continued*) Comparison of main arsenic removal technologies (Adapted from Mohan and Pittman, 2007).

Arsenic removal technologies	Advantages	Disadvantages
<i>Sorption and ion-exchange techniques</i>		
Activated alumina	Relatively well known and commercially available.	Needs replacement after four to five regeneration
Iron coated sand	Cheap; no regeneration is required; remove both As(III) and As(V)	Not standardized; produces toxic solid waste
Ion-exchange resin	Well-defined medium and capacity; pH independent; exclusive ion specific resin to remove arsenic	High cost medium; high-tech operation and maintenance; regeneration creates a sludge disposal problem; As(III) is difficult to remove; life of resins
Activated carbon	Porous structure and high surface areas. AC are available commercially	The adsorption of metal ions on carbon is more complex than uptake of organic compounds because ionic charges affect removal kinetics from solution. Commercial AC is expensive
<i>Membrane techniques:</i>		
Nanofiltration	Well-defined and high-removal efficiency	Very high-capital and running cost, pre-conditioning; high water rejection
Reverse osmosis	No toxic solid waste is produced	High tech operation and maintenance
Electrodialysis	Capable of removal of other contaminants	Toxic wastewater produced

1.2.7 Arsenic remediation by adsorption

In this technique arsenic species are attached on the surface of the adsorbent by physical as well as chemical forces. The active surface area of adsorbent, its surface energy and the pH of the solution highly influence the removal efficiency. The most used adsorbents are iron oxide, granular ferric hydroxide, activated alumina, activated carbon, greensand (KMnO₄ coated gluconite), copper-zinc granules, etc. (Mondal *et al.*, 2006; 2007a; Deschamps *et al.*,

2005). Moreover, Yadanaparthi *et al.* (2009) have been reported a broad view of adsorbents that have been identified for use in cadmium, arsenic and lead removal from waters and a variety of materials have been surveyed, with emphasis on those that are inexpensive and available at various locations around the world (Altundogan, 2002).

1.2.7.1 Biosorption

Biosorption is capable of removing traces of heavy metals and other elements from dilute aqueous solutions. Algae, fungi and bacteria are examples of biomass-derived sorbents for several metals. Such sorbents have produced encouraging results. Biosorption (or bioadsorption) is a passive immobilization of metals by biomass (Pokhrel and Viraraghavan, 2006; 2007). Mechanisms of cell surface sorption are independent of cell metabolism; they are based upon physicochemical interactions between metal and functional groups of the cell wall. The microorganism's cell wall mainly consists of polysaccharides, lipids and proteins, which have many binding sites for metals (Mohan and Pittman, 2007).

A range of equilibrium sorption models, and diffusion and sorption models in different reactor systems were reviewed to correlate fungal biosorption experimental data. Fungi are used in many industrial fermentation processes, which could serve as an economical source of biosorbent for arsenic removal. Fungi can also be easily grown in substantial amounts using unsophisticated fermentation techniques and inexpensive growth media. Lignin has also been used for the metal ions remediation (Mohan *et al.*, 2006b).

Arsenic and other metal ion adsorption on chitosan (Gérente *et al.*, 2010), chitin and biomass from *Rhizopus oryzae* (Mc Caffee *et al.*, 2001) have been studied. Dambies *et al.* (2000) studied the sorption of As(V) on molybdate-impregnated chitosan gel beads. The sorption capacity of raw chitosan for arsenic(V) was increased by impregnation with molybdate. The optimum pH for arsenic uptake was close to pH 3. Arsenic sorption was followed by the release of molybdenum. This can be decreased by a pretreatment with phosphoric acid to remove the labile part of the molybdenum. The As sorption capacity, over molybdenum loading, was almost 200 mg As.g⁻¹ Mo. The exhausted sorbent regenerated by phosphoric acid desorption. Three sorption/desorption cycles were conducted with only a small decrease in sorption capacity.

Chitosan powder derived from shrimp shells, was converted into bead form and used to remove As(III) and As(V) from water in both batch and continuous operations (Chen and Chung, 2006). Furthermore, wastewater containing arsenic discharged from the manufacturing of gallium arsenide (GaAs) supports was also treated in a continuous operation. The optimal pH value for As(III) and As(V) removal was near 5. Adsorption capacities of 1.83 and 1.94 mg As.g⁻¹ bead for As(III) and As(V), respectively, were obtained. Ion coexistence below 50 mg.L⁻¹ did not affect arsenic removal.

Raw agricultural waste or by-products such as rice husks were used for arsenic removal from water. Maximum adsorption occurred at 0.01 mol.L⁻¹ of HNO₃, HCl, H₂SO₄ or HClO₄ using 1.0 g of adsorbent for 5.97×10⁻³ mol.L⁻¹ of arsenic for 5 min. The Freundlich isotherm was followed over concentration range from 8.69×10⁻⁵ to 1.73×10⁻³ mol.L⁻¹ arsenic (1/n = 0.83 and K= 4.43 mmol.g⁻¹). Untreated rice husk was utilized for aqueous arsenic remediation (Amin *et al.*, 2006). Complete removal (using rice husk columns) of both As(III) and As(V) was achieved under the following conditions: initial As concentration, 100 µg.L⁻¹; rice husk amount, 6 g; average particle size, 780 and 510 µm; flowrate, 6.7 and 1.7 mL.min⁻¹; and pH, 6.5 and 6.0, respectively. Desorption (71–96%) was also achieved with 1M of KOH.

1.2.7.2 Activated carbons for arsenic removal

1.2.7.2.1 Commercial activated carbons

Activated carbons are by far the most widely used adsorbents for water purification. Adsorption on activated carbon is strongly dependent on the physico-chemical properties of the solution, and hence on arsenic speciation; for example, adsorption capacities are very low at high pH (Gupta and Chen, 1978).

Commercial activated carbons have been extensively used for As(III) and As(V) adsorption from water (Navarro and Alguacil, 2002; Di Natale *et al.*, 2008). A huge arsenic sorption capacity (2860 mg.g⁻¹) was obtained on coal-derived commercial carbon. Eguez and Cho (1987) studied adsorption of As(III) and As(V) on activated charcoal versus pH and temperature. The capacity of As(III) on carbon was constant at pH 0.16–3.5. However As(V) exhibited a maximum adsorption at pH 2.35 over the pH range of 0.86–6.33. The As(III) isosteric heat of adsorption varied from 4 to 0.75 kcal.mol⁻¹ and that for As(V), from 4 to 2

kcal.mol⁻¹ with increasing surface loading. These magnitudes suggest that physisorption occurred due to weak Van der Waals forces. Activated charcoal adsorbed 2.5 wt.% As(V) and 1.2 wt.% As(III) (based on the weight of carbon) at an equilibrium concentration of 2.2×10^{-2} M of both As(III) and As(V).

Three activated carbons with different ash contents were studied for As adsorption: coconut shell carbon with 3% ash, peat-based extruded carbon with 5% ash and a coal-based carbon with 5–6% ash (Lorenzen *et al.*, 1995). More As(V) was removed from water using carbon with a high ash content.

1.2.7.2.2 Activated carbons from wastes and chars

Lignite, peat chars (Allen *et al.*, 1997; Mohan and Chander, 2006) and biochar (Mohan and Pittman, 2007; Fan *et al.*, 2004) may be good substitutes for activated carbons. Arsenic(V) removal from aqueous solution by mixture of synthetic hydroxyl-apatite and barite or bone-char was carried out (Sneddon *et al.*, 2005) in the concentration range of 4–100 mg/L. Although the hydroxyl-apatite and baryte mixture had a small influence on arsenic concentrations, bone-char was found to be a very effective sorbing agent for As(V) in the pH range of 2–5.

Biochar by-products from fast wood/bark pyrolysis, were investigated as adsorbents for the removal of the As³⁺, Cd²⁺, Pb²⁺ from water (Mohan *et al.*, 2007). Oak bark, pine bark, oak wood, and pine wood chars were obtained from fast pyrolysis at 400 and 450 °C in an auger-fed reactor and characterized. Sorption studies were performed at different temperatures, pHs and solid to liquid ratios in the batch mode. Maximum adsorption occurred over a pH range of 3–4 for arsenic. The equilibrium data were modeled with the help of Langmuir and Freundlich equations. Overall, the data were well fitted with both the models, with a slight advantage for Langmuir model. As(III) removal followed the order: pine wood char (1.20 µg.g⁻¹) < oak wood char (5.85 µg.g⁻¹) < oak bark char (12.1 µg.g⁻¹) < pine bark char (12.15 µg.g⁻¹). This study shows that by-product chars from bio-oil production might be used as plentiful inexpensive adsorbents for water treatment (arsenic remediation) at a value above their pure fuel value. Further studies of such chars, both untreated and after activation, seem warranted

as part of the efforts to generate by-product value from biorefineries (Mohan and Pittman, 2007).

It exist in literature some studies about arsenic removal by activated carbons obtained from agricultural wastes or by products with different activation processes and adsorption capacities (Table 1.6), that also make interesting the utilization of innovative agricultural wastes for activated carbon preparation for arsenic elimination specifically that it is the aim of this work

Table 1.6 –Activated carbons from agricultural wastes for arsenic removal.

Source material	Activation	Adsorption capacity (qm)		Reference
		As (III)	As (V)	
Bean pods waste	Steam/1h	1.01 mg g ⁻¹	---	Budinova <i>et al.</i> , 2009.
Rice husk	ZnCl ₂ /CO ₂	1.22 mg g ⁻¹	---	Kalderis <i>et al.</i> , 2008.
Jute stick	H ₃ PO ₄	---	0.075 mg g ⁻¹	Jahan, <i>et al.</i> 2008.
Rice husk	CaCl ₂	18.2 µg g ⁻¹	---	Mondal, <i>et al.</i> 2007b.
Olive pulp	Steam/2h K ₂ CO ₃	1.39 mg g ⁻¹ 0.86 mg g ⁻¹	---	Budinova <i>et al.</i> , 2006.
Olive stones	K ₂ CO ₃ Steam/HNO ₃	0.74 mg g ⁻¹ 0.21 mg g ⁻¹	---	Budinova <i>et al.</i> , 2006.
Oat hulls	Steam	---	3.1 mg g ⁻¹	Chuang <i>et al.</i> , 2005.
Coconut husk	H ₂ SO ₄ /Cu	158.7 mg g ⁻¹	---	Manju <i>et al.</i> , 1998.

1.2.8 Arsenic elimination by metal loaded activated carbons

Arsenic removal by AC can be improved by doping with metals having a high affinity for arsenate and arsenite as copper (Lorenzen *et al.*, 2005; Manju *et al.*, 1998) and zirconium

(Daus *et al.*, 2004). However, Cu and Zr can be released in the solution, thus presenting other toxic effects (Muñiz *et al.*, 2009).

The technology of adsorption is based on materials having a high affinity for dissolved arsenic. Adsorption of arsenic by iron compounds has been established by several authors. Elementary iron, granular iron hydroxides, and ferrihydrites have been proposed for the removal of arsenic from water (Muñiz, *et al.*, 2009). Most of the adsorption processes investigated so far were reported in a review of Mohan and Pittman (2007), whereas the other techniques were considered in that of Choong *et al.* (2007). There have been some studies focused on arsenic adsorption by modified commercial activated carbons (Muñiz, *et al.*, 2009; Fierro *et al.*, 2009; Chen *et al.*, 2008) surmised that dissolved ferrous iron could diffuse deep into the internal pores of granulated activated carbon.

Gu *et al.* (2005) developed iron-containing granular activated carbon adsorbents for arsenic removal from drinking water. Granular activated carbon (GAC) was a support for ferric ions that were impregnated using aqueous ferrous chloride (FeCl_2) followed by NaClO chemical oxidation. Deliyanni *et al.* (2003) indicated that the varieties of iron oxides differ in their affinity for arsenic. They reported that akaganeite had higher arsenate adsorption capacity than other iron mineral phases such as hydrous ferric oxide and goethite. The combination of activated carbon and iron loading would take advantage of the strength of these two materials. The activated carbon serves as an ideal support media for iron preloading (Mondal *et al.*, 2009). Concertedly, the iron that is preloaded offers high affinity for arsenate and arsenite.

Activated carbon impregnation using a solution of iron salt is the most frequent method for doping activated carbons. In a study realized by Muñiz *et al.* (2009), raw and oxidized activated carbons were doped with iron through treatments with either ferric chloride (FeCl_3) or ferrous chloride (FeCl_2) solutions at different pHs and concentrations. The higher efficiency of the iron-doped materials prepared from low concentration (0.05M) FeCl_3 and FeCl_2 solutions was associated to the higher dispersion of iron in the activated carbons. In that study, a clear relationship between iron content and arsenic adsorption was evidenced, at the condition that iron is well-dispersed. Jang *et al.* (2009) have modified activated carbons by two methods: iron-impregnation/precipitation and iron impregnation/ evaporation using $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. These authors found that iron deposited onto the outer surface peeled off

during use, and that the iron efficiency for removing arsenic was not always proportional to their iron content.

In recent years there have been a lot of researches about the iron loading onto activated carbons for arsenic elimination principally commercial activated carbons (Zhu *et al.*, 2009; Gu *et al.*, 2005; Muñiz *et al.*, 2009; Fierro *et al.*, 2009; Mondal *et al.*, 2008; Jang *et al.*, 2008; Zhuang *et al.*, 2008; Chen, *et al.*, 2007; Gu and Deng, 2007; Reed *et al.*, 2000; Zhang *et al.*, 2007; Vaughan *et al.*, 2007; Payne and Abel-Fattah, 2005) but no researches are focused on iron loading onto activated carbons obtained from wastes or agricultural by-products for arsenic removal specifically that make very interesting and innovative the development of this work.

1.3 TETRACYCLINE CONTAMINATION AND TREATMENT PROCESS

Chlortetracycline and oxytetracycline, both discovered in the late 1940s, were the first members of the tetracycline group to be described. These molecules were products of *Streptomyces aureofaciens* and *S. rimosus*, respectively. Other tetracyclines were identified later, either as naturally occurring molecules, e.g., tetracycline from *S. aureofaciens*, *S. rimosus*, and *S. viridofaciens* and demethylchlortetracycline from *S. aureofaciens*, or as products of semisynthetic approaches, e.g., methacycline, doxycycline, and minocycline (Chopra and Roberts, 2001).

Tetracyclines (TCs) are among the antibiotics that are used extensively for disease control and in livestock feed for several decades due to their great therapeutic values (Sarmah *et al.*, 2006; Kuemmerer, 2009a; 2009b). For example, during the mid-1990s in European countries 2 294 000 kg per year of tetracycline were used for therapeutic in farms animals (Chopra and Roberts, 2001). The widespread use of tetracyclines and other antibiotics has led to dissemination of these compounds into the water and soil environments (Lindsey *et al.*, 2001; Kumar *et al.*, 2005; Xu and Li, 2010). Although environmental concentrations of antibiotics are typically below the threshold levels to exhibit medicinal treatment effects on bacterial populations and other at-risk species, chronic exposure to low levels of antibiotics alone or along with other toxicants may still exert pressure on the development of antibiotic resistant bacteria and minimize the effectiveness and therapeutic value of antibiotics (Kim *et*

al., 2007). Understanding the fate of antibiotic contaminants in the water–soil environment is imperative to better assess their risks and develop mitigation strategies (Chen and Huang, 2010).

1.3.1 Chemical characteristics

Table 1.7 summarizes some of the principal characteristic of the hydrochloride form of tetracycline. This latter is more soluble than tetracycline (only close to 250 mg.L^{-1} at 25°C). Moreover, stock solutions should be stored at $2\text{--}8^\circ\text{C}$ in the dark for no longer than one month because tetracycline hydrolyzes in aqueous solution and it's light sensitive.

Table 1.7: Some characteristics of Tetracycline hydrochloride (adapted from Gu and Karthikeyan, 2005)

<i>Tetracycline properties</i>	
CAS Number	64-75-5
EC Number	200-593-8
Empirical Formula	$\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_8 \text{ HCl}$
Molecular Weight	480.90
Solubility H_2O	10 mg.mL^{-1}
$\log K_{ow}$ (pH dependent)	-1.97 to -0.47
mp	220-223 C

Tetracycline molecule presents 3 acido-basic moieties with specific pK_a (Figure 1.9). So this substance could bear different charges depending on solution pH (Figure 1.10). When solution pH is below 3.3, tetracyclines exist as a cation, TCH_3^+ , due to the protonation of dimethylammonium group. At pH between pH 3.3 and 7.7, tetracyclines exist as a zwitterion, $\text{TCH}_2^\pm$, due to the loss of a proton from the phenolic diketone moiety. At solution pH greater than 7.7, a monovalent anion, TCH^- or a divalent anion TC^{2-} from the tricarbonyl system and phenolic diketone moiety will prevail (Kulshrestha *et al.*, 2004).

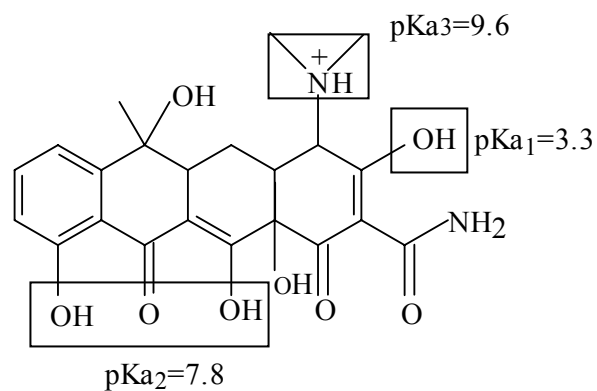


Figure 1.9 - Molecular structure of TC on a planar view.

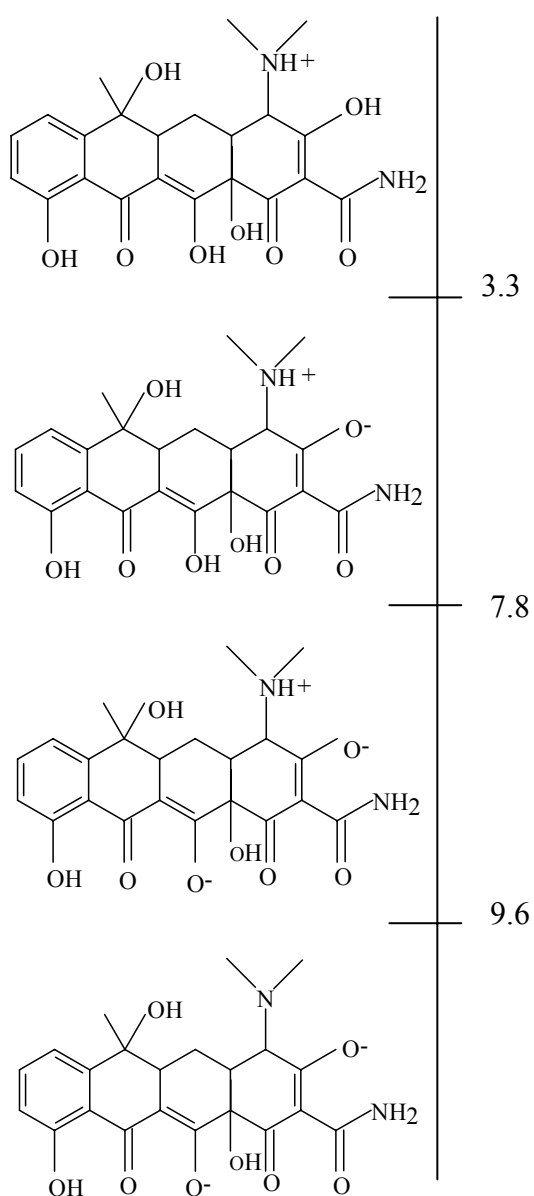


Figure 1.10 – Tetracycline forms at different pH values.

In addition, the conformation of tetracyclines is also affected by solution pH. In basic solutions an extended conformation is the dominant species, while in acid to neutral solutions twisted conformation prevailed (Othersen *et al.*, 2003).

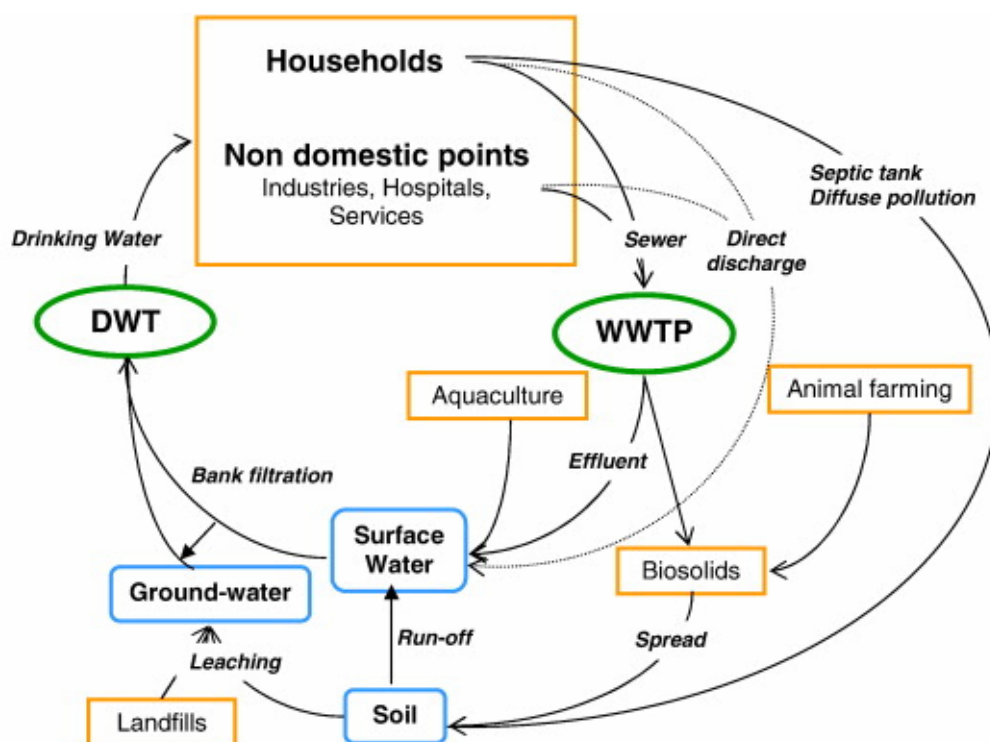
1.3.2 Pharmaceuticals substances in the environment

Traditionally the impact of chemical pollution has focused almost exclusively on the conventional priority pollutants (e.g., PAHs, PCBs, and organochlorine pesticides). However, the growing use of pharmaceuticals worldwide, classified as the so-called emerging pollutants, has become a new environmental problem, which has raised great concern among scientists in the last few years (Zhang *et al.*, 2009).

More than 3,000 chemical products are used in human and veterinary medicine (Ternes *et al.*, 2004). Pharmaceutics products include antiphlogistics/anti-inflammatory drugs, contraceptives, beta-blockers, lipid regulators, tranquilizers, antiepileptics, and antibiotics (Ternes *et al.*, 2004; Petrovic *et al.*, 2005). Although their toxicity to aquatic and terrestrial organisms is relatively unknown, a number of reported investigations have shown that pharmaceutical compounds pose a real threat to the environment (Oaks *et al.*, 2004; Fent *et al.*, 2006; Lacey *et al.*, 2008).

Excessive use of pharmaceuticals substances may also lead to the occurrence of traces of these compounds in the aquatic environment. Accurate assessment of pharmaceutical products impact on the environment is as difficult as there is a multitude of input sources in environment with no evident quantitative data available concerning the relative distribution of them from all emission sources (Figure 1.11).

Wastewater treatment plants (WWTPs) are major contributors of pharmaceuticals in the environment. Because of their high consumption, pharmaceuticals along with their metabolites are continuously introduced to sewage systems, mainly through excreta, disposal of unused or expired drugs, or directly from pharmaceutical discharges. Recently, research has shown that the elimination of some pharmaceutical compounds during wastewater treatment processes is rather low (Zhang *et al.*, 2009).



DWT = Drinking water treatment, WWTP = Wastewater treatment plant.

Figure 1.11. Origin and routes of pharmaceutical substances (from Mompelat, *et al.*, 2009).

The pharmaceuticals may have a potential exposure as persistent pollutants because even their high transformation and removal rates can be compensated by their continuous input into the environment. Nowadays, it is a well-established fact that WWTP effluents are the major source for the introduction of pharmaceuticals into the environment. Most often, these compounds occur at micrograms per liter or sub-micrograms per liter concentrations (Buchberger, 2007; Gros *et al.*, 2006, Roberts and Thomas, 2006). Many believe that of all the emerging contaminants, antibiotics are the biggest concern because of the potential for antibiotic resistance (Erickson, 2002).

A different way of how these pharmaceutical products may directly enter to surface waters is their use in fish farms, where fish feed containing drugs is often used to treat diseases. Since effluents of fish ponds hardly undergo any further treatment, residues of antibiotics can easily contaminate a wider range of the water system. Therefore, reliable analytical methods are required for monitoring residues of these compounds in the aquatic environment (Himmelsbach and Bushberger, 2005).

By-products include both metabolites excreted via urine or faeces, and transformation products which can be formed in environment from pharmaceutical products and/or metabolites released, under physico-chemical and biological factors as in wastewater treatment plants or water works (Figure 1.12), can also increase the environmental pollutant concentration, and maybe present a higher toxic effect (Mompelat, *et al.*, 2009).

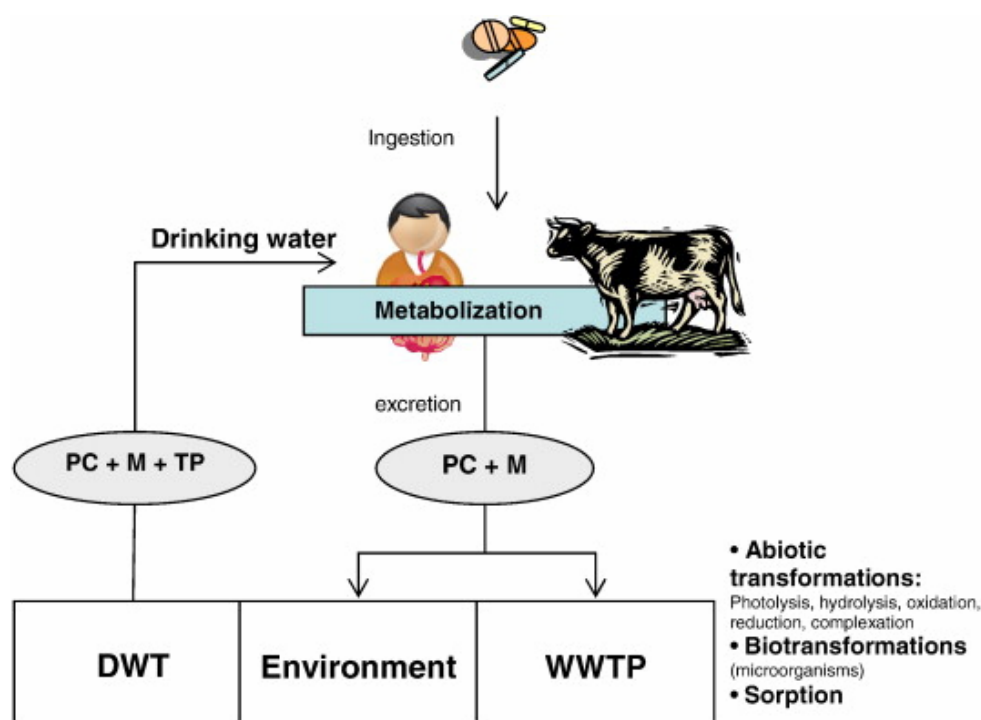


Figure 1.12 - Transformation pathways of PPs (PC: parent compound, M: Metabolite(s), TP: Transformation Product(s), WWTP: Waste Water Treatment Plant; DWT: Drinking Water Treatments) (Mompelat, *et al.*, 2009).

1.3.3 Tetracycline environmental pollution sources

Tetracyclines are one of the most widely-used antibiotics in the world, which are poorly absorbed in the digestive tract, and excreted unchanged in feces and urine (Sarmah *et al.*, 2006). It has been suggested that 90% of administered dose of antibiotics may be excreted through urine and faeces. Tetracyclines are quite persistent in soils and can accumulate with repeated manure application (Jacobsen *et al.*, 2004, Hamscher *et al.*, 2002). The presence of tetracyclines has been also reported in surface waters and groundwater (Lindsey *et al.*, 2001; Batt and Aga, 2005). The strong binding behavior to soil results in low mobility so that aquatic systems may be less affected (Tolls, 2001). Tetracyclines and other play important

roles in the development of antibiotic resistance of microorganisms (Sarmah *et al.*, 2006; Schmitt *et al.*, 2006) and potentially they can be hazardous to non-target organisms in the terrestrial environment (Jia, *et al.*, 2008). For all these reasons the fate and behavior of antibiotics in the environment are becoming a growing concern in most recent research (Tanis *et al.*, 2008).

A survey in 1999–2000 on 139 US streams across 30 states revealed that among 95 organic wastewater contaminants, 82 were found with concentrations ranging from 0.01 to 150 $\mu\text{g.L}^{-1}$. The tetracycline concentration was up to 110 ng.L^{-1} (Kolpin *et al.*, 2002). Analyses of final effluents after treatment from eight WWTPs located in five Canadian cities showed that tetracycline, among others, were frequently detected with a maximum concentration of 0.01 g.L^{-1} (Miao *et al.*, 2004). Samples from several WWTPs in Wisconsin showed an 80% frequency of detection with average influent concentrations of $48 \pm 3 \text{ g.L}^{-1}$ and average effluent concentrations of $3.6 \pm 0.3 \text{ g.L}^{-1}$ for tetracycline and another study realized in the US shown that the tetracycline occurrence in the influent of wastewater treatment plants was 78% and 11% was detected in the effluent (EPA, 2009). Miège *et al.*, (2009) report a mean, minimum and maximum concentration of tetracycline in wastewater treatment plants with activated sludge processes effluent of respectively 0.282 $\mu\text{g.L}^{-1}$, 0.05 $\mu\text{g.L}^{-1}$ and 0.850 $\mu\text{g.L}^{-1}$. When tetracyclines are consumed by human, wastewater treatment plants (WWTPs) are the major source of their release to the environment due to the partial removal efficiency in the treatment process (Miao *et al.*, 2004; Karthikeyan and Meyer, 2006).

While tetracyclines are used by animals, the principal pathway of the antibiotics into the aquatic environment is through manure and waste lagoon water application to fields as fertilizer. Accidental overflow or leakage from storage lagoons or tanks also contributes to their introduction to the environment (Jacobsen *et al.*, 2004).

Another pathway of antibiotic release into the aquatic environment is aquaculture and their occurrence of antibiotic residuals has been found from such operations (Lalumera *et al.*, 2004). Nowadays, oxytetracycline is the preferred tetracycline drug for aquacultures. Despite their widespread use in modern medicine and their ubiquitous presence in the environment, however, knowledge on the behaviour and fate of currently unregulated chemicals, such as tetracyclines into the aquatic environment is still limited.

1.3.4 Toxicity

Tetracycline group of drugs include chlortetracycline, oxytetracycline, demeclocycline, methacycline, tetracycline, doxycycline, and minocycline (WHO, 2008). Of these, oxytetracycline, demeclocycline, tetracycline, doxycycline, and minocycline are currently available in the United States for oral use. Only doxycycline and tetracycline are listed in the International Drug Price Indicator Guide.

Tetracyclines display a wide spectrum of antimicrobial action: apart from a stronger action on the gram-positive bacteria and a weaker one on the gram-negative ones, they exercise action also on mycoplasmas, chlamydiae, rickettsias, spirochetes, actinomycetes, and some protozoa. The sum of tetracycline action is bacteriostatic. The main goal of the antibacterial action of tetracyclines is proteosynthesis inhibition. They bind to the bacterial 30S ribosomal subunit and prevent attachment of aminoacyl-tRNA to the ribosomal receptor site (Roberts, 1996). In cattle, tetracyclines are used when treating general, respiratory, urinary, and local infections. A specific indication for administering tetracyclines in cattle is infectious mastitis.

Most important health aspects which should be taken into account for tetracycline toxicity are possible impact on the emergence of antimicrobial resistance for antimicrobials administered in human therapy, disorders in the intestinal flora and possible occurrence of allergic symptoms (Cerniglia and Kotarski, 2005). Adverse effects on human health after the therapeutic use of tetracyclines are well known. Tetracyclines can develop secondary tooth discoloration in children. Other chronic effects include nephrotoxicity, hepatotoxicity, skin hyperpigmentation in the sun exposed areas, hypersensitivity reactions. Tetracyclines have also been reported to cause hypouricemia, hypokalemia, proximal and distal renal tubular acidosis (Goldfrank *et al.* 2002).

Tetracyclines are deposited in the skeleton during gestation and throughout childhood and may depress bone growth in premature infants. Decrease in fibula growth rate has been observed in premature babies. This is reversible if the period of exposure to the drug is short. Use of this group molecule may cause increased intracranial pressure in young infants, even when given in the usual therapeutic doses.

All tetracyclines can produce a variety of gastrointestinal manifestations. Oesophagitis, esophageal ulcers, and pancreatitis are also reported. Cheilosis, atrophic or hypertrophic glossitis and pruritus ani which can persist for weeks or months after cessation of tetracycline contact is also reported (WHO, 2008).

1.3.5 International legislation for TC concentration in water

There is currently no specific regulatory guidance as to how the significance of the potential presence of pharmaceuticals at trace concentrations in drinking water supplies may be assessed. Nonetheless, numerous evaluations of the potential for adverse human effects arising from indirect exposure to pharmaceuticals via drinking water have been made (Schulman *et al.*, 2002).

By other, Food and Agricultural Organization, World Health Organization and European Union (EU) have established the maximum residual limits (MRL) for veterinary drugs in milk for example (Council Regulation 2377/90/EEC). The maximum residual limit set by the EU legislation for tetracycline, oxytetracycline as well as chlortetracycline in raw cow milk is set to 0.1 mg.kg⁻¹ (100 ng.g⁻¹). The presence of residues at much higher levels in foods may constitute a variety of public health hazards including toxicological, microbiological, immunological, and pharmacological hazards (Navatrilova *et al.*, 2009).

1.3.6 Main tetracycline removal technologies

Wastewater containing organic pollution is commonly treated by biological way with activated sludge processes and anaerobic or aerobic digestion processes. Treatments by biological system, including activated sludge, have proved their efficiency for the decrease of organic and nitrogen loads of wastewater. However, antibiotics could be measured in the effluent after treatment (Miège *et al.*, 2009; Miao *et al.*, 2004; EPA, 2009). Different studies on antibiotics behaviour in bioreactor highlighted three different ways for antibiotics disappearance, the most favourable case is a biodegradation, another way is accumulation on biomass defined as biosorption, which leads to the release of molecules after biomass death, and a third way is hydrolysis (Xu *et al.*, 2007, Kim *et al.*, 2005). Unfortunately, many

antibiotics are none or less biodegradable and they will be present in the treated water. For example, the treatment of wastewater containing tetracycline by a membrane bioreactor shows no biodegradation (Alexy *et al.*, 2004, Prado *et al.* 2009). So, other processes have to be proposed for the tetracycline removal from polluted water. The most common way found in literature is the elimination of tetracycline by adsorption.

1.3.6.1 Tetracycline elimination by sorption

To remove hydrophobic organic compounds from water, a sorbent with higher total organic carbon content will achieve a better effect (Chang *et al.*, 2009a). However, for ionizable compounds, their affinity to solid surface is strongly affected by the solution pH and their hydrophobicity under different pH conditions. TCs are quite hydrophilic. Their water solubility is in the ranges of g/L (Tolls, 2001), which resulted in a lower sorption to activated carbon (Polubesova *et al.*, 2006).

Studies on the adsorption of tetracyclines are limited and have focused mainly on humic materials and minerals (Kulshrestha *et al.*, 2004; Figueroa *et al.*, 2004; Turku *et al.*, 2007; Wang *et al.*, 2008, see also Table 1.8). For those studies, cation exchange was concluded to be the primary adsorption mechanism responsible for the adsorption of tetracyclines especially under acidic conditions, and the adsorption of TCs always decrease with increasing pH (Parolo *et al.*, 2008). Adsorbents materials utilized for tetracycline sorption founded in literature in recent years are shown in Table 1.8. These results highlights that clays minerals present high sorption capacities, for example 0.85 mmol.g⁻¹ for montmorillonite at pH 3. Ionic strength seems to have an effect on tetracycline sorption by mineral phase (Figueroa *et al.*, 2004, Gu and Karthikeyan, 2005). In the case of sorption by aluminum and iron hydrous oxides, it was observed that ligand-promoted dissolution is occurring tetracycline sorption. The ability of tetracycline to form strong complexes with Al or Fe will strongly increase these minerals. Moreover, spectroscopic studies indicate that tricarbonylamide and carbonyl functional groups of tetracycline could be involved in the sorption (Gu and Karthikeyan, 2005).

Sassman and Lee (2005) studied the adsorption of tetracycline, oxytetracycline and chlorotetracycline in several soils varying in pH, clay content and type, and oxytetracycline content under various background electrolyte concentrations. They presumed that batch studies and empirical modeling supported their hypothesis that pH played important role in

the adsorption of TCs. Jones *et al.* (2005) measured the adsorption of oxytetracycline to soils with a wide range of soil properties. They deduced that soil texture and free/crystalline oxide content were the most important factors on the adsorption of oxytetracycline. Figueroa and Mackay (2005) investigated the adsorption of oxytetracycline to iron oxides and iron oxide-rich soils, and found that adsorption models should consider the interaction of oxytetracycline with soil oxide components in addition to clays and organic matter.

It has been reported that when tetracyclines are sorbed onto clay materials, soil, and sediments, tetracycline sorption decreased with increasing pH and increasing ionic strength, and sorption by clays appeared to be enhanced in the presence of Ca versus Na. Tetracycline are dominantly sorbed on soil clays and that humic substances either mask sorption sites on clay surfaces or inhibit interlayer diffusion of tetracyclines (Sassmann and Lee, 2005; Pils and Laird, 2007). But their occurrence in surface waters suggests that their sorption to solids is not irreversible and that there are some factors that could favor their mobility in the environment. Since sorption process is a key determinant of the reactivity, mobility, persistence, volatilization and bioavailability of pollutants in natural waters, there is a need to understand interactions of antibiotics with sediment and aquatic particles.

Limited evidence in the literature points to the reduction in sorption of the antibiotic tetracycline to clay minerals in the presence of other substances. Gu and Karthikeyan, (2008) studied the interaction between humic acids, hydrous Al oxide and the effect of this association on tetracycline sorption. Ligand exchange was proposed as the major mechanism of interaction. Higher organic content resulted in increased nonlinearity of sorption behavior. The authors conclude that the presence of humic substances, in both dissolved and mineral-bound forms, is likely to increase the environmental mobility of tetracycline compounds (Kummerer, 2009). It was also shown that the presence of phosphate affect the tetracycline retention by soils. The presence of 31 mg L⁻¹ of phosphate decrease the Freundlich constant between 30 and 40 % in comparison with the experiments without phosphshate (Wang *et al.*, 2010).

Very few experiments use activated carbon for tetracycline removal (Ji, *et al.*, 2009, Choi *et al.*, 2008). Ji *et al.*, (2009) propose a comparative study between single-walled carbon nanotubes (SWNT), multiple-walled carbon nanotubes (MWNT), activated carbon (AC) and graphite. The isotherm experimental points are well fit with the Freundlich model and the

values for the K_F constant are $1340 \text{ mmol}^{1-n} \cdot \text{L}^n \cdot \text{kg}^{-1}$, $200 \text{ mmol}^{1-n} \cdot \text{L}^n \cdot \text{kg}^{-1}$, $36 \text{ mmol}^{1-n} \cdot \text{L}^n \cdot \text{kg}^{-1}$, $9.6 \text{ mmol}^{1-n} \cdot \text{L}^n \cdot \text{kg}^{-1}$, respectively. The very high adsorption of tetracycline to the carbone nanotubes can be attributed to the strong adsorptive interaction (van der Waals forces, $\pi - \pi$ electron donor acceptor interactions, cation π bonding) with the graphene surface.

1.3.6.2 Tetracycline elimination by oxidation

The use of oxidative processes like, ozonation photo-fenton or photocatalysis, is well known for the treatment of organic pollutant in water. Nevertheless, due to the high diversity in the organic pollutant potentially present in water very few publications treat of the tetracycline degradation by an oxidative process.

Khan *et al.*, (2010) have investigated the ozonation of tetracycline in aqueous media at pHs 2.2 and 7.0 to elucidate the transformation pathway. They detected around 15 ozonation products, and uncovered their production and subsequent degradation patterns. The removal of total organic carbon (TOC) reached a maximum of $\approx 40\%$ after 2 h of ozonation, while tetracycline was completely removed within 4–6 min at both pHs. The low TOC removal efficiency might be due to the generation of recalcitrant products.

The degradation of tetracycline by the photo-Fenton process was evaluated under black-light and solar irradiation by Bautitz and Pupo Nogueira (2007). In this study the influences of iron source ($\text{Fe}(\text{NO}_3)_3$ or ferrioxalate), hydrogen peroxide and matrix (pure water, surface water and a sewage treatment plant effluent—STP) were evaluated. No significant difference in total organic carbon removal was observed between the iron sources, achieving a residual concentration of around $5 \text{ mg} \cdot \text{L}^{-1}$ under black-light and $2 \text{ mg} \cdot \text{L}^{-1}$. Under solar irradiation and in the presence of ferrioxalate, no influence of the matrix was observed, even in the sample of STP effluent, achieving total degradation of tetracycline in 1.5 min.

Another way of tetracycline degradation is the photocatalic oxidation. To compare tetracycline abatement efficiency, Reyes *et al.*, (2006) have irradiated tetracycline solutions in aqueous suspensions of TiO_2 with three different light sources: a UV lamp, a solarium device and a UV-A lamp. They have observed negligible degradation when irradiations were performed in absence of TiO_2 . In contrast, rapid tetracycline degradation was observed in the presence of $0.5 \text{ g} \cdot \text{L}^{-1}$ of TiO_2 . Close to 50% of its initial concentration was eliminated after 10, 20 and 120 min when the irradiation source used was a UV lamp, a solarium device and a

UV-A lamp, respectively. More recently Palominos *et al.* (2009) have performed the photocatalytic oxidation of tetracycline in aqueous suspension containing TiO₂ or ZnO under simulated solar light. The optimal oxidation conditions, determined using multivariate analysis and response surface methodology, were 1.5 g.L⁻¹ and pH 8.7 for TiO₂ and 1.0 g.L⁻¹ and pH 11 for ZnO. For these conditions, after 15 min of irradiation more than 50% of carbon was mineralized in presence of TiO₂. For ZnO, after 10 min, tetracycline was completely eliminated accompanied with a very low mineralization. The complete conversion of tetracycline in CO₂ was reached after 45 min.

Table 1.8 Sorption of Tetracycline by adsorbent materials.

Material	Sorption Conditions	Sorption Capacity	Reference
Palygorskite	pH=8.7	101 mg.g ⁻¹	Chang <i>et al.</i> , 2009a.
Rectorite	pH=4.5 pH=11	140 mg.g ⁻¹ 54 mg.g ⁻¹	Chang <i>et al.</i> , 2009b.
Na- montmorillonite	pH=5.5	0.112 mmol.g ⁻¹	Figuerola <i>et al.</i> , 2004
Montmorillonite	pH=3.0 pH=4.0 pH=5.0 pH=7.0	0.85 mmol.g ⁻¹ 0.75 mmol.g ⁻¹ 0.48 mmol.g ⁻¹ 0.35 mmol.g ⁻¹	Parolo <i>et al.</i> , 2008.
Anthrosol	pH=6.5	27 mmol.kg ⁻¹	Jia <i>et al.</i> , 2008.
Ferrosols	pH=4.4	24 mmol.kg ⁻¹	Jia <i>et al.</i> , 2008.
Quartz/ferrhydrite	pH=5.5 60°C	5.06 µmol.m ²	Tanis <i>et al.</i> , 2008.
Quartz/goethite	pH=5.5 60°C	4.0 µmol.m ²	Tanis <i>et al.</i> , 2008.
Aluminum oxide	pH=5.0	43% of 40µM TC	Chen and Huang, 2010.
Marine sediment	pH=7.5	13 mg.g ⁻¹	Xu and Li, 2010.
Soil humic acid	pH=6.2	17.9 g.kg ⁻¹	Gu and Karthikeyan, 2008.
Carbon nanotubes Single wall nanotubes	pH=3.4-11	Close to 1000 mmol.kg ⁻¹	Ji, <i>et al.</i> , 2009.
Powdered activated carbon	pH=7.0 25°C	78-97% of TC [PAC]=0.7mg.L ⁻¹ , [TC]=0.1-1.0 mg.L ⁻¹	Choi <i>et al.</i> , 2008.

1.4 CONCLUSION

This state of the art highlights that the occurrence in water of inorganic or organic micropollutants like arsenic and tetracycline leads to human health problem or environmental disturbance. One common way to remove from water these kinds of substances is adsorption processes. The use of activated carbon as sorbent is well studied for many applications. But the use of agricultural by-product as precursor of activated carbons devoted to the uptake of arsenic is poorly documented. Moreover, very few papers describe results about the mechanism of tetracycline removal by activated carbon material.

Consequently the aim of this thesis will be the preparation of activated carbons from sugar beet pulp and peanut hulls by physical activation. In order to increase the sorption capacity in the case of arsenic, iron impregnated activated carbon will be also prepared. The new materials will be characterized and then used in sorption studies for the removal of arsenic or tetracycline from water. Two commercial activated carbons will be used as reference.

The following Chapter present the materials and the experimental methods used in this work. Finally, the Chapter 3 gives the characterization data of the new carbonaceous material, and the Chapter 4 the adsorption results of arsenic or tetracycline.

CHAPTER 2

MATERIALS AND EXPERIMENTAL METHODS

The aim of this chapter is to present the method of preparation of activated carbons from sugar beet pulp and peanut hulls, the physical and chemical description of the carbonaceous materials obtained from these agricultural wastes and a comparison with a commercial activated carbon (GAC). In the first part of this chapter, we have characterized the adsorbent materials by determination of:

- Surface specific of the materials (S_{BET})
- Elemental analysis and ash content analysis
- Zeta potential measurement
- Scanning electron microscopy

After that we present the arsenic quantification process by atomic absorption spectrometry (AAS) with a graphite furnace with a calibration curve between 5 and 20 $\mu\text{g.L}^{-1}$ of arsenic(V), that arsenic quantification was realized for the obtaining of experimental results from kinetic and isotherms essays, to describe the sorption process of arsenic onto activated carbons we employed different kinetics model such as pseudo-first and pseudo-second order and isotherms models also like Langmuir and Freundlich.

The ions competition in adsorption was verified by testing arsenic(V) removal in two natural waters (highly and lowly ion charged) and it was compared with that of deionized water doped with arsenic.

In order to study the efficiency of activated carbons prepared from agricultural wastes for organic pollutants, we tested the Tetracycline removal by the application of kinetic and isothermal tests and also the effect of ions presence in the aqueous media.

2.1 ACTIVATED CARBONS FABRICATION

All chemicals were of reagent grade from Sigma. Arsenic solutions were made from $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$. Sugar beet pulp was commercially supplied by Lyven (Cagny, France) and peanut hulls were obtained from a local market. In a previous study, a complete characterization of the raw sugar beet pulp revealed that the polysaccharides accounted for 72.5% of the dry matter and ash content for 3.9% (Reddad *et al.*, 2002). Raw peanut hulls presented 1.7% of ash content. A commercial granular activated carbon (GAC) was used for the performance comparison in the sorption tests.

The sugar beet pulp (BP) and peanuts hulls (PH) were first dried at 110°C for 24 h. The carbonization and activation step was realized in a rotative furnace (model HTR 11/150) from Carbolite® with a quartz reactor. They were heated at 857°C for 80 minutes under a nitrogen atmosphere and with steam as the activating agent ($0.7 \text{ mL} \cdot \text{min}^{-1}$). The temperature decrease was carried out under a nitrogen atmosphere ($0.5 \text{ L} \cdot \text{min}^{-1}$).

The activated carbonaceous materials obtained from beet pulp and peanut hulls were called BP-H₂O and PH-H₂O respectively. These materials were crushed in a hammer mill, the milled particles were then sieved so that the particle sizes of 0.50–1 mm of BP-H₂O and PH-H₂O were used for the arsenic adsorption experiments. This fraction was washed with deionized water ($10 \text{ g} \cdot \text{L}^{-1}$) until the pH remained constant, filtered and dried at 110°C. 1 g of activated carbons (BP-H₂O and PH-H₂O) with particle size $> 1 \text{ mm}$ was also placed in a $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution (0.1 M and pH = 1.7) and the mixture was shaken at 200 rpm for 24 h at room temperature (Haque *et al.*, 2008), this step was realized after carbonization in order to avoid any structure disaggregation of the agricultural wastes at the contact time with the iron acid solution. Iron impregnated beet pulp activated carbon (BP-H₂O-Fe) and iron impregnated peanut hulls activated carbon (PH-H₂O-Fe) were washed several times with deionized water until the water was free from iron ions, as indicated by atomic absorption spectrometry measures. The iron content of BP-H₂O-Fe and PH-H₂O-Fe was then evaluated after by an acid digestion (HCl concentrated). The iron concentration was then measured at $\lambda=248.33\text{nm}$ by a

Perkin Elmer Atomic Absorption Spectrophotometer unit with flame atomization. Finally the adsorbents were dried at 105°C.

2.2 CHARACTERIZATION OF CARBONACEOUS MATERIALS

2.2.1 Physical characterization – BET surface analysis

The adsorption isotherms of gases at temperatures not far removed from their condensation points show two regions for most of the adsorbents: at low pressures the isotherms are concave, and at higher pressures convex, to the pressure axis. The higher pressure convex portion has been attributed to capillary condensation by some workers and to the formation of multimolecular layers by others. The formation of multimolecular layers was explained by assuming that the uppermost layer of the adsorbent induces dipoles in the first layer of adsorbate molecules, which in turn induces dipoles in the second layer, and so on until several layers are built up (Bansal and Goyal, 2005).

Brunauer, Emmett, and Teller (1918) were of the view that the polarization of the second layer of adsorbed gas molecules by the first layer gas molecules will be much too small to constitute a major portion of the binding energy between the two adsorbed layers, at least in those cases in which the gas molecules do not possess considerable permanent dipole moments. These workers proposed that the forces acting in multimolecular adsorption are the same as those acting in the condensation of vapors. Only the first layer of adsorbed molecules, which is in direct contact with the surface of the adsorbent, is bound by adsorption forces originating from the interaction between the adsorbate and the adsorbent. Thus, the molecules in the second and subsequent layer have the same properties as in the liquid state. On this basis they derived an equation for multimolecular adsorption by a method that is a generalization of the Langmuir treatment of unimolecular adsorption. This equation is known as the Brunauer, Emmett, Teller equation or, more commonly, the BET equation. This equation has played a significant role in the studies of adsorption because it represents the shapes of the actual isotherms. Furthermore, it also gives reasonable values for the average heat of adsorption in the first layer and satisfactory values for V_m , the volume of the gas or vapor required to form a unimolecular layer on the surface of the adsorbent.

The pore structure of carbon materials, particularly of activated carbons, is usually characterized by using physical adsorption of various gases. According to the classical BET method, the specific surface area of the adsorbent is usually measured by adsorption of nitrogen at 77 K using molecular area a_m of nitrogen as 0.162 nm^2 .

The adsorption and desorption isotherms were classified from their shapes into 5 types, as shown in Fig. 2.1. Type I isotherms are typical for microporous solids, including most activated carbons, where micropore filling occurs at a relatively low partial gas pressure P/P_o ; in many cases, adsorption is complete at P/P_o below 0.5 (Inagaki and Tascón, 2006).

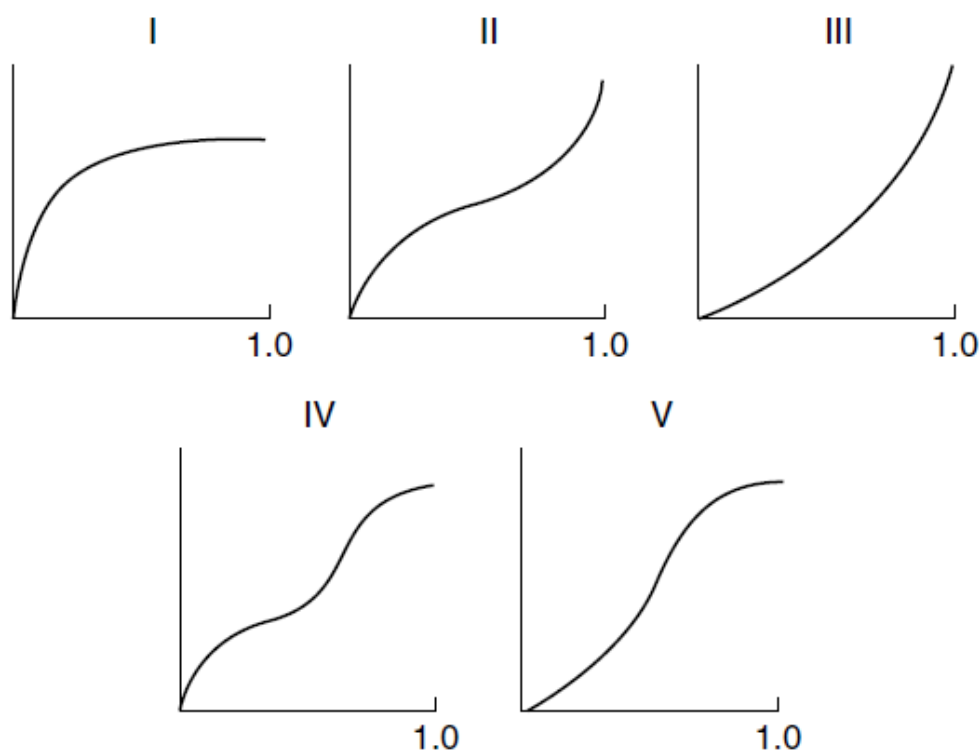


Figure 2.1 Classification of gas adsorption isotherms (from Bansal and Goyal, 2005).

For the Type I isotherms measured by nitrogen at 77 K (Figure 2.2), the BET method has commonly been applied to determine the surface area of solids. However, it has been pointed out that the measured surface area might be larger (by even 40%) than the true area if the sample contains relatively large micropores, and too small if there are ultramicropores in the material. In order to evaluate the surface area and pore size distribution, various procedures

such as the Dubinin-Radushkevich (DR) plot, Barrett-Joyner-Halenda (BJH) method, Horvath-Kawazoe (HK) method, t plot, alpha plot and density functional theory (DFT) method have been proposed, together with theoretical calculations based on the Grand Canonical Monte-Carlo (GCMC) method.

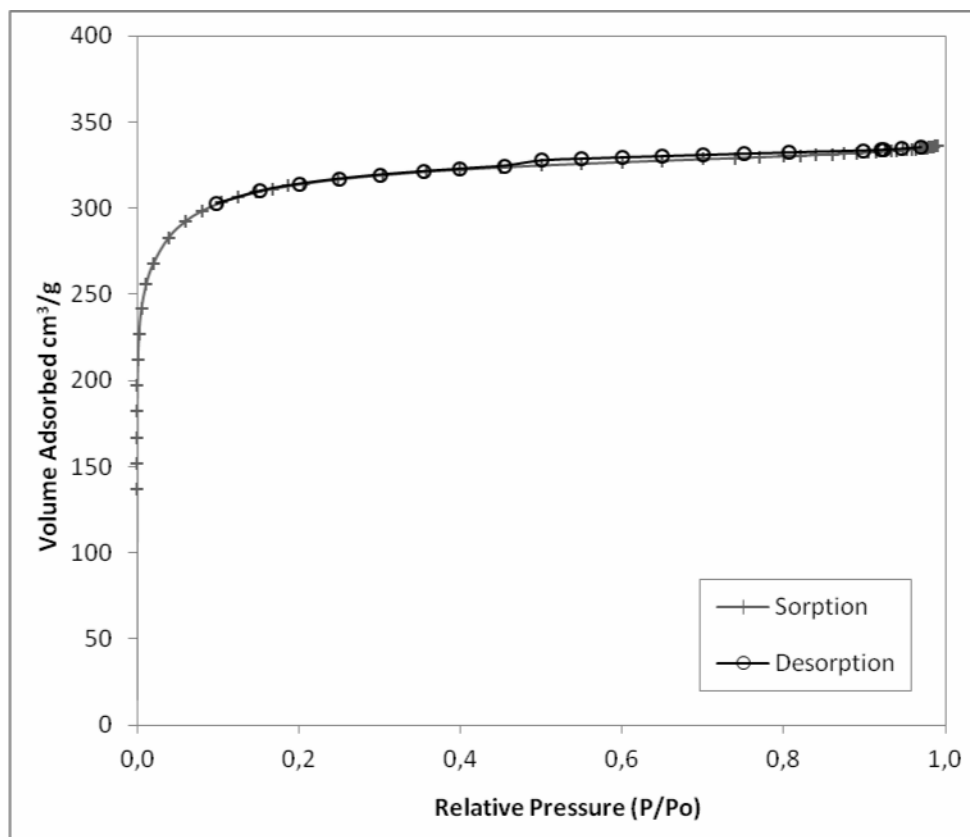


Figure 2.2 . Sorption isotherm of N₂ adsorption on GAC1 for surface BET determination.

In order to characterize the different materials, the BET surface area and pore size distribution of the carbonaceous materials was determined from a nitrogen adsorption isotherm at 77K using the ASAP 2010 Micromeritics analyzer (Figure 2.3) that consists of an analyzer, a control module and an interface controller. Prior to this analysis, the samples were degassed at 350°C for at least 24h at the sample preparations ports, all the results were duplicated.

The micropore volume, $V_{\mu\text{icro}}$ (cm³g⁻¹), corresponding to pores narrower than 2 nm, was calculated according to the Dubinin–Radushkevitch method (Dubinin, 1989) and it was obtained in the Horvath-Kawazoe slit pore geometry from the surface analysis. The total pore

volume, sometimes referred to as the so-called Gurvitch volume $V_{0.99}$, was defined as the volume of liquid nitrogen corresponding to the amount adsorbed at a relative pressure $p/p_0 = 0.99$. The mesopore volume, V_{meso} , was calculated as the difference between the cumulative pore volume ($\text{cm}^3 \text{g}^{-1}$) at average diameter 2 nm and the cumulative pore volume at average diameter 50 nm in the BJH pore distribution. The mesopores d_{50} was determined by adding the cumulative pore volume at 50 nm and that one at 2 nm and then divides by 2, the obtained value of pore volume corresponds to the values of mesopores d_{50} of the material in the BJH adsorption pore distribution.

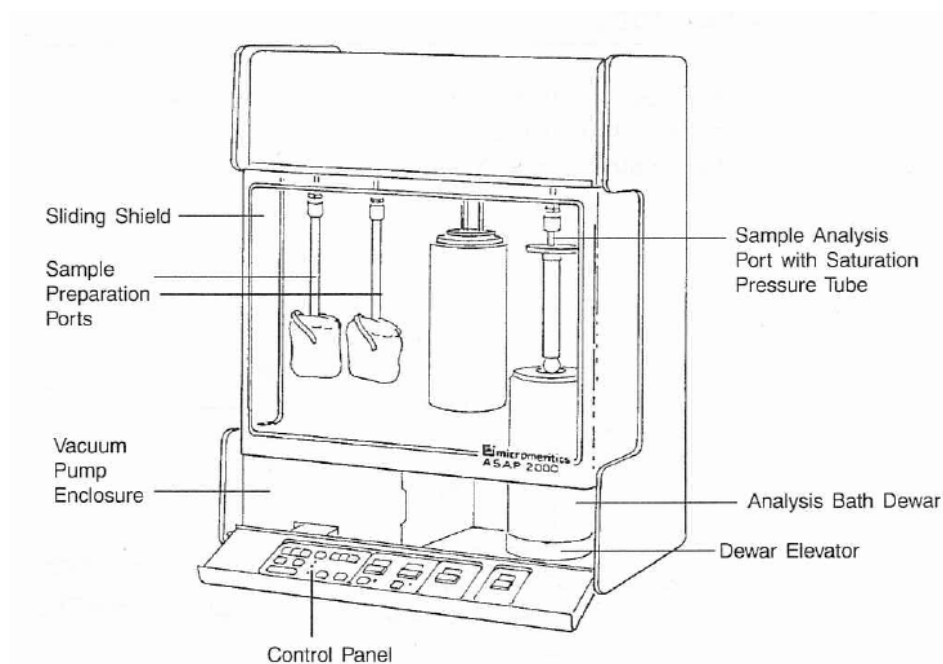


Figure 2.3. Surface BET analyzer components.

2.2.2 Elemental analysis and total ash content

The elemental analysis is based on dynamic flash combustion and involves two different steps, the first one for CHNS analysis and the other one for oxygen analysis. Elemental analysis of the carbonaceous materials samples was performed using Flash EA 1112 (ThermoFinnigan). This analyzer measures the amount of C, H, N, O, and S in samples by the rapid combustion of small amounts (1-2 mg) of the sample in pure oxygen (Dumas method or "flash combustion"). Catalysts are present at high temperature of around 1800° Celsius. The products of combustion are sent through a packed chromatographic column. The column

converts the products into combination of NO_2 , CO_2 , SO_2 , H_2O . These simple compounds are then measured using a thermal conductivity detector.

The calibration is performed by analyzing standard compounds with K-factors calculations. The analysis of all elements in the CHNS/O group is performed simultaneously. Time of full analysis cycle is less than 10 minutes. The high precision micro scale has resolution of 0.1 microgram and works with samples of up to 4-5 milligram.

One interesting feature is special system of calculating the precise amount of Oxygen necessary for full combustion of the sample. The Oxygen is automatically cut at that pre-calculated amount.

For the CHNS/O determination, the samples were ground into fine powders and carefully weighed on tin capsule for CHNS analysis or silver capsule for oxygen analysis and folded before insertion into the instrument; the capsules were introduced in combustion furnace at 920 °C for CHNS analysis and 990 °C for oxygen with constant helium flow like carrier gas. The temperature of flash combustion for CHNS analysis was around 1800 °C to obtain nitrogen oxides (N), CO_2 (C), H_2O (H) and $\text{SO}_2 - \text{SO}_3$ (S), after that there is a reduction reactions in the cuprum tube and then the gases are detected by a catharometer (furnace at 65 °C + chromatographic column + detector by thermal conductivity difference, reference = He) (Figure 2.4), the four chromatogram peaks correspond by apparition order to N_2 , CO_2 , H_2O and SO_2 . For oxygen analysis the furnace temperature was around 1060 °C to obtain CO from oxygen compounds and N_2 , H_2 and CH_4 from another produced compounds, the gases detection was realized by a catharometer (furnace at 75 °C + chromatographic column at molecular sieve + detector by thermal conductivity difference, reference = He), the chromatogram peaks correspond by apparition order to N_2 , H_2 , CH_4 and CO. This analysis was repeated three times for each sample to provide an average reading. Results were indicated as percentages of carbon, hydrogen, nitrogen and oxygen. No sulphur content was detected.

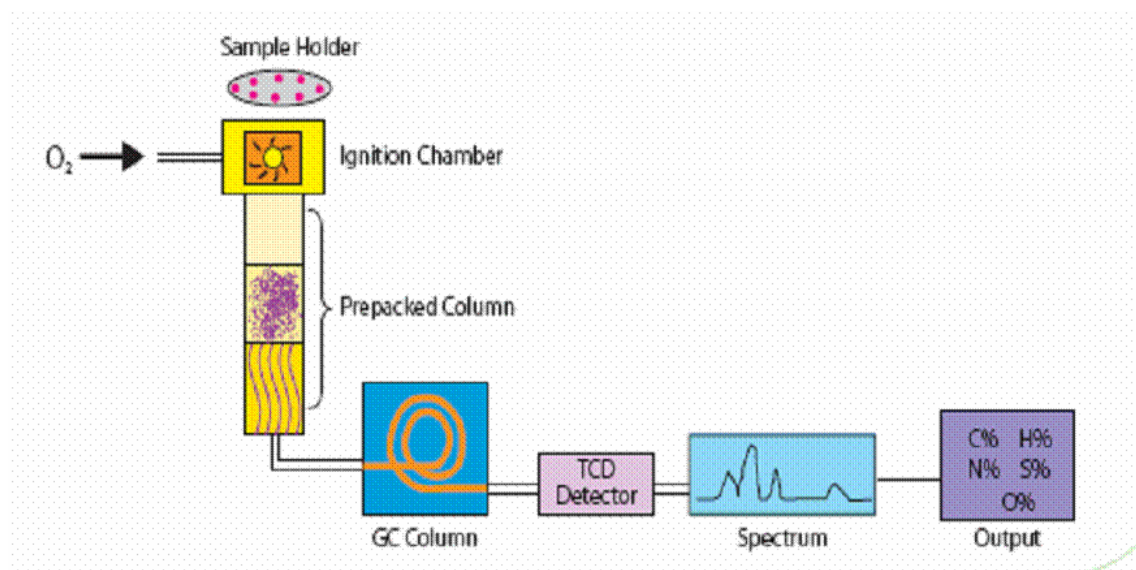


Figure 2.4. Scheme of CHNS/O analysis process.

The total ash content as a percentage was calculated by the standard test method for total ash content of activated carbon D 2866-94 (ASTM, 1994), for the ash determination, a crucible was ignited in the muffle furnace at 650 ± 25 °C for 1h, then it was placed in a dessicator until room temperature and weighed, then about 50 mg of dry activated carbons was weighed and placed into the ignited crucible and heated at 650 ± 25 °C. Ashing was considered complete when constant weight is achieved.

2.2.3 Iron content measurement

The iron content of the samples was determined after ashing the materials (ASTM method) and then, the remaining ashes in the crucibles were taken into liquid phase by leaching with strong HCl (7M) and heating at 80 °C until complete dissolution of the solid phase and the acid solution was diluted with deionized water in a specific volume to fit the values into the calibration curve range (2 to 8 mg.L⁻¹ of Fe). The solutions for the calibration curve were prepared from a reference solution of Fe (1000 ppm) and diluted with a solution of HNO₃ (2% vol). Iron was analyzed on a Perkin Elmer AAnalyst200 Flame Atomic Absorption Spectrometer. Iron hollow cathode lamp was used at a wave length of 248.3 nm with a slit width of 1.8/1.35 nm.

2.2.4 Zeta potential measurement

In almost all electrokinetic phenomena a fluid moves with respect to a solid surface. (An exception is the electrophoresis of emulsions). For the most part we shall be concerned with determining the relation between the velocity of the fluid (which will generally vary with distance from the solid) and the electric field in the interphase region. The electric field will be partly determined by the surface charges on the solid in the liquid but may also include an externally imposed field, either generated deliberately by the experimenter (electroosmosis and electrophoresis) or arising out of the motion of particles (sedimentation potential) or ions (streaming potential). The relation between the potential (or the electric field) at any point and the number of charges is given by Poisson's equation. The charges themselves will respond to three sorts of forces:

- (i) the electrical potential,
- (ii) the diffusion force, tending to smooth out concentration variations,
- (iii) the bulk movement of charge carried along by the flow of the liquid (convective transport).

At the same time the liquid itself is subjected at each point to forces caused by pressure gradients in the system and the electrical charges it contains, as well as shear forces induced by neighboring parcels of liquid moving with different velocities. Even with the powerful tools of vector calculus and high-speed computer solution of the resulting differential equations it is still necessary to make a number of significant simplifications and to treat, at least in the first instance, highly idealized models of the real experimental systems. Nevertheless, a great deal of interesting and valuable information can now be obtained from electrokinetic measurements.

Theoretical treatments generally assume that the solid is a sphere, a cylinder, or a large flat plate; more rarely it may be a disc or ellipsoid. The liquid is assumed to be Newtonian (i.e. its viscosity does not depend on shear rate and moving sufficiently slowly so that turbulence and other non linear effects are absent).

The most important concept which is introduced is that of the surface of shear. This is an imaginary surface which is considered to lie close to the solid surface and within which the

fluid is stationary. In the case of a particle undergoing electrophoresis, the surface of shear forms a sheath which envelopes the particle. All of the material inside that sheath forms the kinetic unit so that the particle moves along with a certain quantity of the surrounding liquid and its contained charge. Measurement of the electrophoretic mobility (i.e. the velocity per unit electric field) therefore gives a measure of the net charge on the solid particle.

The analysis of the forces on the solid or the liquid can be carried out in the terms of either charge or electrostatic potential. In the latter case one calculates the average potential in the surface of shear; this is called the electro-kinetic or zeta potential, and is universally given the Greek symbol, zeta (ζ).

The electrokinetic potential (zeta potential, ζ) is the potential drop across the mobile part of the double layer that is responsible for electrokinetic phenomena, for example electrophoresis (motion of colloidal particles in an electric field). It is assumed that the liquid adhering to the solid (particle) surface and the mobile liquid are separated by a shear plane (slipping plane). The electrokinetic charge is the charge on the shear plane (Stumm, 1992).

At the interface between a charged surface and an electrolytic solution, it exists a solution layer called double layer, it has different properties than an electrolyte. This layer is constituted by the compact layer corresponding to adsorbed ions in the surface of the solid in the way of the mono-layer of Langmuir, and the diffuse layer. Several models have been elaborated to describe the charge evolution (σ_0) and the surface potential (Ψ_0) of the double layer, and it is the triple layer model that allows understanding the zeta potential signification (Stumm and Morgan, 1996). The triple layer model was introduced in 1947, the compact layer is sub-divided into two parts (Figure 2.5). The first part is placed between the surface and the Helmholtz internal plane (HIP). Just one layer or the ions that present a high interaction with the surface can be received, and they loss partially or totally their hydration sphere (internal sphere complexes). The center of these ions is located at HIP level. The second part is between the HIP and the Helmholtz external plane (HEP) and it does not take into account the hydrated ions retained by the electrostatic forces (extern sphere complexes).

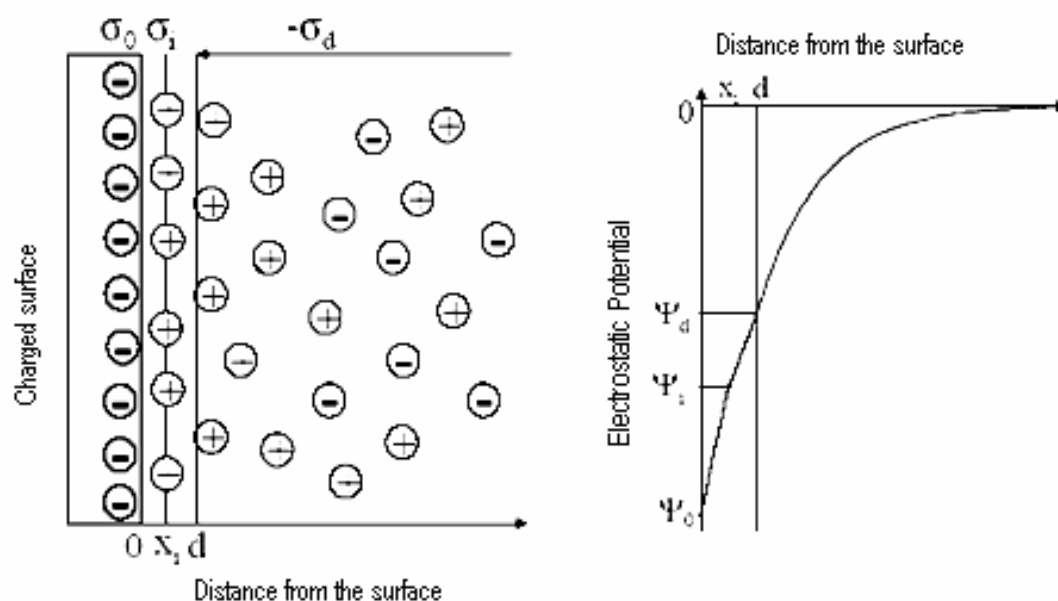


Figure 2.5. Triple layer model. The Helmholtz internal plane is located at the distance x_i of the surface and the Helmholtz external plane is located at the distance d .

In the triple layer model, the thickness of the diffuse layer appears like a essential parameter to characterize the decrease of Ψ potential. This thickness, called Debye length is noted by κ^{-1} and depends of the ionic force in the solution, it is expressed by:

$$\kappa = \left(\frac{2F^2 I}{\epsilon \epsilon_0 R T} 10^3 \right)^{1/2}$$

where:

κ Debye's parameters (m^{-1})

κ^{-1} Debye's length (m)

I Ionic force of the solution (M)

F Faraday (96485 coulombs)

ϵ Water dielectric constant ($\epsilon = 78,5$ à 25°C)

ϵ_0 Permittivity of vacuum ($8,854 \cdot 10^{-12} \text{ C.V}^{-1}.\text{m}^{-1}$ or $\text{C}^2.\text{J}^{-1}.\text{m}^{-1}$)

R Perfect gases constant ($8,31 \text{ J.mol}^{-1}.\text{K}^{-1}$)

T Temperature (K)

The surface potential then is expressed by :

$$\psi = \psi_d \exp(-\kappa d)$$

And the surface charge :

$$\sigma \cong \epsilon \epsilon_0 \kappa \psi_d$$

where

d distance from the surface (m)

ψ The local electric potential (V)

ψ_d The potential of diffuse double layer (V)

σ The surface charge (C.m^{-2})

When the ionic strength increases, the Debye's length decreases, which explains the phenomena of layers contraction. Moreover, in these models, the plane of the solid surface receives ions from the solution such as H^+ and OH^- or from the solid structure, determining the potential. The surface charge is then calculated taking into account those association equilibriums, and therefore depends of equilibrium constants, ion concentrations determining the potential solution, and the total number of surface sites.

When an electric field is applied in a suspension containing charged particles, the particles acquire certain mobility (u) depending on their charge and their ionic accompanying. There exists within the double layer a plan that delimits two different ions comportment. Ions having a specific affinity for the surface go with the particle in its movement, whereas ions with smaller attraction have a gradual separation from the surface. This plan, called the shear plane, is defined from hydrodynamic considerations. However, it is possible to connect it to the chemical description of the double layer. Indeed, it is usually very close to the delimiting plane of the compact layer and of the potential diffuse layer (Ψ_d).

The potential at the shear plane is commonly noted as zeta potential or ζ . It depends mainly of two parameters: the potential at the Helmholtz internal plane (ψ_i) and the ionic

force of the solution, compressing more or less the electric double layer. The zeta potential is experimentally accessible by electrokinetic measurements. The principle of these measures is based on the electrophoretic mobility of charged particles suspended in an electrolytic reservoir. Applying an electric field promotes that the charged particles go towards the electrode with opposite charge. It is the electrophoresis phenomenon.

The electrophoretic mobility, u ($\text{m.s}^{-1}.\text{V}^{-1}$), allows to access to the zeta potential value based on Henry's relationship:

$$u = \frac{2\varepsilon\varepsilon_0\zeta}{3\eta}f(\kappa a)$$

where :

η Liquid viscosity (Po)

a Particle radius (m).

The factor $f(\kappa a)$ depends on the form of the particle. In the case of a spherical particle, and if a is higher than 1, the relationship is simplified by the Smoluchowski equation where $f(\kappa a) = 3/2$ and becomes:

$$u = \frac{\varepsilon\varepsilon_0\zeta}{\eta}$$

This simple relation based on electrophoretic mobility, allows the access to the zeta potential when the applied electric field is known. The zeta potential of the powder activated carbons was determined by using a zeta meter (Zetaphoremeter IV-CAD Instrumentation) with the measure conditions described in Table 2.1. The instrument automatically measures the electrophoretic mobility of particles in dilute suspension and then converts the electrophoretic mobility into zeta potential for aqueous system by utilizing the Smoluchowski equation. Calibration or calibration control of the zeta meter was made with a colloid solution. Suspensions were prepared by first weighing 0.1 g of activated carbon (particle size $< 0.5\text{mm}$) and transferring it into a 125 mL volumetric flask containing about 50 mL of deionized water. For zeta potential measurement, the pH of the sample was adjusted with dilute acid (HCl) or base (NaOH) solutions.

The zeta potential of the suspensions was studied in a wide pH range of 2 to 12 by sampling some volume from the suspension and then following the positioning and measuring procedures for zeta potential measurement. The reproducibility of the tests was verified by measuring 10 times the zeta potential of a number of moving particles at different aliquots of each sample.

Table 2.1 . Zeta measurement conditions

Parameters	Values
Electric field	8.7 V cm ⁻¹
Dielectric constant	78.2
Viscosity	0.9 mPAs
Temperature	25.5 °C
Conductivity	0.001 – 0.01 mS cm ⁻¹

2.2.5 pH_{ZC} determination

The determination of the pH_{pzc} in carbonaceous materials was carried out as follows (Rivera-Utrilla *et al.*, 2001): 50 mL of 10⁻² M NaCl solution was placed in a closed Erlenmeyer flask, the pH was adjusted to a value between 2 and 12 by adding HCl or NaOH 0.1 M solutions. Then, 0.15 g of each sample was added and the final pH measured after 5 days under agitation at room temperature. Faria *et al.* (2004) utilized this method to determinate the pH_{pzc} of commercial activated carbons for anionic and cationic dyes adsorption and they explains that the pH_{pzc} value is found at the point where the curve pH_{final} vs pH_{initial} crosses the line pH_{final} = pH_{initial}.

2.2.6 Scanning electron microscopy (SEM)

Scanning electron microscope is composed of a number of chambers (Figure 2.6). The first is a column filled with an electron source, apertures, scanning coils and lenses, down which an electron beam is first generated, accelerated, demagnified to a small electron *probe*, and then deflected in a raster fashion over the area to be imaged in the main chamber. The

interaction between the impact electrons and the sample generates a number of different electrons such as *back scattered electrons* (BE), *secondary electrons* (SE) and Auger electrons and other emissions such as characteristic and Bremsstrahlung X-rays, visible light through elastic and inelastic scattering processes. Inelastically generated and emitted SEs are classified into two types called SE1 and SE2 which are produced within materials either directly from an incident (primary) electrons or from internally scattered electrons, respectively. Therefore SE1 produces a contrast highly dependant upon sample surface geometry and gives topographic information selectively, while SE2 comes from larger depth and volume than those of SE1, the contribution of SE2 to the image reduces topographic information. It is noteworthy that reduction of SE2 contribution to an image can be made only by reducing the landing energy. Characteristic X-rays, which are used for EDS and WDS measurements, give chemical information. Rutherford scattering of electrons involves high scattering angles of impact electrons, a detectable proportion of which are scattered through a large enough angle such that their resultant trajectory allows them to exit through the sample surface as BE. As Rutherford scattering is highly dependant upon the electrostatic potential of the sample atom nucleus, and therefore the atomic number, BE therefore provides compositional contrast . The electrons generated are collected by a scintillator or solid state detector and the signal is multiplied and delivered as a grayscale value, depending upon the intensity, to a viewing screen that is progressively scanning in synchronization with the scanning beam. The result is an image of the crystal that may be saved to film or digital image file (Stevens *et al.*, 2009).

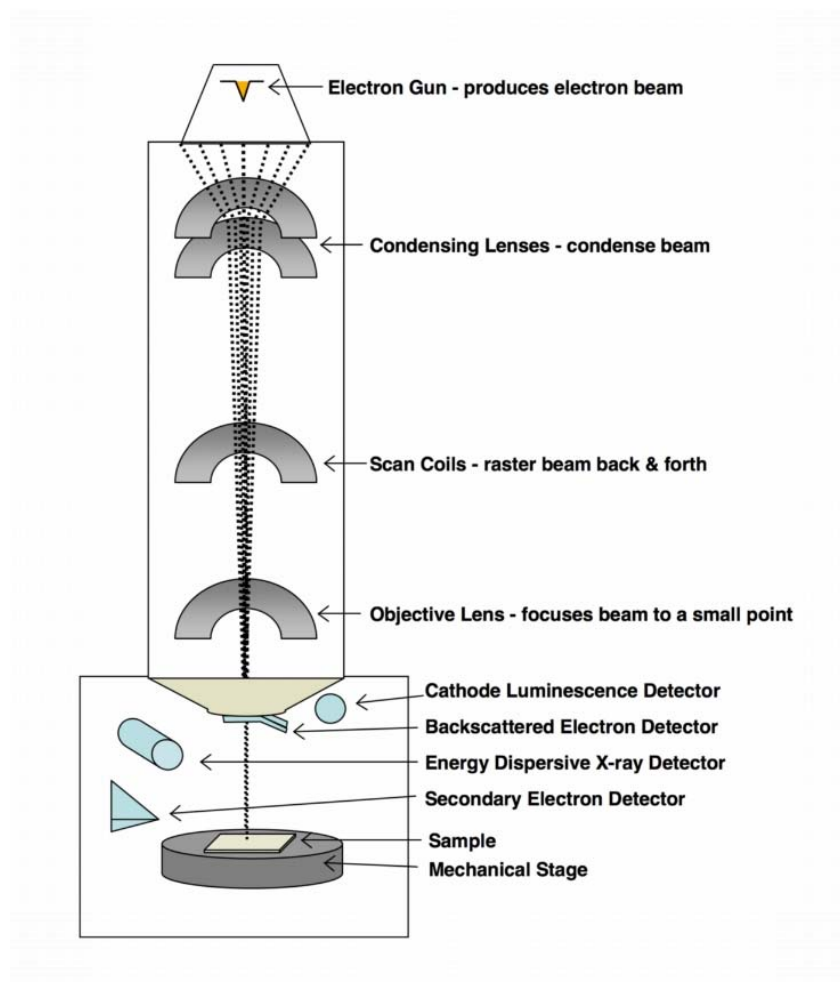


Figure 2.6. Schema of SEM technique

The porous structure of carbonaceous materials and commercial activated carbons was observed using a JEOL 6400F Scanning Electron Microscope. A magnification ranging from 100X to 500X was used for the visualization of the images. Imaging is typically obtained using secondary electrons besting order to obtain the best resolution of the fine surface typographical features. To examine the samples they were coated with a thin metal layer (Au) to make them electrically conductive and minimize the artefacts associated with the charge build up.

2.3 ARSENIC MEASUREMENTS

Methods for determining different chemical forms of arsenic in water have become increasingly important due to the different toxicity and chemical behavior of various arsenic forms. Consequently, various quantification procedures have been proposed and reviewed. Electrochemical methods have been reported as detection systems for traces of arsenic or as

preconcentration techniques prior to the detection of arsenic species by optical instruments. Well-established methods that involve the coupling of separation techniques, such as ion chromatography and high performance liquid chromatography, with a sensitive detection system, such as inductively-coupled plasma-mass spectrometry (ICP-MS), atomic fluorescence spectrometry-hydride generation (AFS-HG), atomic absorption spectrometry-hydride generation (AAS-HG) and atomic absorption spectrometry with graphite furnace (AAS-GF) are the methods of choice for the routine determination of a large number of water samples. AAS-GF allows the determination of the total arsenic and also allows the determination of the arsenic in very low concentrations as parts per billion (ppb or $\mu\text{g.L}^{-1}$).

The AAS-GF is based fundamentally in the Beer-Lambert law that represents a linear relationship between absorbance and concentration of an absorber of electromagnetic radiation. The general Beer-Lambert law is usually written as:

$$A = a_{\lambda} \cdot b \cdot c$$

Where A is the measured absorbance, a_{λ} is a wavelength-dependent of the absorptivity coefficient, b is the path length, and c is the analyte concentration. When the concentration is expressed in units of molarity, the Beer-Lambert law is written as:

$$A = \epsilon_{\lambda} \cdot b \cdot c$$

Where ϵ_{λ} is the wavelength-dependent molar absorptivity coefficient. The λ subscript is often dropped with the understanding that a value for ϵ is for a specific wavelength.

Experimental measurements are usually made in terms of transmittance (T), which is defined as:

$$T = \frac{P}{P_0}$$

where P is the power of light after it passes through the sample and P_0 is the initial light power. The relation between A and T is:

$$A = -\log(T) = -\log\left(\frac{P}{P_0}\right)$$

The figure 2.7 shows the case of absorption of light through an optical filter and includes other processes that decrease the transmittance such as surface reflectance and scattering.

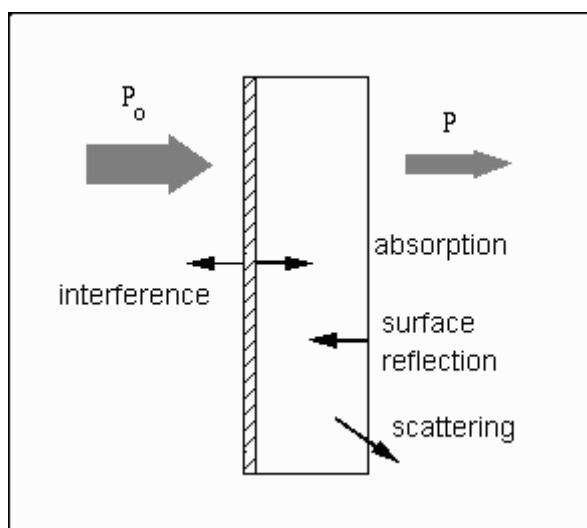


Figure 2.7. Absorption of light through an optical filter in AAS technique.

In analytical applications such as AAS-GF, the concentration of an analyte must be measured independent of the effects of reflection, solvent absorption, or other interferences. The figure 2.8 shows the two transmittance measurements that are necessary to use absorption to determine the concentration of an analyte in solution. The first diagram is for solvent only and the second one is for an absorbing sample in the same solvent. In this case, P_s is the source light power that is incident on a sample, P is the measured light power after passing through the analyte, solvent, and sample holder, and P_o is the measured light power after passing through only the solvent and sample holder. The measured transmittance in this case is attributed to only the analyte.

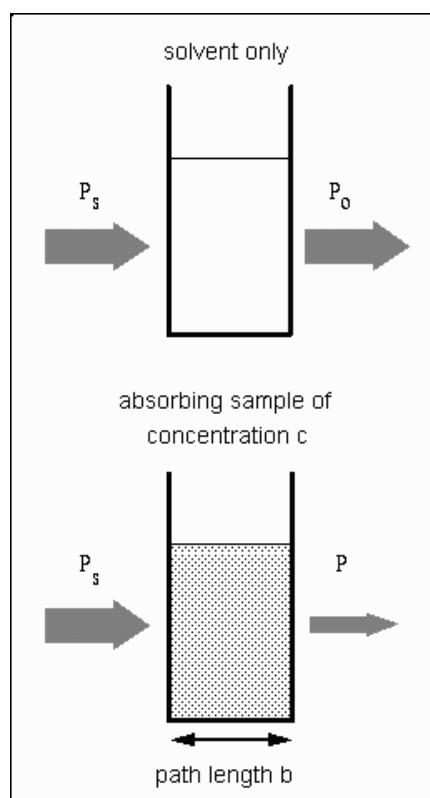


Figure 2.8. Light absorption by a sample.

Absorption instruments can usually display the data as either transmittance, %-transmittance, or absorbance. An unknown concentration of an analyte can be determined by measuring the amount of light that a sample absorbs and applying Beer-Lambert's law. If the absorptivity coefficient is not known, the unknown concentration can be determined using a calibration curve of absorbance versus concentration derived from standards.

A Perkin Elmer Analyst 600 atomic absorption spectrometer equipped with graphite furnace was used. For graphite furnace measurements, argon (high purity) was used as inert gas. The operating parameters for the arsenic determination were set as described in Table 2.2. THGA graphite tubes (Perkin Elmer part No. B3 000641) were used. Samples were injected into the graphite furnace using Perkin Elmer AS-800 auto sampler. All chemicals used in As analysis were of analytical reagent grade and were used without further purification. Deionized water (Milli-Q Millipore $18.0 \text{ M}\Omega \text{ cm}^{-1}$, resistivity) and ultrapure nitric acid at 65% (Normatom, Prolabo) were used for blank (2%) preparation. Magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$) and palladium (Pd) matrix modifiers were also added. Most of the matrix was removed before the atomization step and less interference occurred during atomization.

The atomic absorption signal was measured as a peak height mode against an analytical curve, the calibration curve was made in the range 5 to 20 $\mu\text{g.L}^{-1}$ from a 1000 $\mu\text{g.L}^{-1}$ standard solution of arsenic (Aldrich). For samples analysis, each sample was prepared two times and each preparation analyzed three times to obtain finally 6 arsenic measures from each sample.

Table 2.2. Optimized graphite furnace parameters

Furnace Program					
Step	Temp. (°C)	Ramp time	Hold time	Internal Flow	Gas type
1-Dry	110	5	20	250	Normal
2-Dry	120	5	40	250	Normal
3-Pyrolysis	1000	20	30	250	Normal
4-Atomization	2400	0	3	0	Normal
5-Cleaning	2500	1	3	250	Normal

One of the important aspects in the determination of different compounds (As(V) and TC in this study) by analytical techniques is to report the detection and determination of the smallest concentration or, sometimes, amount of the analyte, that may be achieved with a reasonable certainty when using a given procedure. Consequently, performance of a specified trace analysis method is commonly characterized by the limit of detection (LD) and the limit of quantification (LQ). The following definitions of the limit of detection, LD, given by the International Union of Pure and Applied Chemistry (IUPAC) and the American Chemical Society (ACS), respectively, are commonly accepted:

1. The limit of detection, expressed as a concentration or quantity, is derived from the smallest measure that can be detected with reasonable certainty for a given analytical procedure (IUPAC, 1978; 1976).

2. The limit of detection is the lowest concentration of an analyte that the analytical process can reliably detect. The limit of quantification, LQ, is not defined in the IUPAC publications (IUPAC, 1978; 1976), although its numerical definition is given in an ACS document (ACS, 1980). The LQ has been introduced to provide supplemental statistical separation of the blank measurement and true analyte signal distributions and established because the LD was not considered satisfactory for quantitative analysis. Thus, it can be defined in words that the limit of quantification refers to the smallest concentration or the mass which can be quantitatively analyzed with reasonable reliability by a given procedure (Mocak *et al.*, 1997).

To determine the limits of detection and quantification, the signal value, y_D , corresponding to the limit of detection, must reflect the value of the true signal (related to some non-zero analyte concentration) which is significantly different from the blank signal value. The y_D signal value is defined in the ACS document in terms of population statistics, i.e. the population mean, μ_b , and the population standard deviation, σ_b , of the blank signal, as in the equation:

$$y_D = \mu_b + k_D \sigma_b$$

where $k_D = 3$. This definition corresponds to a $100(1 - \alpha) = 99.865\%$ probability that the blank signal does not exceed the LD ($\mu_b + 3\sigma_b$) value (one-sided statistical test).

For the signal y_Q , which is related to the limit of quantification (LQ), it follows:

$$y_Q = \mu_b + k_Q \sigma_b$$

where $k_Q = 10$.

With the obtained analytical measures, the limits of detection and quantification for As(V) were determined and they are presented in Table 2.3.

Table 2.3 –Limit of detection (LD) and Limit of Quantification (LQ) for As(V).

Pollutant	Technique	LD	LQ
As(V)	AAS-GF	2 $\mu\text{g.L}^{-1}$	4 $\mu\text{g.L}^{-1}$

2.4 EXPERIMENTAL PROCEDURES FOR ARSENIC REMOVAL WITH CARBONACEOUS MATERIALS AND GAC1

All the solutions were realized with deionized water, except for the study realized with spring waters, all the polyethylene reactors were previously washed with diluted nitric acid overnight and rinsed with source water, demineralized water and deionized water three times with each type of water to avoid any contamination in the arsenic solutions. During sorption tests it was verified that no sorption of arsenic occurred in the cellulose filters and in the plastic bottles walls by running a blank reactor. For the entire sorption tests a particle size of 0.5 -1 mm was utilized for steam activated carbons and a particle size > 1 mm was employed for sorption test with iron modified materials, except for the short sorption kinetic and the sorption test in spring water where powder materials (particle size < 0.5 mm) were used.

2.4.1 Sorption kinetic

The removal of arsenic (V) from synthetic aqueous solutions by BP-H₂O, BP-H₂O-Fe, PH-H₂O, PH-H₂O-Fe, and GAC1 is studied. Batch kinetics adsorption experiments were conducted at 20°C by agitating 0.05 g of adsorbent with 100 mL of As (V) solution at three different initial concentrations (100, 500 and 1000 µg.L⁻¹), at 200 rpm and temperature fixed at 20 °C. Initial pH values were close to 6, and they were controlled at the end of the experiment. Bottles were capped and shaken until the sorption equilibrium was reached. Previously, it has been verified that the raw beet pulp (BP) and raw peanut hulls (PH) are inefficient for arsenic removal.

2.4.2 pH effect on As (V) sorption

The pH is an important parameter in water treatment, because proton concentration can modify the redox potential of sorbates and sorbent materials, as well as chemical speciation of sorbates and surface charge of adsorbent materials. The effect of initial pH on arsenic (V) sorption onto carbonaceous material from sugar beet pulp and activated with steam was studied by contacting for 7 days 0.05g of adsorbent with 100 mL of arsenic solution of initial concentration of 100, 500 and 1000 µg.L⁻¹. The initial pH was established in an acid value of

3.5 (arsenic like H_2AsO_4^-) and a basic value of 12.0 (arsenic like AsO_4^{3-}) to compare the sorption efficiencies in two different pH ranges.

2.4.3 Adsorption isotherms

Adsorption isotherm tests were conducted using the bottle-point method: 100 mL of deionized water was doped with arsenic (V) concentrations from 100 to 5000 $\mu\text{g.L}^{-1}$ and then 0.05g of carbonaceous materials was added to plastic bottles. The bottles were sealed and put on a shaker (200 rpm) for 5 days at 20 °C. After shaking, the equilibrium pH was measured and recorded, the samples were filtered through 0.45 μm regenerate cellulose filters and the concentration of arsenic in the filtrate was determined by atomic absorption spectroscopic using a graphite tube (Analyst 600, Perkin Elmer). When necessary, it was verified that no adsorption occurs on the wall of the plastic bottles and nor on the filters. Furthermore the arsenic (V) concentration was measured from a plastic bottle without carbonaceous material to verify no changes in arsenic (V) concentration after 5 days.

2.4.4 Adsorption study in natural water spiked with As(V)

To determined the effect of the presence of ions in solution for As(V) sorption on the carbonaceous materials, two different spring water were utilized, the first one with a high mineral content and the second one a natural water with a lower mineral content, they were designed like HMC and LMC respectively. To investigate the effect of ions on As(V) removal by the carbonaceous materials prepared from peanut hulls (PH- H_2O and PH- H_2O -Fe), batch adsorption tests were conducted, with an initial As(V) concentration between 100 and 5000 $\mu\text{g.L}^{-1}$ spiked into 100 mL of both types of natural water. The concentrations of competitive ions in spring waters tested in this study are shown in Table 2.4. The adsorbent materials mass was 0.05 g, and the As(V) solutions mixed with PH- H_2O and PH- H_2O -Fe were shacked mechanically at 200 rpm. Samples were measured after 5 days of reaction time.

Table 2.4. Mineral content of natural water utilized in this work

	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	NO_3^-	HCO_3^-	SO_4^{2-}	pH
HMC (mg L⁻¹)[*]	230	66	40	8	58	< 1	280	620	7.2
LMC (mg L⁻¹)[†]	4.1	1.7	2.7	0.9	0.9	0.8	25.8	1.1	7.3

^{*} Natural water with high mineral content (HMC), [†] Natural water with low mineral content (LMC).

2.5 TETRACYCLINE MEASUREMENTS

The pure tetracycline used was of analytical grade and purchased from Sigma-Aldrich (St. Louis, MO, USA). All the tetracycline determinations were realized by ultraviolet-visible spectroscopy (UV-Vis) that is a non-destructive technique for determining the chemical species of a material and quantifying their concentration. A light beam of a certain wavelength range interacts with the sample and the intensity of the transmitted or reflected signal is recorded as a function of the wavelength. Because of the interaction with the sample, at certain frequencies the light is absorbed resulting in absorption peaks in the spectrum. The absorption frequencies are specific for certain chemical compounds and associated with electron transitions in the material. The chemical composition of the sample can therefore be determined by analyzing the spectrum using standards that allow quantitative measurement. The basis of this theory is the Lambert-Beer law (described previously in this chapter). In this case, a Shimadzu Recording Spectrophotometer UV-1601 was used. Spectra were recorded at room temperature in the range 190 nm to 600 nm to verify no changes in spectra after sorption process and the wavelength was fixed at 357 nm to TC determination. All the TC measurements were realized at pH values between 4 and 5 due to a change in λ_{max} of TC spectra when pH increases (Figure 2.9 and 2.10).

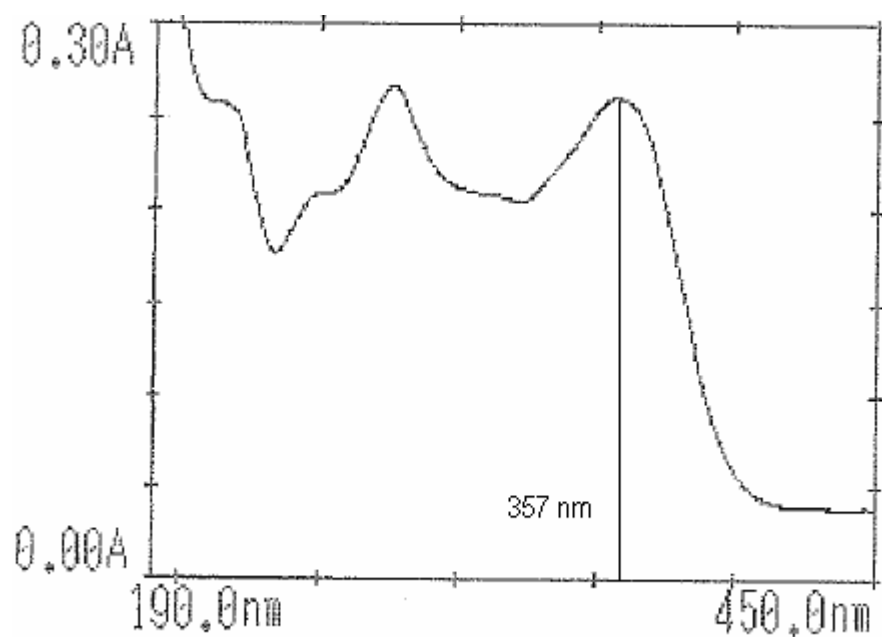


Figure 2.9 - Absorption spectra of the TC at pH 4.5

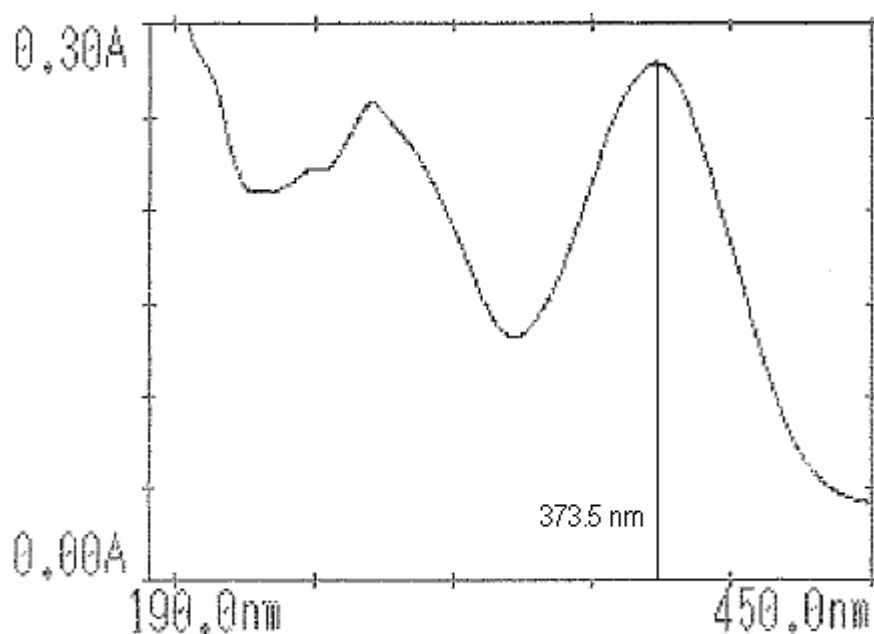


Figure 2.10 - Absorption spectra of the TC at pH 9.5

The spectral measurements were carried out at room temperature (25 ± 1.0 °C). The UV–Vis measurements and spectra were recorded with 1.0 cm Hellma® quartz cells. The corresponding limits of detection and quantification for TC were also determined and they are presented in Table 2.5.

Table 2.5 –Limit of detection (LD) and Limit of Quantification (LQ) for TC.

Pollutant	Technique	LD	LQ
TC	UV-Vis Spectrometry	0.1 mg.L ⁻¹	0.3 mg.L ⁻¹

2.6 EXPERIMENTAL PROCEDURES FOR TETRACYCLINE REMOVAL WITH CARBONACEOUS MATERIALS AND ACTIVATED CARBONS

Experiments were carried out in batch mode, using glass reactors previously washed with diluted nitric acid overnight and rinsed three times with source water, three times with demineralized water and three times with deionized water to avoid any organic contamination in the TC solutions, and then dried overnight in an oven at 105°C. During sorption tests it was verified that no sorption of tetracycline occurred in the cellulose filters and in the glass reactors walls by running a blank reactor. For TC sorption test, powder materials (particle size < 0.5 mm) were utilized. All the flasks were wrapped with aluminum foils to prevent light induced decomposition during mixing and sorption or storage processes.

2.6.1 Sorption kinetic

Sorption kinetics were studied for three different initial concentrations of TC (50, 100, 300 mg.L⁻¹). TC solutions were prepared in deionized water and the initial pH values were around 3.4 and 4.2, found as optimal for TC. For each contact time, stirring was briefly interrupted and an aliquot was removed. The sample was filtered and TC concentration in solution was analyzed. The studied time range was varied in the range 0-500 hours.

2.6.2 pH effect on TC sorption

Before beginning with isotherms experiments, the initial pH effect of TC sorption onto a carbonaceous material (BP-H₂O) and a commercial activated carbon (GAC2) was studied by contacting for 5 days 0.07g of BP-H₂O and 0.06g of GAC2 with 300 mL of TC solution of

initial concentration of 200 mg.L^{-1} . The initial pH was established at values of 4.0, 8.0 and 11.0 to compare the sorption efficiencies at different pH ranges and different TC species. Like the kinetics test, a blank reactor shown that no TC adsorption occurs in the flask, the filter and there are not changes in TC structure during all the experiment.

2.6.3 Adsorption isotherms

For the adsorption isotherm test on the materials, 0.07 g of the PH-H₂O and PH-H₂O (powder) were placed in each of six glass flasks with 100 mL of TC solution at different concentrations (15, 25, 50, 65, 80 and 100 mg.L^{-1}). For the carbonaceous material prepared from beet pulp (BP-H₂O), 0.07 g of powder material was placed in contact with 200 mL of TC solution at concentrations of 70, 100, 150, 200, 250 and 300 mg.L^{-1} . In the case of the first commercial activated carbon (GAC1), the mass was of 0.06 g, in a volume of 300 mL of TC solutions at 50, 80, 100, 120, 150 and 200 mg.L^{-1} and for the second activated carbon utilized (GAC2), the mass of powder material was 0.06 g placed in contact with 300 mL of TC solution at 100, 120, 160, 200, 250 and 300 mg.L^{-1} .

The pH of the all the solutions was between 3.3 and 4.5 depending of the TC solution concentration. The flasks were sealed and shaken mechanically at 25 °C in an agitation table (Bioblock Scientific) at a shaking speed of 300 rpm. The flasks were wrapped with aluminum foils to prevent light induced decomposition during mixing and sorption or storage processes. A blank sorption experiment was conducted following the same test procedure except that no adsorbent material was added. Sorptive losses to the glass flask walls were found to be less than 4% of the tetracycline added.

2.6.4 Adsorption study in natural water spiked with tetracycline

The effects of environmental factors, such as ions content in water, on tetracycline sorption were investigated on the BP-H₂O and the GAC2. To evaluate the ions presence effect in the solution, batch adsorption tests were conducted, with an initial TC concentration between 70 and 300 mg.L^{-1} for BP-H₂O and 100 and 300 mg.L^{-1} for GAC2 into 300 mL of natural water. The adsorbent materials mass was 0.06 g, and the TC solutions were mixed

with the powder adsorbents and shaken mechanically at 300 rpm. Samples were measured after 5 days of reaction time. The tetracycline sorption by these materials in natural spring water with a high mineral content (HMC) (mineral content described in Table 2.4), was studied with pH adjustment at 4.5 at the moment of TC determination by UV-Vis spectrophotometry.

2.7 CONCLUSION

This chapter has described the different techniques and methodologies chosen for the characterization of the sorbents and the sorption study. This does not represent an exhaustive list of what is needed to reach these two objectives. In future works, the characterization could be completed by a better knowledge of the iron form included into the activated carbons. For example, XPS analysis or FTIR spectra would bring interesting new data as well as surface potentiometric titrations such as the Boehm's method. In addition, different methods leading to variable iron contents in the sorbents could be tested. As far as sorption experiments are concerned, it would be interesting to work with arsenic (III) since this form is also present in natural contaminations as well as mixtures of arsenic (V) and (III). The possibility to test real contaminated effluents would also lead to progress on the applicability of these kinds of sorbents. Regarding the tetracycline sorption, concentrations more adapted to those found in natural environment should be used. This means that new analytical methods have to be developed to decrease the quantification limits. Speciation and competing effects with natural organic matter would complete favourably the sorption study in batch reactor.



CHAPTER 3

CARBONACEOUS MATERIALS CHARACTERIZATION

This part is of main importance in this work since the aim is to obtain the most complete physic-chemical characterization of the lab-scale carbonaceous materials. Even if this study is a preliminary work on the activated carbons (AC) production from agricultural wastes, the whole goal is ideally to find some relationships between the properties of the materials and the sorption efficiencies towards specific pollutants. To respond to this question, huge experimental data describing the materials and their behaviour in solution are necessary and a comparison with other activated carbons, produced at industrial scale with a more homogeneous structure is essential. It is the reason why two commercial granular activated carbons (GAC1 and GAC2), with different porosities and chemical properties have been selected for this work. This part is then divided into 3 main sections:

- The production of carbonaceous materials from two types of agricultural wastes : the sugar beet pulp and the peanut hulls,
- An investigation of the porous structure of the carbonaceous materials including nitrogen adsorption measurements for the determination of BET surface area, porous volumes and median diameters. Then SEM pictures are presented to complete this part devoted to the material porosity,
- A study of the chemical characterization based on simple determination like ash content and elemental analysis and then followed by zeta potential measurements and pH_{PZC} determinations.

3.1 PRODUCTION OF CARBONACEOUS MATERIALS

3.1.1 Char and activated carbons

The activated carbons produced from sugar beet pulp and peanut hulls were prepared with the same operating conditions, namely a ramp of heating of $10^{\circ}\text{C min}^{-1}$ until 857°C under nitrogen gas (0.5 mL.min^{-1}), then a physical activation with steam (0.7 mL.min^{-1}) during 80 min always under nitrogen flowrate. Finally, the temperature decreased under the nitrogen flow. The activated carbons were called BP-H₂O and PH-H₂O. In addition, fews grams of chars were also produced only with the sugar beet pulp (BP-C): the pyrolysis was made under nitrogen flow until 600°C and then a cooling until ambient temperature. After the production, all the carbonaceous materials have been separated into 3 parts with 2 sieves of 0.5 and 1 mm, and the mass yields have been calculated with the following equation

$$\text{mass yield} = \left(\frac{w_2}{w_1} \right) \times 100 \quad (3.1)$$

where w_1 is the initial weight of dried agricultural waste (g) and w_2 the weight of the obtained activated carbon (g) or char (g). The table 3.1 presents these different results.

Table 3.1 – Yield and particle size distribution of carbonaceous materials obtained from raw agricultural by-products (%).

Material	Particle size (%)			Yield (%)
	Particles > 1.0 mm	0.5 mm < Particles > 1.0 mm	Particles < 0.5 mm	
BP-C (600 °C)	22.2	46.4	31.4	28
BP-H ₂ O (857°C / steam)	21.0	42.9	35.9	16
PH-H ₂ O (857°C / steam)	42.9	40.4	16.7	24

The obtained yields are the followings: close to 30 % for the carbonized sugar beet pulp (BP-C), 16 % for BP-H₂O and 24% for PH-H₂O. During the pyrolysis, also called thermal carbonization, the devolatilization takes place and consequently many gaseous products rich in hydrogen, light hydrocarbons are generated. This mainly explains a great mass loss of the precursors. Obviously it is also observed with the production of BP-C: the mass loss is close to 72 %. With respect to the solid residue (char) formed, there is an enrichment in both relative carbon content and aromaticity, compared to the precursor. Because a lot of mass is evolved during carbonization, this increase in aromaticity is accompanied by an increase in incipient microporosity, since a lot of functional group and bridge chains are evolved, yielding void spaces (Bandosz, 2006). To enhance the porous structure of the char, a partial oxidation, called activation is needed. When the activating agent is steam the activation is said *physical activation*, which is rather different from *chemical activation* obtained after impregnation of chemical agent. For example, GAC1 is produced by physical activation of coconut shell and GAC2 by chemical activation with H₃PO₄ from wood. The steam reacts with the carbon atoms and removes some of the mass of the internal surface, in the incipient micropores, creating a well developed microporous material. In this step, the mass loss is less than those observed during the pyrolysis (Bandosz, 2006). It explains that the mass yield of BP-H₂O production is only 12 % less in comparison with the corresponding char. All these yields are of course dependent of the selected precursors. Within the same conditions, they represent 16 % for the sugar beet pulp and reach 24 % for the peanut hulls. A last remark about these AC is that both carbonization and activation are carried out simultaneously so the process is called *direct activation* (Bandosz, 2006).

After the thermal treatments, the char and activated carbons were collected from the furnace and a sieving has been realized. It has been decided to keep the (0.5-1 mm) fraction for the adsorption study since it represents 43 and 40 % respectively of BP-H₂O and PH-H₂O. But before that, the AC needs to be rinsed and washed with deionised water. Different washing steps have been performed in order to reach a constant pH of the solution. For example, the pH evolution in function of time corresponding to BP-H₂O and PH-H₂O is shown on Figure 3.1. The same procedure has been applied to GAC1 and GAC2. For all the different materials, the obtained pHs are the followings: 10.1 and 9.8 for BP-H₂O and PH-H₂O and 7.6 and 4.3 for GAC1 and GAC2 respectively. All these pH take basic values which

certainly means that the majority of these AC are basic materials excepted for GAC2. It will be discussed again in the next section devoted to pH_{PZC} . When the pH is stabilized, the AC is then dried at 105 °C and considered as ready to use. The particle size higher than 1 mm counting for 21 % for BP-H₂O and 43 % for PH-H₂O is recycled for the iron impregnation (see Chapter 2). Finally it can be noted that the fine particles (< 0.5 mm) fraction corresponding to 36 % of BP-H₂O and 17 % of PH-H₂O is not reused for further applications since only granular materials have been considered. That could be seen as a drawback would be more attractable in the case of an adsorption study leading on powder materials.

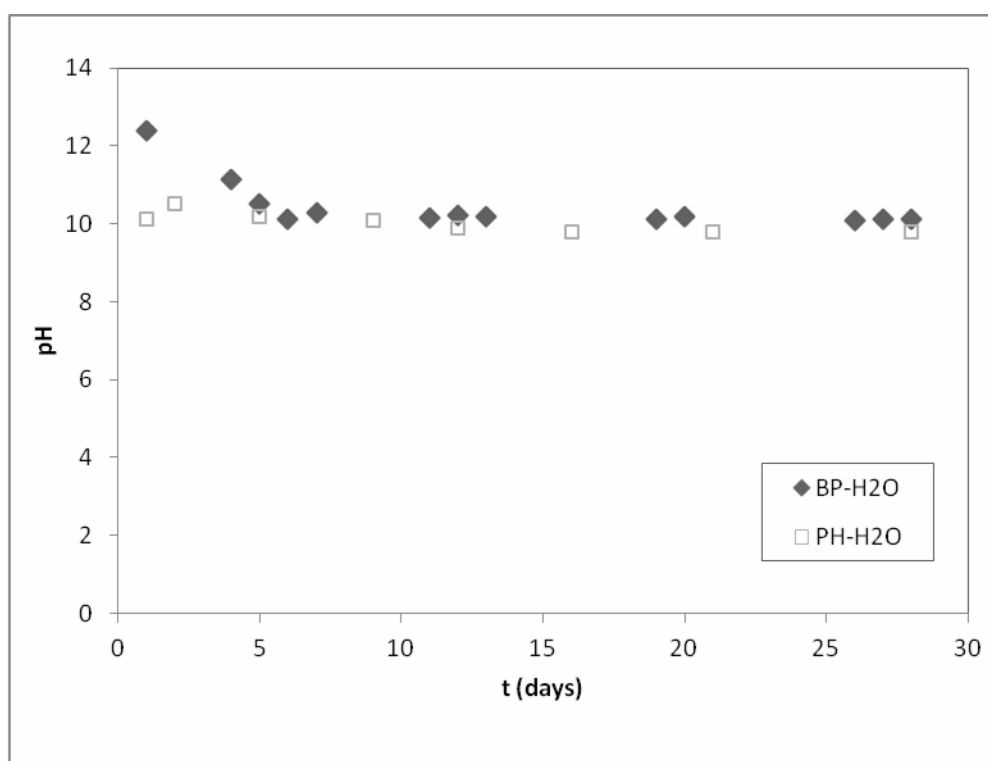


Figure 3.1 – Evolution of the pH during the washing procedure of BP-H₂O and PH-H₂O.

3.1.2 Modified activated carbons

In Chapter 1, it has been shown that it is possible to modify AC in order to give them specific properties regarding selected pollutants. As far as arsenic is concerned, it is well known that iron based adsorbents present better adsorption capacities. A simple procedure has been then followed (Chapter 2) to include iron onto the lab scale AC (> 1mm). The obtained

materials from sugar beet pulp and peanut hulls are called BP-H₂O-Fe and PH-H₂O-Fe. After the chemical reactions, BP-H₂O-Fe and PH-H₂O-Fe are then washed with the procedure described above to have a stabilized pH and it was completed by an iron measurement to be sure that there was no release of this ion. After the drying at 105 °C, these new adsorbents were ready to use. The mass yield from BP-H₂O and PH-H₂O are close to 74 % for BP-H₂O-Fe (12 % from BP) and 78 % for PH-H₂O-Fe (19 % from PH). Since these carbonaceous materials have not a great mechanical resistance, the mass loss is mainly due to their attrition during the chemical treatment. It is the reason why the fraction higher than 1 mm was kept for that purpose and there was not presence of iron precipitation during the impregnation. The stabilized pH measurements are 9.1 and 3.9 for BP-H₂O-Fe and PH-H₂O-Fe respectively. They are lower than their precursors (BP-H₂O and PH-H₂O), and particularly for PH-H₂O-Fe indicating probably that acidic moieties have been created during the treatment.

3.2 POROUS STRUCTURE OF THE MATERIALS

3.2.1 BET surface analysis

In adsorption processes, the main parameters influencing the reaction are notably in relation with the surface area and porous properties of the adsorbent. A study of nitrogen adsorption is then required to access to the porosity characteristics. The parameters provided by the characterization of the produced materials are presented in Table 3.2. The BET surface areas for BP-H₂O and BP-H₂O-Fe are 821 and 762 m².g⁻¹, and 829 and 718 m².g⁻¹ for PH-H₂O and PH-H₂O-Fe, respectively. Previously a determination of BET surface was also done on BP-C which revealed a very low value of 6.6 m².g⁻¹ and as a matter of interest, the BET surface of the raw precursor was 0.2 m².g⁻¹ measured with krypton gas (Reddad, 2002). These values confirm that pyrolysis is a thermal treatment which is not devoted to create the porosity of the material and an activation step is necessary to satisfy to this objective. In comparison with the GAC, the BET surface areas developed by BP-H₂O and PH-H₂O are 25 % lower. Considering that the optimization of the AC production, in terms of carbonization and activation temperature, nature of activating gas, temperature ramp and dwell time, was not the ultimate goal, then they are considered as acceptable for a hand-made activated carbons.

Table 3.2 Textural parameters of produced activated carbons and GACs.

	BP-H ₂ O	BP-H ₂ O-Fe	PH-H ₂ O	PH-H ₂ O-Fe	GAC1	GAC2
S_{BET} (m².g⁻¹)	821	762	829	718	1138	1515
Microporous volume (cm³.g⁻¹) / up to 2nm	0.3478	0.3227	0.3551	0.3084	0.4852	0.6407
Mesoporous volume (cm³.g⁻¹) / (2 to 50 nm)	0.3612	0.3227	0.0699	0.0569	0.1761	0.6131
% microporosity	49	50	84	84	73	51
%mesoporosity	51	50	16	16	27	49
d₅₀ mesoporous (nm)	5.4	4.5	3.8	3.6	4.3	5.9
Total porous volume (cm³.g⁻¹) / BET analysis	0.6430	0.5778	0.4028	0.3446	0.6230	1.2291
Ash Content (%)	13.6	13.9	1.3	1.5	0.4	1.1

Other values extracted from the literature are shown in Table 3.3. It is clear that the BET surface areas measured on materials produced at lab scale depend obviously on the nature of the precursor and the conditions of preparation. For example, El-Hendawy *et al.* (2001) prepared activated carbon from corncob. The carbonization occurred at 500 °C for 2 h. A portion of this char was steam activated at different temperatures (from 600 °C to 850 °C) and times (1 to 2 h). The resulting BET surface areas are ranged between 607 and 786 m².g⁻¹. Another example is given by Juang *et al.* (2002) who shows that an increase of 90 °C on activation temperature induces an enhancement of BET surface from 446 to 607 m².g⁻¹ on a AC produced from bagasse. Finally, CO₂ activations lead to the highest BET surfaces in

Table 3.3. In all cases, the values determined in this work, from sugar beet pulp and peanut hull are quite high in comparison with this literature review.

Table 3.3 Studies of porosity of activated carbon obtained from agricultural by-products.

Material	Activation conditions	S_{BET} ($m^2 g^{-1}$)	Total porous Volume ($cm^3 g^{-1}$)	Reference
Corncob	Steam/850°C (1h)	607	0.296	El-Hendawy <i>et al.</i> , 2001.
	Steam/600°C (2h)	618	0.321	
	Steam/700°C (2h)	786	0.430	
Sawdust	Steam/800°C (1h)	516	--	Malik, 2003.
Bagasse	Steam/750°C (2h)	446	0.287	Juang, <i>et al.</i> , 2002.
	Steam/840°C (2h)	607	0.445	
Pistachio nut-shell	CO ₂ /800°C(1h)	884	--	Yang and Lua, 2003.
	CO ₂ /800°C(2.5h)	964	--	
Macadamia nut-shell	CO ₂ /500°C(4h)	750	--	Wang, <i>et al.</i> , 2002.
Bagasse	CO ₂ /900°C(1h)	614	0.310	Valix <i>et al.</i> , 2004.
Beet pulp	Steam/857°C(1.3h)	821	0.643	This work
Peanut Hulls	Steam/857°C(1.3h)	829	0.403	This work

A last point which needs to be noted is that the iron impregnation on BP-H₂O and PH-H₂O only implies a slight reduction of the BET surface, leading to 762 m².g⁻¹ for BP-H₂O-Fe and 720 m².g⁻¹ for PH-H₂O-Fe. If the precipitation of iron is difficult to control because of the complexity and the black color of the mixture, it can be concluded that the iron impregnation

is not like a homogeneous coating layer but rather some iron oxide fixed in probably specific sites. The SEM pictures and EDX spectra (section 3.2.3) can confirm this assumption.

3.2.2 Porous volumes and median diameters

In terms of total porous volumes determined by nitrogen adsorption analysis, the values obtained with the sugar beet pulp (BP-H₂O) are very close to those relative to the GAC1: 0.643 cm³.g⁻¹ compared to 0.623 cm³.g⁻¹ respectively. PH-H₂O presents a lower volume of 0.403 cm³.g⁻¹ and GAC2 the highest one (1.23 cm³.g⁻¹). In all cases, they are highly improved in comparison with the values shown in Table 3.3 with other precursors and activating gases. The difference between BP-H₂O and GAC1 is the distribution of these porous volumes: the mesoporous volume corresponds to the volume entrapped in pores between 2 to 50 nm and microporous volume in pores less than 2 nm. PH-H₂O is the highest microporous carbon (84 %), GAC1 is 73 % microporous and 27 % mesoporous, BP-H₂O has equal mesoporous and microporous volumes like GAC2. If this distribution plays an important role regarding the size of pollutants needing to be removed, explanations are under discussed and a key point could be the ash content. Valix *et al.* (2004) suppose that a high ash content in AC had some metal oxides that can fill or block some portions of micropore volume. This leads to increase the mesopore volume and to lower the surface area. This observation is verified between BP-H₂O and PH-H₂O where the ash content being higher in BP-H₂O the mesoporous volume is also improved. It means that the mesopores development might be depending on feedstock in physical activation and probably in relation with the ash content of the precursor itself. This parameter would act as a key point in the selection of the feedstock for the production of AC with determined properties. This comparison cannot be done with GAC2 due to the chemical activation of this carbon.

Moreover, in a case of a physisorption process for example, the absolute values of these different volumes are then of interest. Once again the lab-scale AC are attractive since they are centred around 0.33 cm³.g⁻¹ for the microporous ones and comprised between 0.06 and 0.36 for the mesoporous. The resulting classifications, based on microporous and mesoporous volumes are the followings:

$$\text{GAC2} \gg \text{GAC1} > \text{PH-H}_2\text{O} \neq \text{BP-H}_2\text{O} \neq \text{BP-H}_2\text{O-Fe} \neq \text{PH-H}_2\text{O-Fe}$$

$$\text{GAC2} \gg \text{BP-H}_2\text{O} \neq \text{BP-H}_2\text{O-Fe} \gg \text{GAC1} \gg \text{PH-H}_2\text{O}, \text{PH-H}_2\text{O-Fe}$$

Considering a similar type of activation and way of impregnation, the value of micro and mesoporous of each adsorbent are quite different. So the selection of the precursor is a key parameter in accordance with the desired porosity distribution or porous volumes.

As far as iron modified AC are concerned, it can be concluded that the iron impregnation decreases the total porous volumes (- 10% in BP-H₂O and - 14 % in PH-H₂O). But the important point of this impregnation is that it does not modify the percentage balance in terms of micro and mesoporosity.

Table 3.2 also shows that the mesoporous d_{50} corresponding of the diameter which retained 50% of the mesoporous volume. For all the mainly microporous adsorbents (PH-H₂O, PH-H₂O-Fe and GAC1), these diameters are respectively 3.8, 3.6 and 4.3 nm. It means that half of the mesoporous volume is ranged between 2 and 3.8, 3.6 and 4.3 nm. So their mesoporosity are close to microporosity. Concerning the AC developing an equal porosity distribution namely BP-H₂O, BP-H₂O-Fe and GAC2, these diameters get higher values of 5.4, 4.5 and 5.9 nm respectively. Another remark is that the iron impregnation does not highly modify again the median diameter. This parameter is interesting if the size of the pollutant is considered and could be correlated to the adsorption capacity.

3.2.3 Scanning electron microscopy

Surface images of the carbonaceous materials and GAC1 have been analyzed by scanning electron microscopy as shown in Figures 3.2 to 3.8. From these pictures, it is possible to appreciate the macropores in the surface of the materials, the micro and mesopores cannot be distinguished clearly by the limitations on magnification of this analysis technique. Figures 3.2 and 3.5 show SEM images of the rough areas of the raw materials (BP and PH). It can be found that there is poor porosity in their surfaces especially with the sugar beet pulp. In BP-H₂O and PH-H₂O (Figure 3.3 and 3.6), the pore creation can be slightly observed. The Figure 3.4 (BP-H₂O-Fe) only shows clearly the presence of iron traces but only in specific spots of the surface.

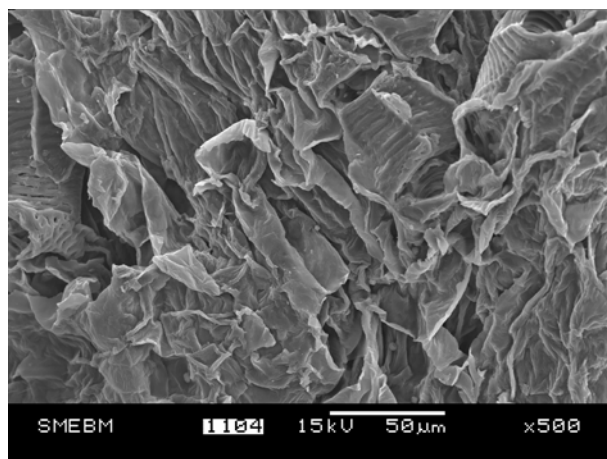


Figure 3.2. SEM micrograph of Raw-BP

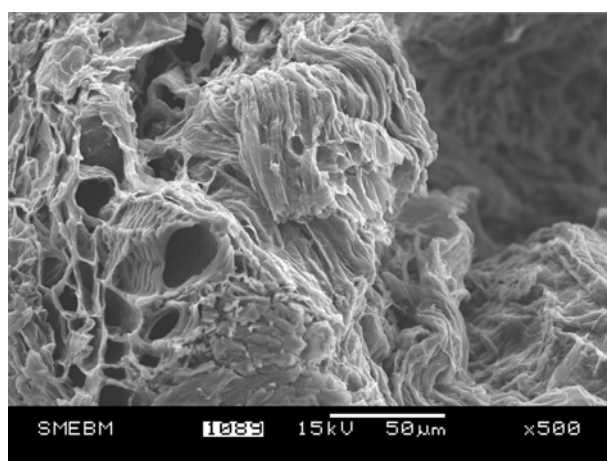


Figure 3.3. SEM micrograph of BP-H₂O

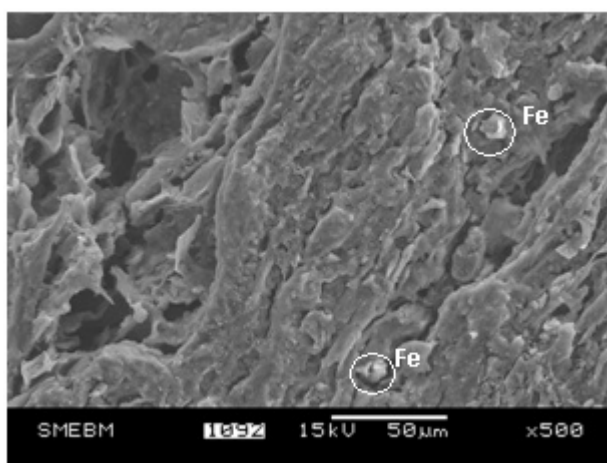


Figure 3.4. SEM micrograph of BP-H₂O-Fe

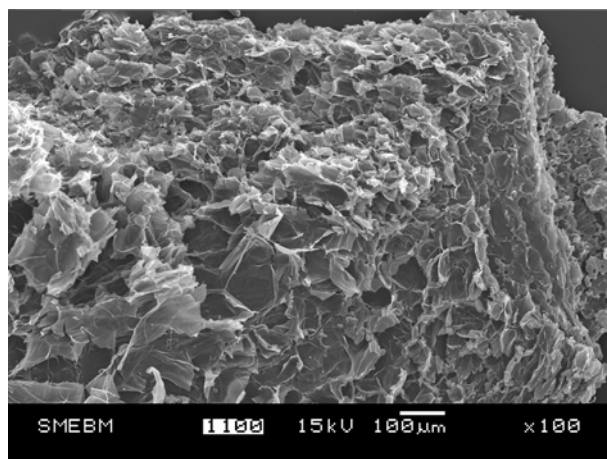


Figure 3.5. SEM micrograph of Raw-PH.

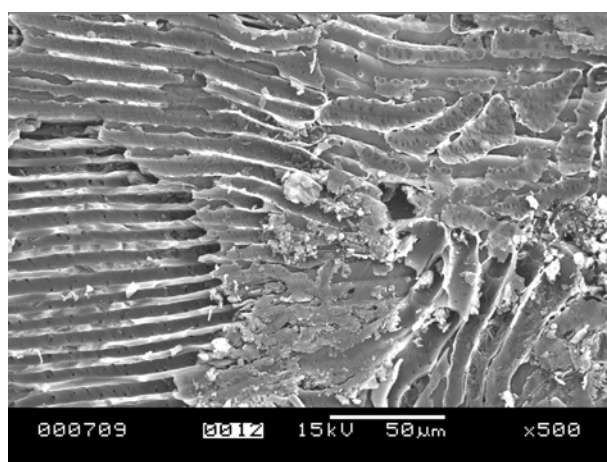


Figure 3.6. SEM micrograph of PH-H₂O

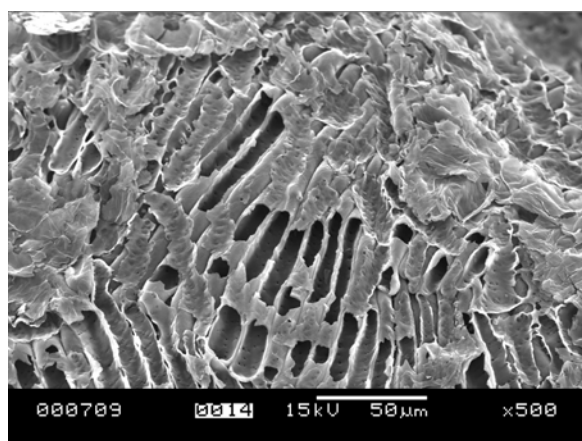


Figure 3.7. SEM micrograph of PH-H₂O-Fe (Fe non-detectable)

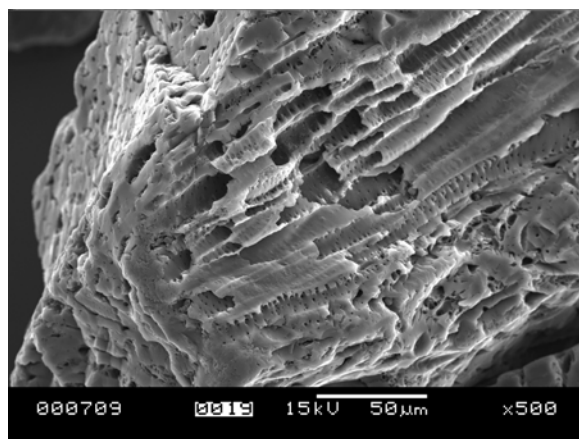
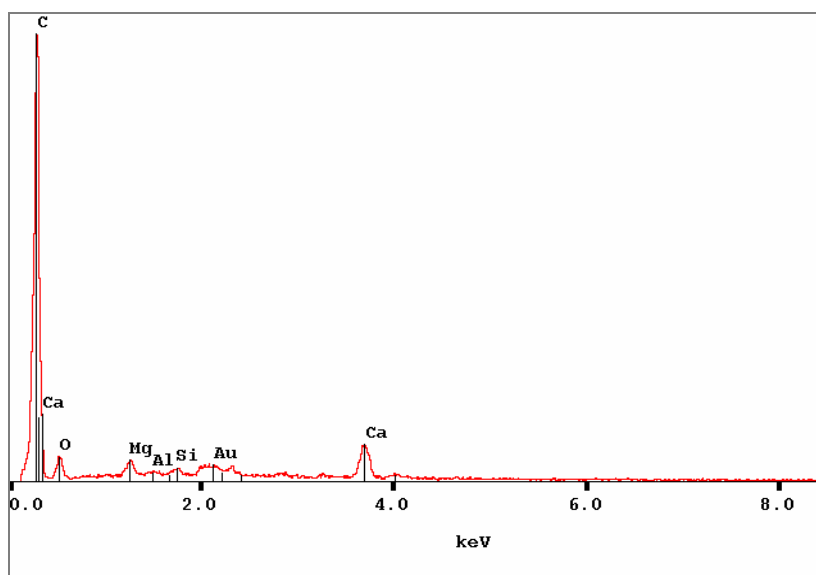


Figure 3.8. SEM micrograph of GAC1

To complete these pictures, EDX spectra have been realized on BP-H₂O, BP-H₂O-Fe, PH- H₂O and PH-H₂O-Fe (figures 3.9 to 3.12). These spectra are only used for a qualitative analysis because the heterogeneity of the materials. Carbon and oxygen are the major elements present in all samples. No iron is observed on BP-H₂O and PH- H₂O but its content in BP-H₂O-Fe is probably higher than in PH-H₂O-Fe because of the size of the peak. This will be confirmed by the results of the next section in relation with the chemical characterization of the AC and particularly the elemental analysis.

Figure 3.9 EDX spectrum of BP-H₂O

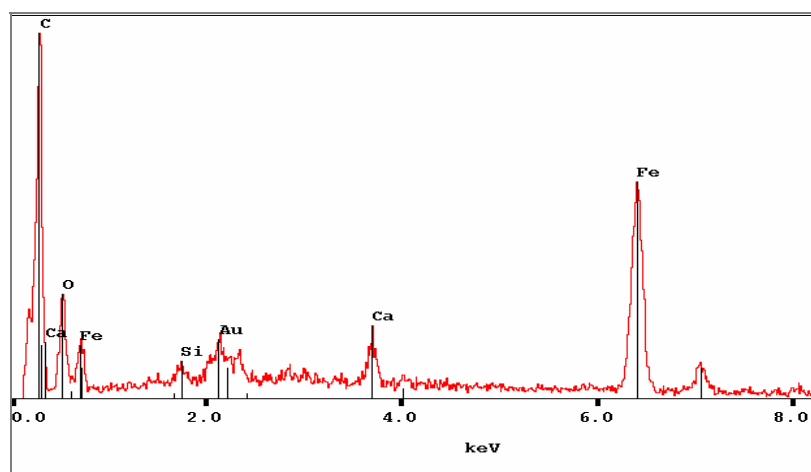


Figure 3.10 EDX spectrum of BP-H₂O-Fe

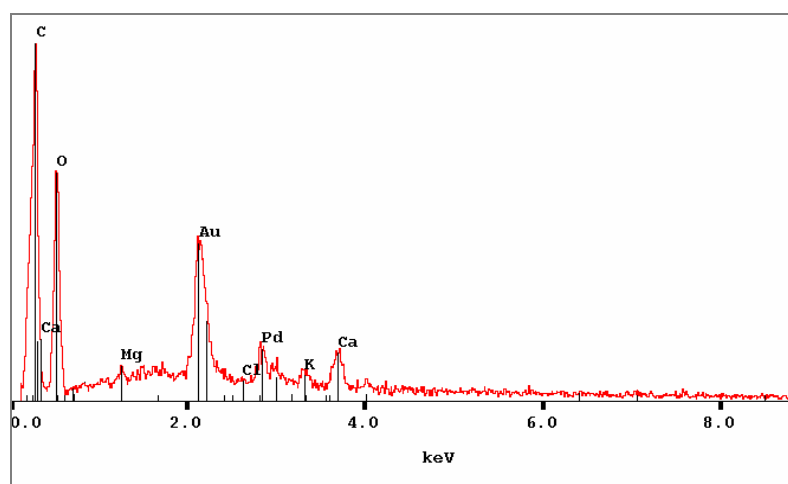


Figure 3.11 EDX spectrum of PH-H₂O

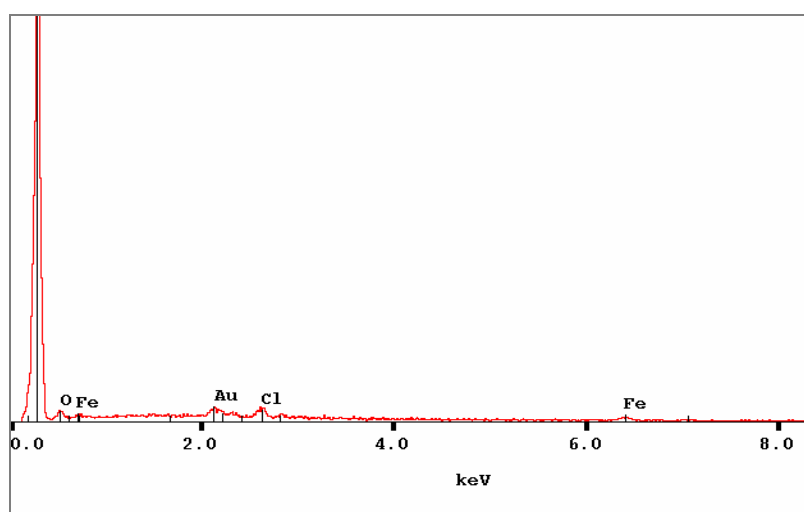


Figure 3.12 EDX spectrum of PH-H₂O-Fe

3.3 CHEMICAL CHARACTERIZATION OF THE ACTIVATED CARBONS

3.3.1 Elemental analysis and total ash content

The major element contents C, H, N and O have been determined (Table 3.4). The carbon percentage is 78 and 68 % for BP-H₂O and BP-H₂O-Fe and 91 and 84 % for PH-H₂O and PH-H₂O-Fe respectively. These values are comparable to the C content of the commercial GAC: 90 et 65 % in GAC1 and GAC2. In that sense, it means that the adsorbents produced from agricultural wastes are really activated carbons, with high carbon content. The second major element is oxygen. Even if the determination by elemental analysis is not always adapted to this analysis, it gives an order of magnitude. BP-H₂O, PH-H₂O and GAC1 present similar content (7, 6 and 9 %) while GAC2 has a huge one (20 %) probably due to the chemical activation by H₃PO₄. After the iron impregnation, the oxygen concentration shows a significant increase in both BP-H₂O-Fe and PH-H₂O-Fe (16 and 14 % respectively). It can be noted that the iron solution (FeCl₃, 0.1 M) get an acidic pH of 1.7 and probably favors some oxidation of the sorbents.

Table 3.4. Total ash content and elemental analysis (wt.%) of carbonaceous materials.

MATERIAL	Ash	C	H	O	N	Fe
BP-H ₂ O	13.6	77.9	0.9	7.0	0.6	0.1
BP-H ₂ O-Fe	13.9	67.8	1.0	16.0	0.7	4.8
PH-H ₂ O	1.3	91.2	0.8	6.0	0.2	ns
PH-H ₂ O-Fe	1.5	83.9	0.6	14.0	0.4	0.5
GAC1	0.4	90.1	0.2	9.0	ns	ns
GAC2	1.1	64.8	2.4	19.5	ns	0.03

ns : not significant

After the contact between the ferric solution and steam activated carbons, the iron in BP-H₂O-Fe and PH-H₂O-Fe was determined following an acid extraction procedure and a measurement by an absorption atomic spectrometer. The iron content deduced from this methodology is 4.8 and 0.5 % for BP-H₂O-Fe and PH-H₂O-Fe respectively, and 0.12 and 0.008 % in BP-H₂O and PH-H₂O. GAC2 has an iron content of 0.03 % which is very low and GAC1 has a non significant value. The iron contents of BP-H₂O-Fe and PH-H₂O-Fe confirm

the qualitative analysis made after the EDX spectra of the materials. In the state of the art, impregnations of commercial activated carbons with different iron solutions have conducted to content ranged between 1.5 to 9.4 % (Fierro *et al.*, 2009), but no results has been obtained on lab-scale produced AC.

In terms of ash content, only the sugar beet pulp based materials present high content: 13.6 and 13.9 % for BP-H₂O and BP-H₂O-Fe respectively. This can be due to the chemical composition of the native pulp which notably contains for example more than 1 % of calcium (Reddad, 2002). This would correspond to 7 % in BP-H₂O. For all AC, ash content are very similar, between 0.4 and 1.5 %.

3.3.2 Zeta potential measurement

With zeta potential measurement, it is possible to evaluate the isoelectric point (pH_{IEP}) of particle suspended in solution, i.e. the pH at which the zeta potential is zero. As a reminder, the determination of ζ potential is based on a mobility measurement of a particle in an electric field. It is then representation of the external charge of the particle, whereas the point of zero charge varies in response to the net total (external and internal) surface charge of the particles (Bandosz, 2006). The difference between pH_{PZC} and pH_{IEP} values would give an indication of the surface charge distribution of the porous activated carbon (Song *et al.*, 2010).

All the measurements were done in a pH range from 2 to 13 after a contact time of 5 days in a NaCl 0.01 M solution. The figures 3.13 to 3.17 give the results of zeta potential measurements of the different activated carbons.

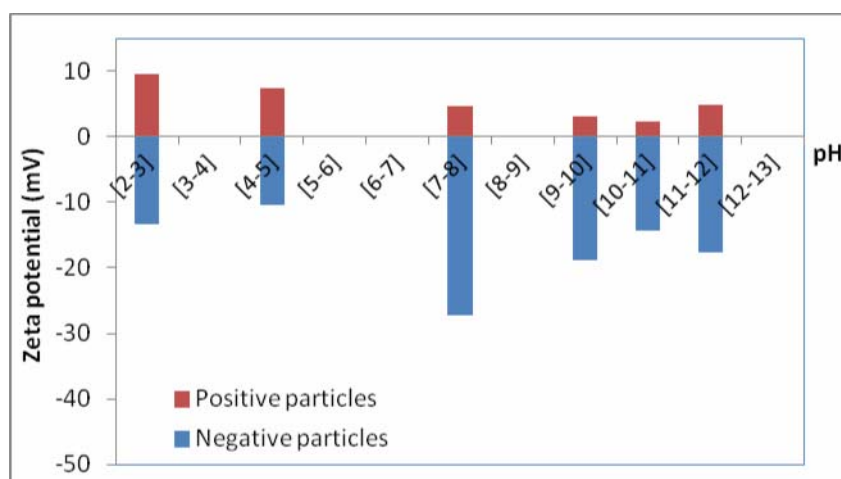


Figure 3.13 – ζ potential for BP-H₂O

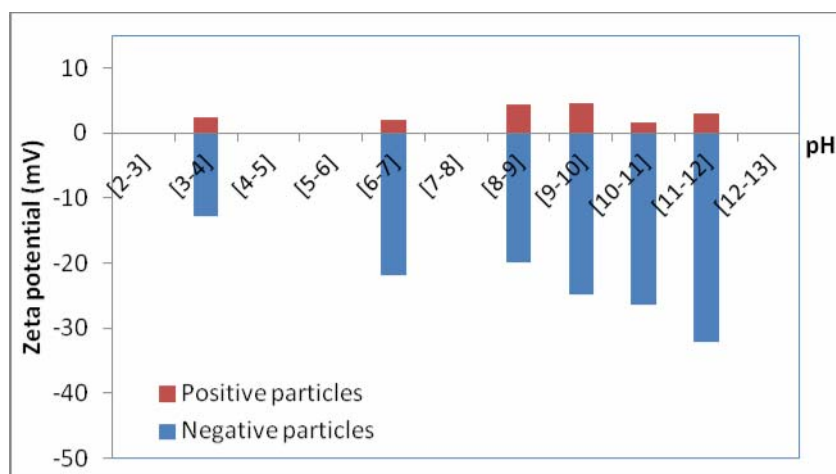


Figure 3.14 – ζ potential for BP-H₂O-Fe

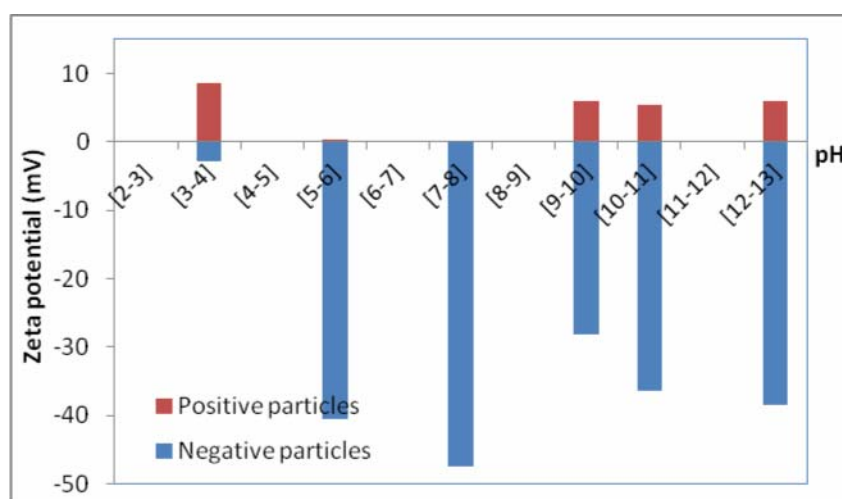
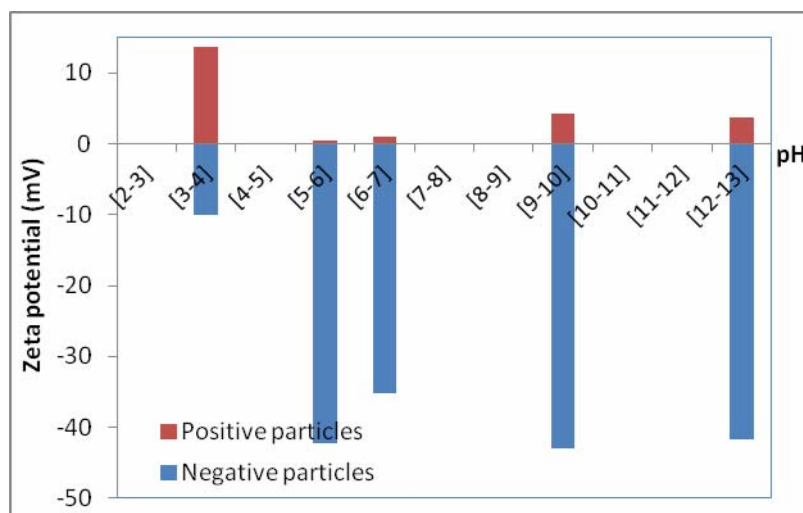
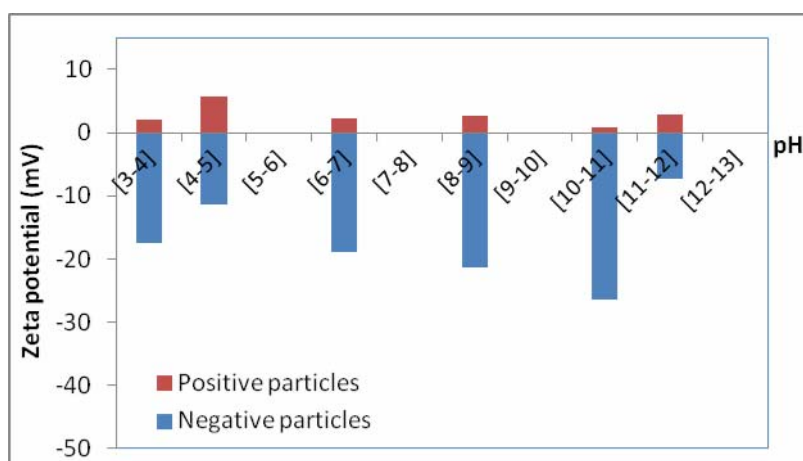


Figure 3.15 – ζ potential for PH-H₂O

Figure 3.16 – ζ potential for PH-H₂O-FeFigure 3.17 – ζ potential for GAC1

Firstly, only 2 groups of particles were detected from each measurement: a bigger one of negative charges and a smaller one of positive charges. This is shown by red and blue bars on all figures. But it is obvious that the negative particles group is always predominant meaning that global charge on the surface is always negative. Secondly, there is no clear tendency in relation with the pH.

For GAC1, the negative values are quite homogeneous from -10 to -20 mV for the studied pH range. It is really different for PH-H₂O and PH-H₂O-Fe: from pH 5 to 6, the ζ potential takes very negative values comprised between -30 and -40 mV. As far as BP-H₂O

and BP-H₂O-Fe are concerned, the behavior is intermediate. At this stage, these determinations cannot bring other information according the characterization of the AC. The quantity of chemical function at the surface of AC are maybe not enough sufficient to impact the value of the ζ potential. In a future work, it could be interesting to correlate these data to Boehm titrations and particularly the basic moieties.

3.3.3 pH_{PZC} determination

As the pH_{IEP} obtaining is not easy by zeta potential measurements, a very simple methodology adapted from Rivera-Utrilla *et al.* (2001) and based on pH measurement is proposed for the determination of the pH of point of zero charge (pH_{PZC}). On an activated carbon the pH_{PZC} depends on the chemical and electronic properties of the functional groups on its surface and is a good indicator of these properties. After an optimized contact time of 5 days in this work, if the final pH is the same of the initial one, then it is called pH_{PZC}. The Figures 3.18 to 3.23 are represented pH_f vs pH_i for all the carbonaceous materials.

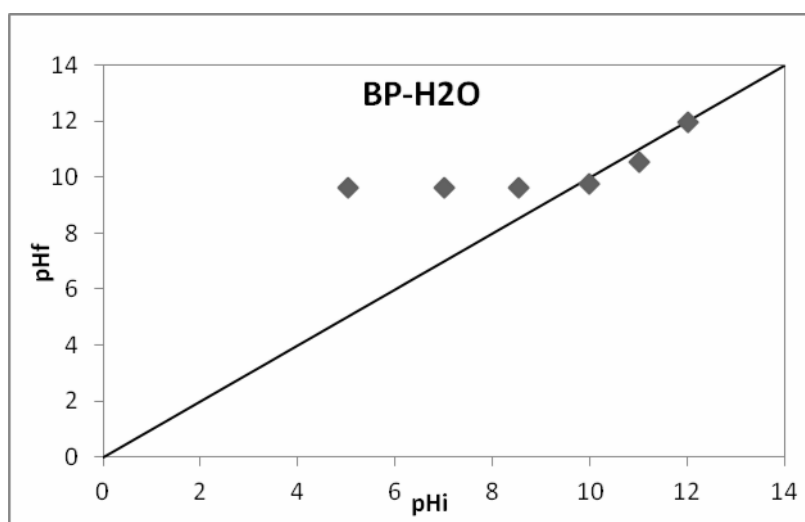


Figure 3.18 Determination of pH_{PZC} for BP-H₂O.

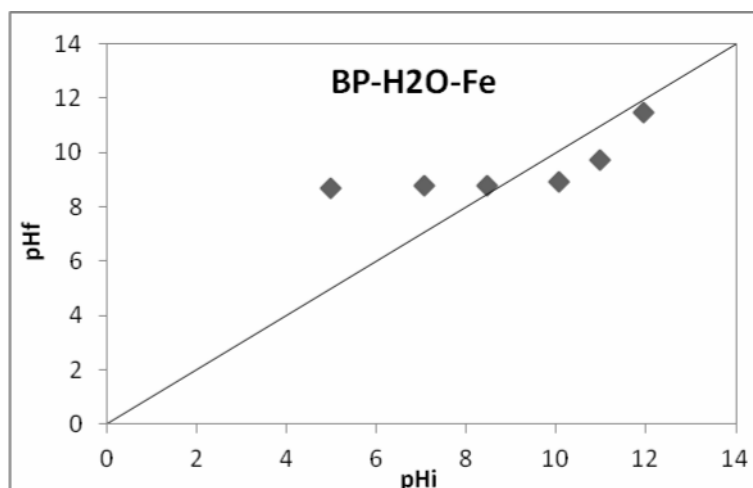


Figure 3.19 Determination of pH_{PZC} for BP-H₂O-Fe.

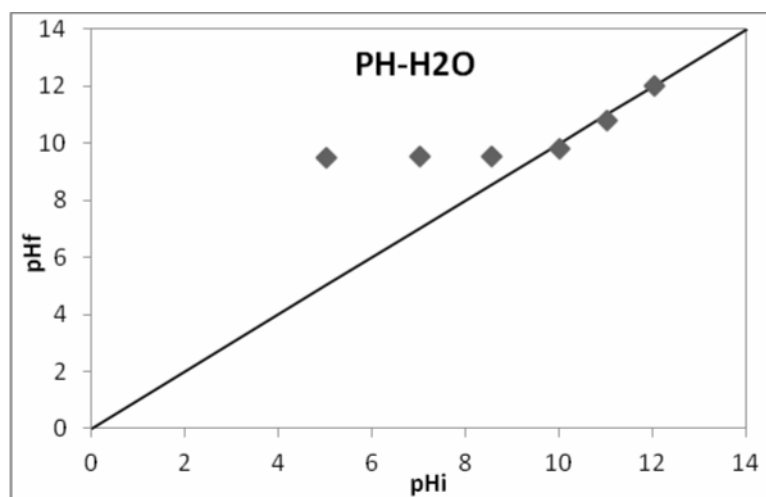


Figure 3.20 Determination of pH_{PZC} for PH-H₂O.

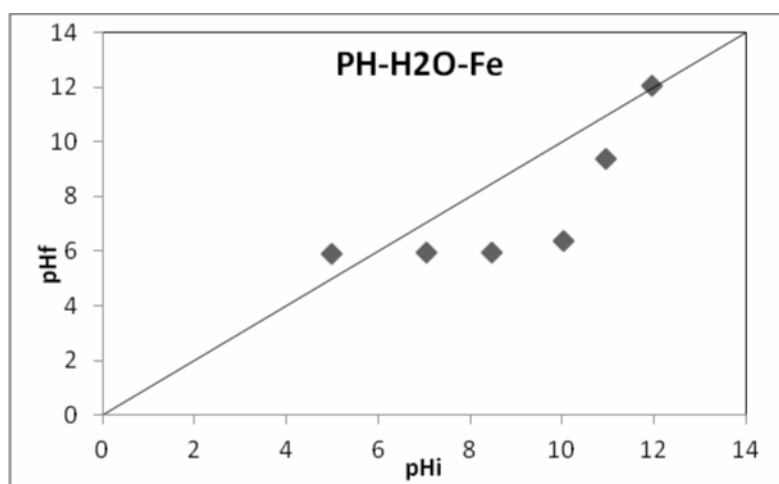
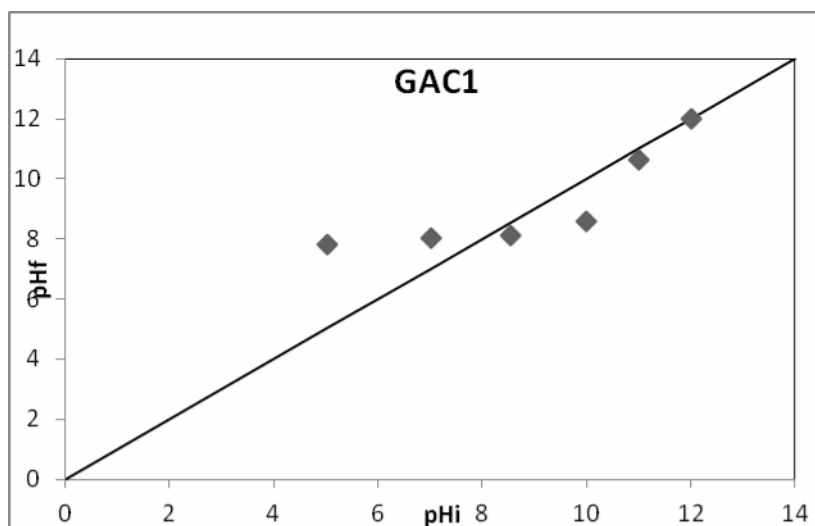
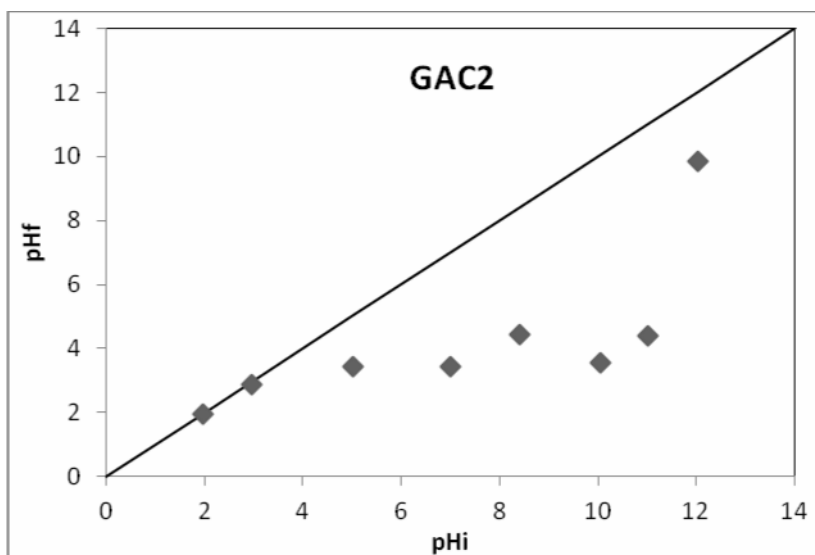


Figure 3.21 Determination of pH_{PZC} for PH-H₂O-Fe.

Figure 3.22 Determination of pH_{PZC} for GAC1Figure 3.23 Determination of pH_{PZC} for GAC2

All experimental curves have a similar shape and only the intersection with the straight line $\text{pH}_i = \text{pH}_f$ is changing. Each pH deduced from this intersection and representing the pH_{PZC} is shown in Table 3.5.

Two groups are distinguished: a majority of AC (BP- H_2O , BP- H_2O -Fe, PH- H_2O and GAC1) has high basic pH_{PZC} from 8 to 9.8, and often correlated with the pH of the washing solution. Only two of them (PH- H_2O -Fe and GAC2) present acidic value (6 and 3.5). These data are useful because they can give an idea of the pH variation during the isotherms, but they cannot clearly be related to the ζ potential measurements. A future work consisting in the

determination of the chemical moieties at the surface of the AC would confirm these pH_{PZC} . When iron is impregnated on BP-H₂O and PH-H₂O, the pH_{PZC} decreases but the difference between BP-H₂O-Fe and PH-H₂O-Fe is not yet explained. An assumption could be however given: GAC2 is a chemical activated carbon of which the activating agent was H₃PO₄ and which was subjected to a thermal treatment. The role of this acid is clearly to oxidize the carbon surface during the pore creation, implying probably an improvement of acidic surface moieties. The oxygen content was then found to 20 %. During the impregnation, the pH of the iron solution was acid (close to 1.7). Since this impregnation was realized at the ambient temperature, the oxidation of the carbons is effective but less. In the other hand, the oxygen content in BP-H₂O-Fe and PH-H₂O-Fe has been increased (see Table 3.4) compared to BP-H₂O and PH-H₂O. However the pH_{PZC} of BP-H₂O-Fe remains surprisingly high.

Table 3.5. pH_{pzc} of the prepared activated carbons and commercial GACs.

MATERIAL	pH_{PZC}	pH of washing solution
BP-H ₂ O	9.8	10.1
BP-H ₂ O-Fe	9	9.1
PH-H ₂ O	9.8	9.8
PH-H ₂ O-Fe	6	4.0
GAC1	8	7.6
GAC2	3.5	4.3

3.4 CONCLUSIONS

In this chapter, the production of AC obtained from sugar beet pulp and peanut hulls has been realised with steam activation and their physico-chemical characterization has been performed and compared with 2 commercial GACs, one physically activated from coconut shell and the second one, chemically activated from wood. In order to give them some specific properties, a chemical modification by iron impregnation has been successfully followed.

In terms of mass yields, values comprised between 16 % (BP-H₂O) and 24 % (PH-H₂O) have been reached depending on the feedstock. Due to the low mechanical resistance of these materials, 17 % (PH-H₂O) to 36 % (BP-H₂O) of them are under powder form (< 0.5 mm) and the mass yields after the iron impregnation are respectively 74 % for BP-H₂O-Fe and 78 % for PH-H₂O-Fe.

Regarding the porous structure, the BET surfaces ranged between 720 and 830 m².g⁻¹ are rather good in comparison with the commercial GAC and higher than those found in the literature. The porous volume and especially the microporous volumes are relatively constant in function of the precursors before and after the iron impregnation. Their values reach 0.33 cm³.g⁻¹. More heterogeneity is observed for mesoporous volumes. In terms of relative values, the percentage of microporosity is not affected by the iron impregnation and the lab-scale AC are rather good compared with the commercial ones.

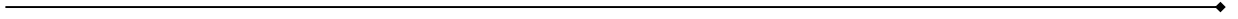
Finally, the chemical analysis shows high content of carbon, and oxygen in Fe rich carbons or oxidized ones. Ash content remains dependant of the precursor and reaches more than 13 % in BP-H₂O and BP-H₂O-Fe while it is under 1.5 % for the others. This could contribute to develop mesoporosity properties. Zeta potential determination has not given a lot of information about the global charge on AC surface, but pHPZC measurement methodology based on pH determination indicates that the AC are basic excepted GAC2 (chemically activated) and PH-H₂O-Fe. All these data are printed in Table 3.6 to give a summary of the carbons characterization.

This Chapter shows that the production of AC from agricultural wastes is possible at lab scale. A comparison with industrial scale AC displays that they have similar physico-chemical properties and these encouraging results justify their use in adsorption processes. This is the main objective of the Chapter 4 in which they will be evaluated in terms of adsorption capacities towards 2 different micro-pollutants: inorganic arsenic (V) and the antibiotic tetracycline.

Table 3.6. Summary of carbonaceous materials from agricultural wastes and commercial GACs characterization.

	BP-H₂O	BP-H₂O-Fe	PH-H₂O	PH-H₂O-Fe	GAC1	GAC2
S_{BET} (m².g⁻¹)	821	762	829	718	1138	1515
% microporosity	49	50	84	84	73	51
Microporous volume (cm³ g⁻¹) / up to 2nm	0.3478	0.3227	0.3551	0.3084	0.4852	0.6407
d₅₀ mesoporous (nm)	5.4	4.5	3.8	3.6	4.3	5.9
Total porous volume (cm³ g⁻¹) / BET analysis	0.6430	0.5778	0.4028	0.3446	0.6230	1.2291
C (%)	77.9	67.8	91.2	83.9	90.1	64.8
O (%)	7.0	16.0	6.0	14.0	9.0	19.5
Fe (%)	0.1	4.8	ns	0.5	nd	0.03
Ash (%)	13.6	13.9	1.3	1.5	0.4	1.1
pH_{PZC}	9.8	9.0	9.8	6.0	8.0	3.5
ζ potential (mV) (global)	-21 to -11	-25 to -15	-37 to -21	-43 to -34	-24 to -15	nd

ns : not significant, nd : not determined



CHAPTER 4

APPLICATIONS OF ACTIVATED CARBONS FOR ADSORPTION OF INORGANIC AND ORGANIC MICROPOLLUTANTS

After the lab scale production of activated carbons from sugar beet pulp and peanut hull and their physico-chemical characterizations, the last objective of this work is now to evaluate their adsorption performance in water treatment process. This feasibility study involves two different pollutants, an inorganic anion as arsenic(V) (arsenate) and the tetracycline (TC), an organic molecule acting as antibiotic. Both of them are called micro-pollutants because they are found in water in low concentrations. These two pollutants are in relation with two different topics. As far as arsenic is concerned, Chapter 1 showed that surface and ground waters contamination is a worldwide public health problem. This natural contamination is mainly due to the release of rocks leading to variable concentrations in solution up to few thousands of $\mu\text{g.L}^{-1}$ and is composed by a mixture of the 2 inorganic forms of arsenic, As(V) and As(III). This study is focused on the adsorption on As (V), in concentrations found in natural environment and with synthetic contaminated solutions. The second problematic is the persistence of molecules with endocrine disruptor effect such, as antibiotics, in treated domestic waters. This contamination of anthropogenic origin is today of great interest and the best available treatment technologies are not yet found. These molecules and their metabolites are difficult to detect because of their very low concentrations (ng.L^{-1}) and their complexity. The last part of this work presents some TC adsorption results on the previously produced activated carbons. To simplify this first study, the selected concentration range is between $\mu\text{g.L}^{-1}$ and mg.L^{-1} .

This chapter is therefore divided into 2 main parts, corresponding firstly to arsenic sorption and secondly to tetracycline one. The followed methodology is rather the same in both cases:

- Experiments conducted in batch reactor, with synthetic solution of As (V) and TC and the experimental data are compared in each case with a commercial GAC,

- A kinetic study including contact time experiments and a deeper analysis with kinetic models,
- Realization of adsorption isotherms in different experimental conditions taking into account the effect of influencing parameters,
- A tentative of correlation between the properties of the AC and their adsorption performances for a sorption mechanism approach.

Partial conclusions are established at the end of each part. The objective is to be able to choose the correct AC with defined properties for a selected pollutant. By this way, these low-cost AC could acquire a real added-value. The overall comment and the perspectives of this work are developed in the last part of this manuscript.

4.1 ADSORPTION STUDY OF ARSENATE IONS

In this section As(V) is selected for the adsorption experiments. It is an oxy-anion, monovalent (H_2AsO_4^-) or divalent (HAsO_4^{2-}) in function of the solution pH. As a reminder, it is the most oxidized and thermodynamically stable form of arsenic in waters. Therefore, no reduction of arsenic is expected in the chosen experimental conditions and after the contact with activated carbons. The selected materials for this study are the followings: BP (raw sugar beet pulp), BP-C, BP- H_2O , BP- H_2O -Fe, PH- H_2O , PH- H_2O -Fe and GAC1.

4.1.1 Kinetic study of arsenate adsorption

The kinetic study presented in this section includes contact times experiments in order to determine the equilibrium time between the solid and the solution, the modeling of the decay curves by different approaches such diffusion model or chemisorption model, and a last part related to the pH effect on the sorption.

4.1.1.1 Contact time experiments

In a classical adsorption study, one of the first parameters to determine is the equilibrium time: it is the time after which there is no mass transfer between the adsorbent and the pollutant. These experiments have been conducted firstly with raw material (BP) and BP-C and in a second set with BP- H_2O , BP- H_2O -Fe, PH- H_2O , PH- H_2O -Fe and GAC1. Three initial concentrations of arsenate were tested (100, 500 and 1000 $\mu\text{g.L}^{-1}$) leading to initial pH comprised between 6 and 7.5. It has not been fixed during the experiment but final values have been noticed.

4.1.1.1.1 Kinetic decay curves obtained with the raw material and char

The first contact time experiments have been carried out with BP and BP-C. It is obvious from Figure 4.1 that no adsorption occurs on the raw material and the char in the

range of selected concentrations. These results are not so surprising because the biosorption of arsenic is not found to be very efficient. In chapter 1, some studies deal with this topic and very few of them present adsorption capacities due to this low potential. As far as chars are concerned, it has not been found again high sorption capacities. These results mean that an activation step is then needed to produce an extended BET surface and maybe completed by a chemical treatment. No kinetic decay curves are presented with the peanut hull but preliminary results have revealed a negligible adsorption on raw PH.

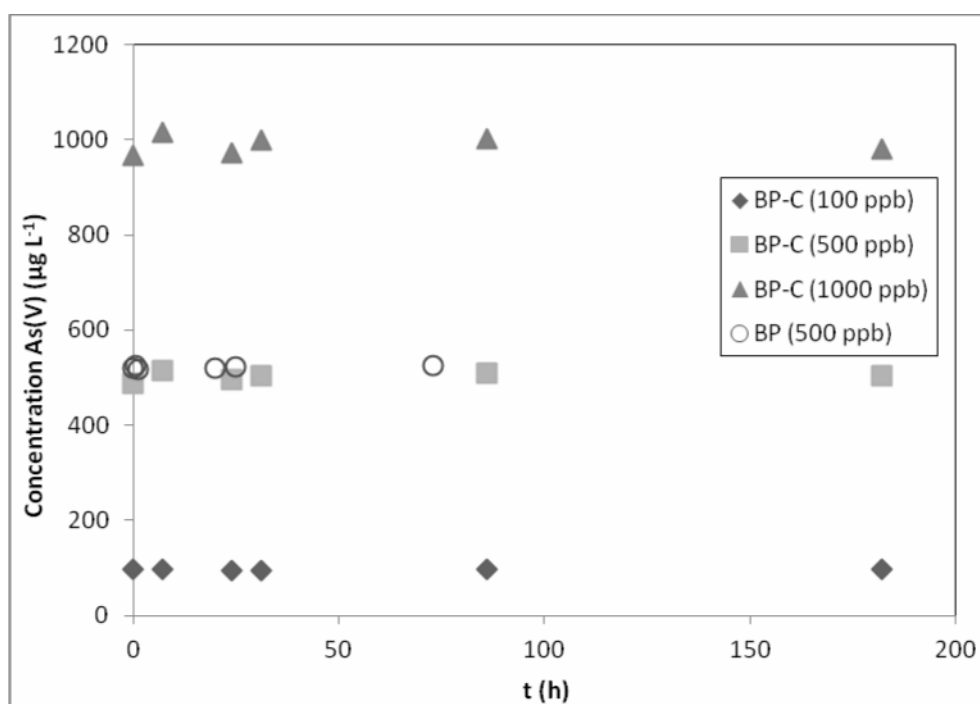


Figure 4.1 Kinetic decay curves for removal of As (V) as a function of time and initial concentration of 100, 500 and 1000 $\mu\text{g.L}^{-1}$ for BP-C and 500 $\mu\text{g.L}^{-1}$ for BP.

4.1.1.1.2 Kinetic decay curves obtained with BP- H_2O , BP- $\text{H}_2\text{O-Fe}$, PH- H_2O , PH- $\text{H}_2\text{O-Fe}$ and GACI

Regarding the sugar beet pulp based adsorbents, the kinetic decay curves are plotted on Figure 4.2. Light symbols correspond to BP- H_2O and plain ones to BP- $\text{H}_2\text{O-Fe}$. Even if some points seem to be close to 0 $\mu\text{g.L}^{-1}$ (for BP- $\text{H}_2\text{O-Fe}$, $C_0=100 \mu\text{g.L}^{-1}$), it always has been verified that all the data are higher than the quantification limit determined by GF-AAS for As measurement (4 $\mu\text{g.L}^{-1}$). A first comment can be done: there is a low adsorption of arsenate in

BP-H₂O and the capacities are greatly improved after the iron impregnation. Secondly, equilibrium times are different according the 2 materials: for BP-H₂O, 24 h (1 day) seem enough to reach the mass balance and for BP-H₂O-Fe, it takes quite 96 h (4 days). These data can be confirmed by the modeling in sections 4.1.1.2. In terms of final pH, the values are (for $C_0 = 1000 \mu\text{g.L}^{-1}$) 8.9 and 9.1 respectively. It confirms the basic behavior of these carbons and the mainly sorbed species is then HAsO_4^{2-} .

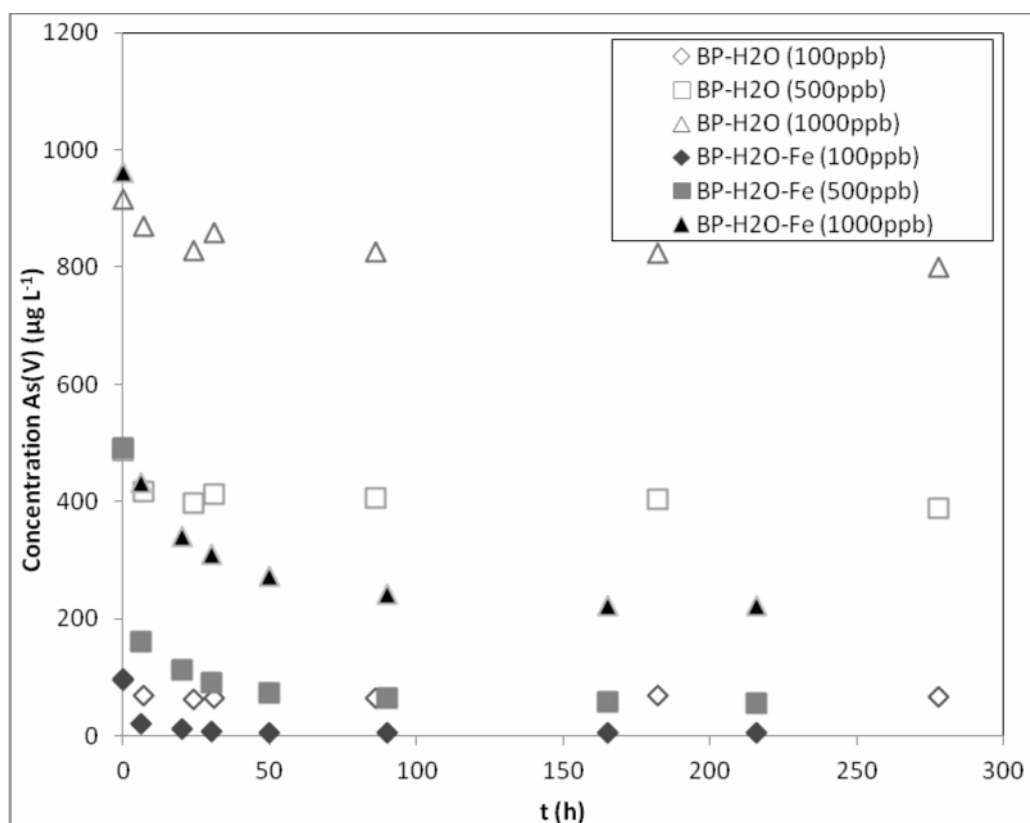


Figure 4.2 Kinetic decay curve for removal of As(V) by BP-H₂O (particle size 0.5-1 mm) and BP-H₂O-Fe (> 1 mm) as a function of time and initial concentration of 100, 500 and 1000 $\mu\text{g.L}^{-1}$.

Similar experiments have been carried out with the peanut hull based actives carbons. It is clear that adsorption performances are better than with BP-H₂O and BP-H₂O-Fe. In terms of equilibrium times, 120h (5 days) are necessary for PH-H₂O and quite less for PH-H₂O-Fe (80-100 h). In this case, the iron impregnation seems slightly speed up the sorption kinetics and the sorption capacity. Final pH values are 7.1 and 5.6 for PH-H₂O, PH-H₂O-Fe. The acid property of PH-H₂O-Fe is confirmed, a mixture of H_2AsO_4^- and HAsO_4^{2-} is sorbed on PH-H₂O and mainly one species H_2AsO_4^- on PH-H₂O-Fe.

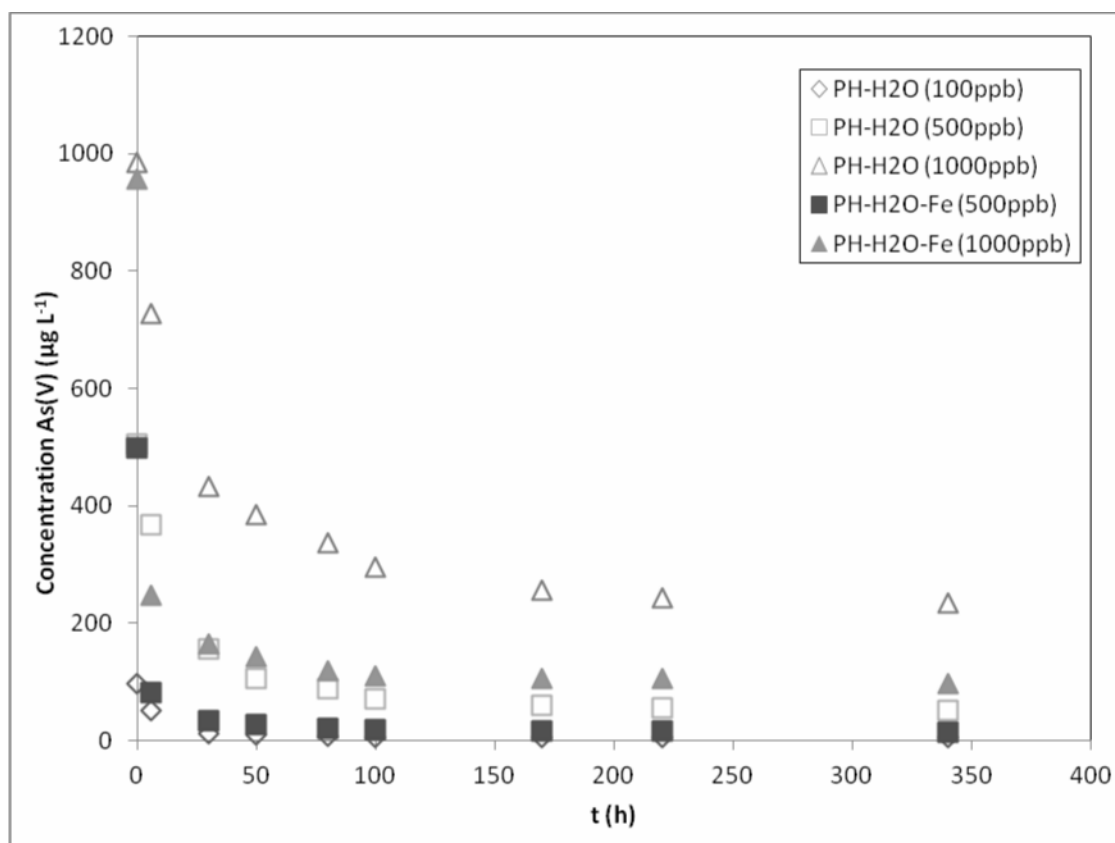


Figure 4.3 Kinetic decay curve for removal of As(V) by PH-H₂O (particle size 0.5-1 mm) and PH-H₂O-Fe (particle size > 1 mm) as a function of time and initial concentration of 100, 500 and 1000 µg.L⁻¹.

The experiments conducted with GAC1 have given the following results (Figure 4.4): the equilibrium times are close to 120 h (5 days) which is rather good taking into account the high porosity of the commercial GAC. As the final pH is 6.9, a mixture of H₂AsO₄⁻ and HAsO₄²⁻ is also sorbed.

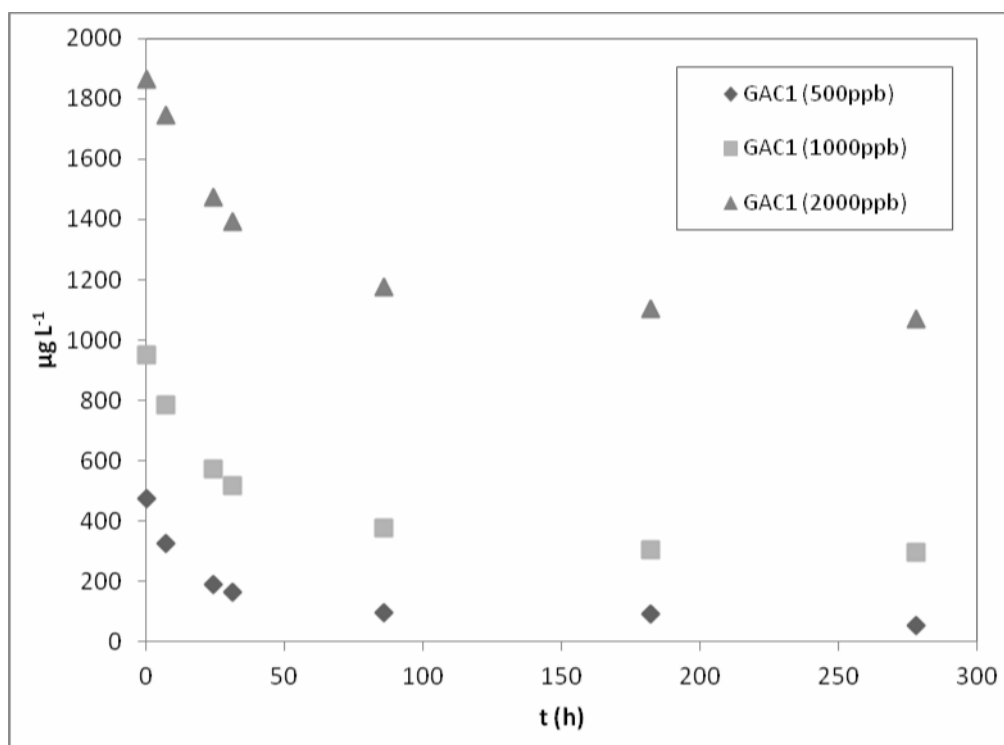


Figure 4.4 Kinetic decay curve for removal of As (V) as a function of time and initial concentration of 500, 1000 and 2000 $\mu\text{g.L}^{-1}$ for GAC1 (particle size 0.5-1 mm).

4.1.1.1.3 Conclusion about contact time experiments

In Figures 4.5 and 4.6 are only presented the kinetic decay curves carried out at 1000 $\mu\text{g.L}^{-1}$ with the lab scale AC and GAC1. For the further experiments, the optimal contact time common for all the materials is then fixed at 120 h (5 days). The comparison between each steam activated materials (Figure 4.4) leads to conclude that PH-H₂O and GAC1 have a similar behavior in terms of capacity, kinetic rate and pH. Moreover it has been shown that their porous structure is quite similar with respectively 84 and 73 % of microporosity. This percentage could play a role in the choice of AC for arsenate removal.

Undoubtedly capacities are enhanced with the iron based materials (Figure 4.6). As the iron impregnation does not greatly affect the porous structure, a mechanism of chemisorption could be probably involved in that case. As the final pH is really basic for BP-H₂O-Fe, it does not seem to be the highest influencing parameter but a section about the effect will add more data. And finally the presence of iron tends to speed up the kinetic rate.

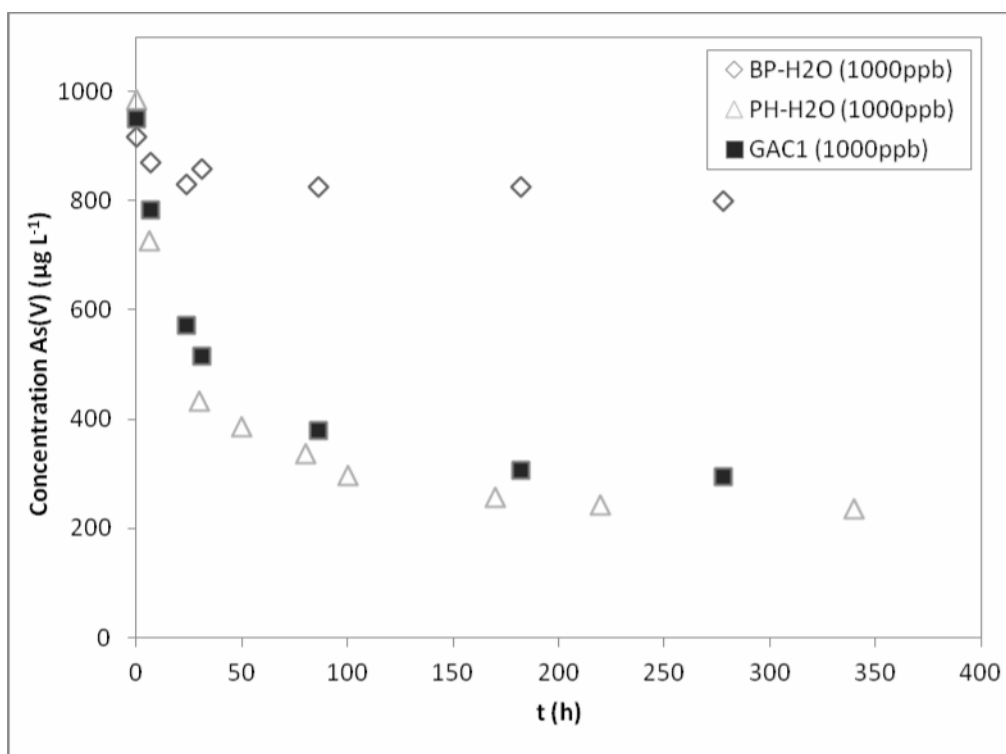


Figure 4.5 Kinetic decay curve for removal of As (V) as a function of time and initial concentration of $1000 \mu\text{g.L}^{-1}$ for BP-H₂O, PH-H₂O and GAC1.

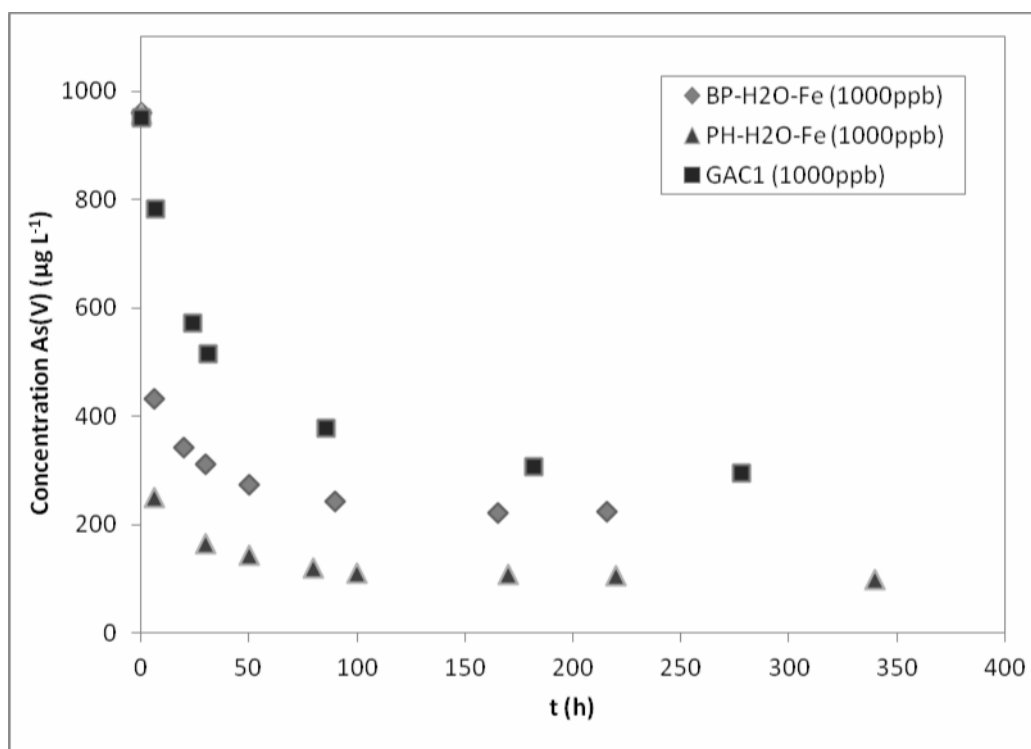


Figure 4.6 Kinetic decay curve for removal of As (V) as a function of time and initial concentration of $1000 \mu\text{g.L}^{-1}$ for BP H₂O-Fe, PH-H₂O-Fe and GAC1.

4.1.1.2 Kinetic modeling

In order to investigate the mechanism of sorption and potential rate-controlling steps such as mass transport and chemical reaction processes, kinetic models have been used to test experimental data. To focus on the first hours of the decay, the sorbents have been grounded to a powder and new kinetic curves have been carried at 300 rpm. Different approaches have been selected to describe these new experimental results including the intraparticle diffusion-controlled adsorption model proposed by Morris and Weber (1962) and the sorption model equations (pseudo-first (eq.1.2) and second-order (eq.1.5) equations).

4.1.1.2.1 Diffusion modeling

Regarding diffusional adsorption, only the intraparticle diffusion has given interesting results. As adsorption is usually controlled by an external film resistance and/or internal diffusion mass transport, it can be concluded that the external transfer is not the limiting step in this reaction. In the earlier stages of the adsorption, when t is relatively small, the equation (1.7) is represented by

$$q_t = k_i t^{0.5}$$

According to Morris and Weber (1962), if the rate-limiting step is intraparticle diffusion, a plot of solute sorbed against square root of contact time should yield a straight line passing through the origin (Gérente *et al.*, 2007). This has been successfully applied to BP-H₂O and BP-H₂O-Fe for the first 1 hour and to PH-H₂O and PH-H₂O-Fe and GAC1 for the first 2 hours due to their higher microporosity percentage. Kinetic plots are shown on Figure 4.7-A for BP-H₂O, BP-H₂O-Fe and GAC1 and Figure 4.7-B pour PH-H₂O, PH-H₂O-Fe and GAC1 and the intraparticle diffusion values in Table 4.1.

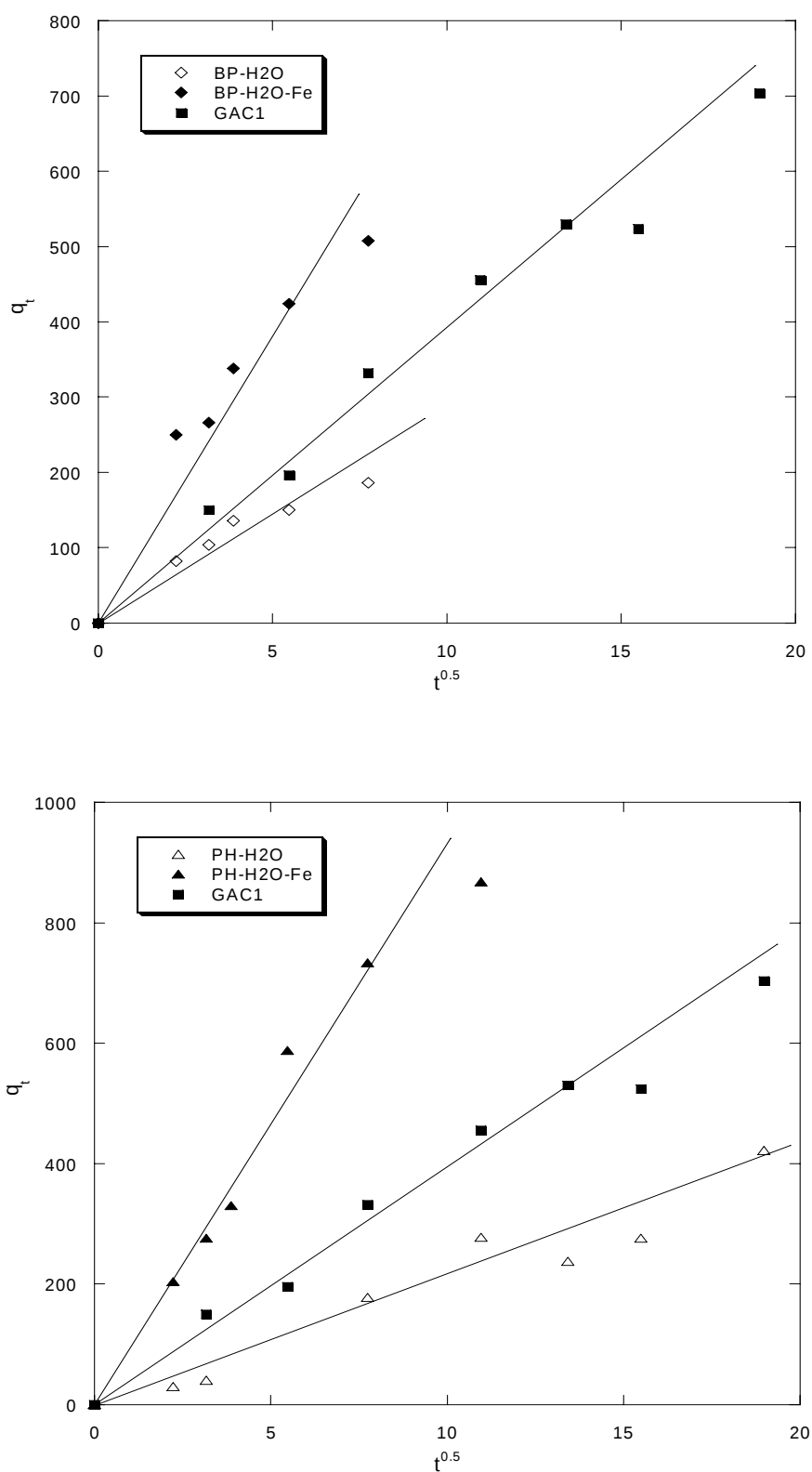


Figure 4.7 Intraparticle diffusion modeling for A) BP-H₂O, BP-H₂O-Fe and GAC1 and B) PH-H₂O, PH-H₂O-Fe and GAC1 (particle size < 0.5 mm).

Table 4.1 Intraparticle diffusion values for As(V) sorption on the different the activated carbons

Material	$k_{id} (\mu\text{g}\cdot\text{g}^{-1}\cdot\text{min}^{-0.5})$	R^2
BP-H ₂ O	31	0.939
BP-H ₂ O-Fe	84	0.947
PH-H ₂ O	24	0.983
PH-H ₂ O-Fe	88	0.959
GAC1	41	0.988

In all cases, the correlation coefficients are good enough to give to an acceptable description of experimental points and to conclude that the intraparticle diffusion is probably a limiting step of this adsorption reaction between AC and As(V). The results also suggest that an iron modification in the materials leads to higher values in the intraparticle diffusion constant. The diffusivity being a function of the solute affinity for the adsorbent material and the activated carbon site density (Axe and Trivedi, 2002), it can be actually confirmed that As(V) has a great affinity to iron loaded sorbents. The higher calculated intraparticle diffusion parameters for iron loaded activated carbons listed in Table 4.1 demonstrate also a higher boundary layer effect indicating that the diffusion of As(V) within the pores of the BP-H₂O-Fe and PH-H₂O-Fe is more rapid than those in BP-H₂O and PH-H₂O.

4.1.1.2.2 Chemisorption model

Pseudo-first-order and pseudo-second-order equations (eq. 1.2 and 1.5) have also been tested and only the second one has perfectly described the experimental data. Figure 4.8 and 4.9 and Table 4.2 show respectively the kinetic plots and the constants. Contrary to the other models, it predicts the behaviour over the whole range of the kinetic curves so the previous experimental data obtained with granular materials and 12 days of contact time are used. It is also in agreement with a chemisorption mechanism being the rate controlling step so this chemisorption is probably again a limiting step. On the second hand, the main deficiency of this extremely useful model stems from the fact that it is a pseudo-kinetic model, so a specific

but different rate constant is obtained for each change in system variable. Anyway, all the curves are obtained in the same experimental conditions and the constants are compared each other. As shown in Table 4.2, the R^2 values are close to unity and the calculated q_e values agree well with the experimental values, demonstrating that the pseudo-second order model can be applied to the entire adsorption process. It is clear from Table 4.2 that the iron impregnation increases the initial sorption rate (h) of As(V) on BP-H₂O-Fe by a factor of 14 ($7.06 \mu\text{g.g}^{-1}.\text{min}^{-1}$) and those on PH-H₂O-Fe by a factor of 7 ($14.27 \mu\text{g.g}^{-1}.\text{min}^{-1}$). Moreover, the h values obtained with PH-H₂O and GAC1 are similar, 1.91 and $1.42 \mu\text{g.g}^{-1}.\text{min}^{-1}$ respectively, and higher than BP-H₂O ($0.5 \mu\text{g.g}^{-1}.\text{min}^{-1}$). These results confirm the first analysis made from Figure 4.7. Finally, we can establish the next classification for the rate of initial arsenic sorption: PH-H₂O-Fe > BP-H₂O-Fe >>> PH-H₂O $\approx$ GAC1 > BP-H₂O (all the obtained values were above the quantification limit). Fierro *et al.* (2009) have also used iron-doped activated carbons derived from a commercial material for arsenic adsorption at a lower concentration ($311 \mu\text{g.L}^{-1}$) in groundwater. They have obtained h values in the range of 0.65 to $38.1 \mu\text{g.g}^{-1}.\text{min}^{-1}$. These values are in the same magnitude order as the initial sorption rate values obtained by the carbonaceous materials prepared in this research.

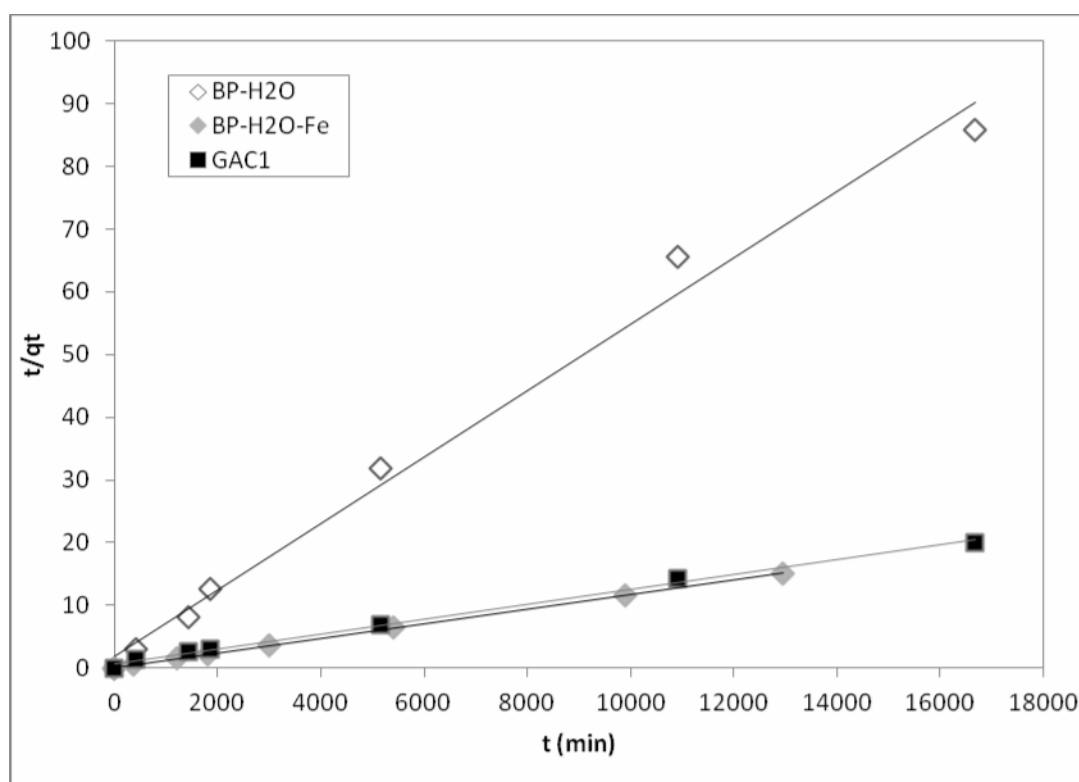


Figure 4.8 Arsenic adsorption by BP-H₂O, BP-H₂O-Fe and GAC1 fitted with pseudo-second order kinetic model (linear).

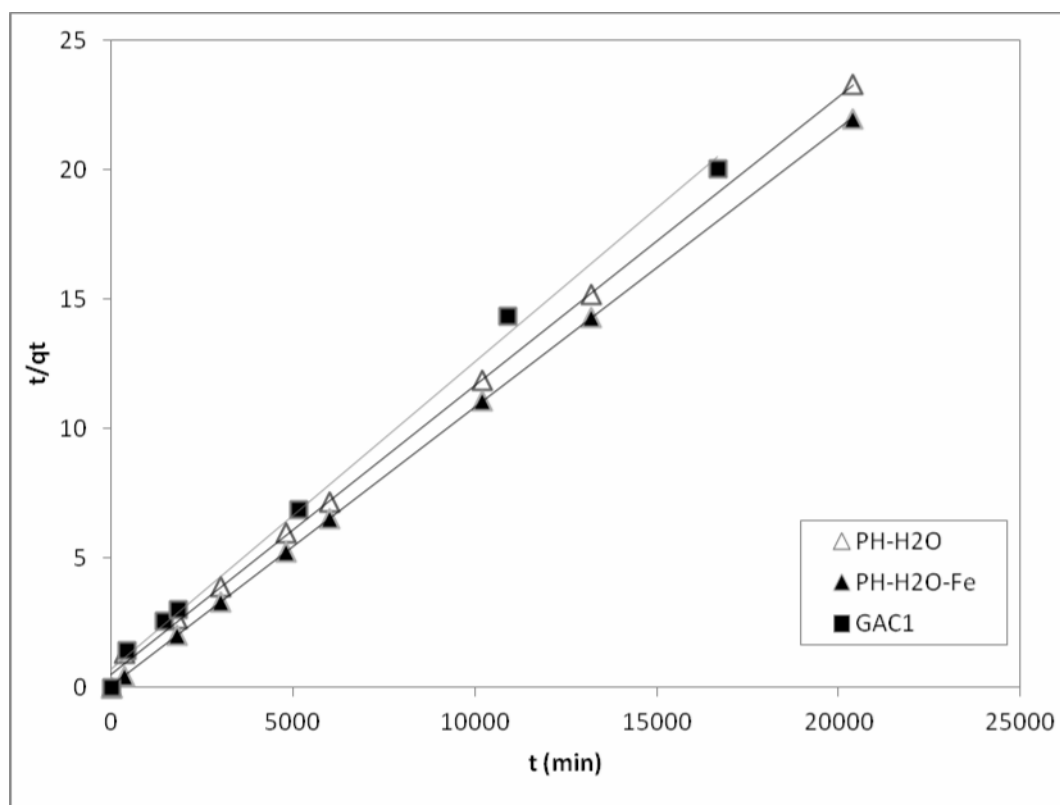


Figure 4.9 Arsenic adsorption by PH-H₂O, PH-H₂O-Fe and GAC1 fitted with pseudo-second order kinetic model (linear).

Table 4.2 Kinetic parameters for arsenic(V) adsorption fitted by the pseudo-second order model.

Material	h ($\mu\text{g}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$)	q_e (cal.) ($\mu\text{g}\cdot\text{g}^{-1}$)	q_e (exp.) ($\mu\text{g}\cdot\text{g}^{-1}$)	k_2 ($\text{g}\cdot\mu\text{g}^{-1}\cdot\text{min}^{-1}$)	R^2
BP-H ₂ O	0.50	188.7	194.5	1.42×10^{-5}	0.990
BP-H ₂ O-Fe	7.06	833.3	853.8	1.02×10^{-5}	1.000
PH-H ₂ O	1.91	909.1	875.6	2.31×10^{-6}	0.999
PH-H ₂ O-Fe	14.27	909.1	928.4	1.73×10^{-5}	1.000
GAC1	1.42	833.3	832.5	2.04×10^{-6}	0.996

4.1.1.3 pH effect

Adsorption of metallic and/or metalloid ions onto activated carbon occurs through parallel and consecutive reactions that involve the active sites on carbon surface and ionic species of the dissolved metal and/or metalloid. In section 4.1.1.3, it was suspected that the pH would not be a great influencing parameter for all the lab-scale AC. To confirm this, experiments were only conducted with the most available material BP-H₂O, at different initial pH values selected in function of its pH_{pzc} (9.8) and As(V) speciation. The tested pH values were 3.5, close 7 and 12. Figure 4.10 shows then the kinetic decay curves obtained at 2 different initial concentrations (500 and 1000 $\mu\text{g.L}^{-1}$).

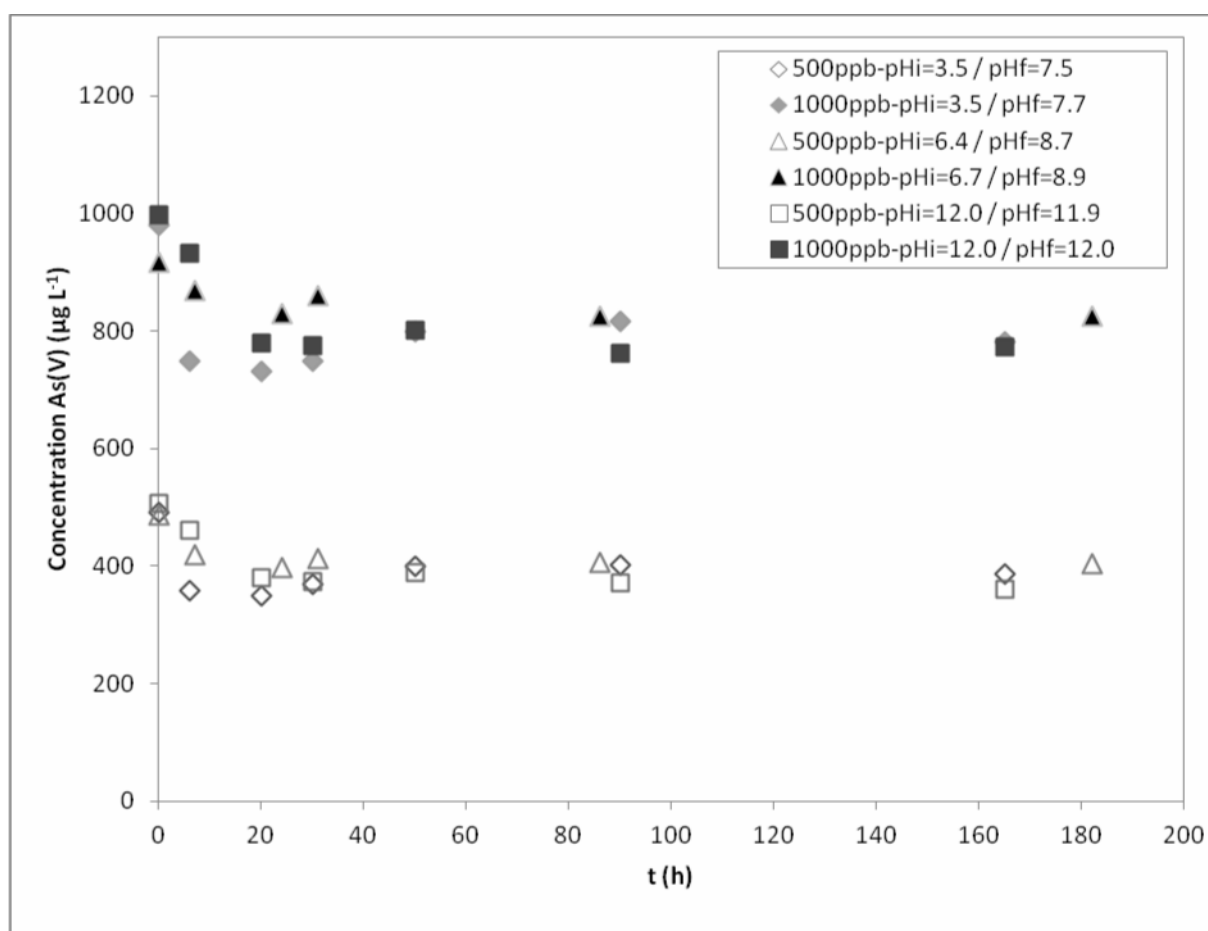


Figure 4.10 Kinetic decay curves of As(V) adsorption onto BP-H₂O at 2 different initial concentrations (500 and 1000 $\mu\text{g.L}^{-1}$) and different pH values (3.5, $\approx$ 7 and 12).

It is obvious that between pH = 3.5 and pH = 12 and for $C_0 = 500$ and $1000 \mu\text{g.L}^{-1}$, the initial pH value does not influence the sorption capacity at equilibrium (120 h). Even at pH = 12 *i.e.* beyond the pH_{pzc} , the As(V) adsorption is not prevented. It only seems that at acidic pH, the decay is more rapid during the first 24 hours, then followed by a slight desorption to finally stabilized at the same sorption capacity. Final pHs have been also reported and Table 4.3 presents the different forms of As(V) determined from the speciation for an initial concentration of $1000 \mu\text{g.L}^{-1}$. This leads to conclude that all the negative forms of As(V) were really considered in these experiments and none of them has a priority for sorption. In the literature, it is generally found that adsorption of anions decreases by increasing pH due to the higher concentration of competitive anions, such as OH^- (Chen and Lin, 2001). But, the assessment of these competitive phenomena depends on the specific interactions between the ions and the adsorption sites. The adsorption of anions on AC is then a complex reaction including surface complexation mechanism with protonated sites (Chen and Lin, 2001) and the presence of electrophilic surface sites (Alfarra *et al.*, 2004).

Table 4.3 Different forms of As(V) determined from the speciation for an initial concentration of $1000 \mu\text{g.L}^{-1}$

BP-H ₂ O, $\text{pH}_{\text{pzc}} = 9.8$, $C_0 = 1000 \mu\text{g.L}^{-1}$			
pHi	Arsenic form	pHf	Arsenic form
3.5	95 % of H_2AsO_4^-	7.7	83 % of HAsO_4^{2-} 17 % of H_2AsO_4^-
6.7	67 % of H_2AsO_4^- 33 % of HAsO_4^{2-}	8.9	99 % of HAsO_4^{2-}
12	72 % of AsO_4^{3-} 28 % of HAsO_4^{2-}	12	72 % of AsO_4^{3-} 28 % of HAsO_4^{2-}

To conclude about this kinetic study, the main results are the followings:

- the carbonaceous sorbents produced from agricultural wastes need to be activated for an efficient adsorption of As(V),
- from contact time experiments, it has been shown that the optimal equilibrium time valid for each AC is 120 h,
- the intraparticle diffusion model on one hand, and the pseudo-second order model on the other describe correctly the experimental data. It means that the adsorption reaction is in agreement with a chemisorption mechanism being the rate controlling step as well as the intraparticle diffusion,
- The pseudo-second order model confirm the better efficiency of iron based materials as well as a faster reaction,
- Finally, the pH does not seem to have a great effect on the sorption capacities.

4.1.2 Adsorption isotherms

Based on these kinetic results, the adsorption study consists in conducting adsorption isotherms, testing adsorption models in order to define a sorption mechanism approach. Adsorption isotherms have been realized with each material with 120 h of contact time between the arsenic solution and the grains of AC. The pH was not fixed but followed and initial values are ranged between 5.9 and 7.3 depending on As concentration (100 to 5000 $\mu\text{g.L}^{-1}$).

4.1.2.1 Langmuir and Freundlich isotherms

Two adsorption models have been tested with Langmuir and Freundlich equations (see Chapter 1). Figure 4.11 and 4.12 show the experimental points of adsorption isotherms conducted with BP-H₂O, BP-H₂O-Fe, PH-H₂O, PH-H₂O-Fe and the GAC1. In the figures we can see the line corresponding to the Langmuir and Freundlich equations. The constants of each model are reported on Table 4.4.

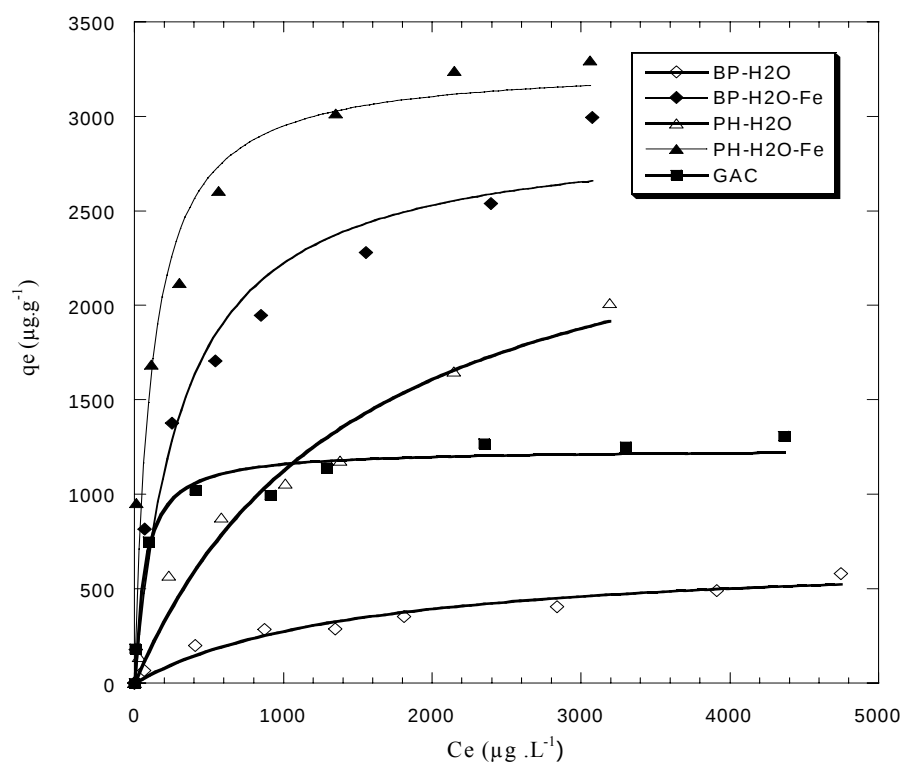


Figure 4.11 Experimental adsorption isotherms of As (V) and modelled results using the Langmuir equation

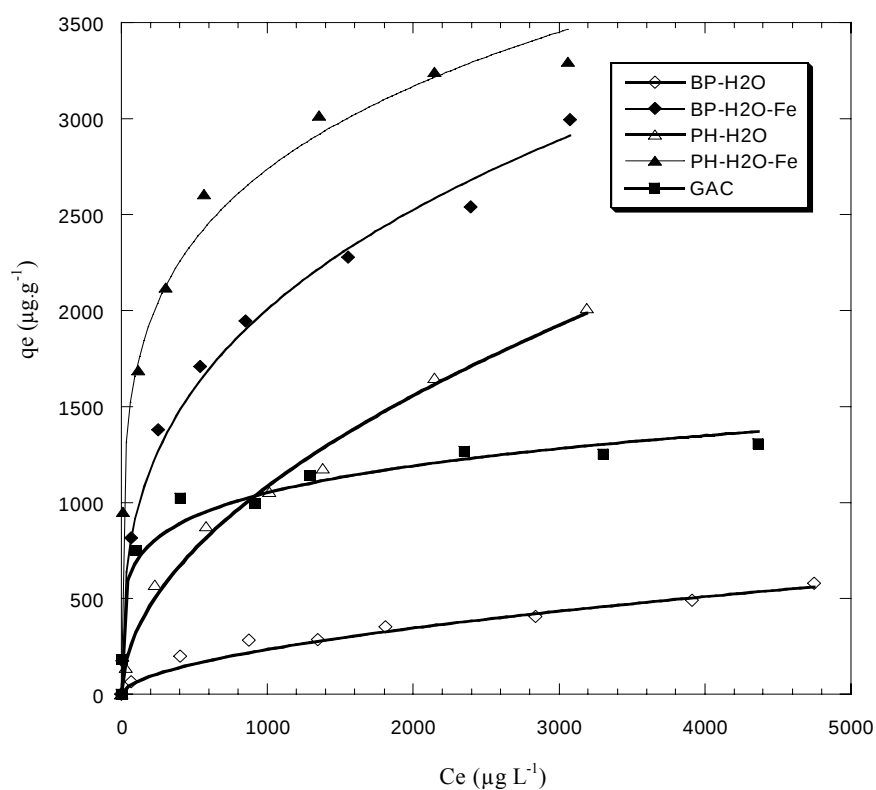


Figure 4.12 Experimental adsorption isotherms of As(V) and modelled results using the Freundlich equation

Table 4.4 Adsorption constants for Langmuir and Freundlich models isotherms.

Material	Langmuir			Freundlich		
	q_m	b_L	R^2	K_F	n	R^2
	($\mu\text{g}\cdot\text{g}^{-1}$)	($\text{L}\cdot\mu\text{g}^{-1}$)		($\mu\text{g}^{1-1/n}\cdot\text{L}^{1/n}\cdot\text{g}^{-1}$)		
BP-H ₂ O	690	0.00066	0.956	5	0.56	0.968
BP-H ₂ O-Fe	2930	0.00312	0.964	205	0.33	0.990
PH-H ₂ O	2820	0.00066	0.971	30	0.52	0.993
PH-H ₂ O-Fe	3280	0.00089	0.945	640	0.21	0.991
GAC1	1240	0.01454	0.966	300	0.18	0.968

Based on determination factor (Table 4.4), the experimental data fit the Freundlich model ($R^2 = 0.968 - 0.993$) better than the Langmuir model ($R^2 = 0.956 - 0.971$) for the carbonaceous materials. The maximum capacities for arsenic (V) deduced from the Langmuir model are 690 and 2820 $\mu\text{g}\cdot\text{g}^{-1}$ for steam activated materials (BP-H₂O and PH-H₂O), 2930 and 3280 $\mu\text{g}\cdot\text{g}^{-1}$ for iron modified carbons (BP-H₂O-Fe and PH-H₂O-Fe) and 1240 $\mu\text{g}\cdot\text{g}^{-1}$ for GAC1. These values calculated from the model are similar to the obtained experimental values and the comparison of efficiencies is quite similar to the latest one based on sorption initial rate: PH-H₂O-Fe > BP-H₂O-Fe $\approx$ PH-H₂O $\approx$ GAC1 > BP-H₂O. Regarding Freundlich model, K_F values are found to be 5 and 30 for steam activated carbons (BP-H₂O and PH-H₂O), 205 and 640 for iron loaded materials and 300 for granular activated commercial carbon (GAC1). The values for n are found to be smaller than 1 in all cases and the curves are concave downward throughout (type I) which indicates that adsorption is favorable (LeVan *et al.*, 1997). In terms of pH, the final values were greatly basic for BP-H₂O (between 9.1 and 9.4) and for BP-H₂O-Fe (8.5 and 9.1), close to the neutrality for PH-H₂O (between 6.5 and 7.1) and for GAC1 (between 6.6 and 7.2) and acidic for PH-H₂O-Fe (4.6 and 5.8). The effect of pH on adsorption isotherms is again not demonstrated. The most significant result of these experiments indicates that the adsorption capacity for As(V) is largely increased by loading iron on carbonaceous materials and exceeds those obtained with a commercial GAC.

Recently, different authors have used iron-impregnated activated carbons (Reed *et al.*, 2000; Chen *et al.*, 2007; Jang *et al.*, 2008; Mondal *et al.*, 2008 and Muñiz *et al.*, 2009) for As(V) removal but all of them concern commercial AC. Table 4.5 report these experiments, the q_m values and the associated iron %. There is a big discrepancy between the q_m values (from 20 $\mu\text{g As(V).g}^{-1}$ to more than 50 mg.g^{-1}), nevertheless these latter seem to be correlated with the iron content. Our results are correctly placed in this topic if we consider activated carbons produced from agricultural wastes at lab scale and trying to increase the iron content of our sorbent should be an interesting perspective.

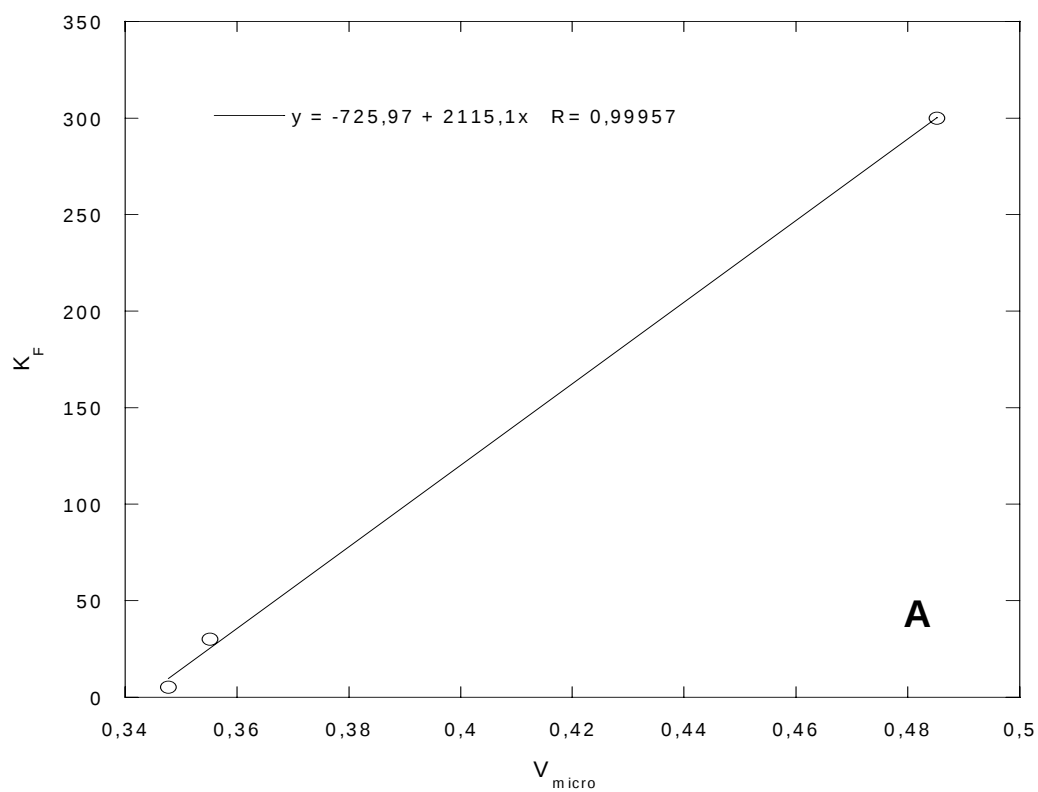
Table 4.5 Iron impregnated carbons reported in literature and adsorption capacity.

Type of carbon	q_m (mg.g^{-1})	Iron content (%)	Impregnation	Reference
Lignite based granular carbon	4.50	7.0	Iron impregnation with Fe(III).	Reed <i>et al.</i> (2000)
Commercial Granular Carbon	0.025	4.8	2.5% Fe^{+3} ferric chloride solution at pH 12.	Mondal <i>et al.</i> (2008)
Commercial (UltraCarb)	51.3	11.7	Impregnation by evaporation of $\text{Fe}(\text{NO})_3 \cdot 9\text{H}_2\text{O}$ solution at pH 6, one Fe precipitation was observed.	Chen <i>et al.</i> (2007)
Commercial (UltraCarb)	43.6	11.7	Impregnation by evaporation of $\text{Fe}(\text{NO})_3 \cdot 9\text{H}_2\text{O}$ solution at pH 8, none Fe precipitation was observed.	Chen <i>et al.</i> (2007)
Commercial granular (Darco)	6.57	2.3	Before oxidation. With 0.1M FeCl_2 solution.	Gu <i>et al.</i> (2005)
Commercial granular (Darco)	3.94	1.6	After oxidation. With 0.1M FeCl_2 solution.	Gu <i>et al.</i> (2005)
Commercial (NC-100)	0.028	2.2	After oxidation. Impregnation with 0.05M FeCl_3 solution in acidic media during 6 hours.	Fierro <i>et al.</i> (2009)
Commercial (NC-100)	0.008	9.4	After oxidation. Impregnation with 0.05M FeCl_3 solution in acidic media during 24 hours.	Fierro <i>et al.</i> (2009)

Table 4.5 (Continued) Iron impregnated carbons reported in literature and adsorption capacity.

Type of carbon	q_m (mg.g ⁻¹)	Iron content (%)	Impregnation	Reference
Commercial (NC-100)	0.008	9.4	After oxidation. Impregnation with 0.05M FeCl ₃ solution in acidic media during 24 hours.	Fierro <i>et al.</i> (2009)
Commercial (NC-100)	0.025-0.03	0.5-0.75	Impregnation in 0.05M FeCl ₃ and 3M HCl solution	Muñiz <i>et al.</i> (2009)
Commercial (NC-100)	0.015-0.02	1.3-1.5	Impregnation in 0.05M FeCl ₃ and 0.5M HCl solution	Muñiz <i>et al.</i> (2009)
Commercial granular (SuperDarco)	4-19	7.5-11	Impregnation with 0.5-1 g/ml [Fe(NO ₃) ₃ ·9H ₂ O] solution dispersed on carbon followed by evaporation for Fe oxide/hydroxide precipitation	Jang <i>et al.</i> (2008)
BP-H ₂ O-Fe	2.93	4.8	Impregnation with 0.1 M FeCl ₃ -6H ₂ O solution (pH = 1.7) during 24 hours.	This work.
PH-H ₂ O-Fe	3.28	0.5	Impregnation with 0.1 M FeCl ₃ -6H ₂ O solution (pH = 1.7) during 24 hours.	This work.

Finally, with the objective to correlate adsorption capacities and AC properties (see Chapter 3), it appears that no simple relationship can be established at this stage. If we consider non ferrous sorbents (BP-H₂O, PH-H₂O and GAC1), the only found relations are between the Freundlich constants, K_F and n , and the microporous volume of the adsorbents (Figure 4.13 – A) K_F vs V_{micro} and B) n vs V_{micro}). A straight line is obtained in both cases ($R^2=1$ and $R^2=0.999$ respectively). Kim *et al.* (2004) have reported that As(V) species sizes were respectively 0.416 nm for H₂AsO₄⁻ and 0.397 nm for HAsO₄²⁻. So a higher microporous (pore size < 2 nm) volume would increase arsenic adsorption. Of course, this results needs to be confirmed because only 3 sorbents are used for comparison but it could be a first approach. When iron is included in the activated carbon, the fixation mechanism is completely changed towards chemisorption reaction due to the high affinity of arsenic for this metal



oxide.

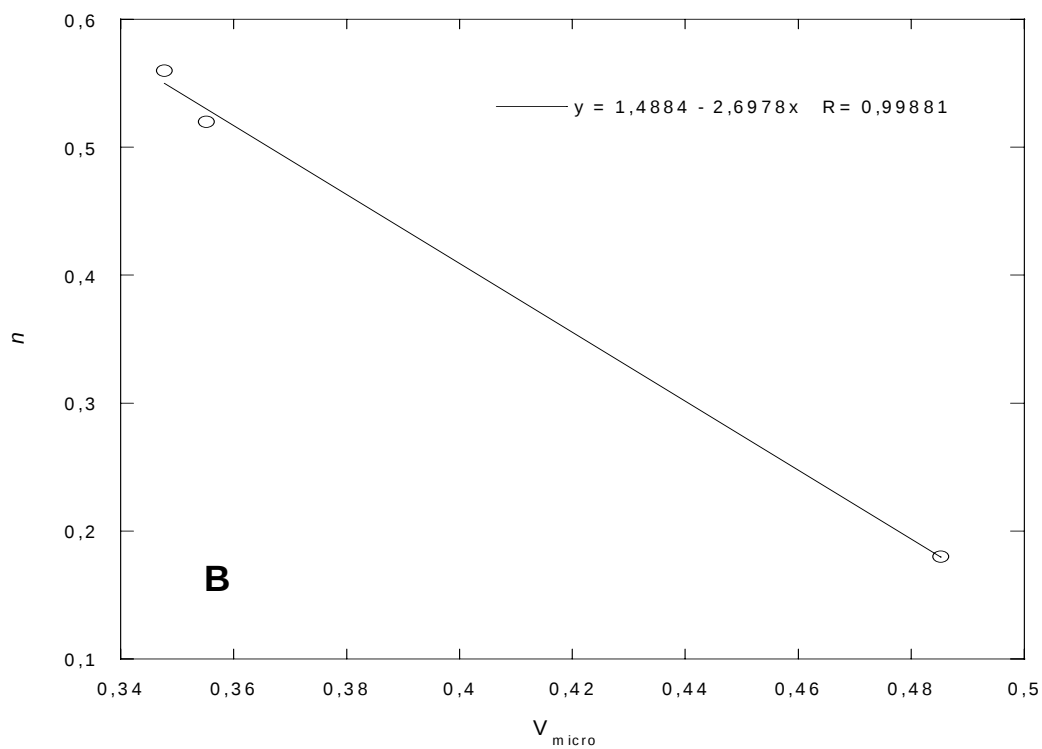


Figure 4.13 A) Freundlich constant (K_F) and B) n constant in function of microporous volume (V_{micro}) fitted to a linear equation.

4.1.2.2 Adsorption in natural waters spiked with arsenic

In order to understand the potential effect of competing ions, adsorption isotherms have been conducted in natural waters (Figure 4.14 - A and B). These waters were commercial spring water in which arsenic has been added. They have been selected due to their difference in their mineral content (Table 4.6) and peanut hull based AC has been chosen because of its highest adsorption capacities. The main concentrated ions in HMC water are: Ca^{2+} , Mg^{2+} , Na^+ , Cl^- , HCO_3^- and SO_4^{2-} .

Table 4.6 Mineral content of spring water utilized for As(V) adsorption.

Water	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	NO_3^-	HCO_3^-	SO_4^{2-}	pH
HMC (mg.L^{-1})*	230	66	40	8	58	< 1	280	620	7.2
LMC (mg.L^{-1})†	4.1	1.7	2.7	0.9	0.9	0.8	25.8	1.1	7.3

* Spring water with high mineral content (HMC), † Spring water with low mineral content (LMC).

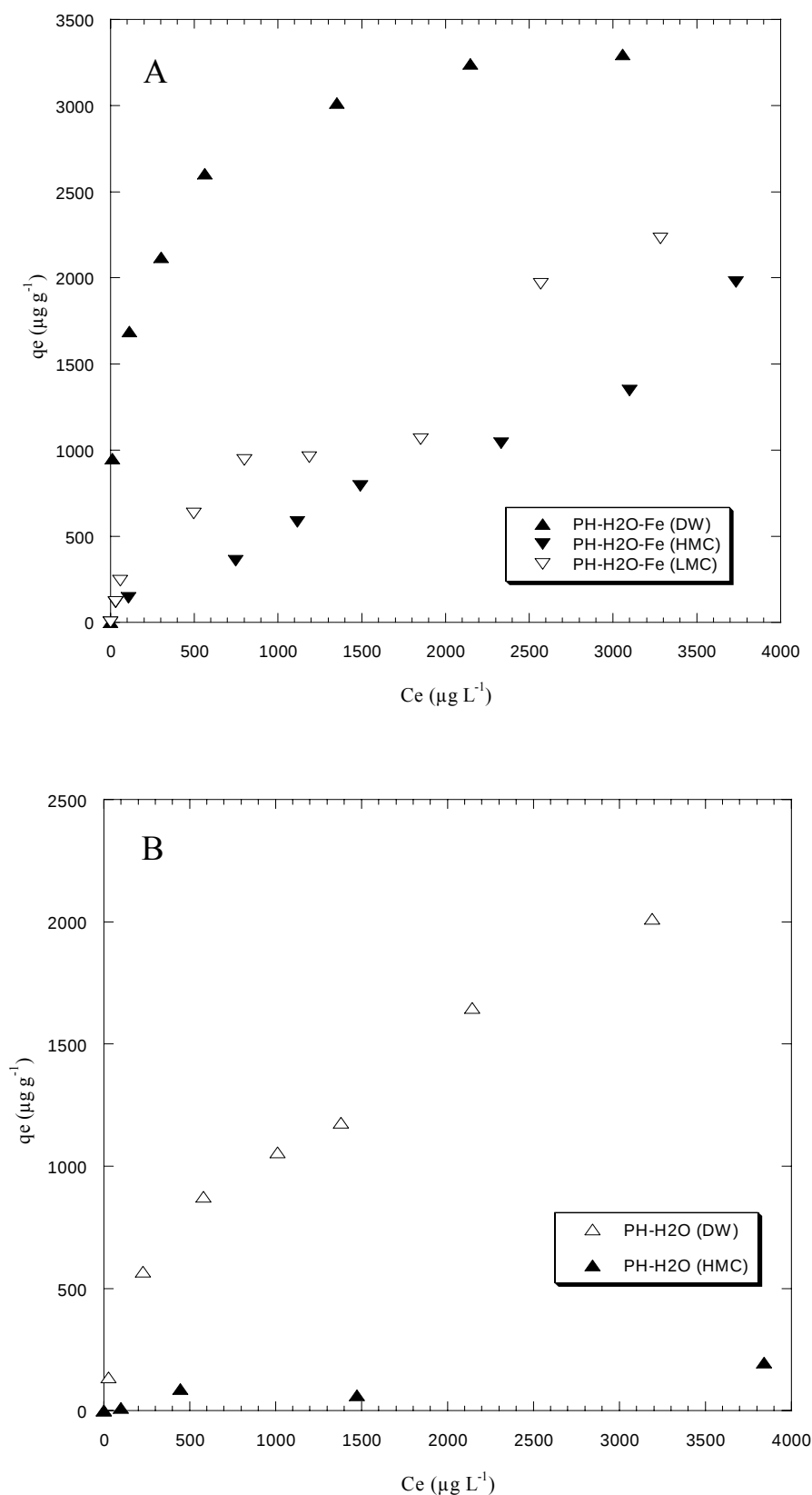


Figure 4.14 A) Sorption isotherm of arsenic(V) onto: A) PH-H₂O-Fe and B) PH-H₂O in deionized water (DW) and spring water with high (HMC) and low (LMC) mineral content.

In comparison with adsorption isotherm conducted in deionized water, the presence of an ionic strength decrease logically the capacities in both natural waters. Considering PH-H₂O (Figure 4.18-B), arsenic adsorption in HMC water is completely negligible. On the contrary, with ferrous sorbents, the decrease does not seem highly related to the minerals content of the 2 waters. The shape of the curves is also very different, showing different waves in function of C_e and preventing to use adsorption model like Langmuir or Freundlich. Another way to compare these data is to plot in deionized water and in HMC water, the adsorption isotherms conducted with PH-H₂O and PH-H₂O-Fe (Figure 4.15). Once again, the benefit of the iron content is obvious in HMC waters. Even if the shape of the curves is different and at $C_e=3000 \mu\text{g.L}^{-1}$ for example, the difference of q_e is close to $1300 \mu\text{g.g}^{-1}$ in both cases. Then, in order to keep adsorption capacities in natural waters, the iron modification of the adsorbent is absolutely necessary.

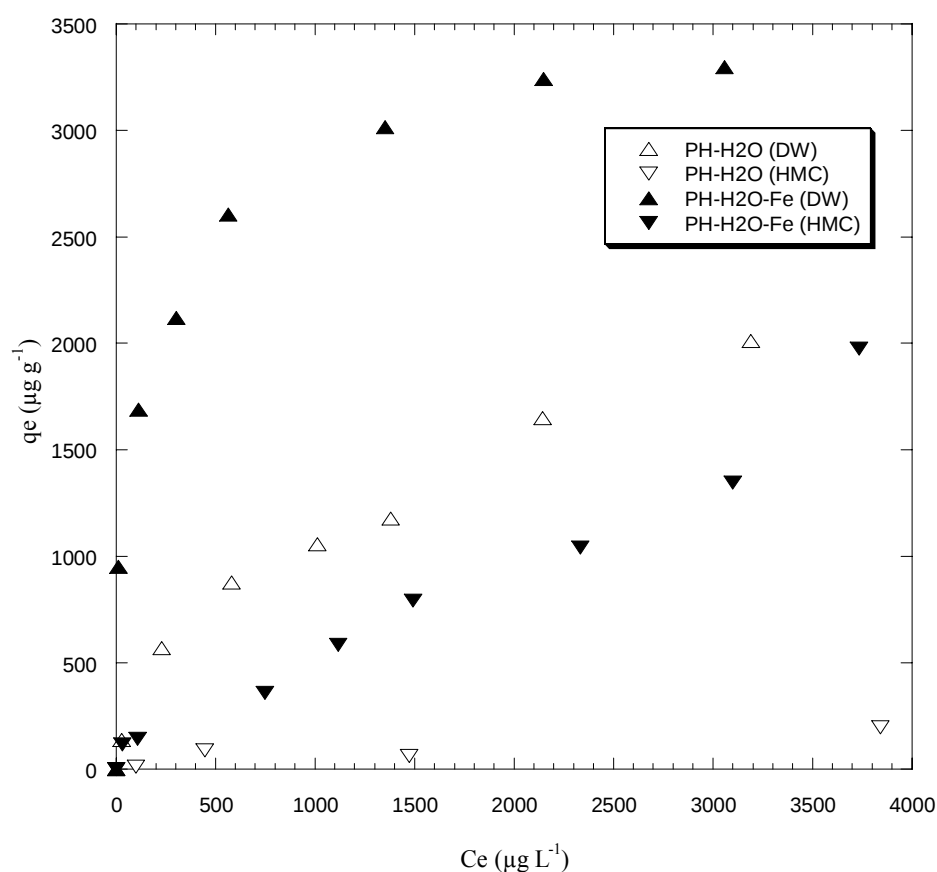


Figure 4.15 Sorption isotherm of arsenic(V) onto PH-H₂O and PH-H₂O-Fe in deionized water (DW) and spring water with high mineral content (HMC).

4.1.3 Sorption mechanism approach and conclusion

It has been shown that it is possible and interesting to produce AC from agricultural waste at lab scale and devoted to arsenic removal in solutions. To increase the As(V) adsorption capacities, the carbonaceous sorbents need firstly to be activated with steam for example, and then impregnated with iron when used in natural waters. In terms of kinetic properties, the optimal contact time was found at 120 h which is in agreement with classical reactions on activated carbons and the rate controlling steps are related to the intraparticle diffusion and the chemisorption reaction. Inclusion of iron in AC increases the initial rate of fixation and leads to a direct and positive effect on adsorption efficiencies. This benefit is also conserved in natural waters. Finally and surprisingly, the pH effect has never been clearly demonstrated in these experiments. In terms of sorption mechanism, no simple relation was found at this stage, but two principles could be retained. The most evident is the presence of iron in the sorbent which creates special affinity between arsenic species and the AC surface. Different ways of impregnation could be tested in future studies in order to produce materials with higher iron content and test them for arsenic removal. The second one needing to be confirmed is the microporosity of the AC. Regarding the smallness of arsenic anions, the interest to produce microporous sorbents could be investigated. Figure 4.16 illustrates the As(V) sorption phenomena on AC and iron impregnated AC.

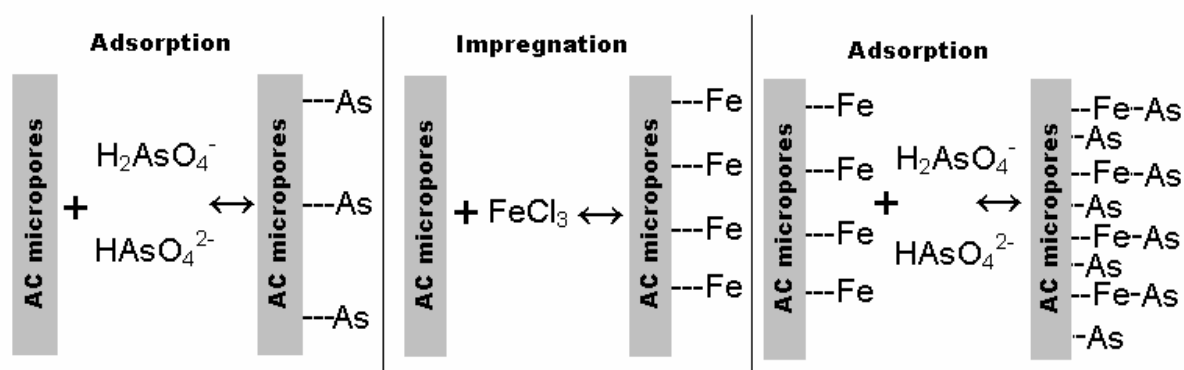


Figure 4.16 As(V) sorption phenomena on AC and iron impregnated AC.

4.2 ADSORPTION STUDY OF TETRACYCLINE

In this section the antibiotic Tetracycline (TC) is selected for the adsorption experiments. It is an organic molecule used extensively for disease control and in livestock feed for several decades due to its great therapeutic value (Sarmah *et al.*, 2006; Kuemmerer, 2009a,b). The widespread use of tetracycline and other antibiotics has led to dissemination of these compounds into the water and soil environments (Lindsey *et al.*, 2001; Blackwell *et al.*, 2007; Xu and Li, 2010). Although environmental concentrations of antibiotics are typically below the threshold levels to exhibit medicinal treatment effects on bacterial populations and other at-risk species, chronic exposure to low levels of antibiotics alone or along with other toxicants may still exert pressure on the development of antibiotic resistant bacteria and minimize the effectiveness and therapeutic value of antibiotics (Kim *et al.*, 2007; Yu *et al.*, 2009). Understanding the fate of antibiotic contaminants in the water–soil environment is imperative to better assess their risks and develop mitigation strategies.

Recent studies have reported strong interactions of TCs with mineral surfaces (Kraemer *et al.*, 1998; Kim *et al.*, 2005; Sassman and Lee, 2005; Pils and Laird, 2007). The electron-rich ketone, carboxyl, amino, and hydroxyl groups of the tetracycline (Figure 4.17) contribute to their strong tendency to complex with metals (Chen and Huang, 2009). In particular, several studies have demonstrated the strong adsorption of TCs with aluminum oxide surfaces and clays (Gu and Karthikeyan, 2005; Pils and Laird, 2007). Adsorption onto carbonaceous porous materials may play an important role in the remediation technologies avoiding the spread of trace organic contaminants such as tetracycline antibiotics. This topic is not developed in the literature, so the potential impact of carbonaceous materials and specifically those obtained from waste materials on the adsorption of tetracycline is investigated in this section.

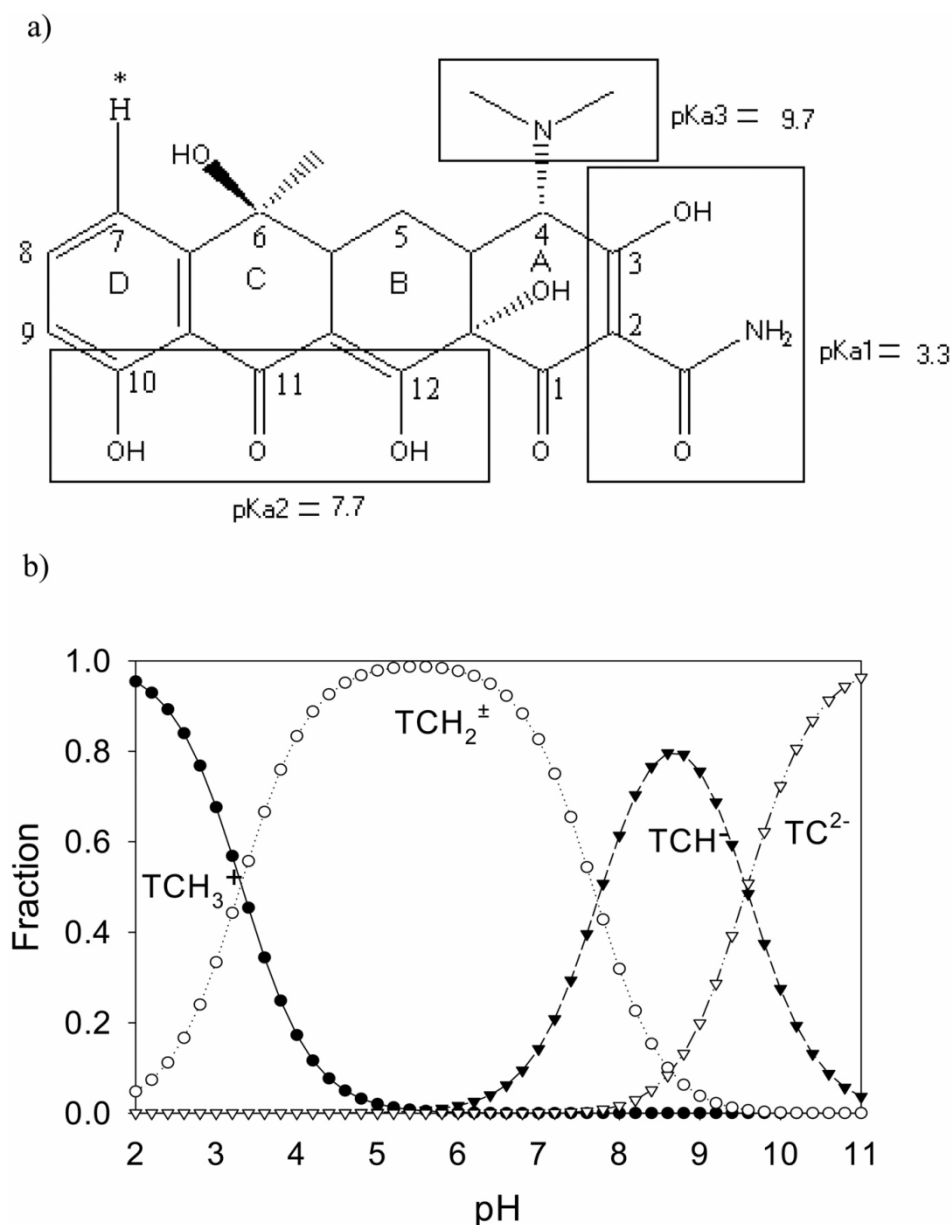


Figure 4.17 a) Structure and (b) pH-dependent speciation of tetracycline (TC) (Gu and Karthikeyan, 2008).

The objective of this part of the work is to study the ability of carbonaceous materials to adsorb tetracycline. Sorption studies are carried out in the same experimental conditions in order to compare sorption performance of the different carbonaceous materials prepared from agricultural wastes. Results are compared to those obtained with commercial activated carbons (namely GAC1 and GAC2) to understand the mechanism governing the tetracycline uptake.

In order to determine the potential rate controlling steps, kinetic data was treated by using two different kinetic models: pseudo-first and the pseudo-second order equation. Rate parameters are also determined. The presence of ions in solution is also studied in order to know if a competing effect affects the tetracycline sorption onto the carbonaceous materials and GACs. The selected materials for this adsorption study are the followings: BP-H₂O, BP-H₂O-Fe, PH-H₂O, PH-H₂O-Fe, GAC1 and GAC2. Powder materials were utilized for all the tetracycline sorption tests in this part of the work.

4.2.1 Kinetic study of tetracycline adsorption

The kinetic study presented in this section includes contact times experiments in order to determine the equilibrium time, the modeling of the decay curves and the final part is related to the pH effect on the tetracycline sorption.

4.2.1.1 Contact time experiments

One of the first parameters to determine is the equilibrium time: it is the time after which there is no mass transfer between the adsorbent and the pollutant. Because of the variation in uptake capacities, different initial concentration of TC has been selected. These experiments have been conducted firstly with PH-H₂O, PH-H₂O-Fe with a fixed initial concentration (50 mg.L⁻¹). Then, a higher initial concentration of TC (100 mg.L⁻¹) was applied to evaluate the equilibrium time with GAC1, BP-H₂O and BP-H₂O-Fe. Finally, another commercial activated carbon (GAC2) with different surface characteristics (see chapter 3) was tested using the highest tetracycline concentration (300 mg.L⁻¹). All the initial concentrations of tetracycline lead to initial pH comprised between 3.4 and 4.2. It has not been fixed during the experiment but final values have been noticed.

4.2.1.1.1 Kinetic decay curves obtained with activated and modified carbonaceous materials

The first contact time experiments have been carried out with BP-H₂O, BP-H₂O-Fe, PH-H₂O and PH-H₂O-Fe. In Figure 4.18 it is obvious that in carbonaceous materials obtained from peanut hulls (PH-H₂O and PH-H₂O-Fe) it has not been found high sorption capacities when they are compared with those of BP-H₂O, BP-H₂O-Fe. However, when PH-H₂O and PH-H₂O-Fe are compared, the iron impregnation increases the tetracycline sorption and it is faster than PH-H₂O. These results mean principally that the characteristics of the AC (precursor, porosity, chemical composition) are important for tetracycline adsorption and the time to reach the equilibrium for BP-H₂O and BP-H₂O-Fe seems to be faster than PH-H₂O and PH-H₂O-Fe. The final pH of the kinetics test was 7.4 and 6.7 for BP-H₂O and BP-H₂O-Fe and 6.3 and 4.4 for PH-H₂O and PH-H₂O-Fe respectively. For these pH values the tetracycline speciation is given on table 4.3. It clearly appears that the main tetracycline species present in solution at the end of the experiments is TCH₂[±] form. All the measurements were verified to be higher than the quantification limit determined by UV-Vis spectrometry for tetracycline measurement (0.3 mg.L⁻¹).

Based on Figure 4.22, two parts can be observed in the curves:

- During the first 12 h, a very fast decrease of the concentration occurs.
- Followed by a slow decrease and the time needed to observe this step depends on the carbonaceous material.

In terms of initial adsorption rate:

- Beet pulp carbons > peanut hulls carbons.
- Iron impregnation seems to speed up the kinetic.

This behavior observed in kinetic tests will be confirmed later. Finally, it will be probably difficult to find a common equilibrium time for each material.

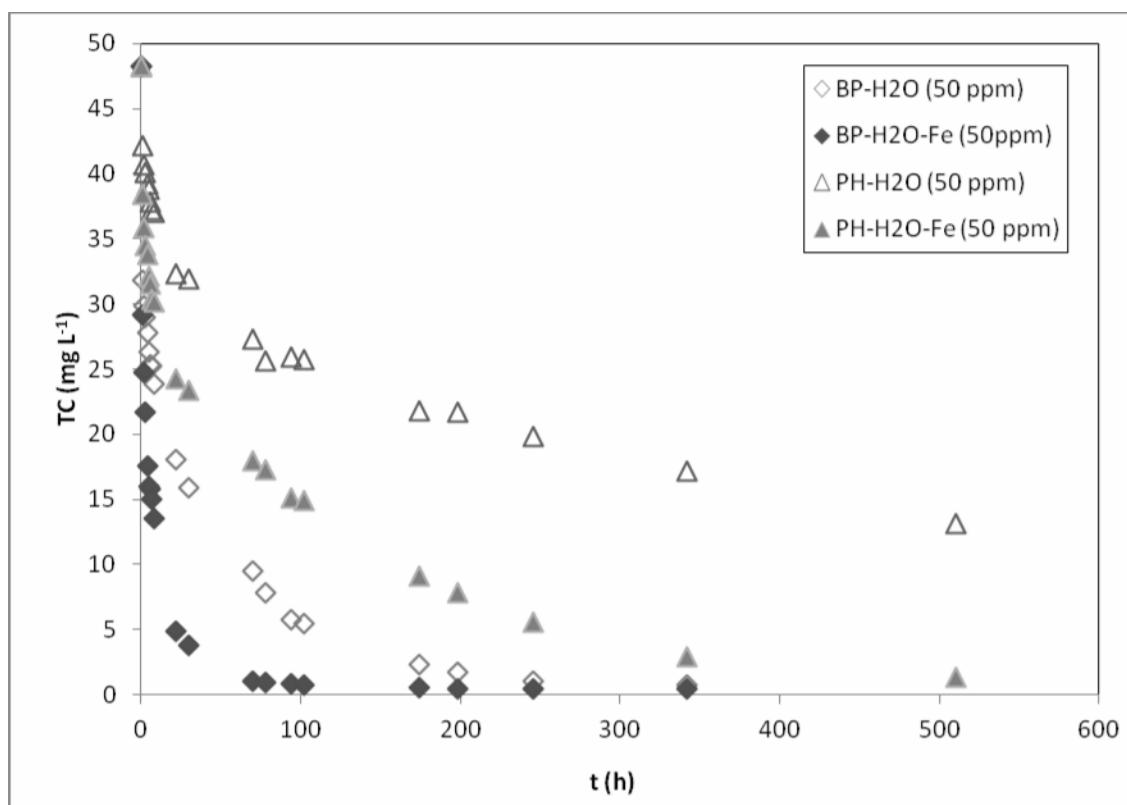


Figure 4.18 Kinetic decay curves for removal of TC as a function of time and initial concentration of 50 mg.L^{-1} for BP- H_2O , BP- $\text{H}_2\text{O-Fe}$, PH- H_2O , PH- $\text{H}_2\text{O-Fe}$.

4.2.1.1.2 Kinetic decay curves obtained with BP- H_2O , BP- $\text{H}_2\text{O-Fe}$, GAC1 and GAC2

In Figure 4.19 the kinetic decay curves for tetracycline adsorption onto the sugar beet pulp based adsorbents (BP- H_2O , BP- $\text{H}_2\text{O-Fe}$) and a commercial activated carbon (GAC1) is represented. From this figure it could be note that there is a low adsorption of tetracycline in GAC1 and the capacities are greatly improved when sugar beet pulp based carbonaceous materials are used. Moreover, the equilibrium time for GAC1 was around of 5 days. This time was longer for BP- H_2O and BP- $\text{H}_2\text{O-Fe}$ because it takes more than 15 days. In terms of final pH, the values for BP- H_2O , BP- $\text{H}_2\text{O-Fe}$ and GAC1 are ($C_0 = 100 \text{ mg.L}^{-1}$) 7.3, 5.8 and 4.0 respectively. In these cases the main species of tetracycline present in solution is also $\text{TCH}_2^\pm$ (Table 4.3, Figure 4.17)

Figure 4.20 present the case of GAC2 where the initial tetracycline concentration was 300 mg.L^{-1} . A great adsorption of tetracycline is observed, the equilibrium time is established at 5 days (120h) and the final pH value does not present important changes.

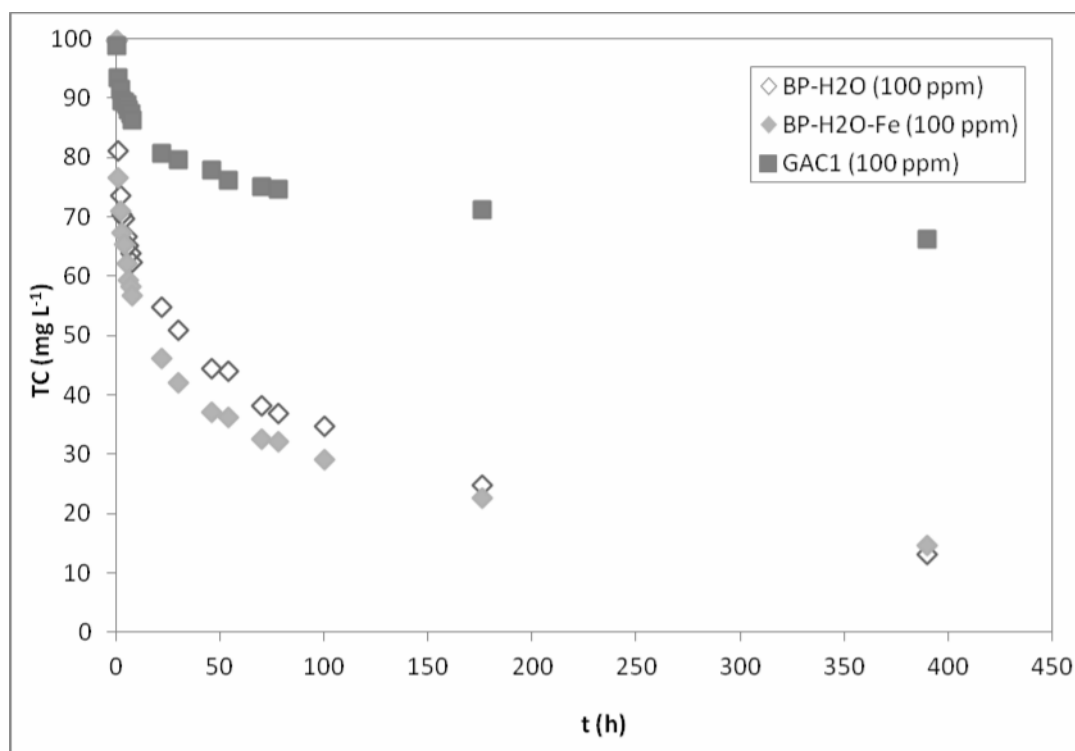


Figure 4.19 Kinetic decay curves for removal of TC as a function of time and initial concentration of 100 mg.L⁻¹ for BP-H₂O, BP-H₂O-Fe and GAC1.

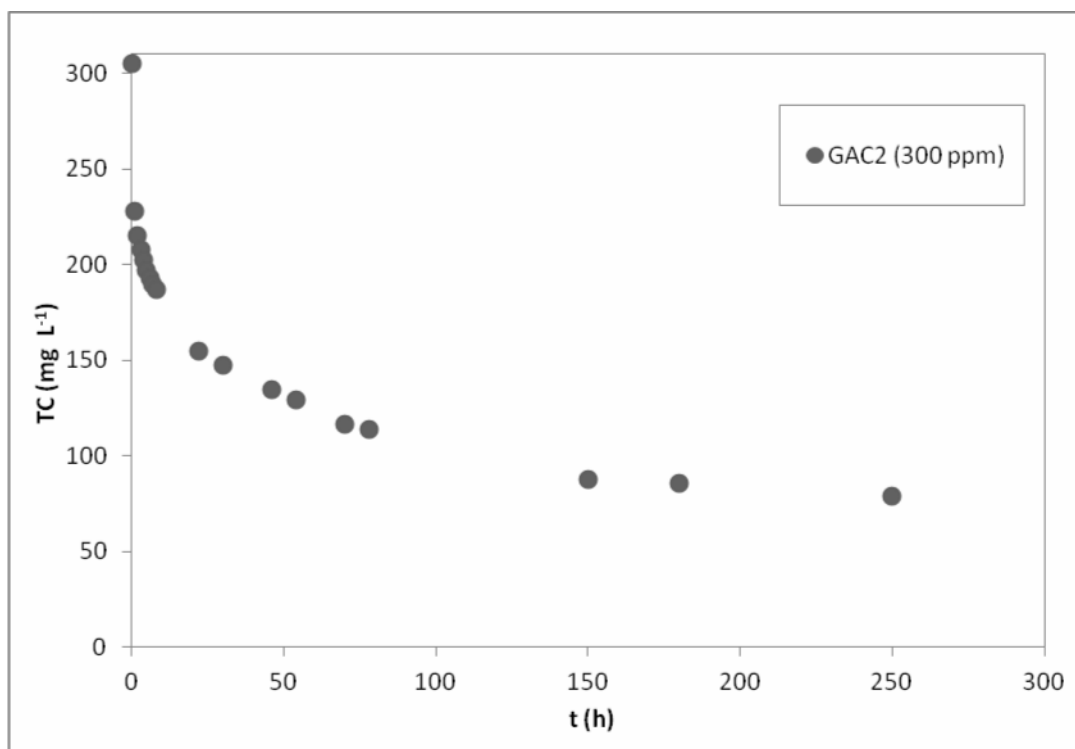


Figure 4.20 Kinetic decay curve for removal of TC as a function of time and initial concentration of 300 mg.L⁻¹ for GAC2.

Table 4.7 Different forms of tetracycline determined from the speciation for the adsorbent materials at pH_i and pH_f in kinetic tests (see also figure 4.17).

Material	pH_i	Tetracycline form	pH_f	Tetracycline form
BP-H ₂ O $C_0 = 50 \text{ mg.L}^{-1}$	4.2	89 % of $\text{TCH}_2^\pm$ 11 % of TCH_3^+	7.4	66 % of $\text{TCH}_2^\pm$ 34 % of TCH^-
BP-H ₂ O-Fe $C_0 = 50 \text{ mg.L}^{-1}$			6.7	90 % of $\text{TCH}_2^\pm$ 10 % of TCH^-
PH-H ₂ O $C_0 = 50 \text{ mg.L}^{-1}$			6.3	96 % of $\text{TCH}_2^\pm$ 4 % of TCH^-
PH-H ₂ O-Fe $C_0 = 50 \text{ mg.L}^{-1}$			4.4	93 % of $\text{TCH}_2^\pm$ 7 % of TCH_3^+
BP-H ₂ O $C_0 = 100 \text{ mg.L}^{-1}$	3.9	80 % of TCH_3^+ 20 % of $\text{TCH}_2^\pm$	7.3	72 % of $\text{TCH}_2^\pm$ 28 % of TCH^-
BP-H ₂ O-Fe $C_0 = 100 \text{ mg.L}^{-1}$			5.8	99 % of $\text{TCH}_2^\pm$
GAC1 $C_0 = 100 \text{ mg.L}^{-1}$			4.0	83 % of $\text{TCH}_2^\pm$ 17 % of TCH_3^+
GAC2 $C_0 = 300 \text{ mg.L}^{-1}$	3.4	56 % of $\text{TCH}_2^\pm$ 44 % of TCH_3^+	3.6	67 % of $\text{TCH}_2^\pm$ 33 % of TCH_3^+

4.2.1.1.3 Conclusion about contact time experiments

In Figures 4.18 to 4.20 are presented the kinetic decay curves carried out at 50, 100 and 300 mg.L⁻¹ with the different prepared carbonaceous materials and GACs. For the further experiments, the optimal contact time common for all the materials is then fixed at 120 h (5 days). Most of materials present a higher adsorption within this time and it is also the equilibrium time for the material that presented the best performance for tetracycline adsorption (GAC2). The comparison between the activated materials from agricultural by-products (Figure 4.18) leads to conclude that an order can be established based on their tetracycline adsorption capacity: GAC2 >> BP-H₂O ≠ BP-H₂O-Fe > GAC1 > PH-H₂O-Fe > PH-H₂O.

As the iron impregnation of peanuts hull carbonaceous material does not greatly affect the porous structure, a mechanism of chemisorption could be probably involved in this case. On the contrary, iron modification of carbonaceous materials from beet pulp (BP-H₂O and BP-H₂O-Fe) only affects the initial adsorption rate and not the sorption capacity at equilibrium time.

4.2.1.2 Kinetic modeling

In order to evaluate the kinetic sorption mechanisms, the pseudo-first order and pseudo-second order models were tested. Based on the poor regression of coefficient (R^2), results for the first-order model are not shown. However, the pseudo-second order rate expression provided a very good fitting to the kinetic model for the experimental data (Figures 4.21 to 4.28).

The pseudo-second order rate constant, h and q_e were calculated from the slope and intercept of the plots of t/q_t versus t . The plots show good linearity, with regression coefficients higher than 0.978 for all the carbonaceous materials obtained from agricultural wastes and the GACs for the entire adsorption period. The calculated kinetic parameters are reported in Table 4.8.

The value of the h constant at tetracycline initial concentration of 50 mg.L⁻¹ was 0.29 and 1.1 mg.g⁻¹.min⁻¹ for BP-H₂O, BP-H₂O-Fe and 0.03 and 0.06 mg.g⁻¹.min⁻¹ for PH-H₂O and

PH-H₂O-Fe which suggested that the sorption of tetracycline for the iron modified materials is faster than only steam activated material. In the case of BP-H₂O, BP-H₂O-Fe and GAC1 where a tetracycline initial concentration of 100 mg.L⁻¹ was employed, the *h* constant values were 0.28 and 0.40 mg.g⁻¹.min⁻¹ for BP-H₂O, BP-H₂O-Fe respectively and 0.18 mg.g⁻¹.min⁻¹ for GAC1 demonstrating that even the carbonaceous materials present a sorption rate for tetracycline higher than a GAC1. In the case of the other commercial activated carbon tested (GAC2), the *h* constant value was 2.41 mg.g⁻¹.min⁻¹ with a higher tetracycline concentration (300 mg.L⁻¹). The different behavior of GACs was probably due to the precursor nature and surface characteristics, specifically the mesoporous volume that presents a high difference between them: 0.176 cm³.g⁻¹ for GAC1 and 0.613 cm³.g⁻¹ for GAC2.

Kinetics of tetracycline sorption on all the carbonaceous materials and commercial activated carbons followed the pseudo-second order model, suggesting that the adsorption rate-limiting step may be chemisorption and the adsorption of tetracycline occurs probably via surface complexation reactions at specific sorption sites (Ho and McKay, 1998a).

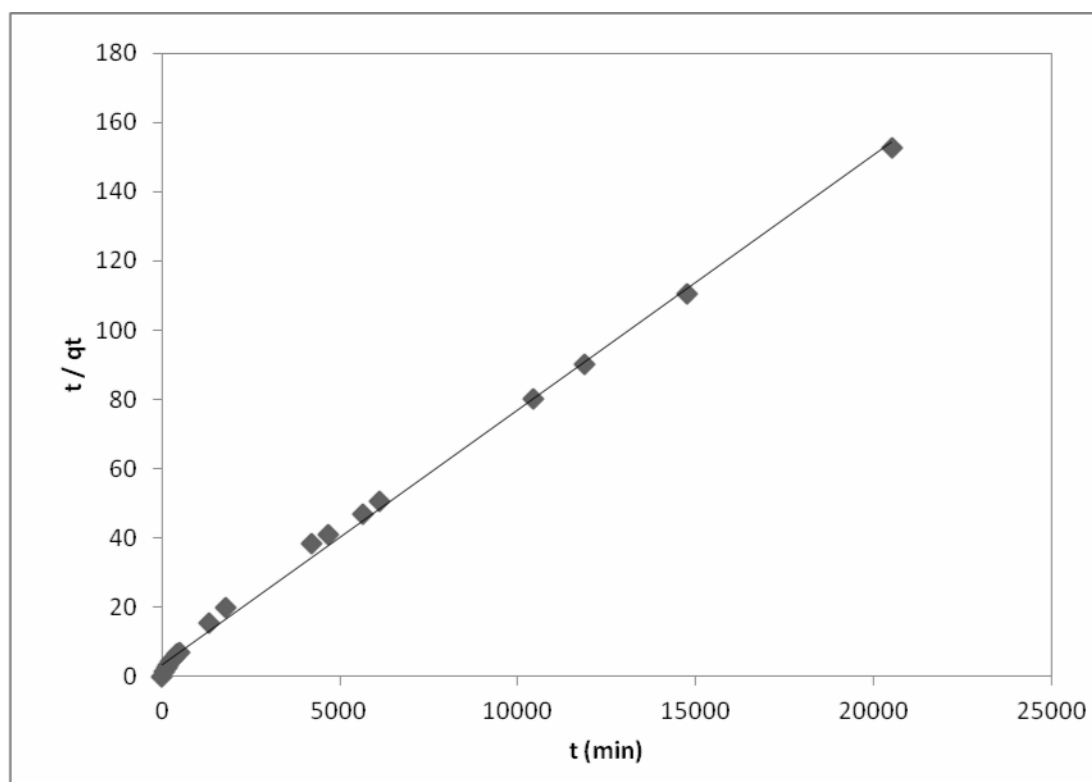


Figure 4.21 Tetracycline adsorption by BP-H₂O fitted with pseudo-second order kinetic model (linear) [TC]=50 mg.L⁻¹.

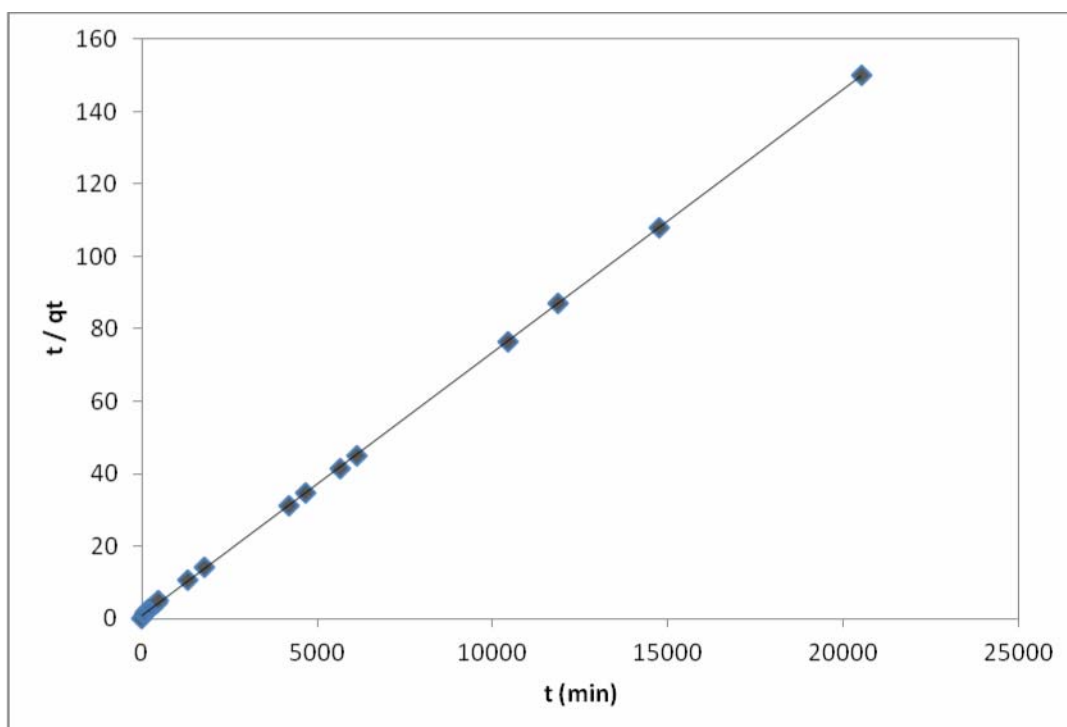


Figure 4.22 Tetracycline adsorption by BP-H₂O-Fe fitted with pseudo-second order kinetic model (linear) [TC]=50 mg.L⁻¹.

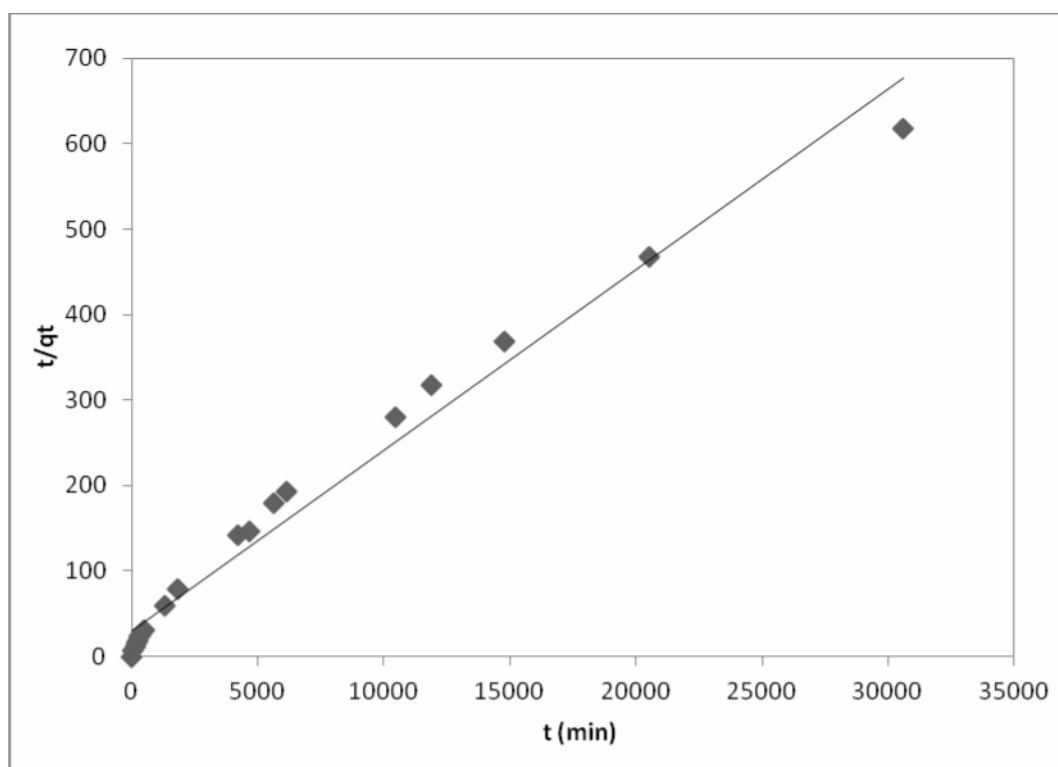


Figure 4.23 Tetracycline adsorption by PH-H₂O fitted with pseudo-second order kinetic model (linear) [TC]=50 mg.L⁻¹.

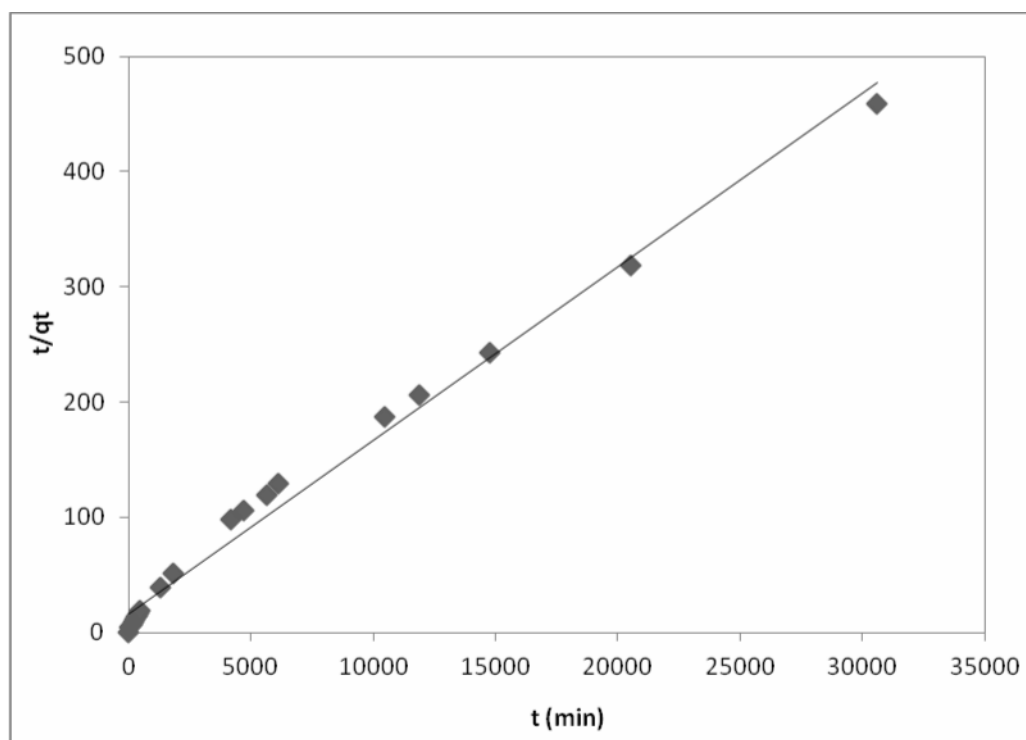


Figure 4.24 Tetracycline adsorption by PH-H₂O-Fe fitted with pseudo-second order kinetic model (linear) [TC]=50 mg.L⁻¹.

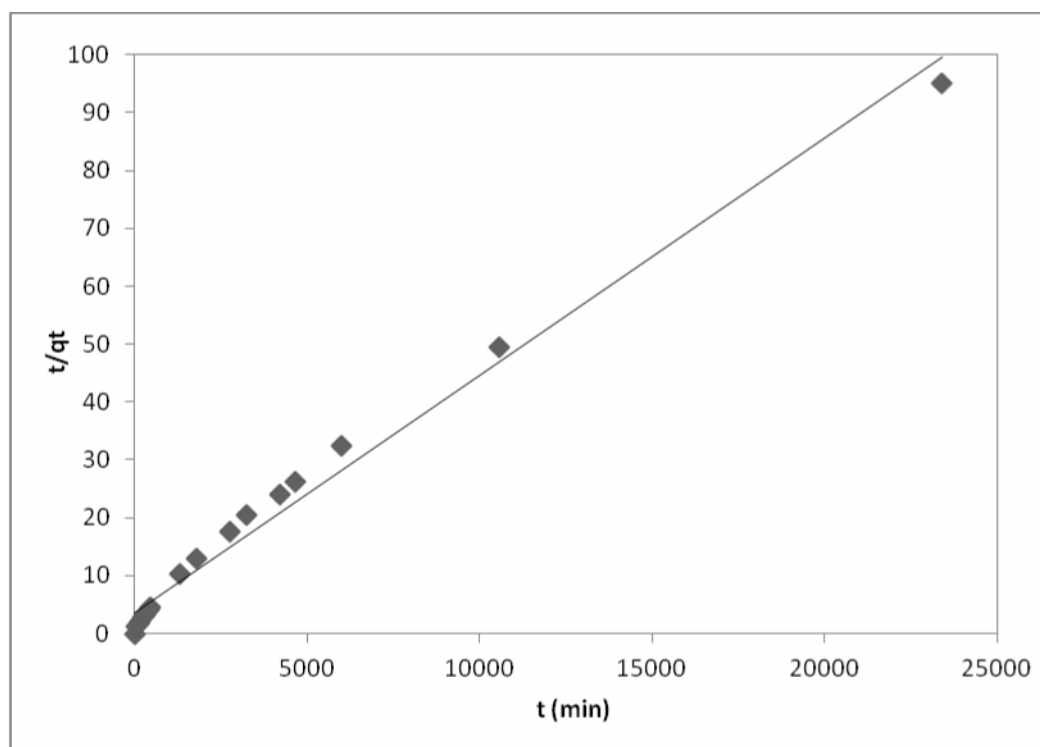


Figure 4.25 Tetracycline adsorption by BP-H₂O fitted with pseudo-second order kinetic model (linear) [TC]=100 mg.L⁻¹.

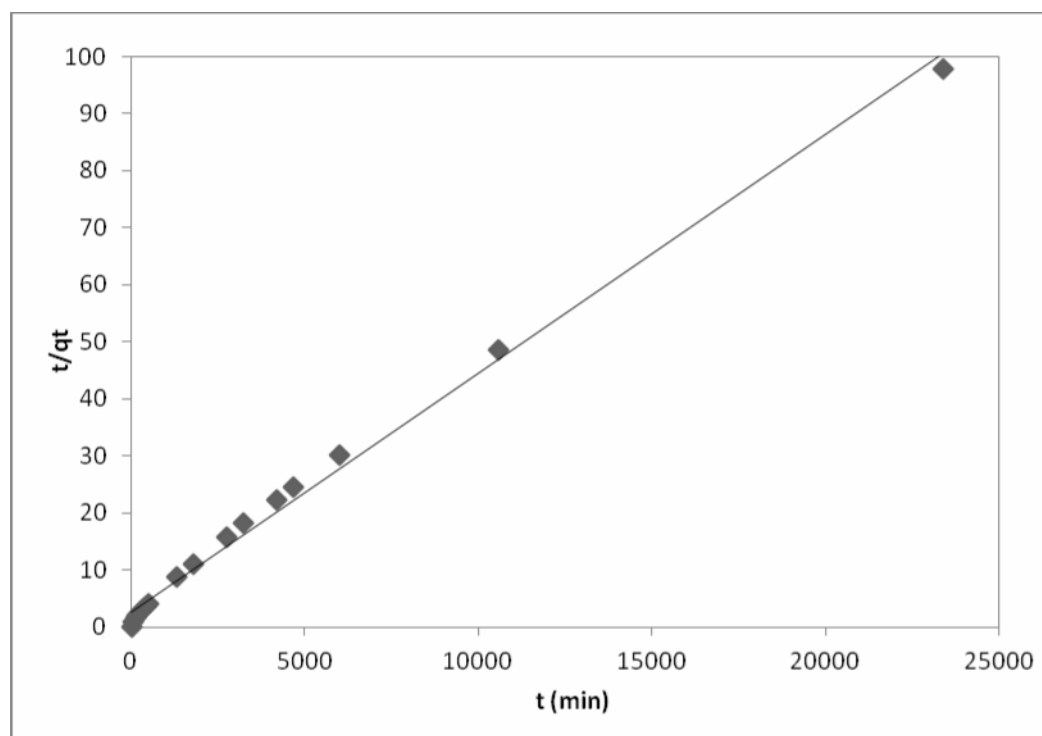


Figure 4.26 Tetracycline adsorption by BP-H₂O-Fe fitted with pseudo-second order kinetic model (linear) [TC]=100 mg.L⁻¹.

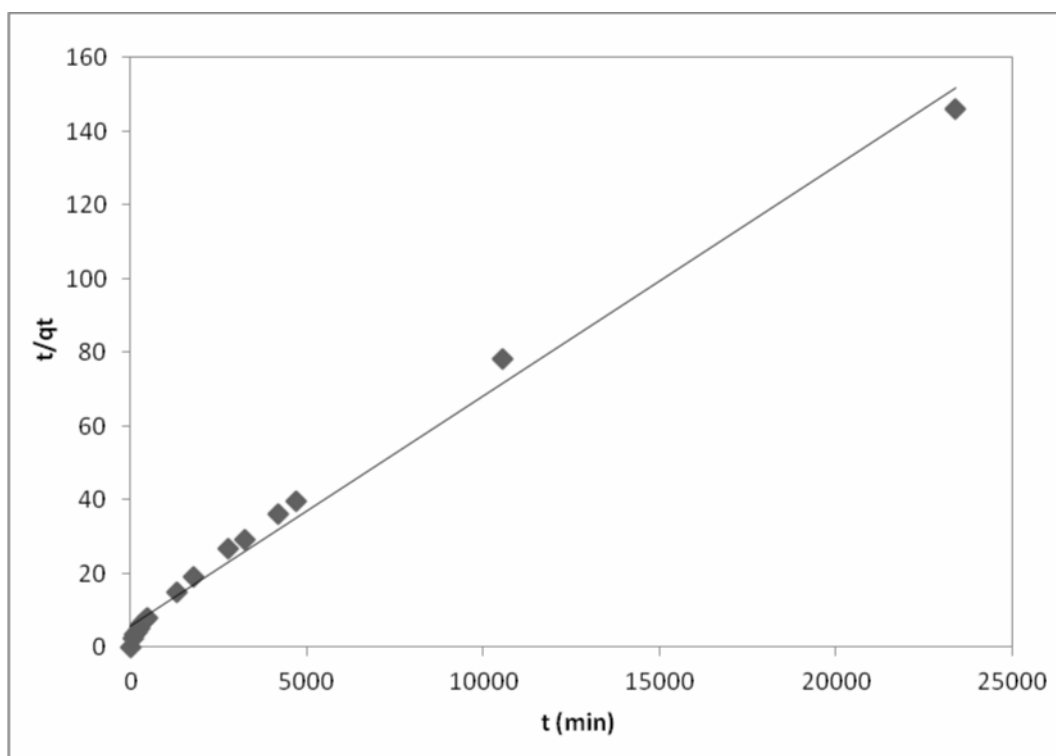


Figure 4.27 Tetracycline adsorption by GAC1 fitted with pseudo-second order kinetic model (linear) [TC]=100 mg.L⁻¹.

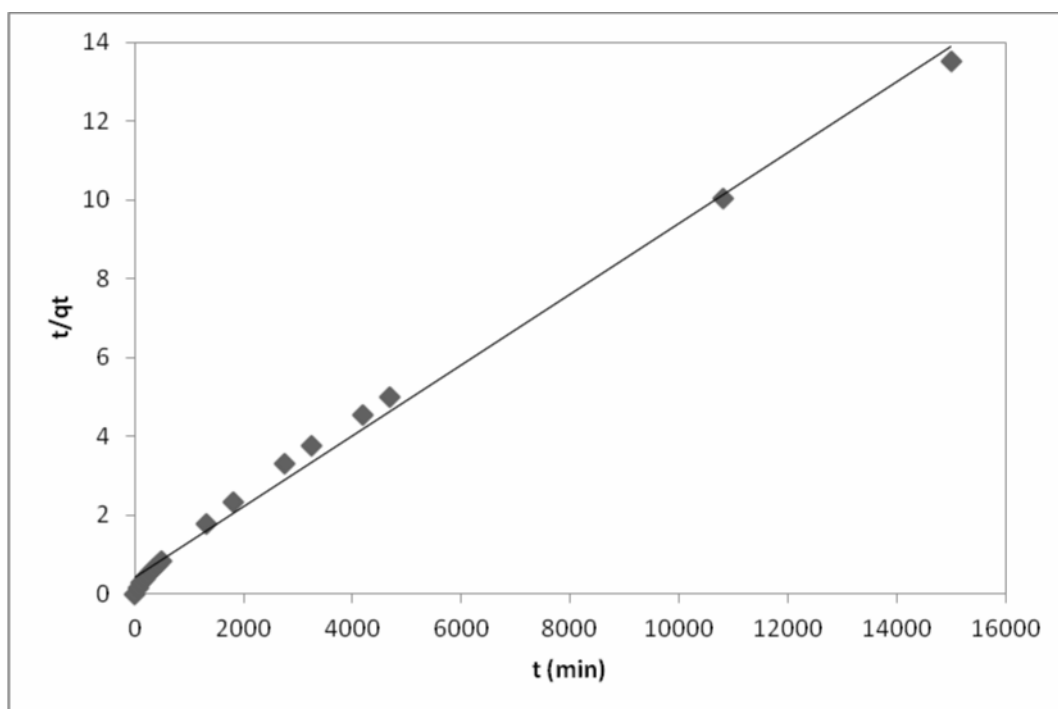


Figure 4.28 Tetracycline adsorption by GAC2 fitted with pseudo-second order kinetic model (linear) $[TC]=300 \text{ mg.L}^{-1}$.

Table 4.8 Kinetic parameters for TC adsorption fitted by pseudo-second order model.

Material	C_0 (mg.L^{-1})	h ($\text{mg.g}^{-1}.\text{min}^{-1}$)	q_e (cal.) (mg.g^{-1})	q_e (exp.) (mg.g^{-1})	k_2 ($\text{g.mg}^{-1}.\text{min}^{-1}$)	R^2
BP-H ₂ O	50	0.29	135.2	134.3	1.6×10^{-5}	0.998
BP-H ₂ O-Fe	50	1.10	137.9	137.0	5.8×10^{-5}	1.000
PH-H ₂ O	50	0.03	47.4	49.5	1.5×10^{-5}	0.978
PH-H ₂ O-Fe	50	0.06	66.2	66.7	1.4×10^{-5}	0.990
BP-H ₂ O	100	0.28	243.9	246.0	4.6×10^{-6}	0.986
BP-H ₂ O-Fe	100	0.40	238.1	239.2	7.0×10^{-6}	0.994
GAC1	100	0.18	158.7	160.1	7.1×10^{-6}	0.990
GAC2	300	2.41	1111.1	1109.0	2.0×10^{-6}	0.994

4.2.1.3 pH effect

The effect of the pH in the sorption of tetracycline was evaluated with the both materials that presented the best performance to adsorb the organic pollutant, the first was the activated carbonaceous material prepared from beet pulp (BP-H₂O) and the second one was the wood based commercial activated carbon (GAC2).

The tetracycline is an amphoteric molecule with multiple ionizable functional groups that exist predominantly as zwitterions in the typical pH in the natural aqueous environment (Figure 4.17). Figure 4.29 shows that solution pH affect the adsorption of tetracycline onto the adsorbent materials. In the case of BP-H₂O when the initial pH of the solution is 4.0, the adsorption capacity was 40% higher (285 mg.g⁻¹) compared with the adsorption capacities for pH values of 8 and 11 that were very similar between them (169 and 156 mg.g⁻¹ respectively).

For GAC2, it is found that for an initial pH value of 4, the sorption is also 20% higher (745 mg.g⁻¹) than at pH value of 8 (599 mg.g⁻¹) and 30 % higher than the capacity obtained at pH = 11 (508 mg.g⁻¹).

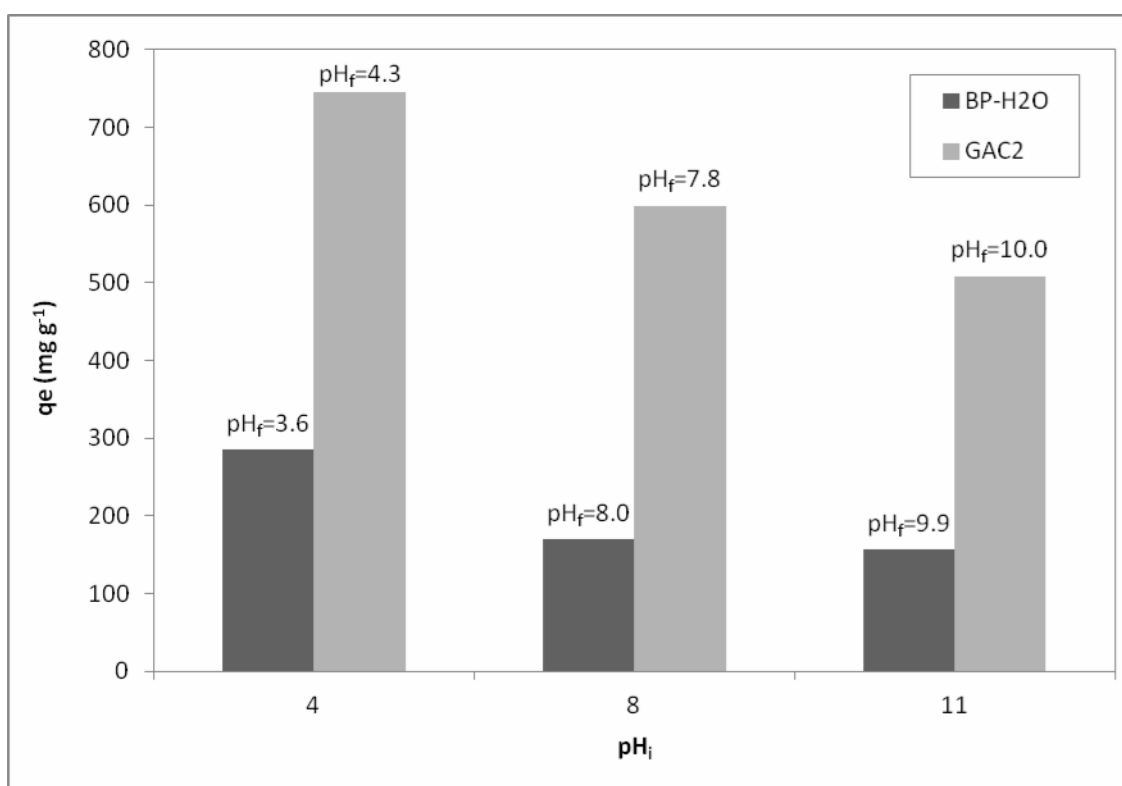


Figure 4.29 - Tetracycline removal by BP-H₂O and GAC2, contact time of 5 days, initial concentration of 200 mg.L⁻¹ and pH_i = 4, 8 and 11.

For the both tested materials, the maximal sorption occurred at $\text{pH}_i = 4$. If cation exchange is the predominant mechanism for tetracycline uptake by mineral sorbent (see Table 1.8 Chapter 1), it clearly appears that for carbonaceous material and the commercial activated carbon other mechanisms takes place. In this study, the better sorption capacity occurs when the TC is in its zwitterionic form $\text{TCH}_2^\pm$. So the sorption could be dominated by other interactions phenomena such as complexation (Chang *et al.*, 2009c) or adsorptive interactions (Ji *et al.*, 2009).

The decrease on tetracycline sorption by the carbonaceous material and GAC2 at high pH may be attributed to the electrostatic repulsion between the anionic tetracycline the negative charge of the adsorbent materials (zeta potential is generally negative and GAC2 shown a $\text{pH}_{\text{zpc}} = 3.5$). On the other hand, probably some sorption was due to another kind of simultaneous interactions between polar and charged functional groups of tetracycline and surface sites on activated carbons. The positively charged quaternary ammonium functional group of tetracycline may interact with negatively charged sites via cation exchange, and the negatively charged tricarbonylmethane keto-enol moiety of tetracycline may interact with negatively charged sites via cation bridging. Hydrogen bonding between polar tetracycline groups and acidic groups on carbonaceous materials may also contribute to tetracycline sorption (Xu and Li, 2010; Pils and Laird, 2007).

4.2.2 Adsorption isotherms

Equilibrium sorption tests have been performed to provide the adsorption capacities of the carbonaceous material and the commercial activated carbon relating to TC. For all the initial concentrations (70 to 300 mg.L^{-1} for BP- H_2O , 15 to 100 mg.L^{-1} for PH- H_2O and PH- $\text{H}_2\text{O-Fe}$, 50 to 200 mg.L^{-1} for GAC1 and 100 to 300 mg.L^{-1} for GAC2), the initial pH values are ranged between 3.3 and 4.5 . The final pH value for BP- H_2O was between 4.5 and 7.5 that means that the zwitterionic form ($\text{TCH}_2^\pm$) was the principal form, For PH- H_2O and PH- $\text{H}_2\text{O-Fe}$ the final pH values was comprised between 4.9 to 7.0 and 3.8 to 4.5 respectively. For GAC1 the final pH values were between 3.6 and 4.4 and for GAC2 between 3.3 and 4.1 . These latter pH conditions mean that both TC forms are present in solution: the positively

charged (TCH_3^+) and the zwitterion ($\text{TCH}_2^\pm$). Figure 4.30 and 4.31 show the experimental points of adsorption isotherms conducted with BP- H_2O , PH- H_2O , PH- H_2O -Fe, GAC1 and GAC2.

4.2.2.1 Langmuir and Freundlich isotherms

Sorption isotherms are determined to assess tetracycline distribution between solid and aqueous phases as a function of sorbate concentration (Figures 4.30 and 4.31). The experimental isotherm data at 20 °C are fitted to the equations of Langmuir and Freundlich. The full line corresponding to the Langmuir and Freundlich equations are presented in figures 4.34 and 4.35 respectively. Based on determination factor (Table 4.8), the experimental data fit the Freundlich model ($R^2 = 0.985 - 1.000$) better than the Langmuir model ($R^2 = 0.939 - 0.998$) for the carbonaceous materials, which indicated that Freundlich equation could be used to describe the adsorption of tetracycline on the tested carbonaceous materials and commercial activated carbons. The maximum capacities for tetracycline adsorption deduced from the Langmuir model are 288.3 and 28 mg.g^{-1} for steam activated materials (BP- H_2O and PH- H_2O), 42.7 mg.g^{-1} for iron modified carbon from peanut hulls (PH- H_2O -Fe) and 133.1 and 816.7 mg.g^{-1} for GAC1 and GAC2 respectively (Table 4.8). These values calculated from the model are very similar to the obtained values from the experimentation and a sequence of efficiencies can be proposed: $\text{GAC2} > \text{BP-}\text{H}_2\text{O} > \text{GAC1} > \text{PH-}\text{H}_2\text{O-Fe} \approx \text{PH-}\text{H}_2\text{O-Fe}$. This efficiency order can be compared with the results obtained from the kinetic models on sorption initial rate.

In Table 4.9 the value of q_m means saturate sorption amount (mg.g^{-1}) and b is the Langmuir equilibrium coefficient (L.mg^{-1}). Langmuir model suggests that the uptake occurs on homogeneous surface by monolayer sorption without interaction between sorbed molecules. It assumes uniform energies of the sorption onto the surface and no transmigration of sorbate in the surface. These sorption capacities values are generally higher than other kinds of materials utilized in other researches for TC adsorption. For example some marine sediment (Xu and Li, 2010) exhibited a q_m value varied from 16.7 to 33.3 mg.g^{-1} and Chang *et al.* (2009a) presented a q_m value of 99 mg.g^{-1} for TC sorption on palygorskite. A clay mineral like rectorite presented a maximum q_m value of 140 mg.g^{-1} (Chang *et al.*, 2009b).

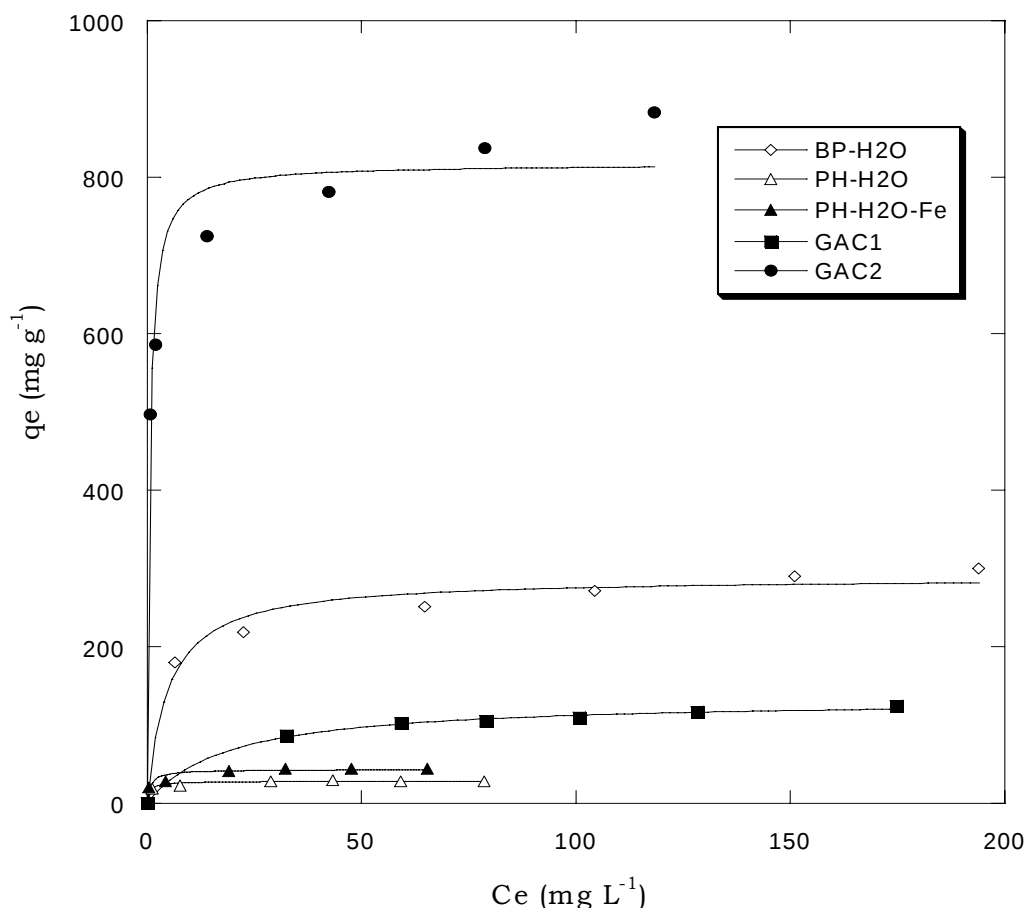


Figure 4.30 - Experimental adsorption isotherms of Tetracycline and modelled results using the Langmuir equation.

The other isotherm equation employed in this work was Freundlich that is a nonlinear sorption model (Figure 4.31), which suggests the existence of heterogeneity on the surface and the exponential distribution of sites and their energies. In Freundlich sorption model, K_F is the Freundlich affinity coefficient and it is found that all of the n values of the Freundlich model are less than 1 (Table 4.9), it is commonly admitted that if $n < 1$ the sorption is favorable, and could reflecting the situation in which at higher tetracycline concentrations, it becomes more and more difficult to adsorb additional molecules on adsorbent materials. This may occurs in cases where specific binding sites become saturated or remaining sites are less attractive to the sorbate molecules. In the case of the carbonaceous materials and activated carbons, the K_F value increases with the increase of mesoporous volume (Table 3.2 and Table 4.9).

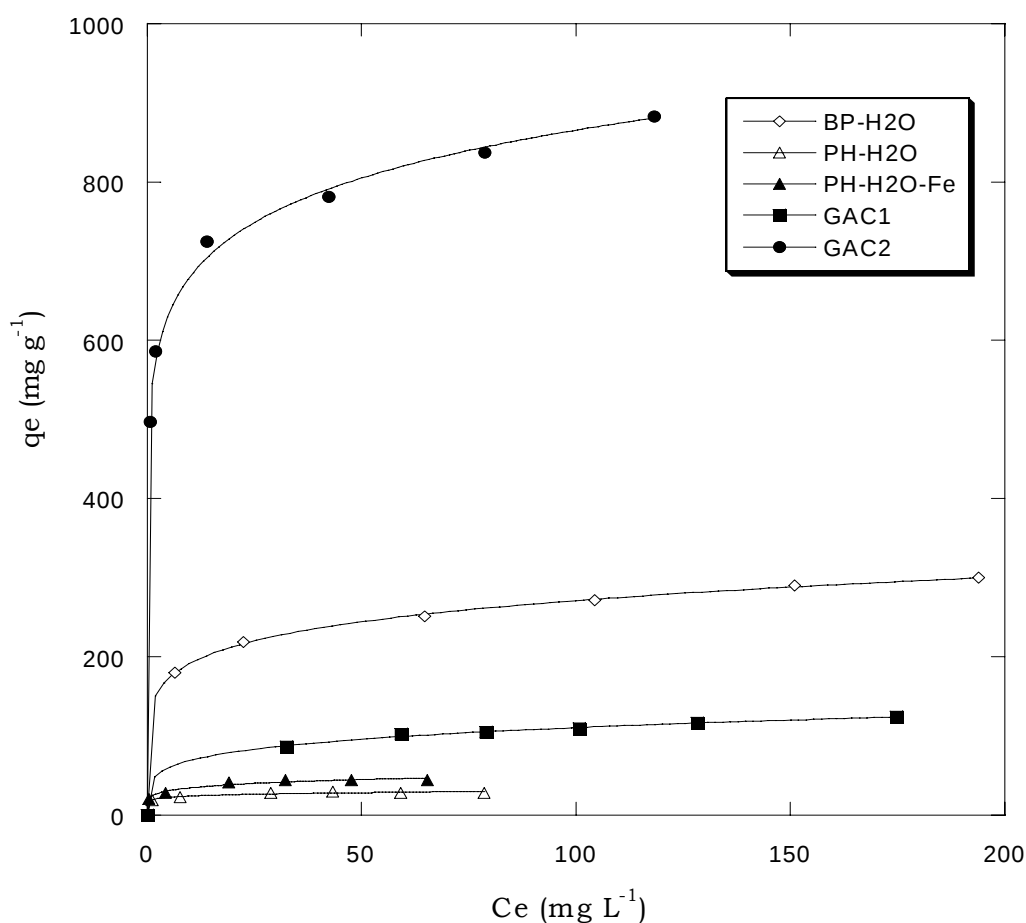


Figure 4.31 - Experimental adsorption isotherms of Tetracycline and modelled results using the Freundlich equation.

Among the two models applied, the Freundlich model presents the best fit of the experimental data and well describes the sorption isotherms of tetracycline on the adsorbent materials. In previous studies, the sorption of tetracycline on humic acids and peat (Sithole and Guy, 1987), soils (Sassman and Lee, 2005), oxytetracycline on clay (Kulshrestha *et al.*, 2004), soils (Rabolle and Spliid, 2000) and marine sediments (Xu and Li, 2010), carbon nanotubes and activated carbon (Ji *et al.*, 2009) were also found to be described as Freundlich type isotherms.

Table 4.9 - Adsorption constants for Langmuir and Freundlich models isotherms.

Material	Langmuir			Freundlich		
	q_m (mg.g ⁻¹)	b_L (L.mg ⁻¹)	R^2	K_F (mg ^{1-1/n} L ^{1/n} g ⁻¹)	n	R^2
BP-H ₂ O	288.3	0.2075	0.990	135.4	0.15	1.000
PH- H ₂ O	28.0	1.5393	0.972	18.6	0.10	0.985
PH-H ₂ O-Fe	42.7	1.2466	0.939	23.1	0.17	0.985
GAC1	133.1	0.0533	0.998	42.7	0.21	0.999
GAC2	816.7	1.7809	0.987	534.8	0.10	0.999
BP-H ₂ O (HMC)	308.8	0.0621	0.929	68.7	0.29	0.969
GAC2 (HMC)	549.5	1.0944	0.990	423.8	0.06	0.995

HMC=Values obtained from sorption isotherm realized in natural water (high mineral content) (see next section)

4.2.2.2 Adsorption in natural water spiked with tetracycline

The ions content may affect the sorption behavior of organic contaminants in water-adsorbent materials systems. Effect of ions content on tetracycline sorption capacity of the activated carbonaceous material obtained from beet pulp (BP-H₂O) and a commercial activated carbon (GAC2) are shown in Figure 4.32. For the case of the BP-H₂O, the results of this study reveals that tetracycline sorption is not significantly affected when the sorption process is realized in the presence of ions in the solution (spring water with high mineral content (HMC) detailed in Table 4.6). In this case the initial pH was between 6.7 and 7.1 and the final pH value was between 7.0 and 7.5 indicating that the main species is TCH₂[±], followed by TCH⁻.

In the case of GAC2, when ions were added to the system, the tetracycline sorption level was highly diminished in the range of 30 to 40%. The pH variation was from 6.9-7.2 at the beginning to 7.4-8.4 at the final of the contact time (5 days).

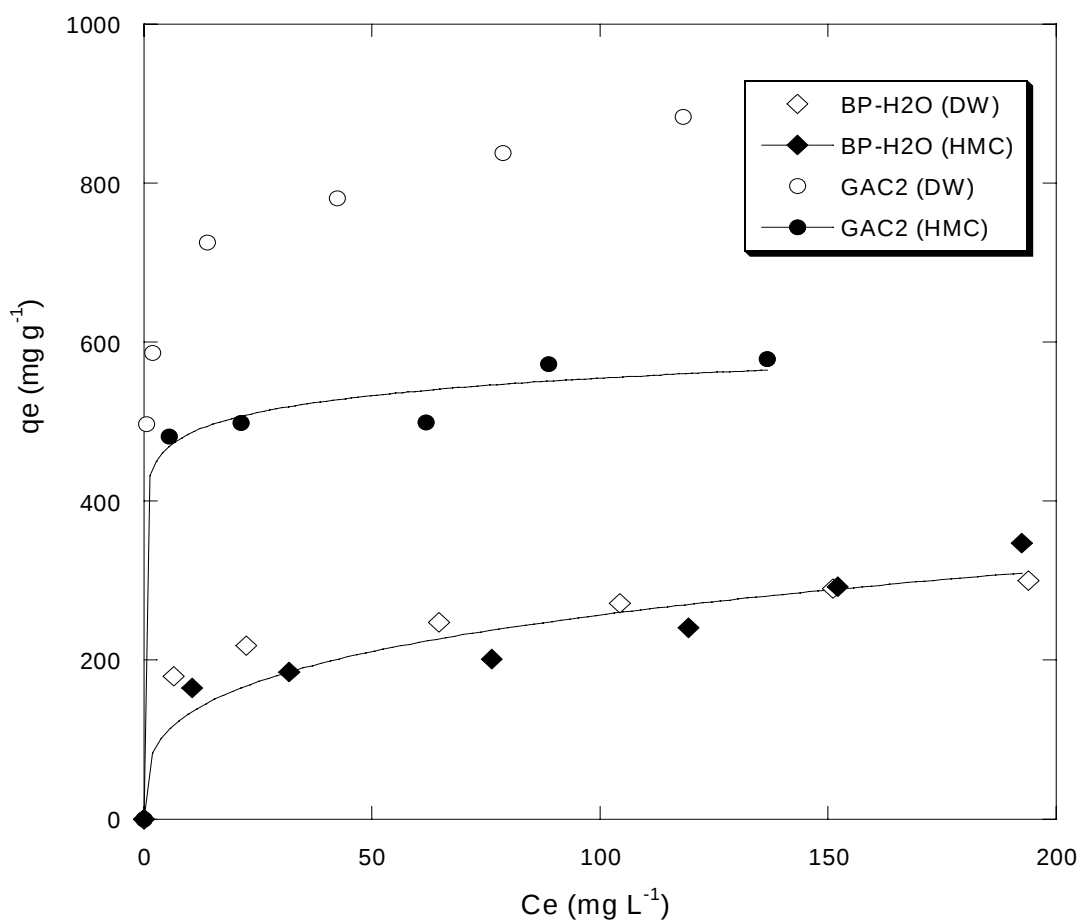


Figure 4.32 –Sorption isotherm of Tetracycline onto BP-H₂O and GAC2 in deionized water (DW) (light symbols) and natural water (HMC) (plain symbols and fitted to Freundlich model).

It is clear from Figure 4.32 that the presence of ions in solution leads to a lower tetracycline sorption capacity principally for the GAC2 and the cation exchange may be used to explain the phenomenon. The change on ions content in the water could affect the tetracycline sorption by changing the interfacial potential and by competing for ion exchangeable sites (Ter Laak *et al.*, 2005). Most adsorbent materials surfaces carry a net negative charge. When the ion content increases, the cations such as Na⁺, Mg²⁺ or Ca²⁺ will be electrostatically attracted by negative material surfaces.

At the final pH of isotherm for the GAC2 ($\text{pH} \approx 7$), the groups of the tetracycline molecule (e.g., amine group) could be slightly positive. Thus, the cations in solution may compete with tetracycline in the sorption process. The result in this case is in agreement with previous studies, it was reported that the increase of ion strength in solution resulted in the decreases of tetracycline sorption in clays (Sithole and Guy, 1987), soils (Sassman and Lee, 2005) and marine sediments (Xu and Li, 2010).

For the experimental points obtained from the isotherm test with natural water with high mineral content (HMC) and the adsorbent materials, the Langmuir and Freundlich models were applied and the tetracycline sorption shown a better fit to Freundlich model (0.969-0.995) (Figure 4.32), the Freundlich parameter (K_F) value for BP-H₂O and GAC2 were lower than those obtained for the sorption in deionized water (DW) (68.7 and 423.8 $\text{mg}^{1-1/n} \cdot \text{L}^{1/n} \cdot \text{g}^{-1}$ respectively) and the n constant value was slightly higher for BP-H₂O (0.29) and for GAC2 remains similar (0.06) than the constant obtained from Freundlich model when tetracycline sorption was carried out in deionized water (Table 4.9).

For BP-H₂O, Figure 4.32 highlights that there is no effect of the ionic strength on tetracycline sorption capacities. At this stage no explanation can be formulated, but it's an advantage of activated carbon prepared from sugar beet pulp.

4.2.3 Sorption mechanism approach

Sorption of tetracycline is a complex process given that it can exist as cations, zwitterions, and anions at environmentally relevant pH values, and undergo epimerization. Although some processes can impact the sorption of tetracycline, batch sorption data in this study clearly demonstrated that tetracycline sorption is dependent on pH and in specific cases also the ions content. To approach the sorption mechanism some correlations need to find. By plotting the mesoporous volume (V_{meso}) of the adsorbent materials versus the Freundlich constant (K_F) and fitting the data to an exponential equation ($K_F = 14.6 \cdot e^{5.9 \cdot V_{\text{meso}}}$) (Figure 4.33), a high R^2 value is obtained (0.999). It can be established that the TC adsorption is strongly correlated to the mesoporous volume of the adsorbent materials and this latter represents a key factor in this adsorption process.

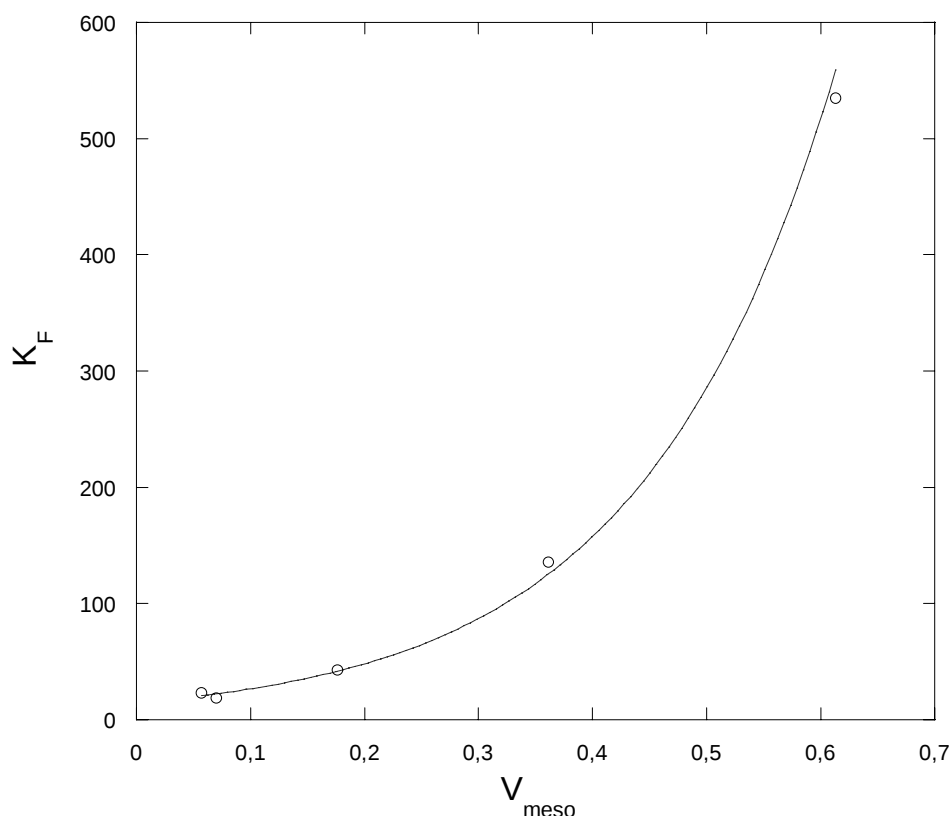


Figure 4.33 – V_{meso} vs Freundlich constant (K_F) fitted to an exponential equation.

Previous studies have involved mechanisms of cation/anion exchange, cation bridging, and/or surface complexation (e.g., H-bonding) to explain the relatively strong sorption of tetracycline by soils (Jones *et al.*, 2005; Sassman and Lee, 2005), iron aluminum hydroxides (Chen and Huang, 2010), clay minerals (Figueroa *et al.*, 2004), humic substances (Pils and Laird, 2007) and chitosan (Caroni *et al.*, 2009).

Within the pH range imposed by the adsorbent materials in this study (3.5-8.0), the zwitterion of tetracycline is predominated and cation exchange reaction, as well as surface complexation, is expected to occur between the zwitterionic tetracycline molecules and the respective ionic/polar sites on the adsorbents surface.

In terms of TC size, it is generally accepted that the conformations for TCs were the twisted one in neutral to acidic solutions, and the extended one in basic solutions. In the twisted conformation, the dimension of TC molecules was 1.29 nm long, 0.62 nm high and 0.75 nm thick (Chang *et al.* 2009c). With hydration shell, the molecular volume concerned is effectively related to mesopores.

The fact that the better adsorption occurs with the $\text{TCH}_2^\pm$ species leads to propose an adsorptive interaction with the graphene surface for the tetracycline uptake.

4.2.4 Conclusion

In this part of the work is investigated the capacity of carbonaceous materials obtained from agricultural by-products (beet pulp and peanut hulls) and two commercial activated carbons (coconut nuts and wood such as precursors) to adsorb tetracycline. After the sorption studies that were carried out in similar experimental conditions, the performance of the different adsorbent materials is compared between them.

By the results obtained from the batch experiments, the sorption behavior of tetracycline on carbonaceous materials obtained from agricultural by-products is lower than the GAC2 but higher than GAC1 for the particular case of those obtained from beet pulp (BP-H₂O and BP-H₂O-Fe).

The sorption of tetracycline on the adsorbent materials follows a pseudo-second order kinetic model and the optimal contact time is fixed at 5 days. The sorption of TC onto the activated carbons follows Freundlich sorption isotherms. According to the data obtained from the Langmuir model, the adsorption capacities (q_m) for the materials reach to 288.3 and 28 mg.g⁻¹ for steam activated carbonaceous materials (BP-H₂O and PH-H₂O), 42.7 mg.g⁻¹ for iron modified carbon obtained from peanut hulls (PH-H₂O-Fe) and 133.1 and 816.7 mg.g⁻¹ for GAC1 and GAC2 respectively, and the next efficiency sequence to TC adsorption can be proposed:

$$\text{GAC2} > \text{BP-H}_2\text{O} > \text{GAC1} > \text{PH-H}_2\text{O-Fe} \approx \text{PH-H}_2\text{O-Fe}.$$

The sorption of tetracycline on a carbonaceous material (BP-H₂O) and a commercial activated carbon (GAC2) is found to decrease with an increase of pH. The effect of ionic strength is greater on GAC2 than BP-H₂O. A correlation is found between the Freundlich constant and the mesoporous volume.

While earlier studies have reported strong adsorption of tetracycline in different kind of existing and commercial adsorbent materials, this study has identified the capacity of

carbonaceous materials prepared from agricultural wastes to adsorb this organic pollutant (TC) from aqueous media with good performances and these results encourage justifying the use of these materials in adsorption processes of organic compounds.

Some perspectives of this work are to study the diffusion mechanisms, to design a continuous process similar to the Cristal process combining adsorption in a batch reactor and a separation step (Memento Technique de l'Eau, 2005).



GENERAL CONCLUSION AND PERSPECTIVES

This work was realized with the aim of utilize activated carbons prepared from agricultural wastes, namely sugar beet pulp and peanut hulls, for arsenic(V) and tetracycline removal from water. They are cheap and available materials with high carbon content that makes them ideal candidates as activated carbons raw precursors. Both carbonization and steam activation have been carried out simultaneously leading to mass yields close to 16 % for BP-H₂O and 24 % for PH-H₂O. In order to enhance the sorption properties for the case of arsenic removal, a chemical modification by iron impregnation has led to materials called BP-H₂O-Fe and PH-H₂O-Fe with respective yields of 74 % and 78 % and iron content of 4.8 and 0.5 %.

An investigation of the porous structure of these materials including nitrogen adsorption measurements for the determination of BET surface area, porous volumes and median diameters has been conducted. SEM pictures are also presented to complete this part devoted to the material porosity. Chemical characterization based on simple determination like ash content and elemental analysis and then followed by zeta potential measurements and pH_{PZC} determinations completes their overall knowledge. Obtained values allow to called them activated carbons: BET surface area are close to 800 m².g⁻¹, total porous volumes are rather high and PH-H₂O is more microporous than BP-H₂O and this balance is not affected by the iron impregnation. Carbon contents are up to 70 % and ash contents depend greatly of the precursor. Zeta potentials determination has shown global negative surface charges for each sample and pH_{PZC} measurements revealed a clear basic behavior except for PH-H₂O-Fe. Based on these results, it is then demonstrated that the production of activated carbons from agricultural residues is successful at lab-scale.

In terms of arsenic removal, it has been shown that the carbonaceous sorbents need firstly to be steam activated and then iron impregnated to increase adsorption capacities. From kinetic study, the equilibrium time was found at 120 h and the rate controlling steps are probably related to the intraparticle diffusion and the chemisorptions reaction. Regarding equilibrium data, experimental isotherms have been correctly described with Langmuir and

Freundlich models. The best fit is obtained with Freundlich equation while the best q_m values provided by Langmuir are $3280 \mu\text{g.g}^{-1}$ for PH-H₂O-Fe, $2930 \mu\text{g.g}^{-1}$ for BP-H₂O-Fe and $2820 \mu\text{g.g}^{-1}$ for PH-H₂O. In natural waters, results also confirmed the good performances of iron rich materials. To conclude, we can say that iron impregnation creates special affinity between arsenic species and the activated carbon surface and this has a direct effect on arsenic sorption capacities. Another conclusion needing to be confirmed is the positive influence of the microporous volumes developed by the adsorbents. In all cases, they can be used in batch reactor for the treatment of solutions contaminated with arsenic(V).

The sorption studies of tetracycline by the new prepared carbonaceous materials and commercial one show that the sorption capacities of BP-H₂O and BP-H₂O-Fe are lower than the GAC2 but higher than GAC1. In all cases the sorption of tetracycline on the materials follows a pseudo-second order kinetic and the optimal contact time is fixed at 5 days. The Freundlich model gives the better fit of the sorption data of tetracycline. According to the data obtained from the Langmuir model, the adsorption capacities (q_m) for the materials reach to 288.3 and 28 mg.g^{-1} for BP-H₂O and PH-H₂O, 42.7 mg.g^{-1} PH-H₂O-Fe and 133.1 and 816.7 mg.g^{-1} for GAC1 and GAC2 respectively. The efficiency order proposed for tetracycline adsorption is:

$$\text{GAC2} > \text{BP-H}_2\text{O} > \text{GAC1} > \text{PH-H}_2\text{O-Fe} \approx \text{PH-H}_2\text{O-Fe}.$$

The sorption of tetracycline on BP-H₂O and GAC2 is found to decrease with an increase of pH. TC uptake by BP-H₂O is less affected by an ionic strength increase than GAC2. An exponential correlation between the mesopore volume values and the Freundlich constant is established. This points out that surface complexation mechanism is predominant in tetracycline uptake by AC.

This work proves that the conversion of some agricultural wastes or by-products such as sugar beet pulp and peanut hulls into activated carbons is efficient. There are also important advantages in the utilization of these sorbents, like their low costs and their availabilities on the local market.

PERSPECTIVES

From these preliminary results, one of the most important points to elucidate is to better understand the sorption mechanism of these micropollutants onto activated carbons. To reach this purpose, two routes could be followed. Firstly, additional experiments are needed related to surface characterisation and sorption experiments. Regarding the characterization, other methods such as the Boehm titration (Boehm, 1994), FT-IR and XPS analysis could be completed the present panel of data. Different iron impregnation leading to different iron content would also confirm this important parameter in the case of arsenic removal. As far as sorption experiments are concerned, other kinetic models could be tested for the tetracycline study and especially the diffusion ones. Secondly and based on the extended characterization results, the use of statistical models as predictive tools would help to find correlations between the kinetic parameters or the equilibrium data and the properties of the activated carbons. The ultimate goal would be to produce these carbons directly with the adequate properties to a given application.

In order to broaden the data about these micropollutants, it would be interesting to work with arsenic (III) since this form is also present in natural contaminations as well as mixtures of arsenic (V) and (III). The possibility to test real contaminated effluents would also lead to progress on the applicability of these kinds of sorbents. Regarding the tetracycline sorption, concentrations more adapted to those found in natural environment should be used. This means that new analytical methods have to be developed to decrease the quantification limits. Speciation and competing effects with natural organic matter would complete favourably the sorption study in batch reactor.

Another important point is to perform a continuous process. As the activated carbons particle produced at lab scale have not a great mechanical strength, they are sensible to attrition phenomena. As a consequence, a process based on the use of powder activated carbons such as the Cristal process developed by Degrémont (Memento Technique de l'Eau, 2005) can be suitable: it includes a continuous stirred tank reactor followed by a separation step by membrane filtration. Otherwise they could be pelletized with a binder in order to design fixed bed columns, but this kind of material have not been tested yet.

Finally this work would not be completed without other analysis taking into account economical and environmental aspects of the activated carbon production. The local source of available wastes or residues, competitiveness of energetic costs and the environmental impacts have to be considered in a global approach of sustainable development.

RESUME EN FRANCAIS

En traitement de l'eau, les charbons actifs sont parmi les adsorbants les plus utilisés du fait de leurs excellentes performances vis-à-vis des polluants organiques. Leurs capacités d'adsorption élevées sont en général reliées à leurs surfaces spécifiques, à leurs volumes poreux et dans certains cas, à leur chimie de surface. A l'échelle industrielle, ils sont élaborés à partir de différents précurseurs (noix de coco, tourbe, bois...) et leurs propriétés dépendent à la fois de la nature du précurseur, mais également de leurs conditions de carbonisation et d'activation. Les déchets et sous-produits de l'agriculture peuvent être des précurseurs potentiels pour la fabrication de ces matériaux carbonés poreux. Dans la littérature scientifique, ces résidus ont été largement utilisés comme adsorbent ou biosorbant pour éliminer de nombreux polluants organiques ou inorganiques présents en solution aqueuse.

D'autre part, la contamination des milieux aquatiques par la présence de micropolluants, ainsi dénommés en raison de leurs faibles concentrations dans le milieu naturel, apparaît aujourd'hui comme une problématique grandissante. Deux cas très différents peuvent être considérés. La pollution par l'arsenic, micropolluant principalement inorganique. Des millions de gens y sont aujourd'hui exposés par une contamination de grande ampleur touchant en particulier l'approvisionnement en eau potable. Le second cas concerne la persistance de molécules et résidus médicamenteux dans les eaux naturelles. Dans cette classe, on retrouve notamment des antibiotiques comme la tétracycline. Etant donné l'avancement des connaissances, peu de technologies de traitement autres que les procédés d'oxydation avancée, sont à ce jour disponibles.

L'objectif de ce travail est donc double : d'une part la valorisation de déchets ou résidus agricoles pour la production de charbons actifs spécifiques avec des propriétés d'usage bien établies, et d'autre part, la faisabilité de les utiliser pour le traitement de solutions synthétiques contaminées par de l'arsenic V ou de la tétracycline. Dans la littérature scientifique, quelques études se sont focalisées sur ce type d'approche pour l'élimination de l'arsenic par exemple, et aucune à notre connaissance pour celle de la tétracycline. Compte tenu de la dimension internationale de cette thèse, il a été choisi de sélectionner un déchet rencontré au Mexique comme les coques de cacahuètes, et un autre se retrouvant à l'échelle française comme la pulpe de betterave à sucre. Cette étude est divisée en quatre parties

incluant une étude bibliographie, puis un chapitre consacré aux matériels et aux méthodes développées pour l'obtention de données expérimentales. La troisième partie décrit les charbons actifs obtenus ainsi que leurs propriétés et enfin, le dernier chapitre est dévolu à l'étude de l'adsorption de l'arsenic V et de la tétracycline en réacteurs fermés parfaitement agités.

Chapitre 1. Etat de l'art

Une étude bibliographique consistante d'environ 40 pages est proposée. Elle débute par une présentation générale sur les charbons actifs, puis ceux élaborés à l'échelle du laboratoire à partir de précurseurs non industriels. Le tableau 1.1 présente une sélection assez récente de 22 publications relatives aux conditions d'activations de certains résidus de l'agriculture pour l'obtention de charbons actifs de faibles coûts.

Cette synthèse est complétée par quelques résultats concernant l'adsorption de métaux lourds et de polluants organiques sur ce type de charbons actifs. Un éclairage particulier est ensuite apporté sur les deux déchets concernés dans ce travail, la pulpe de betterave et les coques de cacahuètes. Cette première partie se termine par une présentation de l'adsorption incluant une description des différents modèles utilisables (modèles cinétiques, modèles de diffusion et modèles de sorption).

Tableau 1.1 – Conditions d’activations de certains résidus de l’agriculture pour l’obtention de charbons actifs de faibles coûts décrites dans la littérature.

Précurseur	Conditions de production	Agent activant	Référence
Coques de noix de pécan	450°C/1h(Carbonisation) 800°C/6h(Activation)	CO ₂	Ahmedna <i>et al.</i> , 2000.
Peau de patate douce	750°C(Carbonisation)	KOH	Sudaryanto <i>et al.</i> , 2006.
Graines d’arbre (<i>Moringa Oleifera</i>)	750°C/2h(Carbonisation) 800°C/1h minutes	H ₂ O	Warhurst <i>et al.</i> , 1997.
Coques des graines d’arbre (<i>Ceiba pentandra</i>)	750°C/2h(Carbonisation) 800°C/1h minutes	H ₂ O	Madhava Rao <i>et al.</i> , 2008.
Noyaux d’olive	--	KOH	Martínez <i>et al.</i> , 2006.
Noyaux d’olive	900°C/12h 850°C/	CO ₂ CaCl ₂	Juárez-Galán <i>et al.</i> , 2009.
Blé	127-375 °C	--	Lanzetta and Di Blasi, 1998.
Paille de maïs	127-375 °C	--	Lanzetta and Di Blasi, 1998.
Olive	750 °C/2h	H ₂ O /CO ₂	Minkova <i>et al.</i> , 2001.
Pin (<i>Radiata</i>)	950 °C	--	Cetin <i>et al.</i> , 2004.
Bagasse de canne à sucre	950 °C	--	Cetin <i>et al.</i> , 2004.
Coques d’amande	800 °C/1h	H ₂ O	Ahmedna <i>et al.</i> , 2004.
Noyaux d’abricot	800°C	ZnCl ₂	Aygun <i>et al.</i> , 2003.

Coques d'amande	400°C(Carbonization) 800°C(Activation)	Physique	Marcilla <i>et al.</i> , 2000.
Paille/Char	550°C(Fluidized bed)	--	Jensen <i>et al.</i> , 2001.
Chêne	700 °C	--	Zhang <i>et al.</i> , 2004.
Ecorces de cacahuètes	500°C(Carbonization) 700-900°C(Activation)	Physique	Girgis <i>et al.</i> , 2002.
Coques de pistaches	500°C(Carbonization) 900 °C/0.5h (Activation)	Physique/CO ₂	Lua <i>et al.</i> , 2004.
Coques de noix de macadamia	500°C	Chimique (ZnCl ₂)	Ahmadroup and Do, 1997.
Épi de maïs	500°C/0.5h	Chimique (ZnCl ₂)	Tsai <i>et al.</i> , 1998.
Balle de riz	400°C/1h(Carbonisation) 600°C/1h(Activation)	H ₂ O	Malik <i>et al.</i> , 2003.
Balle de riz	600°C/3h	ZnCl ₂ /CO ₂	Yalcin and Sevinc, 2000.

La seconde partie est dédiée à la problématique de la contamination des eaux naturelles par l'arsenic à travers le monde. Des rappels de chimie permettant de comprendre les réactions de dissémination de cet élément dans l'environnement sont donnés ainsi les sources de pollutions. Un paragraphe est consacré à sa toxicité puis les législations relatives à la présence de l'arsenic dans les eaux potables sont décrites. Enfin, les principales méthodes d'éliminations sont rappelées et l'accent est mis sur les procédés mettant en l'œuvre les réactions d'adsorption. Des exemples sont donnés sur l'adsorption d'arsenic sur des biosorbants, des charbons actifs (commerciaux ou non) et d'autres adsorbants transformés chimiquement. Le tableau 1.2 présente une synthèse des articles scientifiques qui ont été publiés à ce jour sur l'adsorption d'arsenic sur des charbons actifs industriels ou non.

Tableau 1.2 – Adsorption de l'arsenic sur charbons actifs

Précurseur	Activation/ Modification	Capacité maximale de sorption (q_m)		Référence
		As (III)	As (V)	
Charbons actifs produits à partir de déchets de l'agriculture				
Déchets de haricots	Vapeur d'eau/1h	1,01 mg g ⁻¹	---	Budinova <i>et al.</i> , 2009.
Balle de riz	ZnCl ₂ /CO ₂	1,22 mg g ⁻¹	---	Kalderis <i>et al.</i> , 2008.
Jute	H ₃ PO ₄	---	0,075 mg g ⁻¹	Jahan, <i>et al.</i> 2008.
Balle de riz	CaCl ₂	18,2 µg g ⁻¹	---	Mondal, <i>et al.</i> 2007b.
Pulpe d'olive	Vapeur d'eau /2h K ₂ CO ₃	1,39 mg g ⁻¹ 0,86 mg g ⁻¹	---	Budinova <i>et al.</i> , 2006.
Noyaux d'olive	K ₂ CO ₃ Vapeur d'eau /HNO ₃	0,74 mg g ⁻¹ 0,21 mg g ⁻¹	---	Budinova <i>et al.</i> , 2006.
Ecorces d'avoine	Vapeur d'eau	---	3,1 mg g ⁻¹	Chuang <i>et al.</i> , 2005.
Coques de noix coco	H ₂ SO ₄ /Cu	158,7 mg g ⁻¹	---	Manju <i>et al.</i> , 1998.
Charbons actifs commerciaux modifiés avec du fer				
Charbon de lionite	Fe(III)	---	4,5 mg g ⁻¹	Reed <i>et al.</i> , 2000
Charbon actif	2.5% FeCl ₃	---	0.024 mg g ⁻¹	Mondal <i>et al.</i> , 2008.
Charbon actif	Fe(NO ₃) ₃ ·9 H ₂ O	---	51,3 mg g ⁻¹	Chen <i>et al.</i> , 2007.
Charbon commercial en	FeCl ₂ , 0,1M	---	6,57 mg g ⁻¹	Gu <i>et. al.</i> , 2005.
Charbon commercial	FeCl ₃ , 0,05M	---	0,028 mg g ⁻¹	Fierro <i>et. al.</i> , 2009.

Charbon commercial	FeCl ₃ , 0,05M + HCl	---	0,025- 0,03 mg g ⁻¹	Muñiz <i>et al.</i> , 2009.
Charbon commercial en	0,5-1 g/ml [Fe(NO ₃) ₃ ·9H ₂ O]	---	18-20 mg g ⁻¹	Jang <i>et al.</i> , 2008
Charbon d'houille	FeSO ₄ + NaBH ₄	18,2 mg g ⁻¹	12,0 mg g ⁻¹	Zhu <i>et al.</i> , 2009
Charbon actif Commercial	Phenol formaldehyde + FeO	---	85 % d'une soln. C ₀ =174 mg l ⁻¹	Zhuang <i>et al.</i> , 2008.
Charbon actif- support de silice	FeCl ₃ + Hypochlorite de sodium	5,96 mg g ⁻¹	5,15 mg g ⁻¹	Gu and Deng, 2007.
Charbon actif	FeO	---	0,99 mmol g ⁻¹	Zhang <i>et al.</i> , 2007.
Charbon actif	FeO	---	9,1 mg g ⁻¹	Vaughan <i>et al.</i> , 2007.

Pollution par la tétracycline et procédés de traitement.

La chlortétracycline et l'oxytétracycline ont été découvertes dans les années 1940. Ces molécules sont produites par *Streptomyces aureofaciens* et *S. rimosus*. La tétracycline a été isolée ultérieurement à partir de culture de *S. aureofaciens*, *S. rimosus*, et *S. viridofaciens* (Chopra and Roberts, 2001). Ces antibiotiques sont parmi les plus utilisés pour le contrôle des maladies infectieuses et dans l'alimentation animale (Sarmah et al., 2006 ; Kummerer, 2009). A titre d'exemple, les pays Européens ont utilisé pendant les années 90 jusqu'à 2 294 000 kg par an de tétracycline à des fins thérapeutiques dans les élevages (Chopra and Roberts, 2001). L'utilisation intensive des antibiotiques conduit à la dissémination de ces substances dans les sols et les eaux. Si les concentrations environnementales restent faibles et sont sans effet direct sur les écosystèmes, elles conduisent néanmoins au développement de résistances bactériennes aux antibiotiques ((Lindsey et al., 200 ; Kumar et al., 2005 ; Kim et al., 2007 ; Xu and Li, 2010).

Dans le tableau 1.3 sont regroupées les principales caractéristiques de la forme hydro-chlorure de la tétracycline. Cette dernière est nettement plus soluble que la tétracycline qui ne présente qu'une solubilité proche de $0,25 \text{ mg.mL}^{-1}$ à 25°C . Les solutions de tétracycline doivent être stockées à l'obscurité entre $+2$ et $+8^\circ\text{C}$, pas plus d'un mois du fait sa sensibilité à la lumière et au fait qu'elle s'hydrolyse en solution aqueuse.

Table 1.3: Quelques caractéristiques de l'hydro-chlorure de tétracycline (adapté de Gu and Karthikeyan, 2005)

Nombre CAS	64-75-5
Nombre EC	200-593-8
Formule empirique	$\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_8 \text{ HCl}$
Masse molaire	480,90
Solubilité H_2O	10 mg.mL^{-1}
$\log K_{ow}$ (en fonction du pH)	-1,97 to -0,47
Point de fusion	$220-223^\circ\text{C}$

Comme l'indique la figure 1.1, la tétracycline possède divers groupements fonctionnels acido-basiques présentant 3 pKa différents. Cette configuration confère à la molécule, la faculté de prendre des formes différentes en fonction du pH.

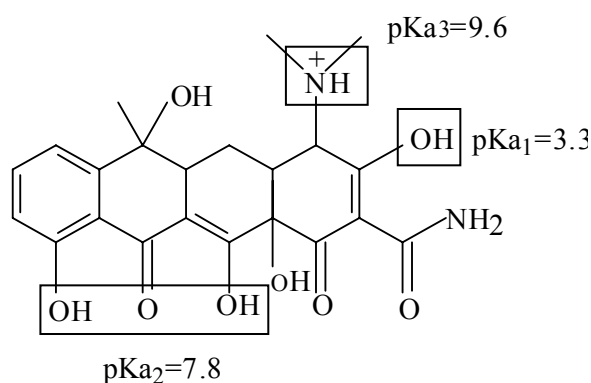


Figure 1.1 –Structure moléculaire plane de la tétracycline.

La figure 1.2 regroupe quant à elle, les formes ioniques possibles de la tétracycline (Kulshrestha et al., 2004).

Les antibiotiques de la famille des tétracyclines sont parmi les plus utilisés à travers le monde. Ils sont très peu absorbés par le tractus digestif et se retrouvent donc dans les excréments et les urines à plus de 90 % de la dose administrée (Sarmah et al., 2006). Ces molécules sont persistantes dans les sols et peuvent donc s'accumuler lors d'épandages répétés de fumier (Hamscher et al., 2002 ; Jacobsen et al., 2004). La présence de tétracycline a également été mesurée dans les eaux de surfaces et souterraines (Lindsey et al., 2001; Batt and Aga, 2005). Dans ce dernier cas, la voie de contamination passe par le rejet des eaux usées, après traitement dans les stations d'épuration. En effet, en plus d'une forte affinité pour les sols, ces substances sont peu biodégradables et de ce fait sont peu éliminées dans les systèmes d'épuration. A titre d'exemple, Miège et collaborateurs (2009) donnent des concentrations comprises entre $0,05 \mu\text{g L}^{-1}$ et $0,850 \mu\text{g L}^{-1}$ dans des effluents de stations d'épuration biologique de traitement des eaux résiduaires urbaines. Si ces traitements biologiques ont prouvé leur efficacité pour la diminution des charges organiques et de l'azote des eaux usées, différentes études sur le comportement des antibiotiques ont mis en évidence trois possibilités de réaction pour les antibiotiques : la biodégradation (cas le plus favorable), la biosorption qui conduit à la libération de molécules après la mort de la biomasse, et enfin l'hydrolyse (Xu et al., 2007, Kim et al., 2005). Malheureusement, de nombreux antibiotiques sont peu ou pas biodégradables, et ils seront présents dans l'eau traitée. Ainsi, d'autres procédés tels que l'adsorption doivent être proposés pour l'élimination de tétracycline dans des eaux polluées.

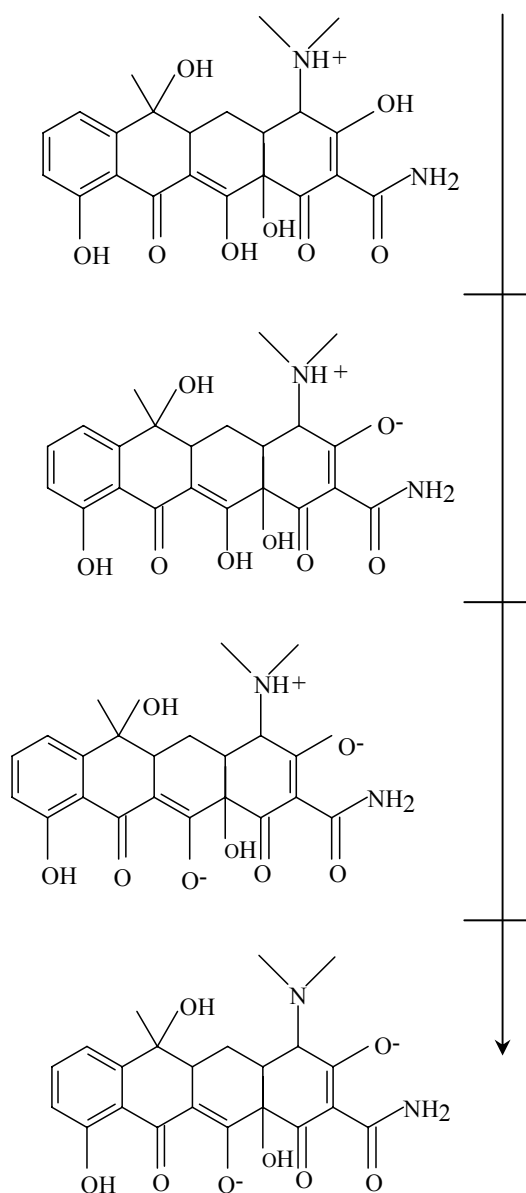


Figure 1.2 – Formes de la tétracycline en fonction du pH.

L'élimination des composés organiques hydrophobes de l'eau par adsorption peut être réalisée à l'aide d'un adsorbant contenant une forte teneur en carbone organique (Chang et al., 2009). Toutefois, pour les composés ionisables, leur affinité à la surface du solide est fortement affectée par le pH de la solution. Les études sur l'adsorption des tétracyclines sont limitées et ont porté principalement sur les matières humiques et minérales (Kulshrestha et al, 2004; Figueroa et al, 2004; Turku et al, 2007; Wang et al, 2008). Il apparaît dans ces études, que le mécanisme d'adsorption principal responsable de la fixation des tétracyclines en milieu acide, est l'échange de cations (Parolo et al., 2008). Par ailleurs, il est retrouvé dans la littérature très peu de résultats quant à l'utilisation de charbons actifs pour la sorption de la tétracycline (Choi et al., 2008 ; Ji, et al., 2009).

Pour toutes ces raisons, le comportement et le devenir des antibiotiques dans l'environnement présentent un intérêt grandissant. Il n'existe pas aujourd'hui de réglementation spécifique sur la concentration de ces substances dans l'environnement. Néanmoins, l'Union Européenne a établi une limite maximale résiduelle pour les substances vétérinaires dans le lait (Council Regulation 2377/90/EEC), qui pour la tétracycline, l'oxytétracycline et la chlortétracycline, est de $0,1 \text{ mg kg}^{-1}$ de lait frais.

Chapitre 2. Matériels et Méthodes

Ce second chapitre présente une description concernant la fabrication des matériaux carbonés poreux puis les méthodes expérimentales nécessaires à leurs caractérisations physiques et chimiques. Il s'agit notamment de l'adsorption d'azote pour la détermination de la surface BET et des propriétés poreuses en général, puis de l'analyse élémentaire, du taux de cendres et celui en fer de ces matériaux. Quelques rappels sur la théorie du potentiel zéta sont donnés ainsi que la description de la procédure expérimentale. Une autre méthode permettant de déterminer le pH_{PZC} est également proposée. La caractérisation se termine par de la microscopie électronique à balayage couplée à de la fluorescence X. La fin de chapitre concerne la description des méthodes analytiques utilisées pour le dosage de l'arsenic et de la tétracycline en solution, ainsi que les expériences réalisées pour l'étude de l'adsorption de ces deux polluants.

Chapitre 3. Caractérisation des matériaux carbonés poreux

Ce chapitre est consacré à la production de matériaux carbonés à partir de pulpe de betterave et de coques de cacahuètes, à leurs modifications chimiques ainsi qu'à leurs caractérisations physique et chimique. Cette approche est essentielle dans le but de corréler les propriétés des charbons à leurs performances en termes d'adsorption. Les propriétés de deux autres charbons actifs commerciaux (appelés GAC1 et GAC2) sont également étudiées. Leur utilisation est justifiée par une comparaison ultérieure des capacités de sorption entre un charbon élaboré à l'échelle du laboratoire et un autre à l'échelle industrielle.

Dans un premier temps, la fabrication de chars et de charbon actif est décrite. Une pyrolyse (ou carbonisation) conduite à 600 °C pendant 1 heure sous azote a été réalisée avec la pulpe de betterave. Le char est appelé BP-C. L'obtention des charbons actifs s'effectue ensuite par une activation dite *activation directe* qui enchaîne simultanément la carbonisation et l'activation proprement dite. Dans ce travail, seule la vapeur d'eau a été considérée comme agent activant : c'est donc une *activation physique*. Les conditions de fabrication sont les suivantes : montée en température jusqu'à 857 °C, puis 80 minutes sous vapeur d'eau (0,7 mL.min⁻¹), l'ensemble de ces opérations étant effectué sous azote. Les matériaux obtenus sont surnommés BP-H₂O pour la pulpe de betterave et PH-H₂O pour les coques de cacahuètes. Les rendements massiques calculés à partir des matériaux précurseurs sont de 28 % pour BP-C, 16 % pour BP-H₂O et 24 % pour PH-H₂O.

Ces nouveaux charbons actifs ont été ensuite tamisés en trois fractions : taille inférieure à 0,5 mm, entre 0,5 et 1 mm et taille supérieure à 1 mm. Les fractions (0,5-1 mm) sont lavées généreusement avec de l'eau désionisée pour supprimer tous les résidus lixiviables en solution. En fin de lavage, les pH sont de 10,1 pour BP-H₂O, 9,8 pour PH-H₂O et concernant les charbons commerciaux 7,6 pour GAC1 et 4,3 pour GAC2. Particulièrement destinés au traitement de solution contaminées par de l'arsenic, des modifications chimiques par imprégnation de fer ont été testées. Elles ont conduit à des teneurs en fer de l'ordre de 4,8 % dans BP-H₂O-Fe et 0,5 % dans PH-H₂O-Fe.

La seconde partie de ce chapitre est consacrée à la caractérisation physico-chimique de ces différents matériaux. La structure poreuse est décrite par l'analyse d'adsorption d'azote permettant la détermination de la surface BET, des volumes poreux et des diamètres de pores. Des images prises au microscope électronique à balayage ainsi que des spectres réalisés par

fluorescence X viennent compléter cette description. D'autre part, l'analyse élémentaire (C, H, O, N), la teneur en cendres, la mesure du potentiel zéta et le pH de point de charge nulle ont permis une bonne caractérisation chimique. Les principaux paramètres de cette caractérisation ont été rassemblés dans le Tableau 3.1.

Les principales conclusions de ce tableau sont les suivantes : les matériaux carbonés poreux synthétisés au laboratoire (BP-H₂O et PH-H₂O) sont réellement assimilables à des charbons actifs (GAC1 et GAC2) en témoignent les valeurs élevées de surface BET (821 et 829 m².g⁻¹), les volumes poreux totaux (0,64 et 0,40 cm³.g⁻¹) et les teneurs en carbone (78 et 91 %). Leur microporosité est également du même ordre de grandeur que celle rencontrée dans les matériaux commerciaux. Les taux de cendres dépendent grandement du type de précurseur sélectionné. Tous ces adsorbants présentent des propriétés basiques (pH_{PZC}) exceptés pour PH-H₂O-Fe et GAC2. Pour ce dernier, l'activation a été réalisée par voie chimique avec de l'acide phosphorique ce qui a dû entraîner la création de fonctions oxydées acides à la surface du charbon. Pour PH-H₂O-Fe, il n'a pas été possible de formuler une explication convaincante. Une autre caractéristique commune à tous est la valeur globalement négative du potentiel zéta et cela, quel que soit le pH de la solution. Il est enfin important de noter que la modification chimique par imprégnation de fer n'affecte pas conséquemment la structure poreuse de ces charbons, la teneur en carbone ainsi que le taux de cendres. Elle a par contre induit une augmentation de la teneur en oxygène.

Tableau 3.1 Principaux paramètres de caractérisation des différents charbons actifs.

	BP- H ₂ O	BP- H ₂ O-Fe	PH- H ₂ O	PH- H ₂ O-Fe	GAC1	GAC2
S_{BET} (m².g⁻¹)	821	762	829	718	1138	1515
Microporosité	49	50	84	84	73	51
Volume microporeux (cm³)	0,3478	0,3227	0,3551	0,3084	0,4852	0,6407
d₅₀	5,4	4,5	3,8	3,6	4,3	5,9
Volume poreux total (cm³ g⁻¹)	0,6430	0,5778	0,4028	0,3446	0,6230	1,2291
C (%)	77,9	67,8	91,2	83,9	90,1	64,8
O (%)	7,0	16,0	6,0	14,0	9,0	19,5
Fe (%)	0,1	4,8	ns	0,5	nd	0,03
Cendres (%)	13,6	13,9	1,3	1,5	0,4	1,1
pH_{PZC}	9,8	9,0	9,8	6,0	8,0	3,5
Potential ζ	-21 to	-25 to	-37 to	-43 to	-24 to	nd

ns : valeur non significative, nd : valeur non déterminée

Chapitre 4. Applications à l'étude de l'adsorption de l'arsenic V et de la tétracycline

Le dernier chapitre de cette thèse présente les résultats obtenus lors de l'étude d'adsorption réalisée avec les deux micropolluants sélectionnés : l'arsenic (V) et la tétracycline. Dans les deux cas, il s'agit d'expériences menées en réacteurs discontinus, avec des solutions synthétiques d'As(V) et de tétracycline. Les performances d'adsorption

déterminées avec les charbons élaborés à l'échelle du laboratoire sont toujours comparées à celles développées par les matériaux commerciaux.

La méthodologie suivie débute par une étude cinétique, permettant l'obtention des temps de contacts régissant l'équilibre dans le cas de l'arsenic et des temps de contact optimaux et communs à tous les matériaux pour la sorption de la tétracycline. Puis, à partir de ces courbes cinétiques, des modèles de diffusion et/ou de chimisorption sont proposés afin de déterminer des constantes de vitesses et d'évaluer les étapes potentiellement limitantes dans la réaction d'adsorption. L'effet du pH sur la cinétique globale de sorption est également pris en compte et il est complété par la spéciation des polluants en solution. Dans un deuxième temps, les résultats expérimentaux obtenus à partir des isothermes de sorption sont présentés. Deux modèles d'adsorption, Langmuir et Freundlich, sont ensuite testés et comparés et les performances en eaux réelles sont enfin évaluées en utilisant des eaux naturelles dopées en arsenic ou en tétracycline.

4.1 Etude la sorption de l'arsenic V

4.1.1 Etude cinétique de l'adsorption de l'arsenic V

La première partie de cette étude s'est attachée à démontrer que les matériaux carbonés poreux devaient être préalablement activés avant tout essai de sorption. En effet, aucune fixation n'est observée sur la figure 4.1, relative à la pulpe de betterave brute et carbonisée alors qu'elle est effective sur les figures 4.2 (pulpe de betterave) et 4.3 (coques de cacahuète) et cela pour des concentrations initiales en arsenic comprises entre 500 et 1000 $\mu\text{g.L}^{-1}$. Comme pour la pulpe de betterave, il est nécessaire que le charbon à base de coques de cacahuète soit activé pour obtenir des performances de sorption. La figure 4.4 est donnée à titre de comparaison puisqu'elle concerne le charbon commercial. A partir de ces courbes, il est possible de déduire un temps d'équilibre de 120 h (5 jours) et commun à tous les matériaux. En termes de pH d'équilibre, les valeurs rapportées pour les expériences menées à 1000 $\mu\text{g.L}^{-1}$ sont respectivement : 8,9 et 9,1 pour BP-H₂O et BP-H₂O-Fe, 7,1 et 5,6 pour PH-H₂O et PH-H₂O-Fe et enfin 6,9 pour GAC1.

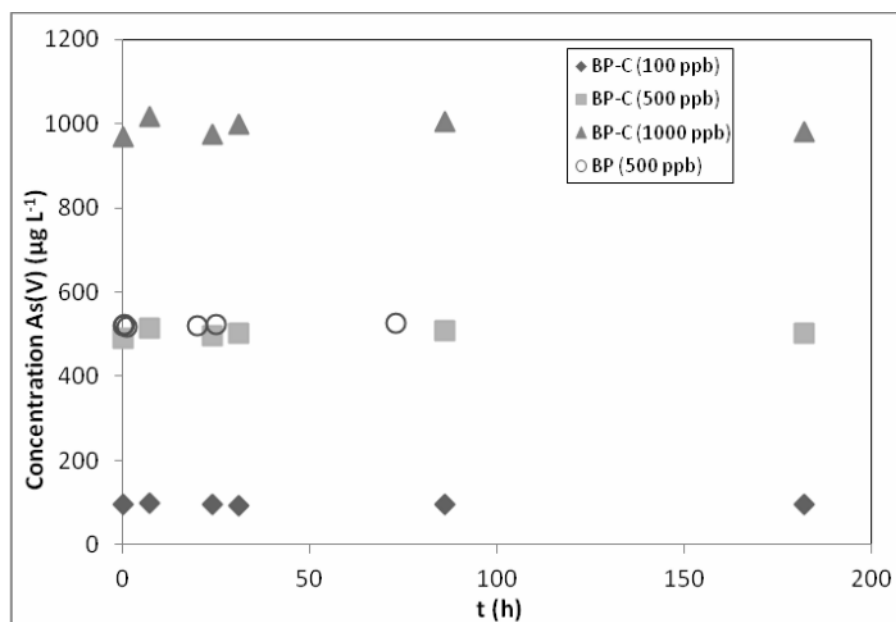


Figure 4.1 Cinétiques d'adsorption d'As (V) sur BP-C et BP

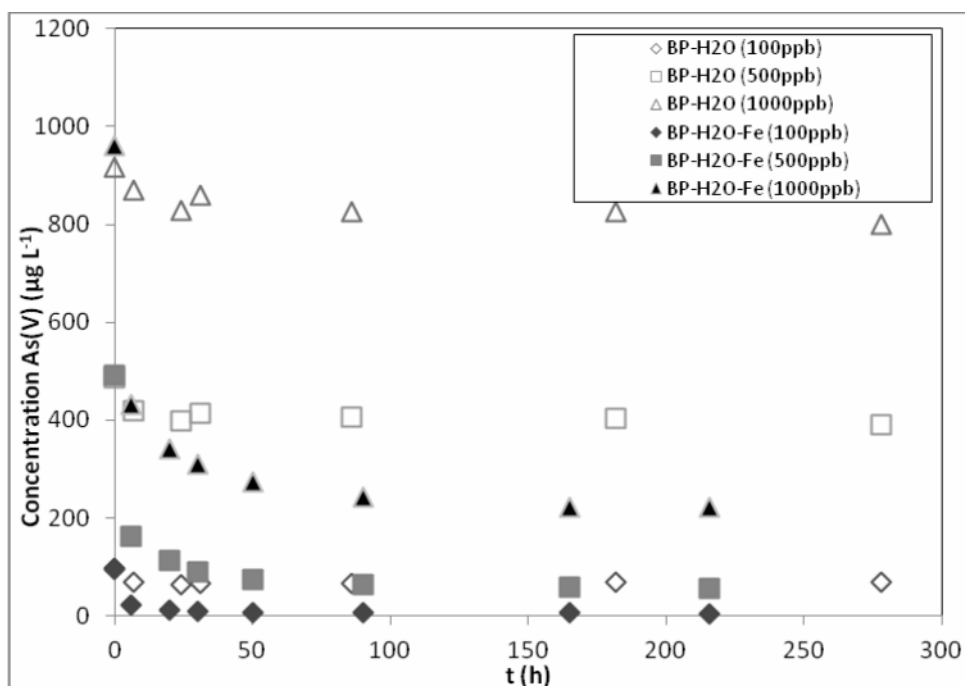


Figure 4.2 Cinétiques d'adsorption d'As (V) sur BP-H₂O et BP-H₂O-Fe

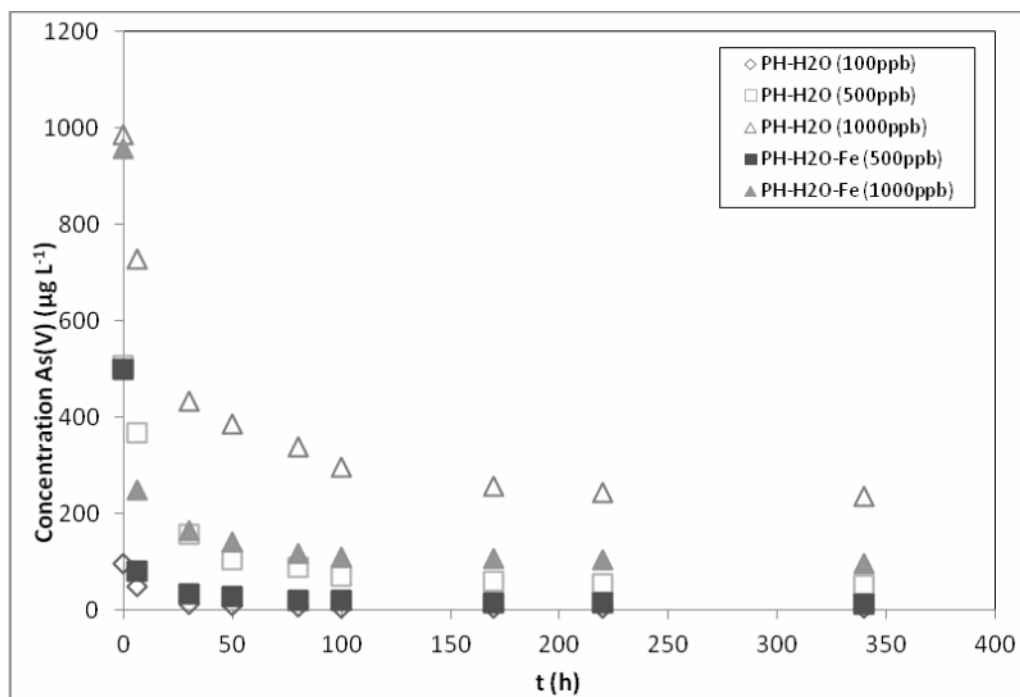


Figure 4.3 Cinétiques d'adsorption d'As (V) sur PH-H₂O et PH-H₂O-Fe

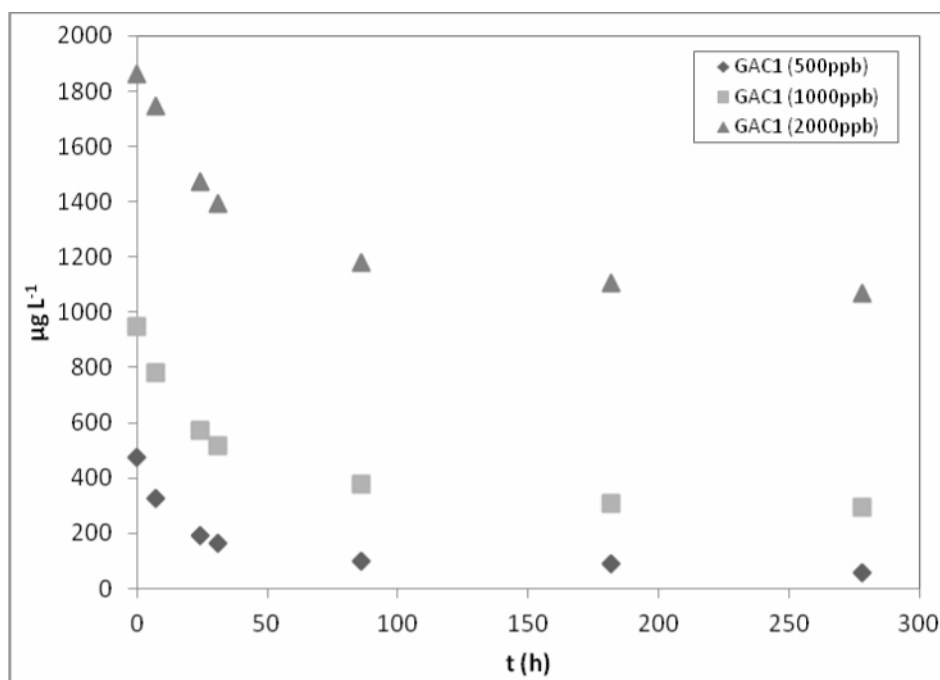


Figure 4.4 Cinétiques d'adsorption d'As (V) sur GAC1

Elles sont assez cohérentes avec les valeurs des pH_{PZC} obtenues au chapitre 3 et elles confirment le caractère basique des charbons, excepté pour PH-H₂O-Fe. Dans tous les cas, les espèces adsorbées sont soit majoritairement $HAsO_4^{2-}$ pour les valeurs les plus basiques, soit un mélange de $H_2AsO_4^- / HAsO_4^{2-}$ pour les valeurs proches de la neutralité. Les figures 4.5 et 4.6 permettent une comparaison plus fine entre les charbons BP-H₂O, BP-H₂O-Fe, PH-H₂O, PH-H₂O-Fe et le charbon commercial. Le comportement de PH-H₂O est très similaire à celui du GAC1 en termes de vitesse d'élimination comme en termes de capacité d'adsorption. Quant aux performances relatives aux charbons imprégnés de fer, il est évident que les capacités de sorption sont accrues et que les vitesses semblent accélérées.

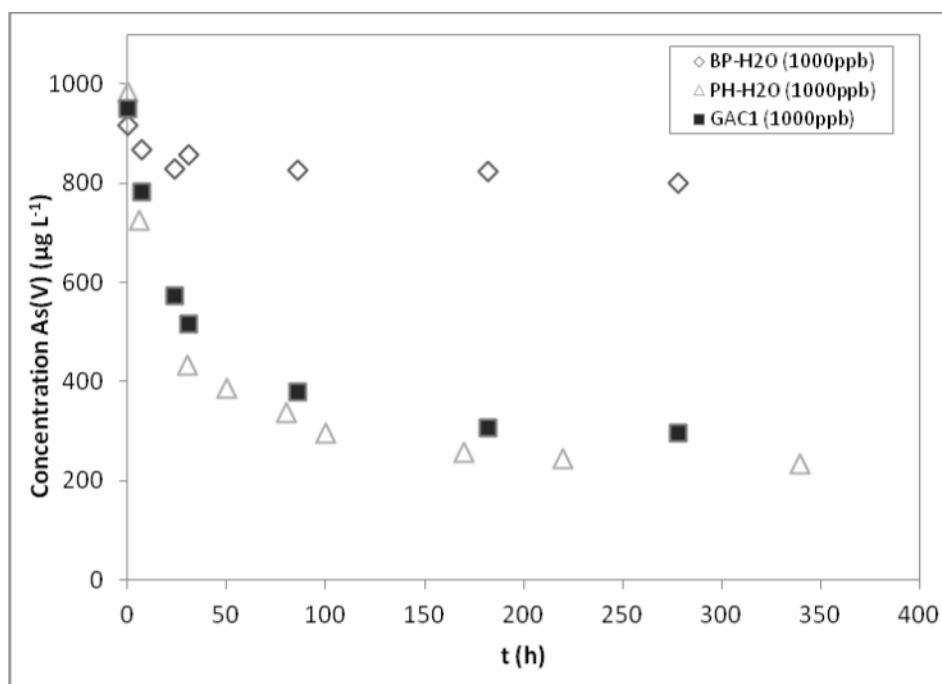


Figure 4.5 Cinétiques d'élimination d'As (V) sur BP-H₂O, PH-H₂O et GAC1 pour une concentration initiale de 1000 µg.L⁻¹.

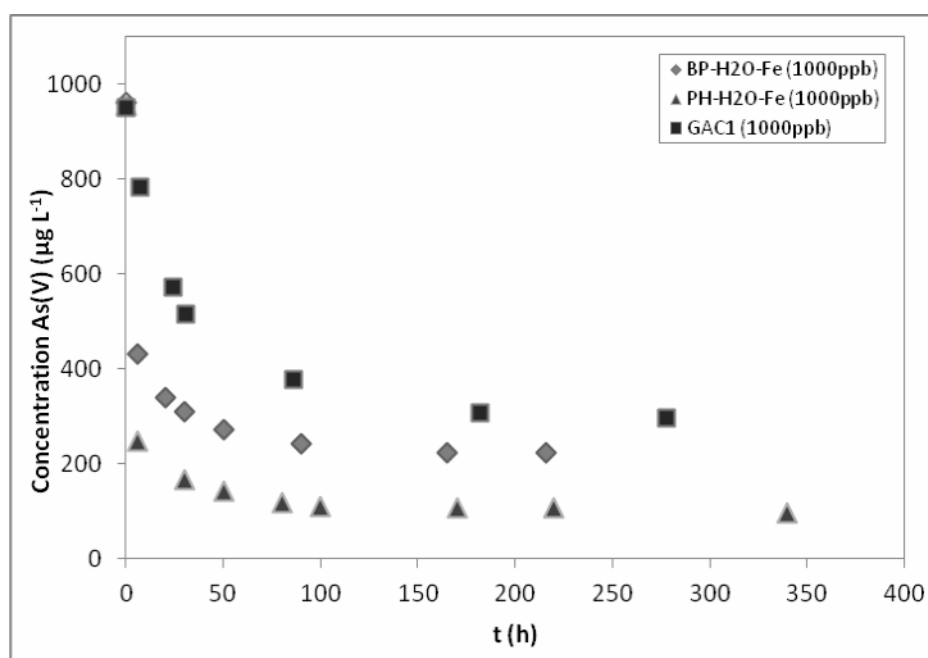


Figure 4.6 Cinétiques d'élimination d'As (V) sur BP-H₂O-Fe, PH-H₂O-Fe et GAC1 pour une concentration initiale de 1000 µg.L⁻¹.

Les deux modèles qui ont permis la meilleure description des données expérimentales sont le modèle de diffusion intraparticulaire et le modèle de pseudo-second ordre. Le premier permet de déterminer une constante de vitesse de diffusion à l'intérieur des particules poreuses en traçant les droites q_t en fonction de $t^{0.5}$ pour les premiers termes de la cinétique. La figure 4.7 représente les tracés de ce modèle et le tableau 4.1 en extrait la constante de vitesse recherchée. La description des données expérimentales est satisfaisante comme en témoignent les valeurs du coefficient de régression (tableau 4.1) et cela traduit que la diffusion intraparticulaire peut être considérée comme l'une des étapes limitantes lors de la réaction d'adsorption. Il est à noter que l'ajout de fer dans les charbons augmente d'un facteur 2 à 3 la constante de vitesse de diffusion intraparticulaire.

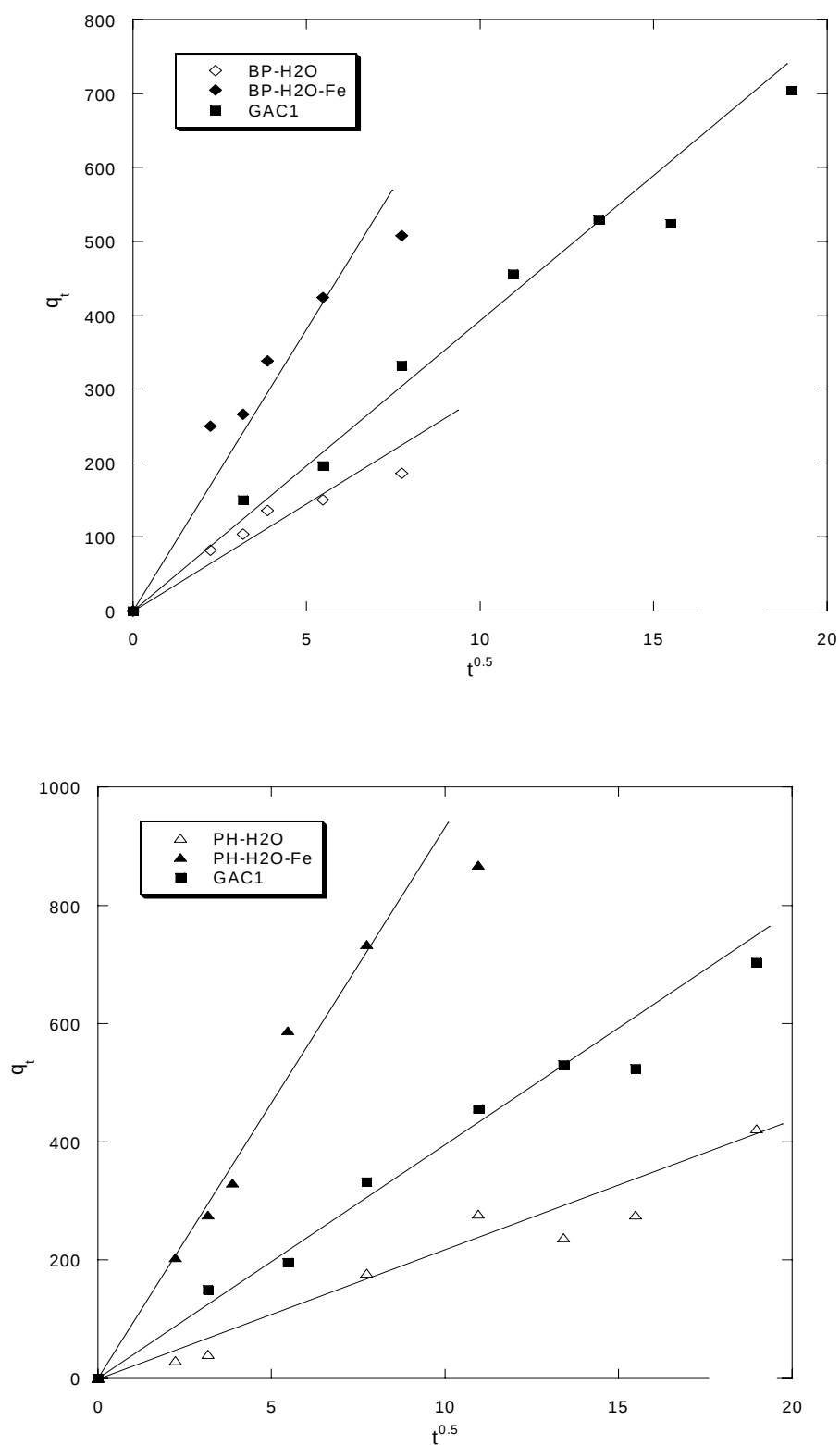


Figure 4.7 Tracés du modèle cinétique de diffusion intraparticulaire ((A) BP-H₂O, BP-H₂O-Fe et GAC1 et (B) PH-H₂O, PH-H₂O-Fe et GAC1).

Tableau 4.1 Paramètres du modèle de diffusion intraparticulaire de l'As V sur les différents charbons

Material	$k_{id} (\mu\text{g}\cdot\text{g}^{-1}\cdot\text{min}^{-0.5})$	R^2
BP-H ₂ O	31	0.939
BP-H ₂ O-Fe	84	0.947
PH-H ₂ O	24	0.983
PH-H ₂ O-Fe	88	0.959
GAC1	41	0.988

Le modèle de pseudo-second ordre permet quant à lui de déterminer une vitesse initiale de sorption (paramètre h) et une constante de vitesse de pseudo-ordre 2 (k_2) en traçant t/q_t en fonction de t (figures 4.8 et 4.9). Le tableau 4.2 rassemblent les paramètres déduits de cette modélisation.

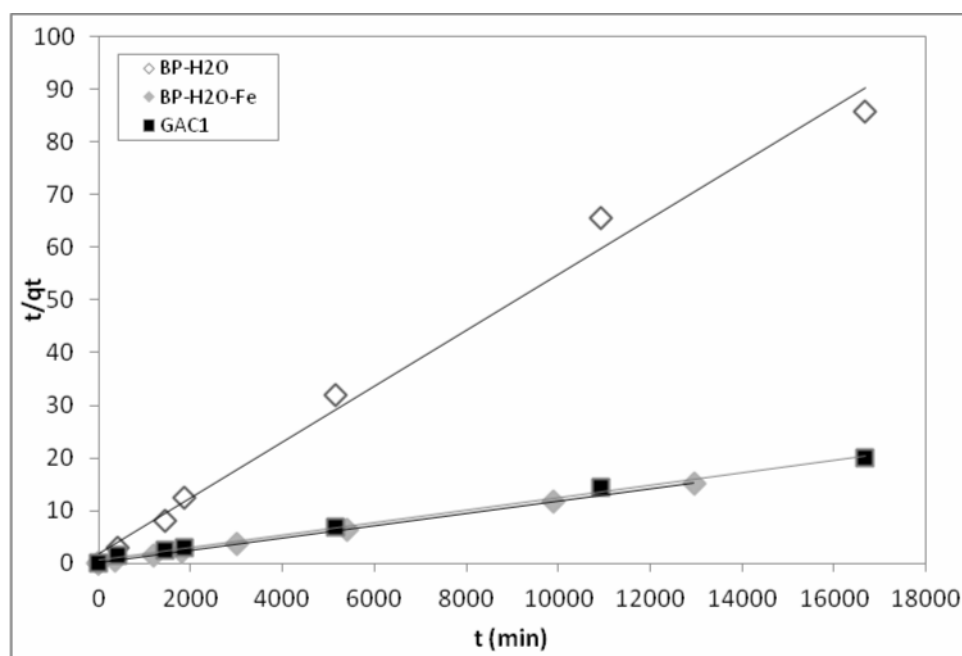


Figure 4.8 Tracés du modèle cinétique de pseudo-second ordre (BP-H₂O, BP-H₂O-Fe, GAC1)

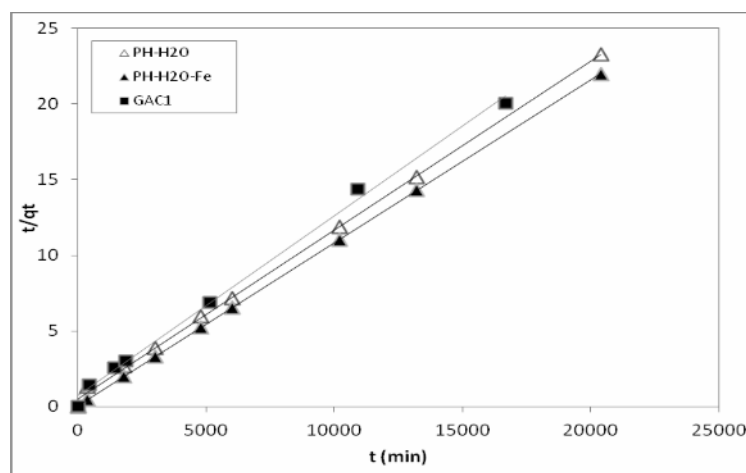


Figure 4.9 Tracés du modèle cinétique de pseudo-second ordre (PH-H₂O, PH-H₂O-Fe, GAC1)

Tableau 4.2 Paramètres du modèle cinétique de pseudo-second ordre de l'As V sur les différents charbons

Charbons	h ($\mu\text{g}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$)	q_e (cal.) ($\mu\text{g}\cdot\text{g}^{-1}$)	q_e (exp.) ($\mu\text{g}\cdot\text{g}^{-1}$)	k_2 ($\text{g}\cdot\mu\text{g}^{-1}\cdot\text{min}^{-1}$)	R^2
BP-H ₂ O	0.50	188.7	194.5	1.42×10^{-5}	0.990
BP-H ₂ O-Fe	7.06	833.3	853.8	1.02×10^{-5}	1.000
PH-H ₂ O	1.91	909.1	875.6	2.31×10^{-6}	0.999
PH-H ₂ O-Fe	14.27	909.1	928.4	1.73×10^{-5}	1.000
GAC1	1.42	833.3	832.5	2.04×10^{-6}	0.996

Ce modèle décrit parfaitement les données expérimentales des cinétiques d'adsorption. Pour une concentration initiale identique, les valeurs de h peuvent être comparées les unes par rapport aux autres. Comme pressenti lors des premières expériences déterminant le temps de contact, l'imprégnation de fer a conduit à une très forte augmentation de la vitesse initiale de sorption de l'As(V), d'un facteur de 14 pour BP-H₂O-Fe et de 7 pour PH-H₂O-Fe. Ce modèle

traduit également qu'un mécanisme de chimisorption est à l'origine de la fixation des ions arsénates et que cette chimisorption peut être la seconde étape limitante de la fixation.

Le dernier paramètre étudié lors de cette étude cinétique est l'influence du pH de la solution d'arsenic (pH initial) avant la réaction d'adsorption. Trois pH initiaux ont été sélectionnés (3,5, ≈ 7 et 12) et les pH finaux (après 120h de temps de contact) ont été relevés lors de différentes cinétiques (à concentrations initiales de 500 et 1000 $\mu\text{g.L}^{-1}$) réalisées sur BP-H₂O (Figure 4.10). Le tableau 4.3 répertorie ensuite les différentes formes de l'arsenic aux pH étudiés.

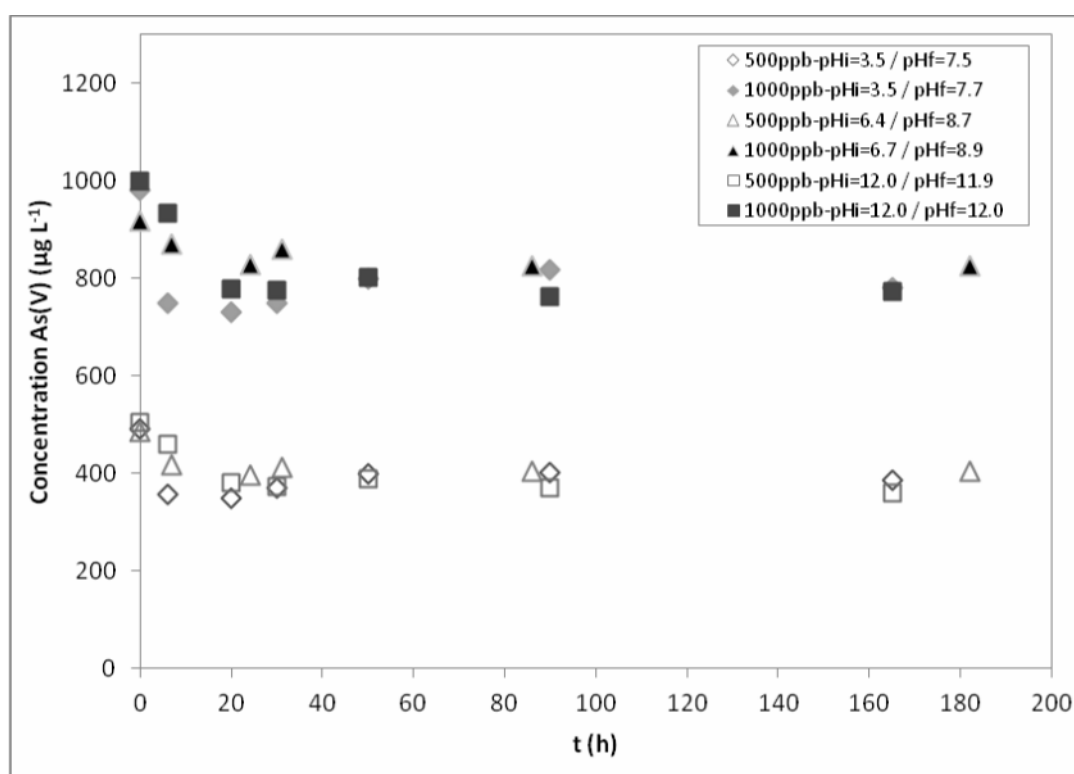


Figure 4.10 Cinétiques d'adsorption d'As(V) sur BP-H₂O à 2 concentrations initiales différentes (500 et 1000 $\mu\text{g.L}^{-1}$) et à différentes valeurs de pH (3,5, ≈ 7 et 12)

La première constatation est qu'entre pH = 3,5 et pH = 12, il n'y a pas de différences importantes sur les capacités d'adsorption. En accord avec le tableau 4.3, toutes les formes

anioniques de l'arsenic sont donc susceptibles d'être adsorbées sur BP-H₂O, sans préférence de l'une par rapport aux autres. Si les capacités d'adsorption sont peu affectées, la vitesse initiale de fixation semble quant à elle plus lente dans le cas des pH basiques (figure 4.10) mais ce résultat reste à confirmer.

Tableau 4.3 Identification des espèces d'As(V) adsorbées aux différentes valeurs de pH

BP-H ₂ O, pH _{pzc} = 9,8, C ₀ = 1000 µg.L ⁻¹			
pHi	Forme de As(V)	pHf	Forme de As(V)
3,5	95 % de H ₂ AsO ₄ ⁻	7,7	83 % de HAsO ₄ ²⁻ 17 % de H ₂ AsO ₄ ⁻
6,7	67 % de H ₂ AsO ₄ ⁻ 33 % de HAsO ₄ ²⁻	8,9	99 % de HAsO ₄ ²⁻
12	72 % de AsO ₄ ³⁻ 28 % de HAsO ₄ ²⁻	12	72 % de AsO ₄ ³⁻ 28 % de HAsO ₄ ²⁻

4.1.2 Isothermes d'adsorption

La seconde partie de l'étude d'adsorption concerne l'obtention et la discussion des données d'équilibre après un temps de contact liquide/solide déterminé précédemment de 120 h. Des isothermes de sorption ont été réalisées avec l'ensemble des adsorbants et les modèles de Langmuir et de Freundlich ont été testés pour décrire les points expérimentaux. La figure 4.11 représente les isothermes de sorption modélisées par l'équation de Freundlich, et le tableau 4.4 les constantes des deux modèles.

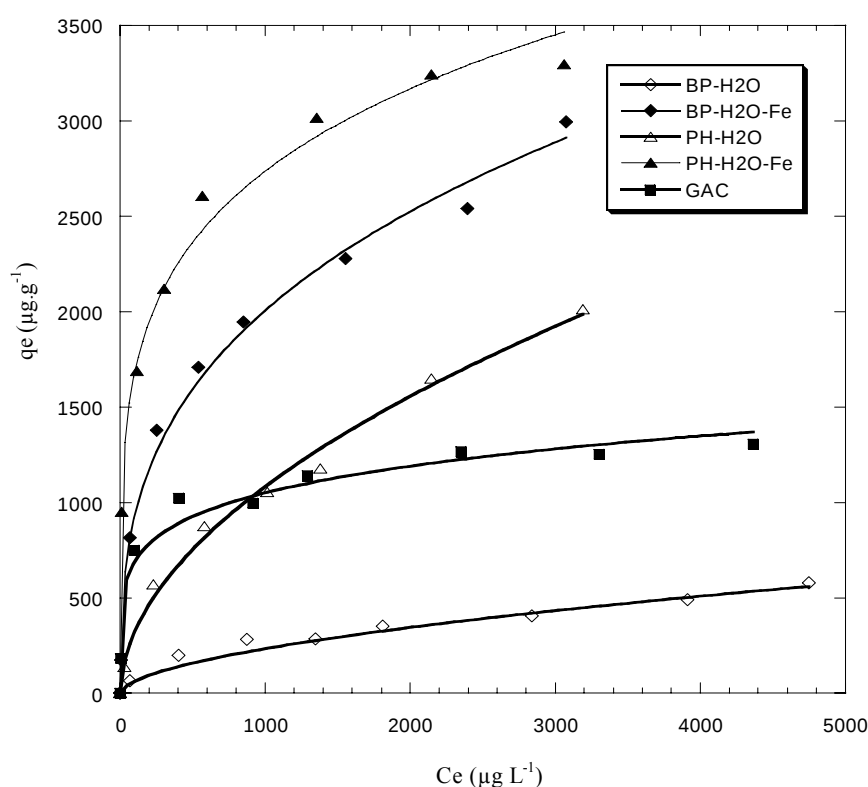


Figure 4.12 Isothermes expérimentales de sorption d'As (V), modélisées avec l'équation de Freundlich

Expérimentalement, les adsorbants présentant les meilleures capacités d'adsorption sont incontestablement ceux imprégnés de fer (Figure 4.12). Cette différence est très forte pour les charbons à base de pulpe de betterave. Par ordre décroissant suivent PH-H₂O, GAC1

et BP-H₂O. Ces capacités dépendent donc du type de précurseur, mais également de la teneur en fer de l'adsorbant.

Tableau 4.4 Constantes des modèles de Langmuir et de Freundlich

Adsorbants	Langmuir			Freundlich		
	q_m	b_L	R^2	K_F	n	R^2
	($\mu\text{g.g}^{-1}$)	($\text{L} \cdot \mu\text{g}^{-1}$)		($\mu\text{g}^{1/n} \cdot \text{L}^{1/n} \cdot \text{g}^{-1/n}$)		
BP-H ₂ O	690	0.00	0.95	5	0	0.96
BP-	293	0.00	0.96	205	0	0.99
PH-H ₂ O	282	0.00	0.97	30	0	0.99
PH-	328	0.00	0.94	640	0	0.99
GAC1	124	0.01	0.96	300	0	0.96

Le modèle de Freundlich est celui qui décrit le mieux les données expérimentales (Tableau 4.4). Les coefficients n sont tous inférieurs à l'unité ce qui traduit une adsorption favorable. Le modèle de Langmuir a permis une description satisfaisante et des valeurs de capacités maximales d'adsorption ont pu être extrapolées. Elles s'échelonnent entre 3280 $\mu\text{g.g}^{-1}$ pour PH-H₂O-Fe et 690 $\mu\text{g.g}^{-1}$ pour BP-H₂O, et elles ont conduit à la séquence suivante : PH-H₂O-Fe > BP-H₂O-Fe $\approx$ PH-H₂O > GAC1 > BP-H₂O.

Afin d'évaluer la potentielle compétition avec d'autres ions présents en solution, des isothermes ont été réalisées avec des eaux naturelles dopées en arsenic V. Ne sont présentées dans ce résumé que l'adsorption d'As(V) sur le meilleur couple d'adsorbants, PH-H₂O et PH-H₂O-Fe (Figure 4.13), dans une eau assez fortement chargée en ions et appelée HMC (Tableau 4.5).

Tableau 4.5 Composition de l'eau HMC.

Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	NO_3^{-}	HCO_3^{-}	SO_4^{2-}	pH
230	66	40	8	58	< 1	280	620	7.2

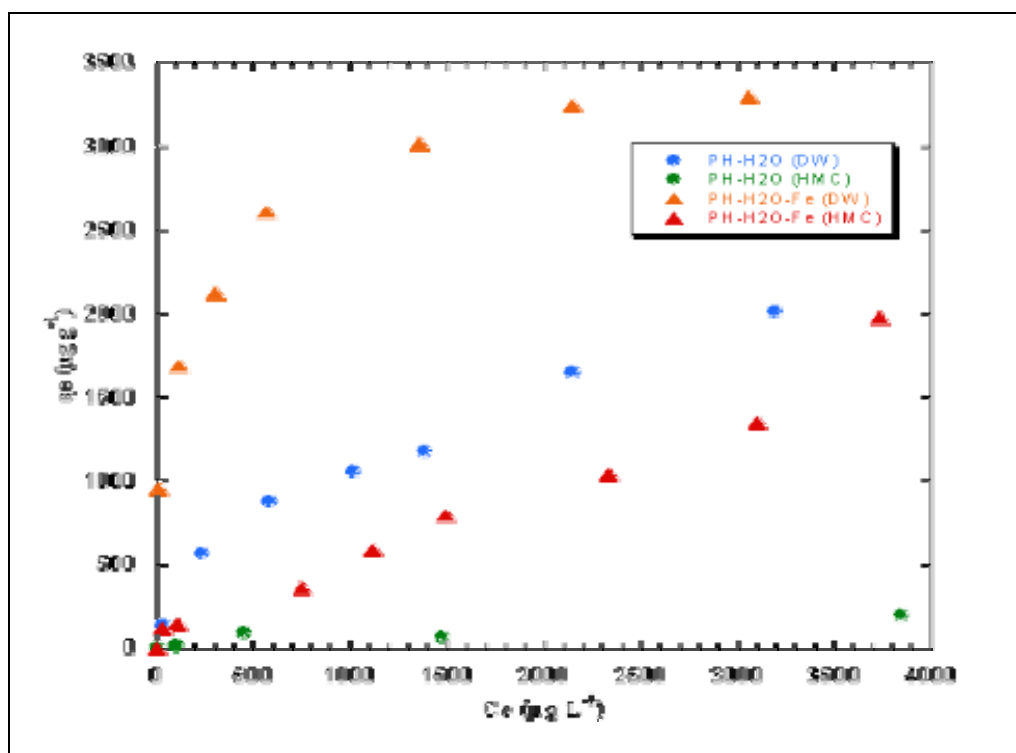


Figure 4.13 Effet d'une eau fortement chargée en ions (HMC) sur les isothermes d'adsorption d'As (V) sur PH-H₂O et PH-H₂O-Fe

La première conclusion concernant ces isothermes est la nette diminution des capacités d'adsorption lors de l'expérience réalisée dans une eau naturelle. Seuls les ions peuvent être incriminés puisque cette eau ne contient pas de matières organiques, et notamment les sulfates et les carbonates présents en forte concentration (Tableau 4.5). Néanmoins, l'adsorbant PH-H₂O-Fe conserve des capacités tout à fait exploitables et montre encore une fois sa nette supériorité par rapport à PH-H₂O. L'importance de l'imprégnation de fer pour la fixation de l'arsenic est à nouveau confirmée.

En conclusion, on peut retenir que pour qu'un matériau carboné soit efficace pour le traitement d'effluents contaminés avec de l'arsenic V, il faut que cet adsorbant soit

préalablement activé (création de volumes poreux). Ses performances sont accrues lorsque du fer, probablement sous forme d'oxyde/hydroxyde est imprégné. La teneur en fer semble ainsi être un facteur clé favorisant l'adsorption. Cette modification chimique permet en outre d'augmenter la vitesse initiale de sorption et la diffusion intraparticulaire. Enfin, si l'influence du pH sur les capacités d'adsorption n'est pas clairement démontrée, l'effet d'autres ions compétiteurs est à prendre en compte.

4.2 Etude la sorption de la TC

4.2.1 Etude cinétique de l'adsorption de la TC

La figure 4.14 présente les courbes cinétiques de sorption de la tétracycline effectuées à 100 mg L⁻¹ avec BP-H₂O, BP-H₂O-Fe et le charbon commercial GAC1. Dans le cas du GAC 2, les expériences ont été réalisées à une concentration de 300 mg L⁻¹. Le temps de contact optimal commun pour tous les matériaux est fixé à 120 h (5 jours).

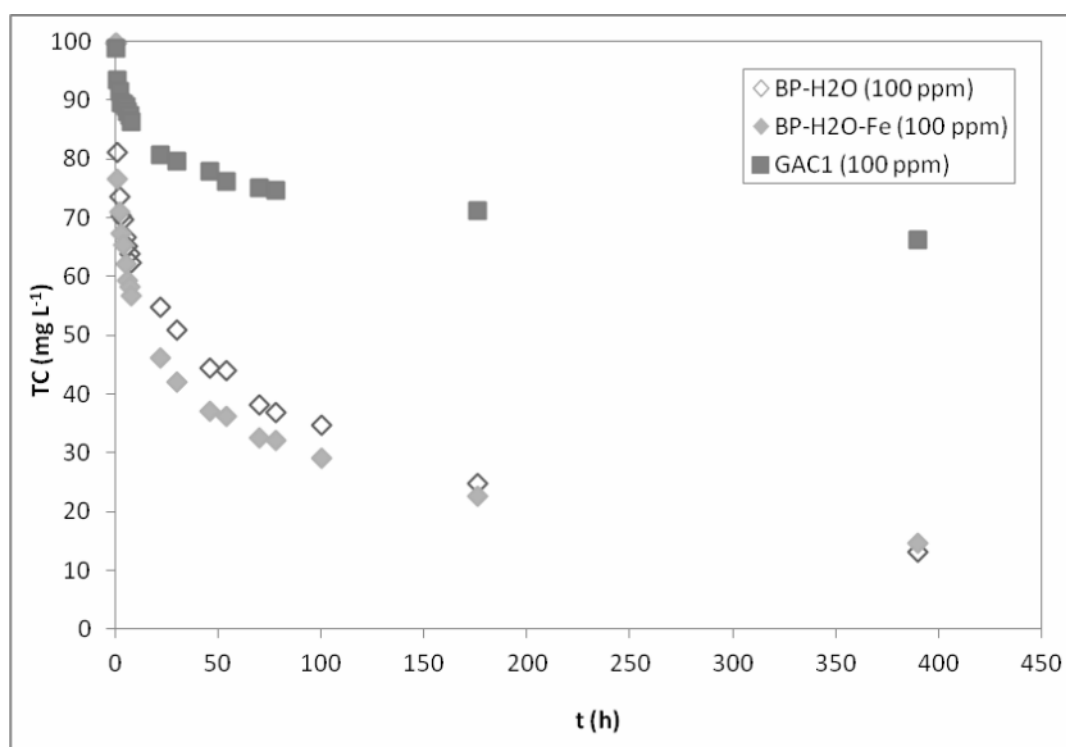


Figure 4.14 Courbes cinétiques de l'adsorption de TC.

Afin d'évaluer les mécanismes cinétiques de sorption, les modèles de pseudo premier et second ordre ont été testés. Seul le modèle de pseudo second ordre permet l'ajustement des points expérimentaux. Ce résultat permet de faire le postulat que l'étape limitante pour la vitesse d'adsorption est la chimisorption et que l'adsorption de la tétracycline est réalisée par un mécanisme de complexation de surface sur des sites spécifiques (Ho and McKay, 1998).

Le tableau 4.6 regroupe les paramètres cinétiques de l'adsorption de la tétracycline sur les matériaux étudiés. La constante de vitesse de pseudo second ordre h et la quantité adsorbée à l'équilibre q_e ont été calculées à partir des courbes t/q en fonction du temps t .

Si l'on compare les valeurs de la constante h pour une même concentration initiale en tétracycline, il est possible d'observer que la présence de fer dans les matériaux augmente la vitesse de fixation. Enfin, la nette différence entre les deux charbons commerciaux est sans doute due à la nature du précurseur utilisé et des propriétés de surface.

Tableau 4.6 Paramètres cinétiques du modèle de pseudo-second ordre.

Matériaux	h ($\text{mg.g}^{-1} \cdot \text{min}^{-1}$)	q_e (cal.) (mg.g^{-1})	q_e (exp.) (mg.g^{-1})	k_2 ($\text{g.mg}^{-1} \cdot \text{min}^{-1}$)	R^2
BP-H ₂ O	0,29	135,2	134,3	$1,6 \times 10^{-5}$	0,998
BP-H ₂ O-Fe	1,10	137,9	137,0	$5,8 \times 10^{-5}$	1,000
PH-H ₂ O	0,03	47,4	49,5	$1,5 \times 10^{-5}$	0,978
PH-H ₂ O-Fe	0,06	66,2	66,7	$1,4 \times 10^{-5}$	0,990
BP-H ₂ O	0,28	243,9	246,0	$4,6 \times 10^{-5}$	0,986

				6	
BP-H ₂ O-Fe	0,40	238,1	239,2	$7,0 \times 10^{-6}$	0,994
GAC1	0,18	158,7	160,1	$7,1 \times 10^{-6}$	0,990
GAC2	2,41	1111,1	1109,0	$2,0 \times 10^{-6}$	0,994

4.2.2 Isothermes d'adsorption

Des expériences de sorption à l'équilibre ont été réalisées afin de déterminer les capacités de fixation de la tétracycline par les matériaux étudiés. Pour toutes les concentrations initiales en tétracycline, le pH initial était compris en 3,3 et 4,5 (70 à 300 mg.L⁻¹ pour BP-H₂O, 15 à 100 mg.L⁻¹ pour PH-H₂O et PH-H₂O-Fe, 50 à 200 mg.L⁻¹ pour GAC1 et 100 à 300 mg L⁻¹ pour GAC2). Les pH finaux ont été mesurés entre 3,3 et 7,5 suivant les matériaux testés, ce qui implique que les formes principales de la tétracycline étaient TCH^{2±} et TCH³⁺. La figure 4.15 présente les points expérimentaux obtenus pour BP-H₂O, PH-H₂O, PH-H₂O-Fe, GAC1 et GAC2, ainsi que les représentations des modèles de Langmuir et Freundlich.

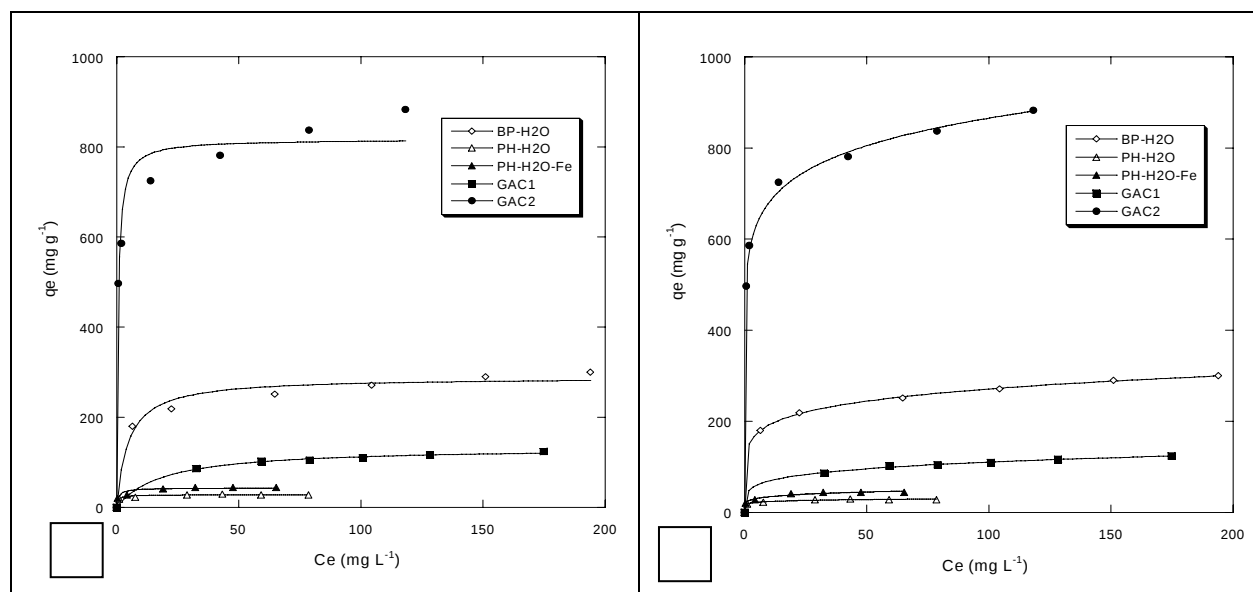


Figure 4.15 Isothermes d'adsorption de la tétracycline par les différents matériaux étudiés. (A) Modèle de Langmuir (B) Modèle de Freundlich.

Les points expérimentaux sont mieux décrits par le modèle de Freundlich que par celui de Langmuir. Ce résultat indique l'existence d'une hétérogénéité de la surface de l'adsorbant ainsi qu'une distribution exponentielle des sites de fixation et de leurs énergies. Les paramètres déterminés à partir de ces deux modèles sont regroupés dans le tableau 4.7. A partir de la comparaison des capacités maximales d'adsorption de la tétracycline déduites du modèle de Langmuir, il est possible de proposer la séquence d'efficacité suivante :

$$\text{GAC2} > \text{BP-H}_2\text{O} > \text{GAC1} > \text{PH-H}_2\text{O-Fe} \approx \text{PH-H}_2\text{O-Fe}$$

De plus, dans le cas des matériaux carbonés et des charbons actifs commerciaux, la valeur de K_F croît avec l'augmentation du volume mésoporeux.

Table 4.7 Paramètres des modèles de Langmuir et Freundlich.

Matériaux	Langmuir			Freundlich		
	q_m ($\text{mg} \cdot \text{g}^{-1}$)	b_L ($\text{L} \cdot \text{mg}^{-1}$)	R^2	K_F ($\text{mg}^{1-1/n} \cdot \text{L}^{1/n} \cdot \text{g}^{-1}$)	n	R^2
BP-H ₂ O	288,3	0,075	0,990	135,4	0,15	1,000
PH- H ₂ O	28,0	1,5393	0,972	18,6	0,10	0,985
PH-H ₂ O-Fe	42,7	1,2466	0,939	23,1	0,17	0,985
GAC1	133,1	0,0533	0,998	42,7	0,21	0,999
GAC2	816,7	1,7809	0,987	534,8	0,10	0,999
BP-H ₂ O (HMC)	308,8	0,0621	0,929	68,7	0,29	0,969
GAC2 (HMC)	549,5	1,0944	0,990	423,8	0,06	0,995

Lors de l'utilisation de BP-H₂O et GAC2 pour l'élimination de la tétracycline présente dans une eau naturelle artificiellement contaminée (précédemment nommée HMC dont la composition est donnée dans le tableau 4.5), il est observé une diminution de la capacité d'adsorption pour le GAC2 (tableau 4.7). Ce résultat peut être expliqué par des mécanismes d'échange d'ions pour la fixation de la tétracycline et donc par des phénomènes de compétitions avec les ions présents dans l'eau (Na⁺, Mg²⁺ or Ca²⁺). En revanche, la capacité de BP-H₂O est entièrement conservée. Ce résultat est évidemment très prometteur pour la mise en œuvre de ce charbon dans des procédés de traitement d'eaux naturelles.

4.2.3 Conclusion

Les études de sorption de la tétracycline par de nouveaux matériaux carbonés et des charbons actifs commerciaux, montrent que les capacités de sorption de BP-H₂O et BP-H₂O-Fe sont inférieures à celles de GAC2 mais supérieures à celles de GAC1. Dans tous les cas, la sorption de la tétracycline suit une cinétique de pseudo-second ordre et le temps de contact optimal est fixé à 5 jours. Le modèle de Freundlich décrit le mieux les points expérimentaux. L'augmentation de la force ionique du milieu implique une diminution de la capacité d'adsorption sur le GAC2 alors qu'elle n'est pas affectée dans le cas de BP-H₂O. Enfin, une corrélation de type exponentiel a été trouvée entre les valeurs des volumes de mésopores et la constante de Freundlich.

5 Conclusions et perspectives

L'ensemble de ces travaux confirme l'intérêt de réutiliser des déchets ou résidus de l'agriculture pour l'élaboration de charbons actifs destinés au traitement de solutions contaminées par de l'arsenic V ou de la tétracycline. Parmi les arguments prometteurs en faveur de cette réutilisation, on peut citer : le faible coût des matériaux précurseurs voire le développement de nouvelles filières de traitement de déchets, la limitation des coûts dus au transport lorsque le précurseur est une ressource locale, la possibilité de fabriquer des charbons à propriétés d'usage (imprégnation de fer pour le traitement de l'arsenic, par exemple)... Cette étude fournit donc des résultats préliminaires qu'il conviendrait de

confirmer ou d'étoffer, afin d'imaginer une filière durable aussi bien d'un point de vue économique qu'environnemental.

Ainsi différentes pistes peuvent être envisagées comme perspectives. La première, dans la continuité directe de ce qui a déjà été réalisé, serait de formuler un schéma réactionnel plus abouti des réactions d'adsorption mises en jeu entre la surface des charbons et ces micropolluants. Deux voies peuvent être suivies pour atteindre cet objectif : des expériences additionnelles seraient nécessaires pour essayer de relier les propriétés de surface aux capacités (ou aux cinétiques) de sorption. Pour cela, la titration des fonctions de surface dite méthode de Boehm, ou des analyses par IRTF ou XPS des charbons pourraient être très intéressantes. D'autre part, d'autres méthodes d'imprégnation de fer pourraient être testées afin de produire des matériaux avec des taux de fer différents pour le traitement de l'arsenic. Pour l'élimination de la tétracycline, des modèles de diffusion pourraient confirmer l'intérêt d'élaborer des adsorbants avec une mésoporosité élevée. L'autre voie consisterait en l'utilisation de modèles statistiques pour trouver des corrélations entre les paramètres cinétiques ou les données à l'équilibre et les propriétés des charbons. L'ultime objectif serait de définir des conditions de production en relation directe avec l'application envisagée.

Une autre perspective serait de se placer au plus près des préoccupations réelles rencontrées sur le terrain. Cela signifie par exemple de travailler avec de l'arsenic III et/ou des mélange AsV et AsIII, ou de diminuer les concentrations en tétracycline donc de trouver des méthodes d'analyse *ad hoc*. Dans tous les cas l'emploi d'effluents réels constitue un atout majeur car cela permet de prendre en compte les effets compétiteurs des autres ions et/ou de la matière organique naturelle, ainsi que les fluctuations dans le temps des concentrations par exemple. Enfin, pour valider ce travail, il faudrait proposer un procédé fonctionnant en continu. Deux approches peuvent être suivies : soit on considère que les charbons produits à l'échelle du laboratoire restent des matériaux très friables et donc il faudrait adapter une technologie de mise en œuvre des poudres. Dans ce cas, un procédé constitué d'un réacteur parfaitement agité couplé à une unité de séparation par membrane pourrait être une bonne option. Ce type de procédé a déjà été développé par Degremont et il est connu sous le nom de procédé Cristal (Mémento Technique de l'Eau, 2005). La seconde approche consiste à trouver des solutions pour renforcer la résistance mécanique des charbons. L'utilisant de liants (comme la cellulose par exemple) pour la fabrication d'extrudés de taille calibrée pourrait être

une voie prometteuse. Des procédés type lits fixes, communément employés avec des charbons actifs en grain, seraient très certainement la meilleure solution.

Enfin, tous ces développements ne peuvent être durables que s'ils sont assortis d'une analyse plus globale prenant en compte les aspects énergétiques, environnementaux et économiques de la fabrication des charbons. La disponibilité locale des déchets ou résidus, la diminution de la demande énergétique, la valorisation énergétique des sous produits liquides et gazeux produits lors de l'activation directe, et le traitement des émissions liquides ou gazeuses doivent être considérés pour la pérennité d'une filière économiquement viable et respectueuse de l'environnement.

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Résumé: Production de charbons actifs à partir de résidus agricoles pour l'élimination de micropolluants

La conversion de deux résidus agricoles, la pulpe de betterave et les écorces de cacahuètes, en matériaux carbonés poreux par activation à la vapeur d'eau est présentée. De plus, leur utilisation dans l'élimination de l'arsenic (AsV) et de la tétracycline (TC) présents en solutions aqueuses est étudiée. Les caractéristiques telles que la surface spécifique, la composition élémentaire, la teneur en cendre, le pH_{pzc} et la capacité de sorption de l'As(V) ou de la tétracycline par ces nouveaux matériaux ont été comparées à deux charbons actifs commerciaux (GACs). Les résultats montrent que les matériaux carbonés poreux obtenus à partir de la pulpe de betterave (BP-H₂O) et des écorces de cacahuètes (PH-H₂O) peuvent être utilisés dans le traitement d'eaux contaminées par de l'As(V) ou de la TC. L'utilisation de matériaux carbonés poreux modifiés par imprégnation de fer a également été étudiée. L'analyse des volumes poreux montre deux différents types de charbon pour les résidus sélectionnés. Il a été mesuré des volumes microporeux et mésoporeux égaux pour BP-H₂O et principalement microporeux pour PH-H₂O. Les matériaux carbonés imprégnés de fer présentent les plus fortes capacités de sorption de l'As(V) : 2930 et 3280 $\mu\text{g.g}^{-1}$ pour respectivement BP-H₂O-Fe et PH-H₂O-Fe. Ces valeurs sont plus élevées que celle mesurée pour le GAC1 (1240 $\mu\text{g.g}^{-1}$). Dans le cas de la tétracycline, le matériau BP-H₂O présente une capacité maximum d'adsorption de 288.3 mg.g^{-1} , alors que les GACs atteignent de 133 à 817 mg.g^{-1} . Cette étude montre clairement que les résidus de faibles coûts tels que la pulpe de betterave et les écorces de cacahuètes peuvent être utilisés comme précurseurs pour la fabrication de charbons actifs présentant des caractéristiques différentes pour le traitement de solutions polluées par de l'As(V) et de la tétracycline.

Mots clefs

Activation vapeur d'eau ; Adsorption ; Arsenic ; Charbons actifs ; Ecorces de cacahuètes ; Imprégnation avec du fer ; Pulpe de betterave ; Résidus agricoles ; Tétracycline.

Abstract: Activated carbons production from agricultural wastes for micropollutants elimination

The conversion of two agricultural wastes, sugar beet pulp and peanut hulls, into porous carbonaceous materials is presented and their potential application for As(V) and tetracycline removal from aqueous solutions is investigated. The properties such as surfaces areas, elemental and ash contents, pH_{pzc} and efficiencies for As(V) and tetracycline removal of these alternatives carbonaceous materials are compared with those of commercial granular activated carbons (GACs). The results show that carbonaceous materials obtained from sugar beet pulp (BP-H₂O) and peanut hulls (PH-H₂O) could be used for the treatment of arsenic and tetracycline contaminated water. Their performances are also improved when the carbonaceous materials are prepared by physical activation (steam) and then modified through iron impregnation especially for As(V) sorption. The pore volume analysis shows that two different carbon surfaces for each by-product were obtained, an equal microporous and mesoporous volume for the BP-H₂O and a predominantly microporous volume for PH-H₂O. According to the experimental results, the activated and then iron modified carbonaceous materials present a great As(V) sorption capacities (2930 and 3280 $\mu\text{g.g}^{-1}$ for BP-H₂O-Fe and PH-H₂O-Fe respectively) that are higher than the sorption capacity of a commercial activated carbon (GAC1) (1240 $\mu\text{g.g}^{-1}$). In the case of tetracycline, the BP-H₂O reaches a maximum sorption capacity of 288.3 mg.g^{-1} while GACs reach sorption capacities from 133 to 817 mg.g^{-1} . It is clear that beet pulp and peanut hulls are cheap and abundant wastes that can be used like precursors to obtain activated carbons with different characteristics for As(V) and tetracycline removal in aqueous media.

Keywords

Activated carbon; Adsorption; Agricultural wastes; Arsenic; Iron impregnation; Peanut hulls; Sugar beet pulp; Steam activation; Tetracycline.