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Option: GÉNIE DES PROCÉDÉS DE L'ENVIRONNEMENT

THÈME

Essais de réduction de la concentration d'un antalgique anti-inflammatoire présent dans les eaux en quantité infimes

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As I begin this study, I want to thank God for His blessings and guidance. I am grateful to my family for their endless support and love. Thank you to my professor for your wisdom and encouragement. Your belief in me has made this journey possible.

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INTRODUCTION GENERAL

Introduction general

Emerging contaminants have been increasingly studied over the past decade to improve the understanding of their fate, occurrence, and toxicological effects on the environment and human health. Originally wastewater treatment plants were not designed to remove these pollutants of emerging concern. However, research is now focusing on determining which existing treatment unit processes are suited to their removal. This research sets out to determine suitable treatment options for thirty-nine emerging contaminants including various pharmaceuticals (Journal of Water Resource and Protection, 2018).

The main role of drugs is to induce a biological effect favorable to the body human or animal. However, their abusive use is the cause of contamination widespread in aquatic environments by a broad spectrum of molecules, The occurrence of pharmaceutical products in various aquatic substances has been proven by numerous researches reporting the toxicity of these substances on aquatic fauna and flora. The first study which demonstrated the presence of drugs in water dates back to 1976 in the United States at the municipal wastewater treatment plant of "Big Blue Rivers" (Kansas City Missouri USA). The study noted the existence of salicylic acid (28.79 g/L, or 8.64 kg/day) and clofibric acid (7.09 g/L, or 2.13 kg/day) (Hignite and Azarnoff, 1977), Since then, numerous studies have shown the presence of drug residues at concentrations that can vary from ng/l to several µg/l in surface water or groundwater, Due to their low concentration, the residue of pharmaceutical products is difficult to detect, characterize and quantify, That's why the advancement of analytical tools has been a miraculous solution to this problem. Although the real risk for humans remains difficult to determine, studies show that residues of certain drugs can have harmful effects on ecosystems, particularly the aquatic environment The techniques for treating water polluted by pharmaceutical compounds can be classic (biological or physicochemical) or advanced (advanced oxidation processes). Several studies have shown that conventional wastewater treatments (primary and biological sectors) more or less effectively eliminate hydrophobic, volatile, and easily biodegradable micropollutants, although they are not designed to eliminate them (Ruel et al. 2012; Mailler et al. 2013). Furthermore, tertiary treatment processes are currently being developed for wastewater because certain hydrophilic micropollutants such as drug residues and pesticides are refractory to conventional treatments. Among the various existing technologies (adsorption, advanced oxidation, membrane filtration), adsorption on activated carbon appears to be a particularly interesting technique due to its simplicity of implementation, its flexibility, its cost, and its efficiency (Abegglen & Siegrist 2012; Boehler et al. 2012; Margot et al. 2013).

CHAPTER 1

I Pollution

I.1 Introduction

Pollution is ubiquitous and takes many forms and shapes. For example, the beautiful sunsets that we may see in the evening are often due to the interaction of light and atmospheric contaminants, as illustrated above.

Pollution can be defined as the accumulation and adverse effects of contaminants or pollutants on human health and welfare, and/or the environment. But in order to truly understand pollution, we must define the identity and nature of potential contaminants. Contaminants can result from waste materials produced from the activity of living organisms, especially humans. However, contamination can also occur from natural processes such as arsenic dissolution from bedrock into groundwater, or air pollution from smoke that results from natural fires. Pollutants are also ubiquitous in that they can be in the solid, liquid, or gaseous state.[1]

Pollution occurs in various forms, including air, soil, noise, light, thermal, and radioactive pollution, each posing significant environmental and health challenges. Air pollution from vehicles and factories leads to respiratory diseases, while soil pollution from pesticides and heavy metals reduces soil fertility. Noise and light pollution disrupt human and wildlife behavior, and thermal pollution from industrial processes affects aquatic life. However, water pollution, caused by industrial discharges, agricultural runoff, and plastic waste, is the most pressing issue today.

I.2 Soils and Water Pollution

Mining, agriculture, and deforestation are important energy-intensive activities that impact economies and at the same time directly and indirectly cause soil and land pollution. Mining produces vast quantities of almost sterile and structureless geologic materials, such as crushed rock that often contain significant amounts of toxic metals, such as lead and cadmium, and salts. Mine overburden and tailings are often stockpiled next to large open pit excavations. Modern agricultural production requires the use of large quantities of commercial fertilizers and pesticides and produces animal wastes, all of which can pollute land and water.[2]

I.3 Pharmaceutical products

I.3.1 Pharmaceutical drugs

The utilization of pharmaceutical drugs keeps rising due to improvements in the health care system and expectations of people for longer life. The global utilization of different pharmaceutical drugs by human beings is to investigate, the consumption of pharmaceuticals, 836 tons of acet`ylsacylic acid [non-steroidal anti-inflammatory drugs (NSAIDs)], 622 tons of paracetamol (NSAIDs), 517 tons of metformin (antidiabetic), 345 ton of ibuprofen (NSAIDs), 88 ton of carbamazepine (antiepileptic) was found in Germany, whereas 35 ton of naproxen (NSAIDs) was observed in England in the year 2001.[3]

I.3.2 Definitions

Medications are grouped under the acronym PPCPs (or Pharmaceuticals and Personal Care Products). This acronym refers to any product used by individuals for health, cosmetic reasons,

or by the agro-industry to stimulate livestock growth or health. We can distinguish different types of medications based on their usage, components, and their mode of regulatory registration, for example. Medication is composed of two types of substances: one or more active substances or active ingredients with demonstrated pharmacological effect and clinically proven therapeutic interest, and one or more excipients; inert substances on a pharmacological level.

Medications can be grouped into six broad categories:

Table 1 Medication Reference Table: Conditions, Treatments, and Side Effects

Medication	Conditions	Action	Effect Time	Side Effects	Common Examples
Anti-depressants	Depression, some Anxiety Disorders	Increase certain NTs, such as dopamine	4-8 Weeks	Nausea, headaches, sexual dysfunction	Prozac, Cymbalta
Anti-Anxiety	Anxiety Disorders, Panic Attacks	Reduce brain activity, promote relaxation	Immediate to several weeks	Drowsiness, dizziness, memory problems	Valium, Xanax, BuSpar
Stimulants	ADHD, Narcolepsy	Increase NT activity	Immediate to several hours	Insomnia, appetite suppression	Adderall, Ritalin
Sedatives	Insomnia, Sleep Disorders	Decrease NT activity	Immediate to several hours	Dizziness, drowsiness	Ambien, Restoril
Mood Stabilizers	Bipolar Disorder	Balance NT activity	Days to several weeks	Weight gain, nausea	Lithium, Depakote
Anti-psychotics	Schizophrenia, BP, severe Depression	Normalize NT activity	Days to several weeks	Weight gain, drowsiness	Risperdal, Zyprexa

I.3.3 Dangers and Toxicity of Medications

Medications are biologically active substances. While their properties and mechanisms of action are well understood in humans, their fate in the environment is still poorly understood. The action of medications on specific biological targets raises questions about the ecological and health risks associated with their presence in the environment. One of the difficulties in monitoring medications in the environment is the wide variety of molecules, both in terms of their pharmacological properties and their chemical structures and physicochemical properties. The fate of medications after their release into the environment depends on their biodegradation, transformation, and distribution among different compartments.

I.3.4 Types of Pharmaceutical Waste

- Expired Medications: Medications that have passed their expiration date are considered as pharmaceutical waste.
- Pharmaceutical Manufacturing Waste: The waste generated during the production of medications can include various by-products, unused materials, and residues.
- Contaminated or Spoiled Medications: Pharmaceuticals that have been compromised in some way, such as through exposure to extreme temperatures or contamination.

I.3.5 Environmental Impact

Improper disposal of pharmaceutical waste can lead to environmental pollution. When medications are flushed down the toilet or thrown in the trash, they can end up in water systems and soil, affecting aquatic life and potentially entering the human food chain.

Although pharmaceuticals persist low in environment, they are ubiquitous in environment due to their higher rate of release as compared to the rate of transformation. Composition of sewage, weather conditions, design and operation of treatment plants determine the transformation of various active pharmaceutical products. The pharmaceutical products contaminated sludge, when used as an agricultural fertilizer can reach to the terrestrial environment and through chain it may enter into surface as well as ground water.[4]

I.3.6 Ibuprofen

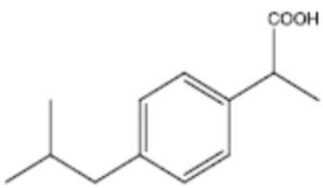
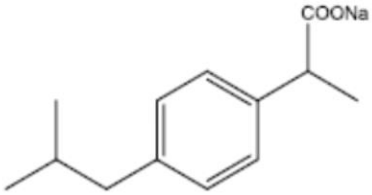
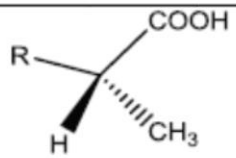
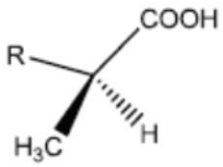
As previously mentioned, one of the most widely consumed medications is ibuprofen, a nonsteroidal anti-inflammatory drug (NSAID), with an annual consumption of 345 tons.

Ibuprofen is one of the safest drugs employed today for the treatment of pain, inflammation, and fever. The development and extensive clinical use of this drug is one of the success stories of the pharmaceutical industry.

In this day and age, such successes are few since we tend to hear more of the negative or unsafe aspects attributed to the actions of many drugs. In respect of relative safety, this is the success for ibuprofen since it has a wide range of tolerance while at the same time being often more effective on a dose-for-weight basis than aspirin and paracetamol in the treatment of many painful conditions.[5]

Figure 1 Ibuprofen Capsules in Blister Pack

Table 2 Formula, chemical structure, dimensions, and physicochemical properties of

Property	Ibuprofen	
	Acid form	Sodium salt
Formula	$C_{13}H_{18}O_2$	$C_{13}H_{17}O_2Na$
CAS number	15687-27-1	31121-93-4
Chemical structure		
Enantiomers	  R enantiomer S enantiomer (inactive) (pharmacologically active)	
Dimensions [a]	1.03 (length) × 0.52 (width) × 0.43 (thickness) (in nm)	-
Molecular weight	206.28 g mol^{-1}	228.26 g mol^{-1}
Water solubility (25 °C)	21 mg L^{-1} [f]	100 mg mL^{-1}
Log K_{ow} [b]	3.5-3.97	-
Log K_d [c]	0.85	-
pK_a [d]	4.91	-
Vapor pressure (40 °C)	1.7×10^{-2} Pa [g]	-
Henry's law constant [e]	6.1×10^{-6} atm m^3 mol^{-1}	-

The high consumption of ibuprofen results in substantial accumulation, leading to a serious environmental pollution problem.

Pharmaceuticals are quickly absorbed by humans or animals after intake; the exceeding dose is either eliminated unmetabolized or subjected to metabolic degradation processes before excretion (via urine or feces), and it might enter aquatic systems via different pathways, as illustrated in the simplified scheme presented in Figure1. Regarding human consumption,

disposal by flushing of unused or expired medication also contributes to water pollution though to a lesser extent.[6]

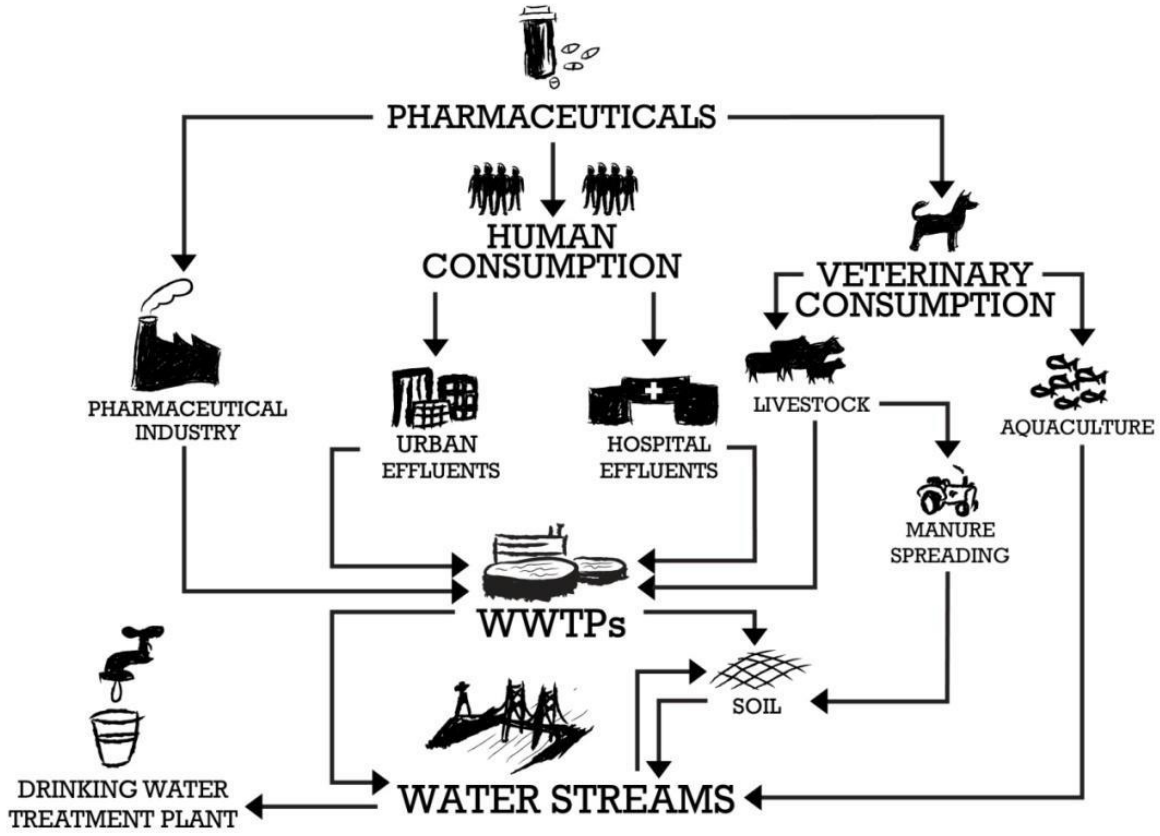


Figure 2Simplified scheme of the main routes of water streams pollution by pharmaceutical

Soil contamination can also arise from the use of reclaimed water for irrigation purposes, or to the use of treated sludge as agricultural fertilizer when low concentration levels of pharmaceuticals are present.[7]

I.4 Ibuprofen Pollution Reduction Methods in Water

To address the issue of accumulated pollution effectively, the field employs several scientifically rigorous methods. These include Advanced Oxidation Processes (AOPs), Reverse Osmosis (RO), Nanofiltration, Biofiltration, and the widely utilized Activated Carbon Adsorption method.

I.4.1 Advanced Oxidation Processes (AOPs)

- **Mechanism:** Involves generating highly reactive species (e.g., hydroxyl radicals) through chemical reactions involving ozone, hydrogen peroxide, or UV light. These species degrade ibuprofen into less harmful compounds.

- **Benefits:** Effective at breaking down a wide range of contaminants.

I.4.2 Reverse Osmosis (RO)

- **Mechanism:** Utilizes a semi-permeable membrane to remove dissolved contaminants, including ibuprofen, by applying pressure to water.
- **Benefits:** Highly effective for a broad spectrum of pollutants.

I.4.3 Biofiltration

- **Mechanism:** Employs microorganisms in biofilters to biologically degrade ibuprofen.
- **Benefits:** Sustainable and can be integrated with natural treatment processes.

I.4.4 Activated Carbon Adsorption

- **Mechanism:** Activated carbon materials have a high surface area that adsorbs organic pollutants, including ibuprofen.
- **Benefits:** Widely studied, effective, and can be used in various water treatment setups.

Given its paramount importance, we have opted to utilize this method in our study.

CHAPTER2

II Adsorption

II.1 Introduction

Understanding of engineering design methods of adsorption systems is an important aspect of process engineering design not only in the chemical industry but also in the fields of environmental pollution control and energy utilization.[8]

II.2 Definition

Adsorption occurs whenever a solid surface is exposed to a gas or liquid. it is defined as the enrichment of material or increase in the density of the fluid in the vicinity of an interface. Under certain conditions, there is an appreciable enhancement in the concentration of a particular component, and the overall effect is then dependent on the extent of the interfacial area.[9]

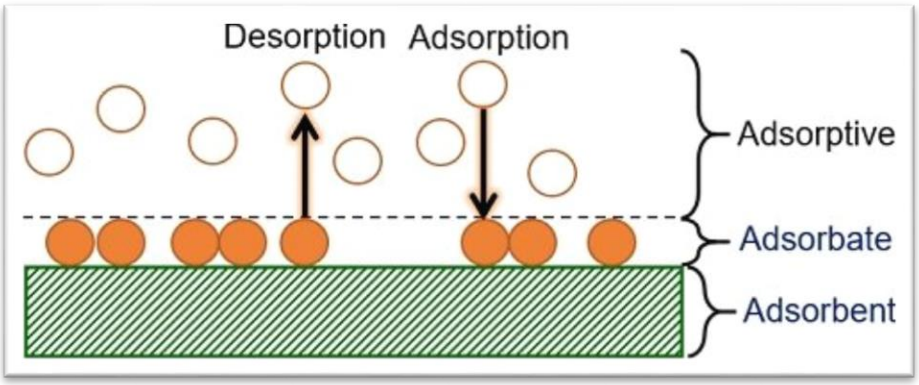


Figure 3. Adsorption phenomenon

II.3 Types of Adsorptions

Adsorption is classified into physical (physisorption) and chemical (chemisorption) types, with further categorizations such as gas-solid, liquid-solid, and liquid-gas adsorption. Understanding these distinctions is pivotal for optimizing processes and addressing environmental challenges.

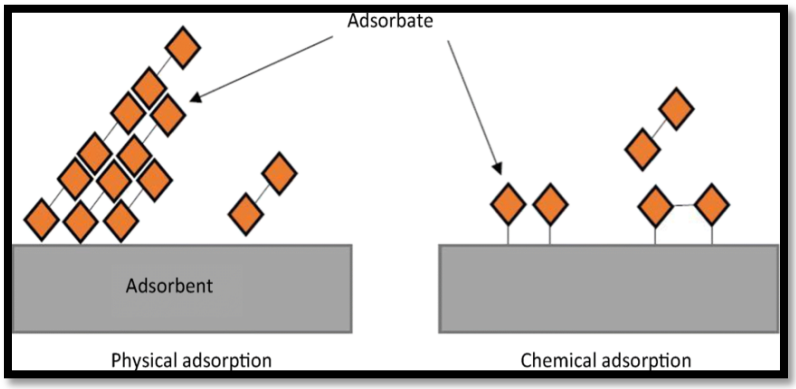


Figure 4. Physical and chemical adsorption

II.3.1 Chemical adsorption

On approaching the surface, each atom or molecule encounters an attractive potential that ultimately will bind it to the surface under proper circumstances. The process that involves trapping of atoms or molecules that are incident on the surface is called adsorption. It is always an exothermic process.[10]

II.3.2 Physical adsorption

Physical adsorption is caused mainly by van der Waals force and electrostatic force between adsorbate molecules and the atoms which compose the adsorbent surface. Thus, adsorbents are characterized first by surface properties such as surface area and polarity. [11]

II.4 Factors influencing adsorption

There are several factors that influence adsorption The degree and nature of adsorption are influenced by various factors, including

II.4.1 Concentration effect

The concentration effect in adsorption is often described by isotherms, which illustrate how the amount of adsorbate on the surface of the adsorbent varies with its concentration in the surrounding medium.[12]

II.4.2 pH effect

adjusting the pH to match the isoelectric point enhances interactions between molecules and the surface.

II.4.3 Temperature effect

Temperature has a significant effect on adsorption processes, influencing both the adsorption capacity and the overall kinetics of the adsorption reaction. The impact of temperature on adsorption can be explained through thermodynamics and kinetics.

II.4.4 The specific surface area

Generally, materials with larger surface areas have more sites available for adsorption, leading to increased adsorption capacity.

Adsorption of a molecule may take place at different surface sites and in diverse molecular orientations.[13]

II.4.5 The nature of adsorbate and adsorbent

the successful outcome of adsorption is influenced significantly by the complementary characteristics of the adsorbate and adsorbent, including their chemical properties, sizes, and the nature of their interactions.

II.5 Adsorption isotherms

An adsorption isotherm is a graphical representation or mathematical equation that describes the relationship between the amount of adsorbate adsorbed onto an adsorbent at a specific temperature and pressure

There are several types of adsorption isotherms, among the most commonly encountered ones are Langmuir, Freundlich, and Temkin models.

II.5.1 Langmuir adsorption

The Langmuir isotherm assumes a monolayer adsorption and is based on the following assumptions.[14]

- Adsorption occurs at specific sites on the surface.
- Each adsorption site can only accommodate one molecule.
- All adsorption sites are identical and energetically equivalent.
- There is no interaction between adsorbed molecules.

The Langmuir isotherm equation is given by:

$$\frac{C_{eq}}{q_e} = \frac{1}{K_L\, b} + \frac{1}{b}\, C_{eq}$$

where:

- C_{eq}**:** Equilibrium concentration of the adsorbate (mg/L).
- q_e**:** Amount of substance adsorbed per unit mass of adsorbent (mg/g).
- K_L**:** Constant related to the energy of adsorption.
- b**:** Maximum adsorption capacity.

II.5.2 Freundlich adsorption

The Freundlich isotherm is more flexible and applicable to multilayer adsorption. It is expressed as an empirical equation [15]

$$q_e = K_F . C_{eq}^{1/n}$$

where:

- q_e: is the amount of adsorbate adsorbed per unit mass of adsorbent.
- C_{eq}: is the equilibrium concentration of the adsorbate in the fluid phase.
- K_F: is the Freundlich constant related to adsorption capacity.
- n: is the Freundlich constant related to the intensity of adsorption.

II.5.3 Temkin adsorption

The Temkin isotherm is a model used in the field of adsorption science to describe the interaction between an adsorbate molecule and a solid surface. It is named after the Soviet scientist Isaak M. Temkin, who proposed this isotherm in the mid-20th century.(Temkin, 1940).

The Temkin isotherm assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to the adsorbate-adsorbate interactions. The equation for the Temkin isotherm is given by

$$q_e = B \ln\left(A e^{\frac{RT}{q}}\right)$$

Where:

- q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (usually in moles per gram),
- B: is the Temkin isotherm constant,
- A: is the equilibrium binding constant (related to the heat of adsorption),
- R: is the ideal gas constant,
- T: is the temperature in Kelvin.

II.6 Adsorption Kinetics

The kinetics of adsorption are of considerable practical interest for the optimal use of an adsorbent in an adsorption process. It allows us to understand the specific nature of the physicochemical interactions between the solute and the adsorbent. Through this, we can determine the initial rate of adsorption, the equilibrium time, the mass transfer coefficient, and the diffusion coefficient. The kinetics of adsorption, are not yet satisfactorily described. Various kinetic models are proposed:

II.6.1 First-order kinetics

The Lagergren equation (1898), which governs the kinetics of first-order adsorption, is the most widely used.

$$\frac{dQ_t}{d_t} = K_1(Q_e - Q_t)$$

- Q_e *et* Q_t : sont respectivement les quantités de soluté adsorbées en mg g^{-1} à l'équilibre et à un instant t,
- K_1 :la constante de vitesse de premier ordre (min-1).

The equation allows the determination of the rate constant for the adsorption of solutes. The linearized form of this equation is obtained by integration between the initial time and time *t*:

$$\log(Q_e - Q_t) = \log(Q_e) - \frac{K_1.t}{2.303}$$

II.6.2 Second-order kinetics

The differential equation that governs the kinetics of second-order adsorption is in the following form [17]

$$\frac{dQ_t}{d_t} = K_2(Q_e - Q_t)^2$$

K2 is the second-order rate constant (g mg-1 min-1).

The integration of this equation leads to:

$$\frac{1}{Q_e - Q_t} = \frac{1}{Q_e} + K_2.t$$

It is mainly used in the following linearized form:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{1}{Q_e}t$$

The initial rate of adsorption *h* is given in this case by the equation:

$$h = K_2 Q_e^2$$

CHAPTER 3

III The adsorbents

III.1 Introduction

The importance of adsorption for different carbon materials and, conversely, the contribution of each type of carbon to the field of adsorption is very different. This reflects the wide variability in properties of solid carbons, which makes their surface properties important in very different fields and for different reasons.[18]

III.2 Historical perspective

Activated carbons are the microporous carbonaceous adsorbents whose history can be traced back to 1600 B.C., when wood chars were used for medicinal purposes in Egypt. In Japan, a well for underground water equipped with a charcoal filter at the bottom was found at an old shrine (Kashiwara Jingu, Nara) constructed in the 13th century A. D. In Europe, wood char and later bone char were used for refining beet sugar, a practice started in France because of the blockade against the Continent during the Napoleonic era. In the 20th century, during the World Wars, the need to develop gas masks stimulated rapid growth in adsorption research.[19]

III.3 Structures of elemental carbon

Carbon has an atomic number of 6 and its ground-state electron configuration is [He]$2s^2 2p^2$. Like some other *p*-block elements (e.g., P, S, Sn), solid elemental carbon exhibits the phenomenon of allotropy (i.e., occurrence of the element in different forms that vary in structure and equation of state).[20]

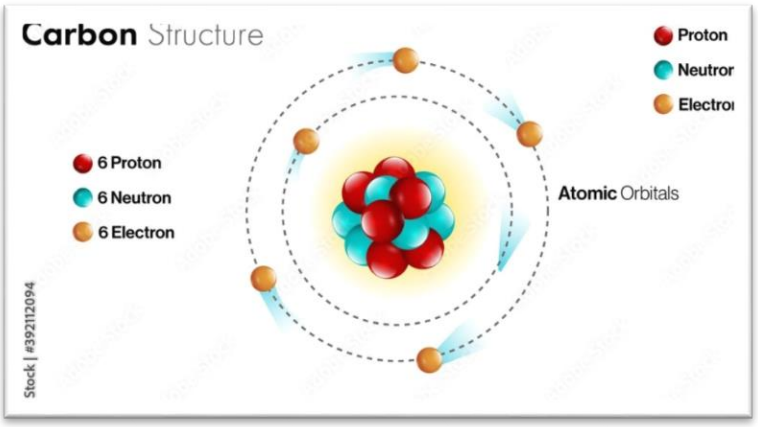


Figure 5. Atomic structure of carbon atom

III.4 Preparation of activated carbons

The process involves producing activated carbon from source materials like coal, wood, nutshells, petroleum, or synthetic high polymers. These materials undergo pyrolysis and

carbonization at high temperatures to remove volatile fractions. The resulting carbonaceous material then undergoes activation using oxidizing gases such as steam or carbon dioxide, forming micropores. The activation yield is typically below 50%, sometimes dropping below 10%. Alternatively, activation can be achieved using inorganic chemicals like zinc chloride or phosphoric acid, which catalyze pyrolytic condensation of carbohydrates, producing larger micropores suitable for adsorbing larger molecules.[21]

III.5 The types of activated carbon

Activated carbon comes in various types, each with specific characteristics and applications. Here are some common types:

Figure 7. Granular Activated Carbon (GAC)

Figure 6.Powder activated carbon(PAC)

- Powdered Activated Carbon (PAC): Fine powder with a large surface area, commonly used in water treatment and air purification.
- Granular Activated Carbon (GAC): Larger particle size than PAC, suitable for water treatment, gas purification, and industrial processes.
- Pelletized Activated Carbon: Compacted form of GAC, often used in gas-phase applications.

CHAPTER 4

IV Materials and equipment

Major glassware and equipment used in this study are summarized in the following table:

Table 3. Accessories and glassware

 Erlenmeyer	 Flask	 Graduated cylinder	 Volumetric flask
 Pipette and pipette filler	 Watch glass	 Spatulas	 Funnel
 Test tubes	 Magnetic stir bar	 Wash bottle for distilled water	 pH meter electrode
 Electronic balance	 Photo spectrometer	 Glass desiccator	 Magnetic stirrer
 Immersion thermostat	 Centrifuge	 Drying oven	 Laboratory Bottles

IV.1 Steps carried out in this part

Study of the main physicochemical parameters influencing the adsorption of ibuprofen from aqueous solutions.

Modelling of the obtained results:

- Application of adsorption isotherms.
- Kinetics studies
- Thermodynamics studies

IV.2 Equipments

Spectrophotometry is an analytical method that allows for the measurement of absorbance (or optical density) of a substance in solution. Using this analytical method, Absorbance is measured, which consists of a light source, a prism to select a specific wavelength of light, and a photosensitive sensor).

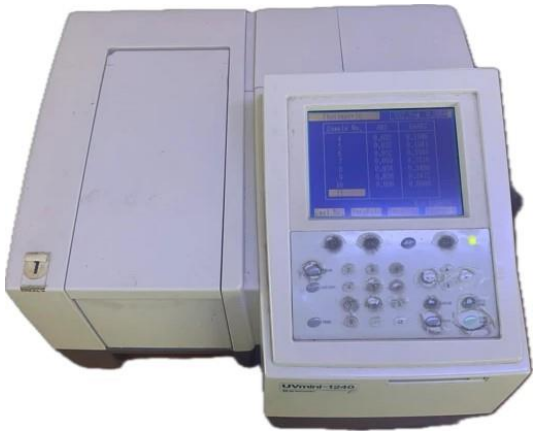


Figure 8 The Photo spectrometer used

In practice, any substance in solution is capable of absorbing certain wavelengths of light, whether in the spectrum of visible or invisible light, from ultraviolet to infrared, passing through all the colours of the rainbow.

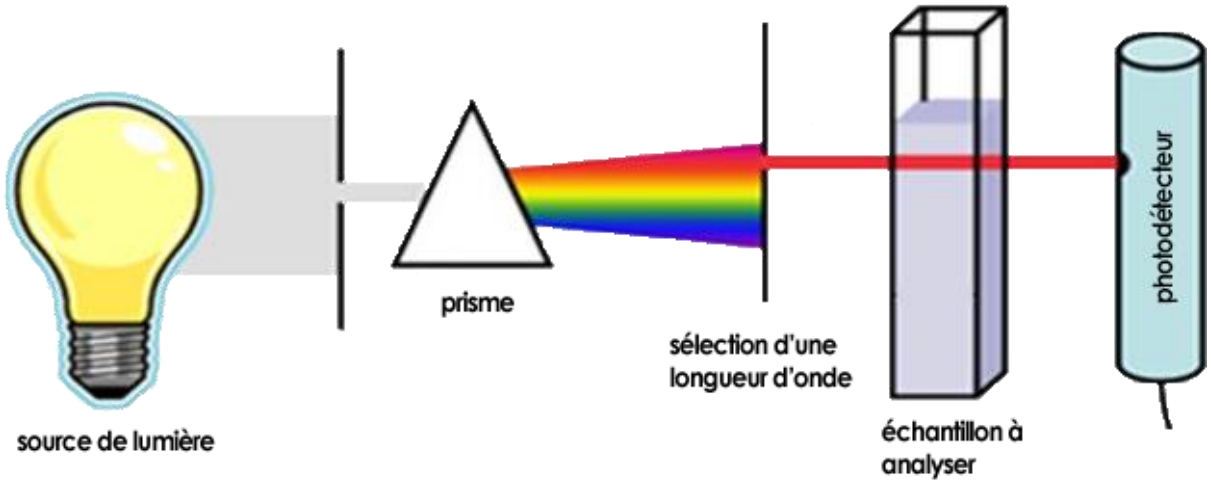


Figure 9 Principle of spectrophotometry

IV.3 Products used

IV.3.1 Commercial Activated Charcoal from Merck

Merck produces activated charcoal, but specific characteristics of their activated charcoal products may vary depending on the intended use. Merck is a large multinational company, and they likely offer activated charcoal for various applications, including pharmaceutical, industrial, and laboratory uses.

IV.3.2 Pharmaceuticals Products

By considering ibuprofen as a pharmaceutical pollutant, below are some of its major characteristics:

The characteristics and chemical profile of ibuprofen were discussed comprehensively in Chapter 1. This included its molecular structure as 2-(4-isobutylphenyl) propanoic acid, molecular formula ($C_{13}H_{18}O_2$,) molecular weight of approximately 206.28 g/mol, and its physical properties such as being a white crystalline solid with a melting point around 77-78°C. The discussion also covered its solubility properties, acidity ($pK_a \approx 4.91$)

Ibuprofen was used in solution form because it was essential to the experimental methodology

IV.3.3 Chemicals used for pH adjustment

- NaOH Solution (0.1N) for pH adjustment in basic media.
- HCl Solution (0.1N) for pH adjustment in acidic media.

IV.4 Preparation of the principal solution

To make a solution of a pharmaceutical product at 20 mg/L concentration, first, weigh out 20 milligrams of the product. Put the weighed product in a clean flask. Then, add distilled water until the total volume reaches 1 litre. Stir well to dissolve the product completely.

IV.5 Establishment of the calibration curve

From the original solution, a series of solutions with well-defined concentrations ranging from 2 to 20 mg/L are prepared through successive dilutions. These solutions are then analysed by UV-visible spectrophotometry after centrifugation. The calibration curve thus established represents the optical density at the maximum absorption wavelength as a function of concentration C, following the Beer-Lambert equation.

The absorption spectrum of adsorbate shows a peak at the wavelength λmax = 220.5 nm, so this wavelength was used for subsequent measurements. The calibration curve presented in the Figure for the analyte demonstrates good linearity. It should be noted that the samples were separated before analysis to avoid any disturbance caused by the presence of suspended solids. The obtained results are grouped in the next table.

Table 1 Values of: A = f(C) from the calibration curve of adsorbate

C_0 (mg/C)	2.0	4.0	6.0	10.0	12.0	20.0
V (mL)	2.5	5.0	7.5	12.5	15.0	25.0
Abs	0.127	0.173	0.263	0.42	0.494	0.788

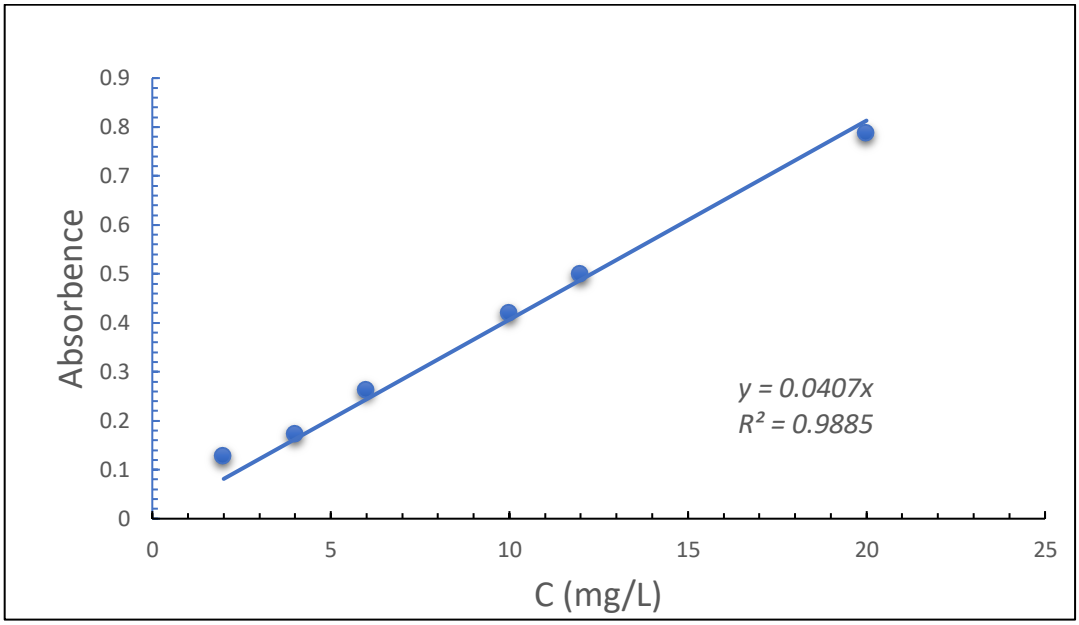


Figure 10 Calibration Curve of adsorbate

We observe that the curve is a straight line with a correlation coefficient equal to **0.997**, representing a good linear fit.

The equation of the line giving the absorbance A as a function of the concentration of the absorbate is: **A = 0.0407*C**. This equation will be used to calculate the concentration of an unknown solution of the pharmaceutical product.

IV.6 Enhancement of adsorption parameter and optimization

In order to determine the best adsorption conditions, our study focused on the variation of the following parameters.

IV.7 Impact of adsorption contact time

In order to examine the contact time needed to achieve adsorption equilibrium, we prepared a solution with a concentration of 4 mg/L and followed the subsequent procedure.

In a series of beakers, we introduced a known mass of **1mg** of prepared activated charcoal and **25 mL** of the prepared solution successively. The mixture was then stirred for varying durations ranging from **5 to 120 minutes,** followed by centrifugation and analysis via spectrophotometry to determine the concentration. The obtained results are compiled in the table and graphically represented in the figure.

Tableau 2 Results obtained from the adsorption isotherm

t(min)	5	30	60	90	120
abs	0.273	0.241	0.303	0.319	0.29
Ceq(mg/L)	6.707617	5.921376	7.444717	7.837838	7.125307
Q(mg/g)	-0.6769	-0.48034	-0.86118	-0.95946	-0.78133
T%	-67.6904	-48.0344	-86.1179	-95.9459	-78.1327

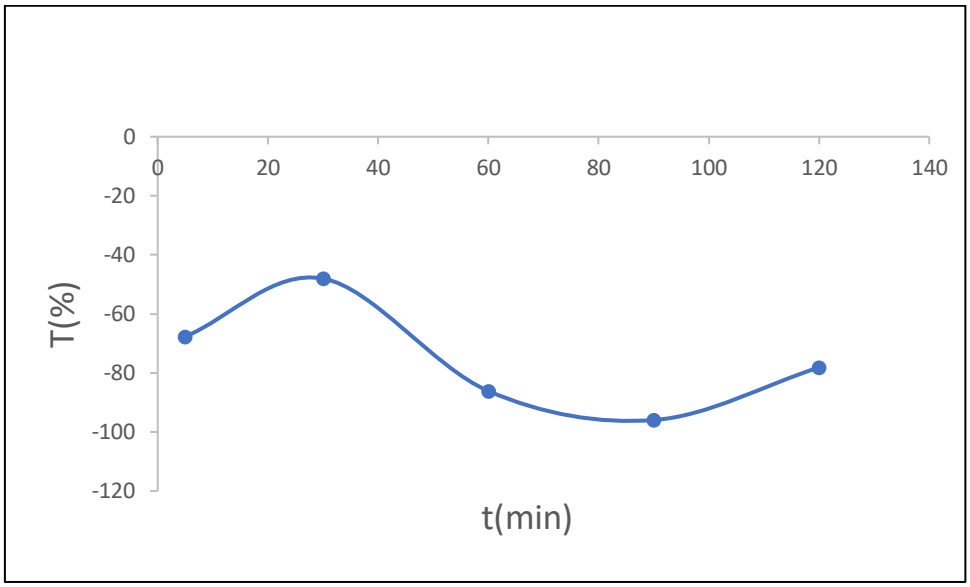


Figure 11 Evolution of the removal rate over time.

The graph (10) shows the time-dependent adsorption behavior of the adsorbate onto the adsorbent. It demonstrates a progressive increase in adsorption efficiency until reaching a plateau, indicative of adsorption equilibrium. Notably, this equilibrium state is achieved around the 30-minute mark, suggesting optimal adsorption-desorption dynamics.

Consequently, subsequent experiments will be conducted with a fixed 30-minute adsorbent-adsorbate contact time to ensure consistency and reliability in the experimental conditions.

IV.7.1 The Influence of Adsorbent Dosage on Adsorption

We introduce into a series of beakers, successively containing masses of 0.025; 0.05; 0.075; 0.125 grams of our adsorbent, and 25 ml of the solution of pharmaceutical product with a concentration of 4 mg/L at a temperature of 25°C. The mixture is stirred for 30 minutes, then centrifuged and analysed by a spectrophotometer. The results of these measurements are grouped in the table (3) and represented graphically in the figure (11).

Tableau 3 Influence of the dosage on the adsorption

m(g)	0.025	0.05	0.075	0.125
abs	0.106	0.173	0.18	0.339
Ceq(mg/L)	2.604423	4.250614	4.422604	8.329238
Q(mg/g)	0.000872	-0.00031	-0.00079	-0.01353
T(%)	34.88943	-6.26536	-10.5651	-108.231

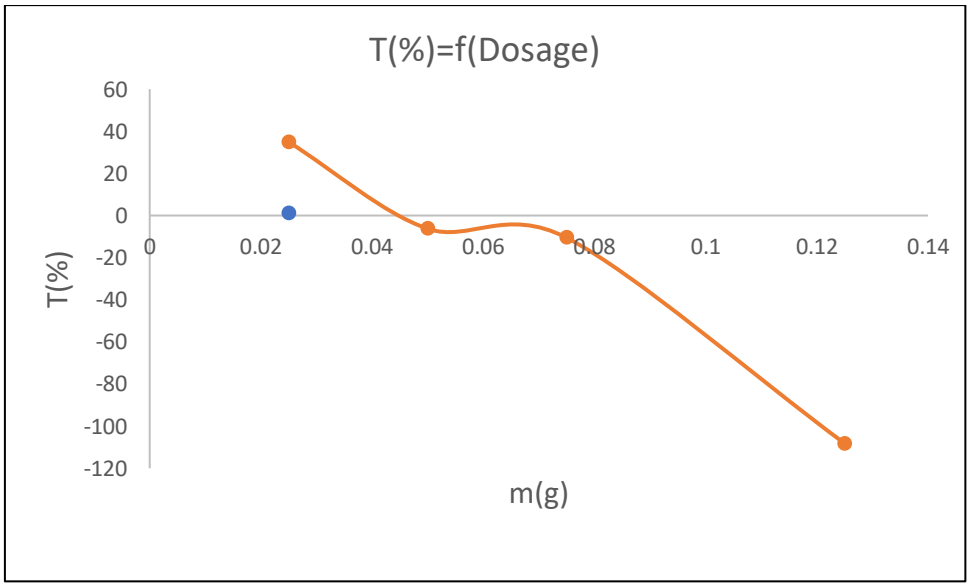


Figure 12 Variation of elimination rate based on dosage.

The graph shows that the maximum adsorption rate of the pharmaceutical product is reached at a charcoal dose of 0.025 g/L. Therefore, we will use this new dose for all subsequent adsorption experiments.

IV.8 The impact of solution pH on adsorption.

The pH plays a significant role in the adsorption process. Many studies have shown that pH is important for determining the adsorption potential of both cationic and anionic compounds.

In a series of flasks, we introduced 25 mL of a known solution of pharmaceutical product with a concentration of 4 mg/L at various pH levels. The pH levels were adjusted using either 0.1 N sodium hydroxide or 0.1 N hydrochloric acid to reach arbitrarily chosen pH values.

To each flask, we added 0.025 g of activated charcoal at a temperature of 25°C. The mixture was stirred for 1 hour and 30 minutes, then filtered and analysed using a spectrophotometer.

The results showing the variation of adsorption rate as a function of pH are compiled in the table (4) and depicted graphically in the figure (12).

pH	2	4	5.5	8	10
Abs	0.089	0.073	0.112	0.113	0.167
Ce q(mg/L)	2.186732	1.793612	2.751843	2.776413	4.103194
Q (mg/g)	0.001133	0.001379	0.00078	0.000765	-6.4E-05
T(%)	45.3317	55.15971	31.20393	30.58968	-2.57985

Tableau 4 Influence of pH on the adsorption.

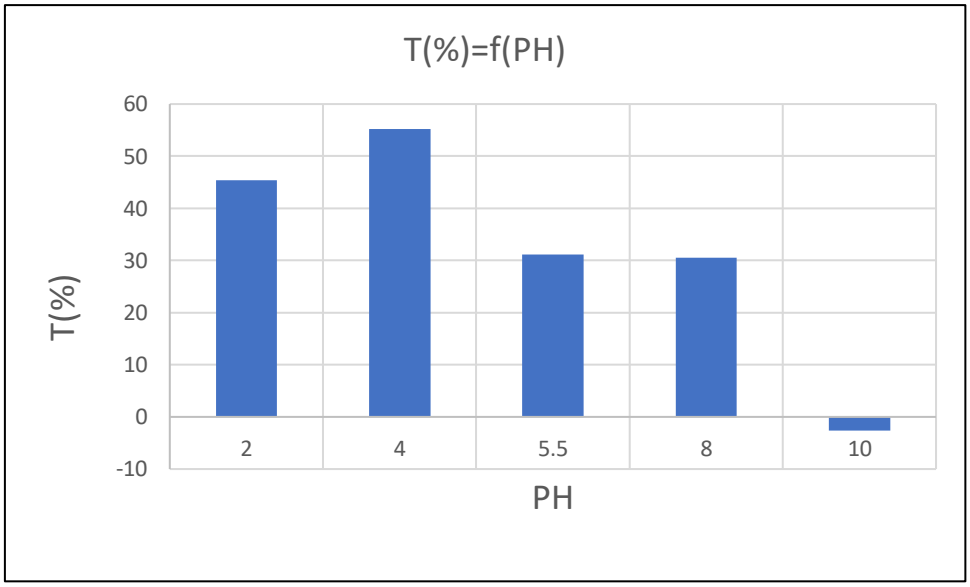


Figure 13 Elimination rate as a function of pH.

According to Figure (12), it is observed that the optimal elimination rate is generally obtained under acidic conditions, with the elimination rate reaching its maximum at a pH of 4. This pH will be established as the adsorption isotherm.

IV.9 Study of the influence of temperature on adsorption

To investigate the influence of temperature on the adsorption of the pharmaceutical product by our charcoal, we prepared flasks containing 25mL of pharmaceutical product solution with a concentration of 4 mg/L and pH 4. To each flask, we added 0.025g of activated

charcoal. These flasks were then placed in a water bath equipped with a thermostat allowing temperature adjustment (25°C, 30°C, 35°C 40°C). The mixture was stirred for 30 minutes, then centrifuged and analyzed by spectrophotometry.

The results of these measurements are recorded in the table (5) and depicted in the figure (13).

Tableau 5 The effect of temperature on adsorption

T(K)	298	303	308	313
abs	0.161	0.104	0.059	0.11
Ceq(mg/L)	3.955774	2.555283	1.449631	2.702703
Q(mg/g)	0.044226	1.444717	2.550369	1.297297
T(%)	1.105651	36.11794	63.75921	32.43243
Kd	0.01118	0.565385	1.759322	0.48
Kd	2.306236	116.6275	362.9129	99.0144
Kd	128.1114	6478.66	20159.81	5500.25
ln kd	4.8529	8.776269	9.911447	8.612549
1000/t	3.355705	3.30033	3.246753	3.194888
ΔG(KgJ/mol)	-12023.4	-22108.7	-25380.4	-22412.3

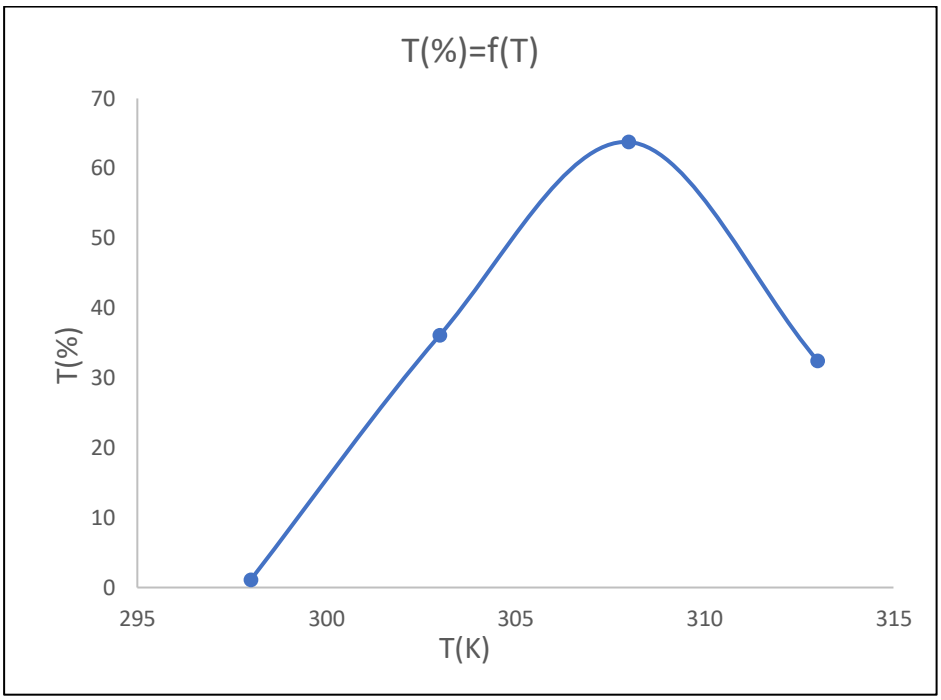


Figure 14 Elimination rate at different temperatures.

According to Figure (13), it is observed that the elimination rate of the pharmaceutical product increases initially and then decreases with increasing temperature.

To confirm these results, we calculated the thermodynamic parameters (ΔG, ΔH, and ΔS) related to the adsorption process and the distribution coefficient Kd.

The plot of Ln Kd as a function of 1000/T, for all samples, is represented in Figure (13).

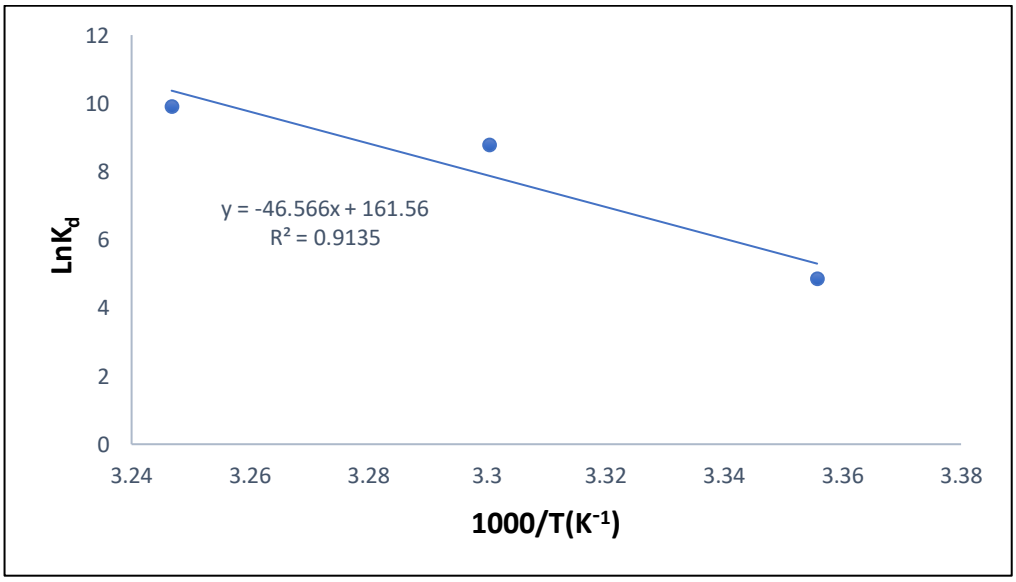


Figure 15 Variation of Ln K_d with 1/T.

From the plot in Figure (14), ΔH and ΔS are respectively deduced from the slope and the y-intercept.

The analysis of the thermodynamic parameters indicates that the adsorption process of methyl orange occurs through spontaneous and favourable reactions (ΔG < 0).

IV.10 Adsorption isotherm of the pharmaceutical product

In a series of beakers, we successively introduced the optimized quantity of adsorbent and 25 ml of known adsorbate solutions, with concentrations ranging between 1 and 8 mg/L. The mixture is agitated for a determined time (30 minutes), then filtered and analysed. Subsequently, the quantity adsorbed per mass of adsorbent is calculated. The values of this study are summarized in the table (06) and graphically represented in figures (14), (13), (12).

Tableau 6 Results obtained from the adsorption isotherm

C_0 (mg/L)	1	2	3	4	5	6	7	8
V(mL)	3.125	6.25	9.375	12.5	15.625	18.75	21.875	25
Abs	0.115	0.113	0.114	0.125	0.139	0.148	0.156	0.16
C_{eq}(mg/L	2.825553	2.776413	2.800983	3.071253	3.415233	3.636364	3.832924	3.931204
Q(mg/g)	-1.82555	-0.77641	0.199017	0.928747	1.584767	2.363636	3.167076	4.068796
T(%)	29.36118	30.58968	29.97543	23.21867	14.61916	9.090909	4.176904	1.719902
C_{eq} /Q	-1.54778	-3.57595	14.07407	3.306878	2.155039	1.538462	1.21024	0.966184
lnQ	/	/	-1.61436	-0.07392	0.460437	0.860201	1.152809	1.403347
ln C_{eq}	1.038704	1.02116	1.02997	1.122086	1.228246	1.290984	1.343628	1.368946

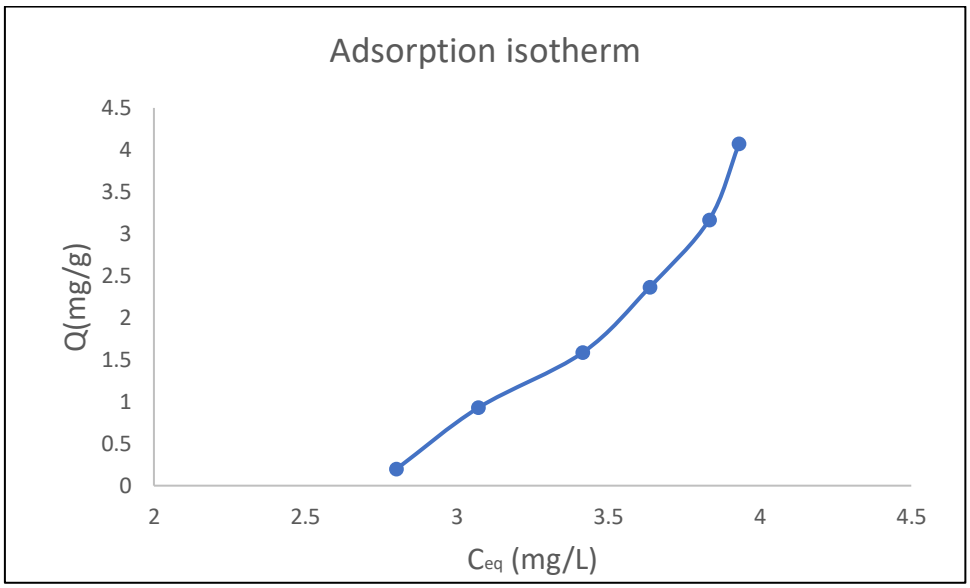


Figure 16 Adsorption isotherm of pharmaceutical product.

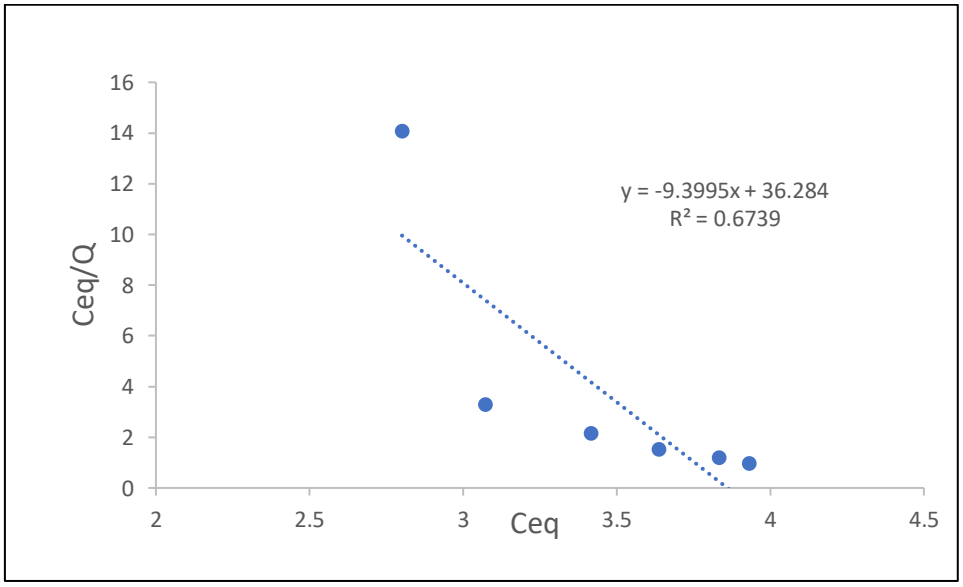


Figure 17 Application of the Langmuir model for the adsorption of ibuprofen.

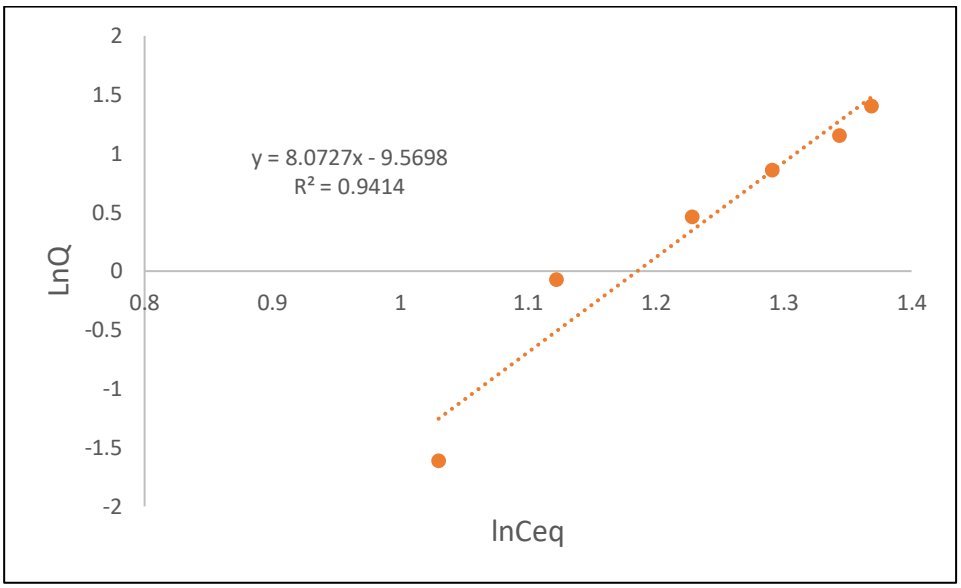


Figure 18 Application of the Freundlich model for the adsorption

From the results plotted in figures (15), (16) (17), and presented the table (6) we can conclude that:

- The adsorption capacity of the pharmaceutical product by the adsorbent increases remarkably with the increase in initial concentration.
- The adsorption isotherm presents a plateau indicating the saturation of surface sites and thus formation of the monolayer.
- The lines obtained with a good correlation coefficient show that under our experimental conditions, the adsorption of pharmaceutical product on activated carbon follows the two models: Langmuir, Freundlich in an acceptable manner in both figures: (16) and (17).
- The slope and the ordinate at the origin determine the maximum adsorption capacity b as well as the constant K for the studied adsorbent.

As a result of this, we obtained the following table:

adsorbent	equation	ΔG			ΔH(KJ/mole)	ΔS(KJ/mol.K)
		T1(303K)	T2(308K)	T3(313K)		
Activated carbon	y = -46.566x + 161.56	-406991.93	-413707.98	-420424.02	0.3871	1343.2

- Since the value of **ΔH(KJ/mole)** is positive, it suggests that the reaction is **endothermic**
- Since the value of **ΔS(KJ/mol.K)** is positive, it suggests an increase in entropy. This indicates that the products of the reaction or process are more **disordered** or have greater **randomness**.
- The negative value of **ΔG** indicates that the reaction is **spontaneous**. Spontaneous reactions occur without needing external energy input, and they proceed in the direction written under standard conditions.

CONCLUSION

Conclusion

The presence of pharmaceutical products for human or veterinary use in the environment has been known since the 70s. On the other hand, it is only in the last two decades that analytical techniques have made significant progress to make it possible to quantify their presence in water (effluent from domestic wastewater treatment plants, surface water, groundwater…....), Specially during the COVID-19 pandemic which has affected the whole world has generated unlimited quantities of medicinal waste, particularly antibiotics and anti-inflammatories which have been consumed abusively.

The purpose of this study was the elimination of pharmaceutical compounds through adsorption of powdered activated carbon. Therefore, the aim was to study several influencing parameters, in particular: pH, dosage of adsorbent, contact time, and temperature, to optimize the adsorption of pharmaceuticals on activated carbon.

A study of the effect of pH showed that at pH = 4, the maximum efficiency was 55.19%. The activated carbon rapidly retained product within the first few minutes of contact until reaching adsorption equilibrium after 30 min at a dose of 0.025 g/L.

The adsorption on activated carbon was modeled using the most common isotherms such as the Langmuir, Freundlich, and Temkin models.

The isotherm that best describes the different adsorption tests is that of Freundlich, with a correlation coefficient of 0.997.

The calculation of thermodynamic quantities confirmed that this reaction is a phenomenon exothermic ($\Delta H < 0$), the reaction is chemical in nature. The adsorption process is spontaneous, due to the negative value of the free enthalpy ($\Delta G < 0$).

Finally, we can conclude that activated carbon presents quite considerable performance concerning the elimination of pharmaceutical products. This study opens a wide door for future research for the application of these results on media real aqueous containing drug residues.

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