# REMOVAL OF NAPROXEN FROM AQUEOUS MATRICES USING OLIVE STONES BASED CARBON MATERIALS AS ADSORBENTS

Vinicius Ferreira de Assis Reis

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**Supervisors**

Prof. Ana Maria Alves Queiroz da Silva

Prof. Paulo Miguel Pereira Brito

Prof. Davi Zacarias de Souza

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*“Naquela mesa ele juntava a gente*

*E contava contente o que fez de manhã”*

*Nelson Gonçalves*

*Dedico este estudo inteiramente a Juracy Antônio de Assis*

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**Abstract**

Emerging micropollutants are substances found in the range of micrograms to nanograms per liter that are present in the various aqueous matrices of the world bringing adverse effects to the health of living beings. Naproxen, the object of study of this work, is a non-steroidal anti-inflammatory with analgesic and antipyretic properties commonly used in sore throats, muscle aching, tendinitis, synovitis, etc.

The present work aims to study the removal of naproxen through adsorption using activated charcoal from the olive pit. Therefore, this work is based on developing a method of quantification of naproxen using high performance liquid chromatography, prepare 4 types of adsorbents from the olive stone by changing the activation conditions, make the physicochemical characterization of the main adsorbent (Ads 3) and study the process of removal of naproxen with HPLC from the adsorption balance isotherms with the Langmuir and Freundlich models.

For the calibration straight line, concentrations of 1 to 10 ppm of naproxen were prepared and injected into the HPLC-Vis, returning a calibration line with linear characteristic with $R^2 = 0.9976$. From the 0.25 mm crushed olive stone, 4 types of adsorbents were prepared: without treatment (Ads 1), carbonized (Ads 2), chemically activated and charred (main adsorbent - Ads 3) and chemically activated and pyrolyzed (Ads 4). Adsorbent 3 has 0.52% ash content and 84% of its volume with micropores and presented good conditions to continue the analysis of the effect of temperature and pH on adsorption. The results pointed to Ads 3 as the best absorber ($q_m$ = 37.01 mg $g^{-1}$ ads) with high efficiency and better cost-benefit because it did not need to undergo pyrolysis although Ads 4 had very optimistic results ($q_m$ = 23.46 mg $g^{-1}$ ads), but lower than Ads 3. Ads 1 as expected was the least efficient although even without treatment it has adsorption capacity ($q_m$ = 22.46 mg $g^{-1}$ ads). The temperature and pH isotherms indicate that the temperature has little significant effect, where the temperature at 35°C obtained the best results of naproxen adsorption capacity ($q_m$ = 86.24 mg $g^{-1}$ ads) but not very different from 25°C ($q_m$ = 77.68 mg $g^{-1}$ ads). For pH, isotherms indicate that the natural pH of the solution (4.4) is the best option for the removal of naproxen ($q_m$ = 37.01 mg $g^{-1}$ ads), since the results for the pH increase were not favorable.

The isotherms adjusted with the Langmuir and Freundlich models have distinct characteristics: for temperature analyses the Freundlich model had better behavior with higher $R^2$, while for pH analysis and analysis of the 4 adsorbents the Langmuir models showed better fit. The difference in the use of the models is due to optimization throughout this work, in which the time and temperature studies were the precursors, and adjustments such as the ratio of naproxen mass with adsorbent mass were optimized in the comparison studies of pHs and adsorbents.

**Keyword:** Activated Carbon; Emerging micropollutants; Environment; High Performance Liquid Chromatography UV-Vis; Naproxen; Olive Stone.

**Resumo**

Micropoluentes emergentes são substâncias encontradas na faixa dos microgramas a nanogramas por litro que estão presentes nas diversas matrizes aquosas do mundo trazendo efeitos adversos a saúde dos seres vivos. O Naproxeno, objeto de estudo deste trabalho, é um anti-inflamatório não esteroidal com propriedades analgésicas e antipiréticas usado comumente em dores de gargantas, dores musculares, tendinites, sinovites, etc.

O presente trabalho tem como objetivo estudar a remoção do naproxeno através da adsorção utilizando carvão ativado a partir do caroço de azeitona. Portanto este trabalho baseia-se em desenvolver um método de quantificação do naproxeno utilizando cromatografia liquida de alta performance, preparar 4 tipos de adsorvente a partir do caroço de azeitona alterando as condições de ativação, fazer a caracterização físico-química do adsorvente principal (Ads 3) e estudar o processo de remoção do naproxeno com o HPLC a partir das isotermas de equilíbrio de adsorção com os modelos de Langmuir e Freundlich.

Para a reta de calibração foi preparando concentrações de 1 a 10 ppm de naproxeno e injetado no HPLC-Vis retornando uma reta de calibração com característica linear com $R^2 = 0,9976$. A partir do caroço de azeitona triturado a 0,25 mm foi preparado 4 tipos de adsorventes: sem tratamento (Ads 1), carbonizado (Ads 2), ativado quimicamente e carbonizado (adsorvente principal – Ads 3) e ativado quimicamente e pirolisado (Ads 4). O adsorvente 3, possui 0,52 % de teor de cinzas e 84% de seu volume com microporos apresentou boas condições para dar prosseguimento as análises do efeito da temperatura e pH na adsorção. Os resultados apontaram para o Ads 3 como melhor absorvente ($q_m$ = 37,01 mg $g^{-1}$ ads) com alta eficiência e melhor custo-benefício por não precisar de passar por pirólise embora o Ads 4 apresente resultados promissores ($q_m$ = 23,46 mg $g^{-1}$ ads), porém inferiores ao Ads 3. O Ads 1 como esperado foi o menos eficiente embora mesmo que sem tratamento possua capacidade de adsorção ($q_m$ = 22,46 mg $g^{-1}$ ads). Os ensaios de variação de temperatura e pH apontam que a temperatura tem efeito pouco significativo, onde a temperatura a 35°C possibilitou o melhor resultado de capacidade de adsorção de Naproxeno ($q_m$ = 86,24 mg $g^{-1}$ ads) porém não muito diferente de 25°C ($q_m$ = 77,68 mg $g^{-1}$ ads). Já para o pH as isotermas apontam que o pH natural da

solução (4,4) seja a melhor opção para a remoção do naproxeno ($q_m$ = 37,01 mg $g^{-1}$ ads), uma vez que os resultados para o aumento do pH não foram favoráveis.

As isotermas ajustadas com os modelos de Langmuir e Freundlich tem características distintas: para as análises de temperatura o modelo de Freundlich teve melhor comportamento com $R^2$ maior, enquanto para análise do pH e as análises dos 4 adsorventes os modelos de Langmuir apresentaram melhor ajuste. A diferença da utilização dos modelos é devido a otimização ao longo deste trabalho, em que os estudos de tempo e temperatura foram os precursores, e ajustes como a relação massa de naproxeno com massa do adsorvente foram otimizados nos estudos de comparação de pHs e adsorventes.

**Palavras-Chave:** Caroço de Azeitona; Carvão Ativado; Cromatografia Liquida de Alta Performance UV-Vis; Meio Ambiente; Naproxeno; Poluentes Emergentes.

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## LIST OF ABREVIATIONS

**ACN** Acetonitrile

**Ads 1** Adsorbent 1

**Ads 2** Adsorbent 2

**Ads 3** Adsorbent 3

**Ads 4** Adsorbent 4

**CV** Variation Coefficient

**EC** Emerging Contaminants

**ED** Endocrine Disrupter

**ETP** Effluent Treatment Plan

**EU** Europe Union

**DAD** Diode-Array Detection

**HPLC** High Performance Liquid Chromatography

**LLE** Liquid–Liquid Extraction

**LOD** Limit of Detection

**LOQ** Limit of Quantification

**NSAID** Non-Steroidal Anti-Inflammatory Drug

**OSAC** Olive Stone Activated Carbon

**PPCP** Pharmaceutical and Personal Care Product

**RP** Reverse Phase

**SPE** Solid Phase Extraction

**TFA** Trifluoroacetic Acid

**UV-Vis** Ultraviolet-Visible Spectroscopy

**WHO** World Health Organization

## NOMENCLATURE

| | |
|---|---|
| **A** | Absorbance |
| **C** | Concentration of the sample (mol/L) |
| **$C_e$** | Naproxen concentration in the aqueous solution (mg $L^{-1}$) |
| **$CV_m$** | Coefficient of Variation of Least Square Method |
| **ε** | Molar absorptivity coefficient of the sample |
| **I** | Intensity of transmitted light |
| **$I_0$** | Incident light intensity in the detection cell |
| **$K_F$** | Freundlich constant for a heterogeneous adsorbent t ($mg^{1-1/n}\ L^{1/n}\ g^{-1}$) |
| **$K_L$** | Langmuir isotherm constant L $g^{-1}$ |
| **l** | Length of the optical path in the detection window |
| $n$ | Amount of adjusted points |
| $n_F$ | The heterogeneity factor of Freundlich Equation |
| **r** | Product-moment correlation |
| **$q_e$** | Amount of adsorbed Naproxen (mg $g^{-1}$ adsorbent) |
| **$q_m$** | Maximum adsorption capacity (mg $g^{-1}$ adsorbent) |
| **$S_{BET}$** | BET method surface area ($m^2\ g^{-1}$) |
| **$S_{ext}$** | External surface area ($m^2\ g^{-1}$) |
| **$S_{Langmuir}$** | Langmuir specific surface area ($m^2\ g^{-1}$) |
| **$S_{mic}$** | Microporous surface área ($m^2\ g^{-1}$) |
| **Sm** | Standard deviation |
| **$S_{y/x}$** | Error associated to the slop and intercept |
| **$V_{mic}$** | Micropore Volume ($mm^3\ g^{-1}$) |
| **$V_{Total}$** | Total pore Volume ($mm^3\ g^{-1}$) |

| | |
|---|---|
| $\mathbf{W_{mic}}$ | Average pore witdth (nm) |
| $x$ | Analyte concentration |
| $\bar{x}$ | Mean analyte concentration |
| $xi$ | Analyte concentration |
| $y$ | Area of the peak |
| $\bar{y}$ | Mean area of peak |
| $yi$ | Area of the peak |
| $\hat{yi}$ | Values estimated with the regression line equation |

## LIST OF EQUATIONS

# 1. MOTIVATION AND OBJECTIVES

## 1.1. Introduction

It was inevitable that the growth of industrial production and the rise of technology caused by the first industrial revolution changed the entire way of life and consumption of modern society (Pott and Estrela, 2017). With the development of new technologies that increased human longevity, medicine had to keep up with the boom of the world population. The portal *Our World in Data* (2013) shows that from early 19$^{th}$ century until today, the world population has increased almost eight times from its first billion to approximately 7.7 billion inhabitants, bringing a series of consequences such as a great increase in the use of natural resources and consequently, waste generation (Roser *et al*., 2013).

Water is a renewable natural resource and an essential for the survival of the mankind. This resource is present in several society sectors, such as, the domestic sector, medicine, agriculture, industries, energy production, and pharmacology (Stefanakis e Becker, 2019). It is mandatory that water resources present adequate physicochemical conditions for the maintenance of life and be free of substances with potential harmful effects on the health of living beings (Braga *et al*., 2005).

The actual technology, allows us to understand that compounds that were not normally found in nature, can now be quantified in aqueous matrices. These pollutants are named as emerging contaminants (EC) and when found in the concentration range of nanograms up to micrograms per liter can be also named as emerging micropollutants. These pollutants, even at very low concentrations have an enormous effect on the health of living beings (Viali, 2014). Emerging contaminants are released from various sources: direct discharge of effluent from pharmaceutical industries, chemical industries, hospitals, domestic wastewater, mining, and so forth and nonpoint sources like agricultural run-off (SyedSaquib *et al*., 2021).

Pharmaceutical drugs are emerging micropollutants that are produced to have great effects over a long period of time using a small quantity (Nunes, 2010). A practical example is naproxen that is normally marketed with pills of approximately 500g to combat effects on an adult body over 50 kg i.e. 25000 times larger than the pill.

Pharmaceutical drugs can be divided in different therapeutic classes: analgesics, anti-inflammatory drugs, antibiotics, antiepileptics, synthetic steroids, among others (Pinto, 2011).

The removal of micropollutants from contaminated soils or aqueous matrices can be done using natural or synthetic adsorbents, i.e., introducing a species or material capable of chemically interacting with various functional groups of unwanted substances such as toxic metals (Pietrobelli, 2007; Rodrigues *et al*., 2006).

The actual number of published studies on the removal of emerging pollutants it is scarce since, until very recently, these compounds were not considered toxic to humans due to the limitations in detection and quantification levels of the past instrumental methods of analysis. As a result, legislation on the monitoring and control of micropollutants in aqueous matrices is advancing in slow steps. Nevertheless, it is possible to see the need to expand the range of studies to assist both in the development of a method to quantify, monitor and mechanisms to remove the pollutant like activated carbon from olive stones to remove naproxen, as well as to develop legislation that can define limits for the concentration found of each one of these pollutants in aqueous matrices.

## 1.2. Objectives

### 1.2.1. Main Objective

The main objective of this work is to study the removal of naproxen by adsorption using different types of activated carbons obtained from olive stones.

### 1.2.2. Specific Objectives

- To develop a quantification method of naproxen using high performance liquid chromatography (HPLC).

- To prepare 4 types of activated carbons from olive stones changing the operational conditions.
- To perform the physicochemical characterization of the main adsorbent.
- To study the adsorption removal process for each material by the experimental measuring of the equilibrium adsorption isotherms.

# 2. LITERATURE REVIEW

## 2.1. Water Resources

There is no life form of our biosphere that can survive without water. Even the toughest organism needs water for maintaining its metabolic activities and energy production. In addition to being applied directly in the vital functions of the human being, water is a resource that indirectly is present in the life of the human being. For example, to produce one kilogram of meat, cotton or rice, thousands of liters of fresh water are required (Bard and Cann, 2011). In the energy sector, water represents a large energy matrix with a renewable source. In the case of Brazil, hydraulic energy represents about 12.6% of the country's energy matrix with approximately 65% supplying the Brazilian electricity matrix (Empresa de Pesquisa Energética, 2021). Itaipu, which is the largest binational hydroelectric power plant with origin in Brazil and Paraguay, supplied in 2020 approximately 76 GWh for both countries (Itaipu Binacional, 2020). However, only 3% of this water is suitable for the consumption of living beings, in which only a quarter of this percentage is usable, since the other three quarters is found in glaciers. The other 97% of the planet's waters are salty and inappropriate for the consumption of living beings (Bard and Cann, 2011; Braga *et al*., 2005).

### 2.1.1. Water Quality

Large urban centers, industrial centers and irrigation areas require intensely large amounts of water in which they often exceed the supply of local water, due to scarcity or pollution of water bodies affecting the quality of local water (Braga *et al*., 2005). Therefore, it is important to maintain water quality at acceptable levels for consumption in order to be safe for the health of living beings in the long, medium, and short terms. According to the World Health Organization (WHO) 1.9 million of the deaths in 2016 could have been prevented if there was better water quality and basic sanitation demonstrating the importance of maintaining water quality (World Health Organization, 2019).

### 2.1.2. Water Pollution

The most commonly water pollution observed in the world is usually has a chemical or biological nature. Additionally, there are few areas in the world that are not affected by some type of pollution in aqueous matrices (Bard and Cann, 2011; Boelee *et al*., 2019). The contact and ingestion of contaminated water can bring several harmful effects to the health of living beings and is greatly associated with diseases that affect the entire population of the world (Amin *et al.*, 2014).

Biological pollution of water occurs when there are pathogenic microorganisms present in water bodies, these organisms are usually originated from industrial activities and domestic sewage. Microbiological pollution can be expressed with the appearance of pathogenic bacteria, viruses, protozoa, fungi among others. (Boelee *et al.,* 2019).

The characterization of chemical pollution of water is the result of the persistence and reach of organic and inorganic molecules, toxic and non-toxic (Cruz *et al*, 2015). Considering the law of mass conservation together with the first and second law of thermodynamics we can justify the identification of chemicals in animals and living beings through biological amplification, explaining, for example, how mercury that is used for gold mining in rivers and lakes passes through the whole food chain until it reaches the final consumer (Braga *et al*., 2005).

## 2.2. Emerging pollutants

Among the chemical pollutants that are released into water bodies are also present some emerging pollutants. These chemical substances are identified in different environmental matrices and may have a potential, real or expected damage to the health of living beings and to their ecosystem by the partial absence of technologies that allow their identification, thus generating a difficulty in their standardization. Its main source is the domestic, commercial, and industrial sewage sectors (Fonseca, 2013). Since almost of them are not biodegradable, the conventional

water treatments cannot eliminate these pollutants, resulting in an increase on the amount of pollutant reaching the user through bioaccumulation over time (Mostafalou, 2016). When these pollutants are found at low concentrations on the microgram levels (µg/L) or nanogram levels (ng/L), they can be considered as emerging micropollutants. The concern with this tiny category is due to being persistent and reach even in low amounts where they can cause serious damage to organisms that have had contact (Viali, 2014).

### 2.2.1. Types of emerging micropollutants

Emerging micropollutants can be divided into pharmaceutical and personal care products (PPCPs), persistent organic pollutants, endocrine disrupting compounds, surfactants, among others. Their sources can be found in several sectors, such as: pharmaceuticals, personal care products, cleaning products, pesticides, illicit drugs, among others (Nunes, 2010; Pinto, 2011; Santana, 2013). Pharmaceutical and personal care products, which contains at least one active principle, are products that are receiving great attention due to the world's high consumption and due to the bioaccumulation and resistance of microorganisms to drugs, these PPCPs can expose living beings to great risks with the aquatic ecosystem (SyedSaquib *et al*., 2021).

When a pollutant can inhibit or modify the function of human and/or animal natural hormones, it is classified as Endocrine Disruptors (ED). This class of compounds represents a great health danger since they can be active even in very small concentrations (up to µg/L) and may change the behavior, reproduction, or development of microorganisms (Mostafalou, 2016; Queiroz, 2011)

PPCPs are characterized by a huge part being present in aqueous matrices due to their solubility with water where they can be found in septic tanks, sewers, and landfill leaches (Queiroz, 2011). The PPCPs are released into the environment through excretion or improper disposal of medicine or pharmaceutical scans (Valcárcel *et al.,* 2011). These products include medicines, fragrances or perfumes, disinfectants, sunscreens, X-ray residues, illicit drugs, veterinary medicines, cosmetics, among others (Ebele *et al.*, 2017; Wang and Wang, 2016; Katsumata, 2014).

### 2.2.2. Legislation

Since emerging micropollutants are found, in most cases, at very low concentrations and because of the difficulty in their detection by the old analytical methods and equipment, there are few regulations about these substances that have not been previously identified. This directly affects the regulatory parameters that these substances should be found in the nature (Viali, 2014). Even with the deficiency of the methods to identify the micropollutants, there are rather some guidelines that put these compounds on a watch list for future regulation, or sets expected maximum values.

In Brazil, as example, according to Health Ordinance No. 2,914 of December 12, 2011, which governs guidelines for water quality, a table of chemical substances and their maximum permitted values is presented in Annex VII. However, the table is not subdivided into drugs in isolation and there is only a generalization of some chemicals that can be found in the drugs, which makes it difficult to set a standard for the values of each drug (Ministério da Saúde, 2011).

Concerning to water policy from EU, the Implementing Decision 2015/495 of 20 March 2015 presents a watchlist for 10 chemicals that should be monitored for future contributions. This Decision brings with it, a table that in addition to compounds such as diclofenac, 17-alpha-ethinilestradiol (EE2), 17-beta-estradiol (E2), estrone (E1) among others, also has the method of analysis of the compound and the values of the maximum detection limit of each substance (Jornal Oficial da União Europeia , 2015).

In the European Union, the Directive 2013/39/EU which is transposed to Portugal through Decree Law 2018 of 2015, da establishes a watchlist for 45 priority compounds in the field of water policy. These compounds presented are under surveillance because they indicate a risk to aquatic fauna. And even on observation, the monitoring data is still insufficient to declare some standardization (Jornal Oficial da União Europeia , 2013).

### 2.2.3. Pharmaceuticals and Personal Care Products

PPCPs are a group of environmental micropollutants that have only been perceived due to the development of new and more sensitive analytical technologies (Duca and Boldescu, 2009). This pollutant class is designed to be persistent due to its pharmacological nature, which directly reflects in its resistance to degradation and consequently its longevity. Drugs are administered topically, i.e., inhalation and application on the skin; internally, by oral or parenterally administration, and through injections and infusions (Tambosi, 2008).

With the increase of the population and with the growing search for care with vanity and health, the human being desires more and more consumption of PPCPs. Following this logic, PPCPs can be found in the soil in landfills and near the household waste when they are discarded because they are no longer useful to the consumer or because they are outside the expiration date. When ingested, the drugs can follow two paths: the drug can be excreted without being transformed by the body, or they can be metabolized by biochemical reactions in which they can be excreted by urine or bile. (Rivera-Utrilla *et al.*, 2013). These excretes that, in turn, are mostly intended for sewage treatment contaminate the wastewater with the drug that are stable in the external environment and metabolized only by some living being and initiating the bioaccumulation process (Ribeiro *et al.*, 2016).

For the identification of these substances, the development of more accurate analytical methods for the study of micropollutants is a reality that is increasingly present. Research already finds evidence of contamination of water bodies by drugs in which, combined with their high pharmacological potential, leads the body that meet these drugs to suffer long-term adverse reactions (Amin *et al.*, 2014; Montagner e Jardim, 2011). With these analytical methods developed it is possible to start studies of methods, mechanisms and materials that help in the removal of these pollutants.

### 2.2.4. Naproxen

Naproxen is a non-steroidal anti-inflammatory with analgesic and antipyretic properties typically used in sore throats, myalgia (muscle pain), bursitis, tendinitis, synovitis, tenosynovitis, low back pain, arthralgia, leg pain, tennis elbow, and various other types of inflammations (See Fig. 1 and Table 1).

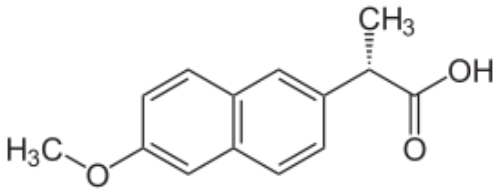


**Figure 1** – Naproxen structural formula.

This drug is sold in doses of 250 mg, 275 mg, 500 mg and 550 mg and are found on the market has brand names such as Naprosyn, Naprox, Naxotec, Naproflen, Flanax and Napronax (Ministério da Saúde, 2015). Due to its long half-life (approximately 13 hours), rapid absorption and since does not require a medical prescription, the drug is one of the most popular NSAIDs for more than 40 years (Wojcieszyńska and Guzik, 2020). In 2019, in the USA there are records of 11,762,233 medical prescriptions with naproxen (ClinCalc, 2019). A wrong ingestion of this drug can lead to several adverse effects such as: getting dizzy, headaches, bruising, allergic reactions, and gastrointestinal disorders (Popov, 2020).

**Table 1** - Properties of Naproxen (National Center for Biotechnology Information, 2022).

| | |
|---|---|
| **Formula** | $C_{14}H_{14}O_3$ |
| **Molar mass (g/mol)** | 230.26 |
| **Visual appearance** | White powder |
| **Solubility in water (mg/L)** | 15.9 |
| **pKa** | 4.15 |

### 2.2.4.1. Natural Degradation of Naproxen

The degradation of naproxen is the subject of studies to better understand its physicochemical characteristics and act on its remediation. Naproxen demonstrates a low natural degradation capacity representing great stability of molecules in aquatic environment resulting in a constant concentration over a period of 24 weeks (Borges *et al.*, 2009). Wojcieszyńska and Guzik (2020) also show that among non-steroidal drugs such as ibuprofen, the degradation of naproxen is lower, evidencing the need to search for microbiological alternatives for its degradation.

## 2.2.5. Analytical methodologies for Naproxen quantification

To quantify the concentration of Naproxen, in 2019, Ana Nemoto selected some analytical methods found in the literature for various drugs, as it can be observed in Table 2. In this same work, Nemoto (2019) optimized an HPLC analytical method using a mobile phase composition of 60% acetonitrile and 40% of ultrapure water containing 0.01% of trifluoroacetic acid. The naproxen retention time of 3.403 min, was obtained using a Nucleosil C18 analytical column and the DAD detector set at 224 nm.

**Table 2** – Analytical methodology for naproxen determination.

| Matrix | Extraction Method | Quantification Method | LOQ (ppb) | Concentração média (ppb) | Reference |
|---|---|---|---|---|---|
| Affluent ETP | SPE (Oasis MAX 6cc 150 mg) | HPLC-DAD | 0.4 | 17.5 | Madikizela and Chimuka, 2017 |
| Effluent ETP | SPE (Oasis MAX 6cc 150 mg) | HPLC-DAD | 0.4 | 0.85 | Madikizela and Chimuka, 2017 |
| Hospital Effluent | LLE (Clorofórmio) | HPLC-UV | 8 | 119 | Ashfaq *et al*., 2017 |

### 2.2.6. Naproxen removal process

Two viable options for the removal of naproxen are degradation and adsorption. There are several studies of the degradation of a drug, which includes methods, such as photocatalytic processes, ozonation and biodegradation (Besbes *et al.*, 2018). For naproxen, ozonation combined with biodegradation was efficient at concentrations of 22 to 67 µg/L using *Cyperus ligularis plants* (Lancheros *et al.*, 2019).

The adsorptive process is a treatment that results in a pollutant adsorbed on a porous surface. The most common adsorption methods use adsorbents, such as activated carbon, graphite oxide, water soluble proteins and biological waste.

#### 2.2.6.1. Activated Carbon

Commonly used in the treatment of waters, activated carbon is a porous substance that is produced on an industrial scale from several different organic materials such as hard coal, coal coke, petroleum coke, coconut shell and other materials. Several organic wastes, such as nutshells, bamboo, algae, sugarcane, and bark can be processed to obtain adsorbents promoting the recycling of food waste. Activated carbon also acts on the removal of PPCPs and is obtained in the powder and granular forms (Krzeminski *et al*., 2019; Wang and Wang, 2016). Today, there are many techniques to activate an absorbent like physical and chemical processes. The chemical activation is responsible to interact the activating agent ($H_3PO_4$, $ZnCl_2$, NaOH, KOH, $NH_4Cl$, $K_2CO_3$, and others) with the organic matter. To activate the solid is necessary to open the pores of the closed carbon material. This can be done thermochemically (pre-impregnated with a solution of zinc chloride, potassium carbonate or some other compounds, and heated without air), or by treatment with pyrolysis, i.e., superheated nitrogen, steam or carbon dioxide or a mixture of the last two at a temperature of 800 to 850 °C. (Krzeminski *et al*., 2019; Wang and Wang, 2016).

### 2.2.7. High-Performance Liquid Chromatography

To identify and quantify a compound, liquid chromatography separation process can be used. The response obtained by the equipment is due to the time difference between the interaction of the analyses with the mobile phase that occurs through polar interactions in the adsorption column that is filled with the moving phase causing a longer delay in the time to cross it (Madikizela and Chimuka, 2017; Viali, 2014; Queiroz, 2011). Figure 2 Illustrates with a flowchart the operation of an HPLC equipment:

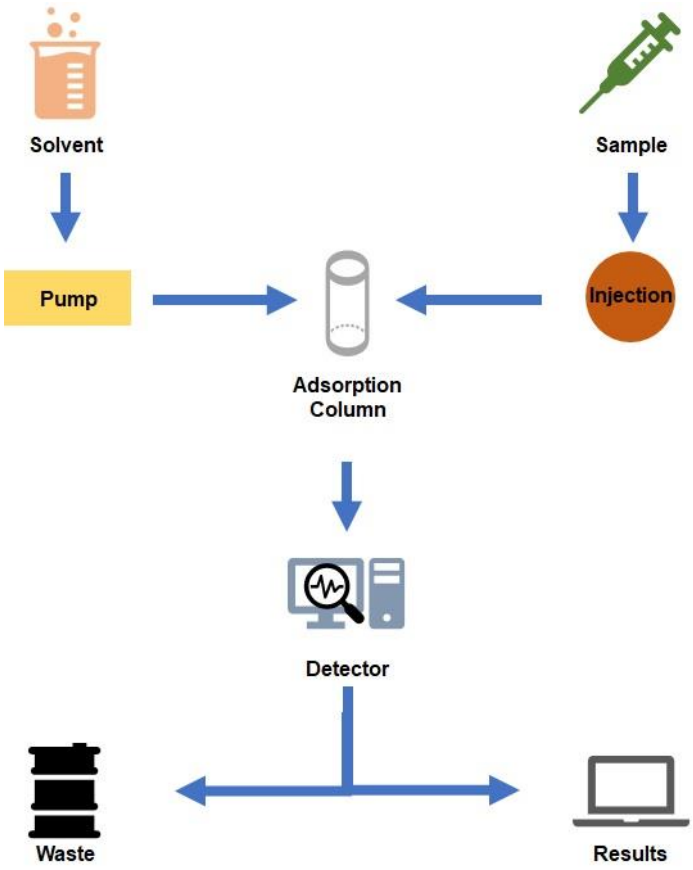


**Figure 2** - Operation of an HPLC equipment.

In general, reverse phase - liquid chromatography (RP-HPLC) is used to analyze pharmaceutical drugs. This type of chromatography mode employs a less

polar column than the mobile phase, which is usually a mixture of acetonitrile with water. The main used stationary phases are based on silica support modified with a carbon chain, such as C8 or C18 (Nemoto, 2019; Caldas, 2009; Kurz, 2007). Due to the short analysis time compared to normal phase chromatography, this type of mechanism is suitable for polar compounds. This is because, for the same set of experimental conditions, the retention of the compound in the RP-HPLC depends on its polarity. Molecules with higher polarity tend to interact more with the stationary phase, thus increasing their retention time, while molecules with lower polarity interact more with the mobile phase than the stationary phase and have shorter retention time. (Caldas, 2009; Kurz, 2007)

### 2.2.8. Ultraviolet-Visible Detector

The ultraviolet-visible detector can measure the absorption of light emitted from the analyte using one previously selected wavelength ranging from ultraviolet and visible light regions. The detection of the analyte through the UV detector takes place through the concentration in relation to the range of light transmitted by the detector cell (Hartmann, 2017). This relationship is explained through the Beer-Lambert Law:

$$A = log\left(\frac{I_0}{I}\right) = \varepsilon \times C \times l \quad (1)$$

$I_0$ = Incident light intensity in the detection cell;

I = Intensity of transmitted light;

**ε** = Molar absorptivity coefficient of the sample;

l = Length of the optical path in the detection window;

C = Concentration of the sample (mol/L);

A = Absorbance

This type of detector can operate with detection limits in the order of nanogram to picogram per liter, being much less influenced by temperature variations and composition of the mobile phase compared to fluorescence detectors. The absorption of light by molecules in the range between 190 and 700 nm depends on the characteristics of the molecules is usually in the form of bands (Hartmann, 2017).

## 2.3. Tools for analytical quantification and adsorption balance modeling

The validation of the analytical model expresses the efficiency of the process so that the results are reliable given several parameters that will be equated (Queiroz F. B., 2011).

### 2.3.1. Calibration curve and linearity

The calibration curve is an extremely important instrument to understand the behavior of the analyses in various concentrations. The graph is represented by two axes: Standard analyte solution (X axis) and equipment response value (Y Axis) and that with the least square's method obtains a regression line of the data obtained if the experimental data are linear equation (2) (Nemoto, 2019).

$$y = ax + b \quad (2)$$

$a$ = slope of the straight line,

$b$ = graph interception on y-axis

$y$ = area of the peak

$x$ = is the analyte concentration.

The Minimum Squares Method are based on two main equations:

$$b = \frac{\sum_i \{(x_i - \bar{x})(y_i - \bar{y})\}}{\sum_i (x_i - \bar{x})^2} \quad (3)$$

$$a = \bar{y} - b.\bar{x} \quad (4)$$

b = coefficient that gives the slope of least squares line,

$a$ = coefficient that intercept of least squares lines

$\bar{x}$ = mean analyte concentration

$\bar{y}$ = mean area of peak

$xi$ = concentration

$yi$ = area

To estimate how well the behavior was the experimental data fit into a line. The closer the correlation coefficient is to the unit, the better the description of the experimental data by this model (Nemoto, 2019).

$$r = \frac{\sum_i \{(x_i - \bar{x})(y_i - \bar{y})\}}{\sqrt{\sum_i (x_i - \bar{x})^2 \sum_i (y_i - \bar{y})^2}} \quad (5)$$

r = product-moment correlation

The error ($S_{y/x}$) associated with the slope of the line and the interception of the linear regression is calculated through the equation (5):

$$s_{y/x} = \left\{ \frac{\sum_i (y_i - \hat{y}_i)^2}{n-2} \right\}^{1/2}$$

(6)

$n$ = amount of adjusted points

$\hat{yi}$ = values estimated with the regression line equation

$S_{y/x}$ = Error associated to the slop and intercept

The standard deviation of terms *a* and *b* following equation 6 and 7, respectively:

$$s_b = \frac{s_{y/x}}{\{\sum_i (x_i - \bar{x})^2\}^{1/2}}$$

(7)

$$s_a = s_{y/x} \left\{ \frac{\sum_i x_i^2}{n \sum_i (x_i - \bar{x})^2} \right\}^{1/2}$$

(8)

As criterion for elimination of Outliers is when ($y_i - \hat{y}_i$) is greater than twice the result of $S_{yx}$.

The Standard Deviation of the Method and the Coefficient of Variation can be calculated according to equations 9 and 10:

$$S_m = \frac{S_{y/x}}{b}$$

(9)

$$CV_m = \frac{S_m}{\bar{x}} \times 100$$

( 10 )

### 2.3.2. Limit of detection (LOD) and limit of quantification (LOQ)

Detection limit is lower amount that analysis can be detected while quantification limit is the lowest value that analysis can be measured under established experimental conditions. (Nemoto, 2019). For this work was considered the lowest value of the concentration range as the LOQ, while for the LOD was obtained with the following equation:

$$LOD = \frac{3 \times LOQ}{10}$$

( 11 )

## 2.4. Adsorption Models

An adsorption isotherm is a mathematical equation used to quantitatively describe the adsorption of a solute by a solid at a constant temperature. An adsorption isotherm shows the amount of a given solute adsorbed by an adsorption surface as a function of the equilibrium concentration of the solute. In principle, the technique used to generate adsorption data is very simple because a known amount of solute is added to a system containing a known amount of adsorbent (Alleoni *et al.*, 1998).

### 2.4.1. Langmuir

The Langmuir equation originally used to describe the adsorption of a solid to a gas is based on three assumptions: (a) the adsorption surface is homogeneous, i.e., adsorption is constant and independent of the degree of surface coverage; (b) adsorption occurs in a specific location, does not interact with solute molecules; (c)

adsorption is maximized when the monolayer completely covers the adsorbent surface (Alleoni *et al.*, 1998). The following equation is based on the original Langmuir equation for the removal of naproxen from this study:

$$q_e = \frac{q_m \times K_L \times C_e}{1 + (K_L \times C_e)}$$

*( 12 )*

$q_e$ = Amount of adsorbed Naproxen (mg $g^{-1}$ adsorbent);

$C_e$ = Naproxen concentration in the aqueous solution (mg $L^{-1}$);

$q_m$ = Maximum adsorption capacity (mg $g^{-1}$ adsorbent);

$K_L$ = Langmuir isotherm constant L $g^{-1}$.

### 2.4.2. Freundlich

The Freundlich equation shows that the adsorption energy decreases logarithmically when the surface is covered with solute, unlike the Langmuir equation. The Freundlich model can be derived theoretically considering that the decrease in adsorption energy with increased surface solute coverage is due to the heterogeneity of the surface (Bohn *et al.*, 1979)

$$q_e = K_F \times (C_e)^{\frac{1}{n_F}}$$

*( 13 )*

$q_e$ = Amount of adsorbed metal (g $g^{-1}$ adsorbent);

$C_e$ = Naproxen concentration in the equilibrium solution (mg $L^{-1}$);

$K_F$ = Freundlich constant for a heterogeneous adsorbent t ($mg^{1-1/n}$ $L^{1/n}$ $g^{-1}$)

$n_F$ = The heterogeneity factor of Freundlich Equation

# 3. TECHNICAL DESCRIPTION AND PROCEDURES

The experimental methodology includes:

- Determination of a HPLC-DAD calibration curve for naproxen quantification.
- Preparation of 4 types of adsorbents obtained from olive stones.
- Adsorption equilibrium studies.

## 3.1. Chemicals and adsorbent

The present work used the following chemicals:

- Acetonitrile for HPLC plus Gradient
- Trifluoroacetic acid (TFA)
- Ultrapure Water
- Distillated Water
- Ethanol
- Methanol
- $H_2SO_4$ 10%
- KOH 0.1 M
- Pure naproxen [*(S)-(+)-2-(Methoxy-2-naphthyl)-propionic acid*] 99%

And the following adsorbent based on olive stone 0.25 mm:

- Without activation
- Carbonized (550°C)
- Acid activation and carbonized (550°C + $H_2SO_4$)
- Acid activation and pyrolised (550°C + $H_2SO_4$ + 800°C)

## 3.2. Equipment

The following equipment was used in this work:

- HPLC-UVis Varian ProStar
- Column for HPLC Inertsil 5 150 X 02.1 mm
- Ultra-centrifugal mill RETSCH ZM 200
- Analytical Balance ADA 210/c
- HANNA edge pH meter
- M6 CAT Stirrer
- Thermolyne Furnace 6000 Mufla
- Shaker Incubator Shell Lab
- Stove Scientific Series 9000
- Syringe Filter 0.45 mm
- Funnel Filter at 1
- Water System, Ultrapure, Millipore® Synergy
- Quantachrome Nova Touch Pore Size Analyzer
- Glass Syringe for HPLC 100 μm

### 3.3. HPLC-DAD calibration curve for naproxen quantification

Based on Nemoto (2019) previous work, the initial operation parameters were selected. For mobile phase composition a mixture of 60% of acetonitrile, 40% of ultrapure water and 0.01% of trifluoracetic acid (%v/v/v) was used. The UV-vis detector was set at 224 nm, the flow-rate was 1 mL/min and the injection volume was 20 μL. The first experimental step for the determination of the HPLC calibration curve, it was the preparation of a naproxen stock solution with a concentration of 40 mg/L using ultrapure water as solvent. From this stock solution 11 standard solutions were prepared from 10 mg/L to 1 mg/L. The dilutions were made using a micropipette and 5 and 10 volumetric flasks.

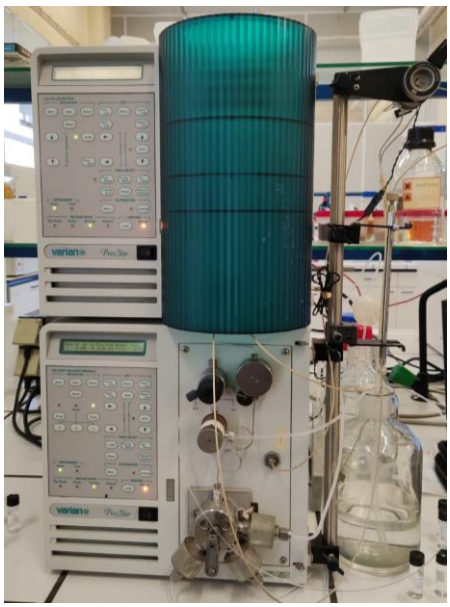

**Figure 3 –** HPLC-UV Vis Varian Pro Star.

### 3.4. Preparation and activation of the adsorbent

The four types of adsorbents quoted above were prepared as follows:

- Without treatment – Ads 1
- Carbonized (550°C) – Ads 2
  Acid activation and carbonized (550°C + H2SO4) – Ads 3
- Acid activation and pyrolised (550°C + H2SO4 + 800°C) – Ads 4

#### 3.4.1. Without treatment

The preparation of this adsorbent consisted of the granulated olive stone crushed to 0.25 mm in an ultra-centrifugal mill RETSCH ZM 200. Approximately 600 grams of adsorbent were prepared and allocated in a clean bottle.

### 3.4.2. Carbonized (550°C)

With the olive stone crushed in the previous step, it was possible to carbonize the adsorbent in a muffle for 1h30min at a temperature of 550°C. The mass of 2 crucibles was annotated and filled with approximately 30 grams in each and measured the mass on an analytical scale. By placing in the muffle, the crucibles were capped to avoid the volatilization of carbon, thus obtaining the best yield.

### 3.4.3. Acid activation and carbonized (550°C + $H_2SO_4$)

The adsorbent that will be used in adsorption tests is the powdered olive stone (0.25 mm) that was ground in an ultra-centrifugal mill RETSCH ZM 200 in the first step.

With the powdered pit it is necessary to prepare a solution of 10% of $H_2SO_4$. In a ratio 1:3 put for every 50 grams of lump, 150 ml of acid in a beaker of 600 mL and leave in constant agitation for 24 hours. After this time, it is necessary to wash the lump. For every 50 grams of stone use a total of one liter of distilled water divided into 5 steps (each step with 200 mL of distilled water). At each stage you will add 200 mL of distilled water in the 600 mL beaker that had the stone solution with acid and left in agitation for 20 minutes. After stirring let the lump decant enough to separate the solution in two phases and pass the liquid carefully into a Funnel Filter No. 1, and then with a spatula collect the lump that was retained in the filter and put back into the beaker.

After washing 5 times with the above step, the pit should be at rest for 24 hours to go to greenhouse at 110 °C for another 24h. After the stove the adsorbent is ready to be burned at 550°C in a Muffle for 1h30min. For this will be annotated the mass of 6 Crucibles and add 200g of adsorbent distributed in all of them. When carrying in Muffle, the crucibles with adsorbents should be capped for better performance of the burning process.

### 3.4.4. Acid activation and pyrolised (550°C + $H_2SO_4$ + 800°C)

The pyrolysed adsorbent was the olive stone already previously activated at 550°C and $H_2SO_4$ 10%. So, this previously activated carbon was burned at 800°C for four hours in an inert environment with Nitrogen gas.

## 3.5. Physicochemical characterization of the adsorbent 3

The textural properties of the materials were determined from $N_2$ adsorption–desorption isotherms at 77 K, obtained in a Quantachrome NOVATOUCH XL 4 adsorption analyzer. The degasification of the materials was conducted at 120 ºC during 16 h and then BET, Langmuir specific surface area ($S_{BET}$, $S_{Langmuir}$) were determined using BET and Langmuir methods. The external surface area ($S_{ext}$) and the micropore volume ($V_{mic}$) were obtained by the t-method (thickness was calculated by employing ASTM standard D-6556-01). The microporous surface area ($S_{mic}$) was determined as the subtraction of $S_{ext}$ from $S_{BET}$ and the average pore width ($W_{mic}$) by approximation ($W_{mic}= 4\ V_{mic}\ S_{mic}^{-1}$). The total pore volume ($V_{Total}$) was determined at $p/p^0$ = 0.98. Calculations of those methods were all done by using TouchWin™ software v1.21.

## 3.6. Removal of Naproxen using Activated Carbon prepared from Olive Stones

Adsorption tests was the heart of this work. With them it is possible to see the variation of the concentration of Naproxen under different conditions. These tests will be done in an Incubator with rotation and controlled temperature with de the adsorbent with acid and heat activation (item 3.4.3). After incubation time the samples will be analyzed in HPLC-UV Vis at a wavelength of 224 nm and injection of 20 μm.

### 3.6.1. Time

To analyze the speed of the adsorbent removing naproxen, will be done tests with 250 mg and 50 mg with varying times of 10, 20, 30, 40, 50, 60, 90, 120, 180, 240, 360, 1440 and 1800 minutes at 25°C and 150 rpm (See Table 3 and Table 4). These tests will allow you to observe the time required to achieve an equilibrium concentration necessary to use in statistical models.

**Table 3** – Adsorption tests on time variation for 250 mg of Adsorbent 3 with Naproxen solution of 20 mg $L^{-1}$ and pH = 4.31.

| Sample | Adsorbent Mass (mg) | Naproxen solution (mL) | Time (min) |
|---|---|---|---|
| **1** | 250.7 | 50 | 10 |
| **2** | 250.7 | 50 | 20 |
| **3** | 250.9 | 50 | 30 |
| **4** | 250.3 | 50 | 40 |
| **5** | 250.1 | 50 | 50 |
| **6** | 250.1 | 50 | 60 |
| **7** | 250.1 | 50 | 90 |
| **8** | 250.3 | 50 | 120 |
| **9** | 250.0 | 50 | 180 |
| **10** | 250.4 | 50 | 240 |
| **11** | 250.8 | 50 | 360 |
| **12** | 250.2 | 50 | 1440 |
| **13** | 250.4 | 50 | 1800 |
| **14** | 250.0 | 50[1] | 1800 |
| **15** | 0.0 | 50 | 1800 |

[1] Ultrapure water

**Table 4** – Adsorption tests on time variation for 50 mg of Adsorbent 3 with Naproxen solution of 20 mg $L^{-1}$ and pH = 4.39.

| Sample | Adsorbent Mass (mg) | Naproxen solution (mL) | Time (min) |
|---|---|---|---|
| **1** | 50.6 | 50 | 10 |
| **2** | 50.3 | 50 | 20 |
| **3** | 50.5 | 50 | 30 |
| **4** | 50.7 | 50 | 40 |
| **5** | 50.3 | 50 | 50 |
| **6** | 50.1 | 50 | 60 |
| **7** | 20.7 | 50 | 90 |
| **8** | 50.8 | 50 | 120 |
| **9** | 49.9 | 50 | 180 |
| **10** | 50.4 | 50 | 240 |
| **11** | 50.4 | 50[1] | 240 |
| **12** | 0.0 | 50 | 240 |

### 3.6.2. Temperature

Analysis was made with 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 150, 200 and 250 mg activated carbon also with 50 mL of solvent at 150 rpm in a 24-hour period to ensure that the solution is already in equilibrium concentration, and at temperatures of 25, 35 and 45 °C.

**Table 5** – Adsorption tests on adsorbent variation from 10 to 250 mg of adsorbent 3 at 25 °C at a Naproxen solution of 20 mg/L and pH=4.39.

| Sample | Adsorbent Mass (mg) | Naproxen solution (mL) | Time (min) |
|---|---|---|---|
| **1** | 10.0 | 50 | 1440 |
| **2** | 20.1 | 50 | 1440 |
| **3** | 30.0 | 50 | 1440 |
| **4** | 40.1 | 50 | 1440 |
| **5** | 49.9 | 50 | 1440 |
| **6** | 60.3 | 50 | 1440 |
| **7** | 70.3 | 50 | 1440 |
| **8** | 80.3 | 50 | 1440 |
| **9** | 90.3 | 50 | 1440 |
| **10** | 100.3 | 50 | 1440 |
| **11** | 150.2 | 50 | 1440 |
| **12** | 200.4 | 50 | 1440 |
| **13** | 250.3 | 50 | 1440 |
| **14** | 250.5 | 50[1] | 1440 |
| **15** | 0.0 | 50 | 1440 |

**Table 6** – Adsorption tests on adsorbent variation from 10 to 250 mg of adsorbent 3 at 35°C at a Naproxen solution of 20 mg/L and pH=4.41.

| Sample | Adsorbent Mass (mg) | Naproxen solution (mL) | Time (min) |
|---|---|---|---|
| **1** | 10.0 | 50 | 1440 |
| **2** | 20.1 | 50 | 1440 |
| **3** | 30.0 | 50 | 1440 |
| **4** | 40.1 | 50 | 1440 |
| **5** | 49.9 | 50 | 1440 |
| **6** | 60.3 | 50 | 1440 |
| **7** | 70.3 | 50 | 1440 |
| **8** | 80.3 | 50 | 1440 |
| **9** | 90.3 | 50 | 1440 |
| **10** | 100.3 | 50 | 1440 |
| **11** | 150.2 | 50 | 1440 |
| **12** | 200.4 | 50 | 1440 |
| **13** | 250.3 | 50 | 1440 |
| **14** | 250.5 | 50[1] | 1440 |
| **15** | 0.0 | 50 | 1440 |

**Table 7** – Adsorption tests on adsorbent variation from 10 to 250 mg of adsorbent 3 at 45°C at a Naproxen solution of 20 mg/L and pH=4.39.

| Sample | Adsorbent Mass (mg) | Naproxen solution (mL) | Time (min) |
|---|---|---|---|
| **1** | 10.0 | 50 | 1440 |
| **2** | 20.3 | 50 | 1440 |
| **3** | 29.7 | 50 | 1440 |
| **4** | 39.9 | 50 | 1440 |
| **5** | 50.0 | 50 | 1440 |
| **6** | 59.7 | 50 | 1440 |
| **7** | 70.8 | 50 | 1440 |
| **8** | 79.6 | 50 | 1440 |
| **9** | 90.2 | 50 | 1440 |
| **10** | 100.4 | 50 | 1440 |
| **11** | 149.6 | 50 | 1440 |
| **12** | 199.5 | 50 | 1440 |
| **13** | 249.8 | 50 | 1440 |
| **14** | 250.7 | 50[1] | 1440 |
| **15** | 0.0 | 50 | 1440 |

### 3.6.3. pH

To study the influence of pH, naproxen solutions from 1 to 10 mg $L^{-1}$ with pH of 4.44, 5.51 and 7.44 were prepared with 10 mg of activated carbon still at 150 rpm for 24 hours at a temperature of 25°C with 50 mL of solvent. KOH 0.1 M was used to increase pH to the alkaline range.

**Table 8** – Adsorption tests on time variation for 10 mg of adsorbent 3 with pH of 4.44.

| Sample | Adsorbent Mass (mg) | Naproxen Concentration (mg $L^{-1}$) | Naproxen solution (mL) | Time (min) |
|---|---|---|---|---|
| **1** | 9.7 | 1 | 50 | 1440 |
| **2** | 10.2 | 2 | 50 | 1440 |
| **3** | 10.4 | 3 | 50 | 1440 |
| **4** | 10.4 | 4 | 50 | 1440 |
| **5** | 10.1 | 5 | 50 | 1440 |
| **6** | 10.1 | 6 | 50 | 1440 |
| **7** | 10.1 | 7 | 50 | 1440 |
| **8** | 9.9 | 8 | 50 | 1440 |
| **9** | 10.4 | 9 | 50 | 1440 |
| **10** | 10.4 | 10 | 50 | 1440 |
| **11** | 0.0 | 10 | 50 | 1440 |

**Table 9** – Adsorption tests on time variation for 10 mg of adsorbent 3 with pH of 5.51.

| Sample | Adsorbent Mass (mg) | Naproxen Concentration (mg $L^{-1}$) | Naproxen solution (mL) | Time (min) |
|---|---|---|---|---|
| **1** | 10.3 | 1 | 50 | 1440 |
| **2** | 10.2 | 2 | 50 | 1440 |
| **3** | 9.9 | 3 | 50 | 1440 |
| **4** | 10.1 | 4 | 50 | 1440 |
| **5** | 10.3 | 5 | 50 | 1440 |
| **6** | 10.5 | 6 | 50 | 1440 |
| **7** | 10.4 | 7 | 50 | 1440 |
| **8** | 10.0 | 8 | 50 | 1440 |
| **9** | 10.2 | 9 | 50 | 1440 |
| **10** | 10.5 | 10 | 50 | 1440 |
| **11** | 0.0 | 10 | 50 | 1440 |

**Table 10** – Adsorption tests on time variation for 10 mg of adsorbent 3 with pH of 7.44.

| Sample | Adsorbent Mass (mg) | Naproxen Concentration (mg $L^{-1}$) | Naproxen solution (mL) | Time (min) |
|---|---|---|---|---|
| **1** | 10.2 | 1 | 50 | 1440 |
| **2** | 10.2 | 2 | 50 | 1440 |
| **3** | 10.0 | 3 | 50 | 1440 |
| **4** | 10.3 | 4 | 50 | 1440 |
| **5** | 10.3 | 5 | 50 | 1440 |
| **6** | 10.1 | 6 | 50 | 1440 |
| **7** | 10.4 | 7 | 50 | 1440 |
| **8** | 10.3 | 8 | 50 | 1440 |
| **9** | 10.4 | 9 | 50 | 1440 |
| **10** | 10.4 | 10 | 50 | 1440 |
| **11** | 0.0 | 10 | 50 | 1440 |

## 3.7. Adsorption tests with different types of adsorbents

With the results of the characterization, analyses were made using the other 3 types of prepared adsorbents (without activation. 550°C and pyrolyzed) with a naproxen solution from 1 to 10 mg $L^{-1}$, pH 4.4, 10 mg of adsorbent at 150 rpm and 25°C on incubator (same conditions in table 8).

**Table 11** – Adsorption tests on time variation for 10 mg of an adsorbent 1 (without activation) with Naproxen solution of 10 to 1 mg $L^{-1}$ and pH = 4.38.

| Sample | Adsorbent Mass (mg) | Naproxen Concentration (mg $L^{-1}$) | Naproxen solution (mL) | Time (min) |
|---|---|---|---|---|
| **1** | 10.2 | 1 | 50 | 1440 |
| **2** | 10.4 | 2 | 50 | 1440 |
| **3** | 10.3 | 3 | 50 | 1440 |
| **4** | 10.1 | 4 | 50 | 1440 |
| **5** | 10.0 | 5 | 50 | 1440 |
| **6** | 10.0 | 6 | 50 | 1440 |
| **7** | 10.0 | 7 | 50 | 1440 |
| **8** | 10.2 | 8 | 50 | 1440 |
| **9** | 10.1 | 9 | 50 | 1440 |
| **10** | 10.1 | 10 | 50 | 1440 |
| **11** | 0.0 | 10 | 50 | 1440 |

**Table 12** – Adsorption tests on time variation for 10 mg of an adsorbent 2 (550°C activation only) with Naproxen solution of 10 to 1 mg $L^{-1}$ and pH = 4.28.

| Sample | Adsorbent Mass (mg) | Naproxen Concentration (mg $L^{-1}$) | Naproxen solution (mL) | Time (min) |
|---|---|---|---|---|
| **1** | 10.5 | 1 | 50 | 1440 |
| **2** | 10.3 | 2 | 50 | 1440 |
| **3** | 10.2 | 3 | 50 | 1440 |
| **4** | 10.1 | 4 | 50 | 1440 |
| **5** | 10.4 | 5 | 50 | 1440 |
| **6** | 10.3 | 6 | 50 | 1440 |
| **7** | 10.3 | 7 | 50 | 1440 |
| **8** | 10.1 | 8 | 50 | 1440 |
| **9** | 10.4 | 9 | 50 | 1440 |
| **10** | 10.3 | 10 | 50 | 1440 |
| **11** | 0.0 | 10 | 50 | 1440 |

**Table 13** – Adsorption tests on time variation for 10 mg of an adsorbent 4 (550°C. $H_2SO_4$ and 800°C activation (pyrolyzed)) with Naproxen solution of 10 to 1 mg $L^{-1}$ and pH = 4.40.

| Sample | Adsorbent Mass (mg) | Naproxen Concentration (mg $L^{-1}$) | Naproxen solution (mL) | Time (min) |
|---|---|---|---|---|
| **1** | 10.3 | 1 | 50 | 1440 |
| **2** | 10.0 | 2 | 50 | 1440 |
| **3** | 10.2 | 3 | 50 | 1440 |
| **4** | 10.4 | 4 | 50 | 1440 |
| **5** | 10.1 | 5 | 50 | 1440 |
| **6** | 10.1 | 6 | 50 | 1440 |
| **7** | 10.2 | 7 | 50 | 1440 |
| **8** | 9.9 | 8 | 50 | 1440 |
| **9** | 10.1 | 9 | 50 | 1440 |
| **10** | 10.0 | 10 | 50 | 1440 |
| **11** | 0.0 | 10 | 50 | 1440 |

## 4. RESULTS AND DISCUSSION

### 4.1. HPLC calibration curve for naproxen quantification

As shown in Figure 3, the results of the calibration curve for naproxen at 60ACN:40TFA:0.01W to 224 nm, was a linear behavior with $R^2$ = 0.9976 for pH 4.4, $R^2$ = 0.9978 for pH 5.5 and $R^2$ = 9.9973 for pH 7.4 (See Fig. 4). This behavior can be explained by Nemoto (2019) who in a range of 5 to 50 ppb under the same conditions obtained an $R^2$ = 0.9876 showing the linear comportment of Naproxen. When comparing the equation of the straight line of the three pHs, there is a little difference in linearity between them, leaving pH 4.4 more able to be used for the initial experiments of this study because it is the natural pH of the solution of naproxen in ultra-pure water.

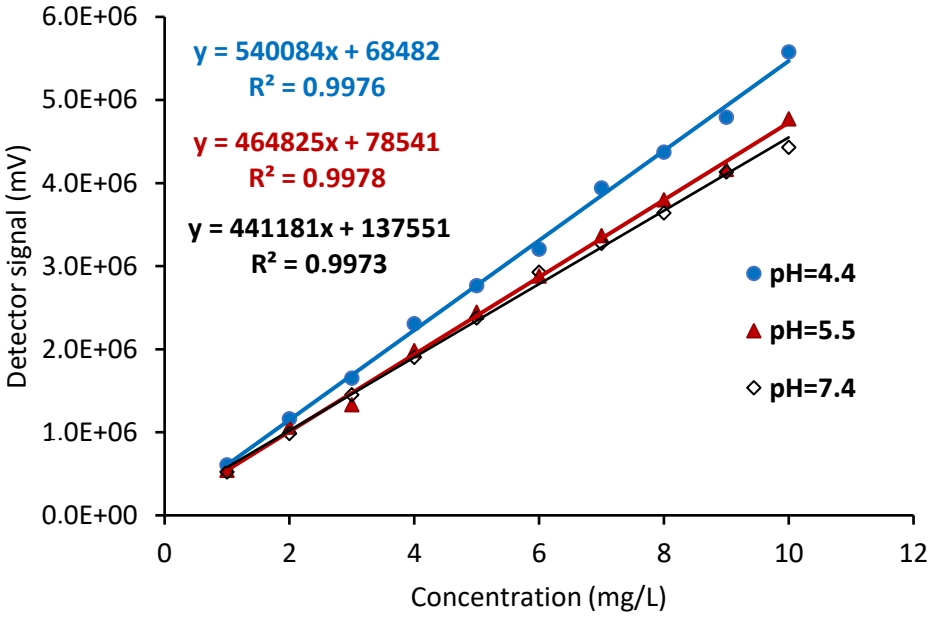


**Figure 4** – HPLC-DAD calibration curve for naproxen from 10 to 1 mg/L on pH 4.4, 5.5 and 7.4.

Nemoto (2019) in his study, found a LOD and LOQ of 5.09 and 16.98 ppb respectively studying an interval of 5 to 50 μm $L^{-1}$, while Madikizela and Chimuka (2017) also studying an interval 5 to 50 μm $L^{-1}$ for naproxen obtained a LOD of 0.04

ppb and LOQ of 0.1 ppb. The LOD and LOQ shown in table 14 for studies in this concentration range. No references were found in this range for the same method and the difference between Nemoto (2019) and this study even using close methodologies is justified by the range of concentration used in each study. However, it is necessary to be noted that the difference of Nemoto (2019) and Madikizela and Chimuka (2017) it's also justified due to the methodologies to find LOD and LOQ.

**Table 14** – Calibration curve and naproxen linearity parameters.

| Parameters | Values |
|---|---|
| **Range** | 1 – 10 mg $L^{-1}$ |
| **LOD** | 1.00 mg $L^{-1}$ |
| **LOQ** | 0.33 mg $L^{-1}$ |
| **a** | 29941 ± 49581 |
| **b** | 469519 ± 7991 |
| **$R^2$** | 0.9976 |
| **n** | 10 |
| **CV** | 2.81% |
| **Sm** | ± 0.155 |

## 4.2. Characterization of Adsorbent

It was observed that in the activation process of the main adsorbent of this study (550°C + $H_2SO_4$), the pit when activated by burning was presented a yield close to 20%. However. the total yield is reduced due to accidents with the Crucible cap C3 and C6 that were the damaged within the muffle (See Table 15) that have obtained these results (5 and 7%) because they were without the cap had a greater loss due to carbon volatilization.

**Table 15** – Experimental yield obtained for OSAC carbonization.

| Crucible | Initial mass of OSAC- before carbonization (g) | Final mass of OSAC after carbonization (g) | Yield |
|---|---|---|---|
| **C1** | 25.0071 | 5.1715 | 21% |
| **C2** | 18.5897 | 3.5125 | 19% |
| ***C3*** | *34.1663* | *1.7671* | *5%* |
| **C4** | 35.1650 | 7.58 | 22% |
| **C5** | 31.4230 | 6.6993 | 21% |
| ***C6*** | *35.7330* | *2.592* | *7%* |
| **Total** | **180.0841** | **27.3224** | **15%** |

Data on moisture and ash rate (See Table 16) present lower percentages than Larous and Meniai (2016) found in their experiments. The low amount of ash content indicates low presence of inorganic materials such minerals pointing to a good quality of adsorbent (Larous & Meniai. 2016), To Miranda *et al. (*2008), olive stone has excellent combustion properties, second only to pulp and its ash has the least amount of minerals such as Nitrogen, Chlorine, Sodium and Potassio.

**Table 16** – Moisture and Ash rate (g $g^{-1}$).

| Properties | % |
|---|---|
| Moisture | 7.68 |
| Ashes | 0.52 |

The textural results of the activated and pyrolyzed adsorbent were very similar. The lump resulting from chemical activation and burning with $O_2$ obtained results with a total volume of micropores of 84% of the total volume of the adsorbent while pyrolyzed has 92% of its volume with micropores. The average pores ($W_{mic}$ = 2.2 nm) and $S_{BET}$ (411 and 409 $m^2$ $g^{-1}$) are also similar indicating here another promising characteristic for non-pyrolyzed charcoal. The main advantage because they have similar characters is that it is not necessary to spend resources and unnecessary time for pyrolysis in the adsorbent 550°C + $H_2SO_4$ + 800°C and the 550°C + $H_2SO_4$ produces a very similar effect (See Fig. 5 and Table 17).

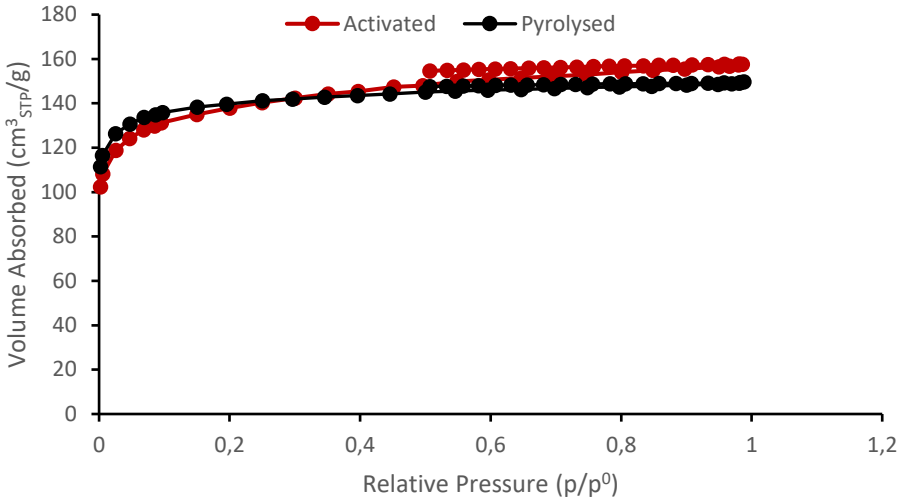


**Figure 5** – $N_2$ isotherms adsorption of the materials.

**Table 17** – Textural properties of activated and pyrolyzed adsorbent.

| | $S_{BET}$ ($m^2 g^{-1}$) | $S_{Langmuir}$ ($m^2 g^{-1}$) | $S_{ext}$ ($m^2 g^{-1}$) | $S_{mic}$ ($m^2 g^{-1}$) | $V_{mic}$ ($mm^3 g^{-1}$) | $V_{mic}/V_{Total}$ (%) | $W_{mic}$ (nm) |
|---|---|---|---|---|---|---|---|
| **Activated** | 411 | 594 | 35 | 376 | 205 | 84 | 2.2 |
| **Pyrolyzed** | 409 | 608 | 16 | 393 | 213 | 92 | 2.2 |

## 4.3. Optimization of the adsorption experimental conditions

### 4.3.1. Time

The adsorption assay of 250 mg results in a removal percentage of approximately 99% in 10 minutes (See Fig. 6).

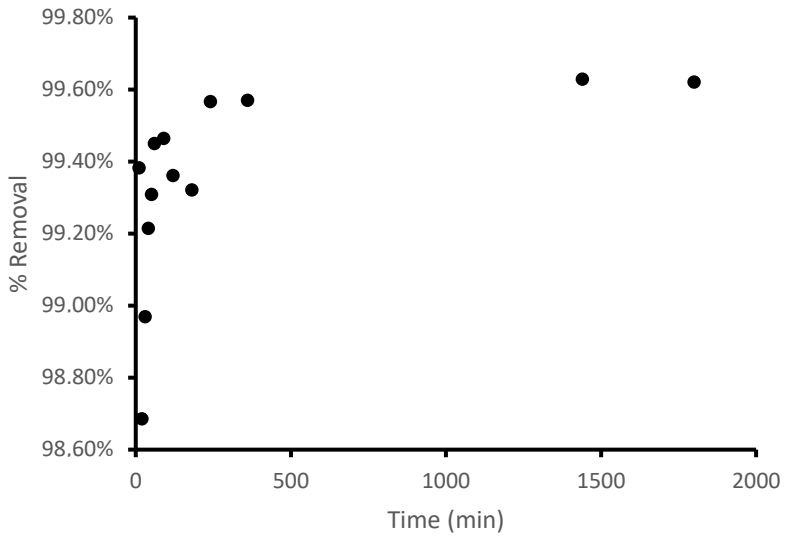


**Figure 6** – Percentage of removal of naproxen with 250 mg activated carbon 0.25 mm in assays of up to 1800 min with 20 mg $L^{-1}$ solution and pH 4.31.

The 50 mg assay also demonstrates high efficiency in removal over time. Unlike the 250 mg assay, the results of this sample are required by 60 minutes to remove approximately 90% of Naproxen. (See Fig. 7).

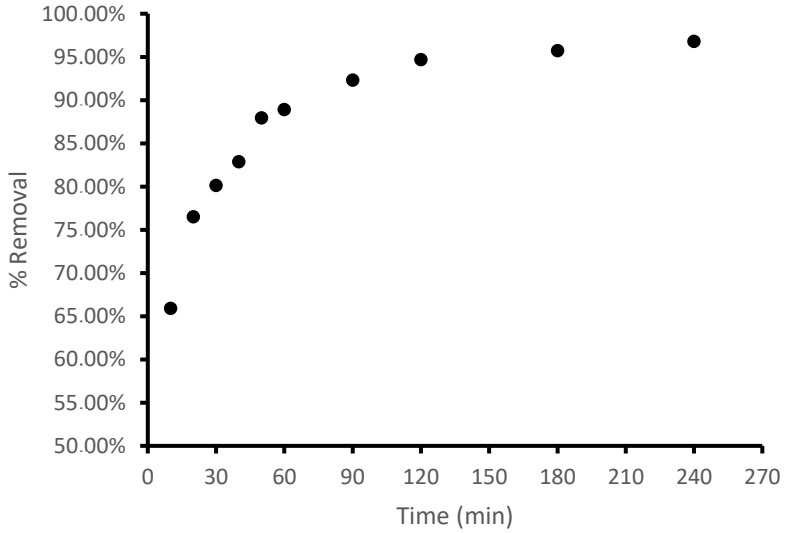


**Figure 7** – Percentage of removal of naproxen with 50 mg activated carbon 0.25 mm in assays of up to 240 min with 20 mg $L^{-1}$ solution and pH 4.39.

The results of this section point to the preliminary results as a starting basis for understanding the removal of Naproxen from Adsorbent 3 in which, for reasons of economics, the study with 50 mg adsorbent was the best option to follow the studies for experimental convenience, like temperature measurement, not ruling out the need for fine adjustments as was actually done in pH and adsorbents measurements.

### 4.3.2. Temperature

With the variation of the mass of activated charcoal of olive stone, it was observed that the assay with a temperature of 25°C, 35°C and 45°C in a period of 24h it is possible to obtain a removal of almost 100% of naproxen with approximately 33 mg of adsorbent (See Fig. 8).

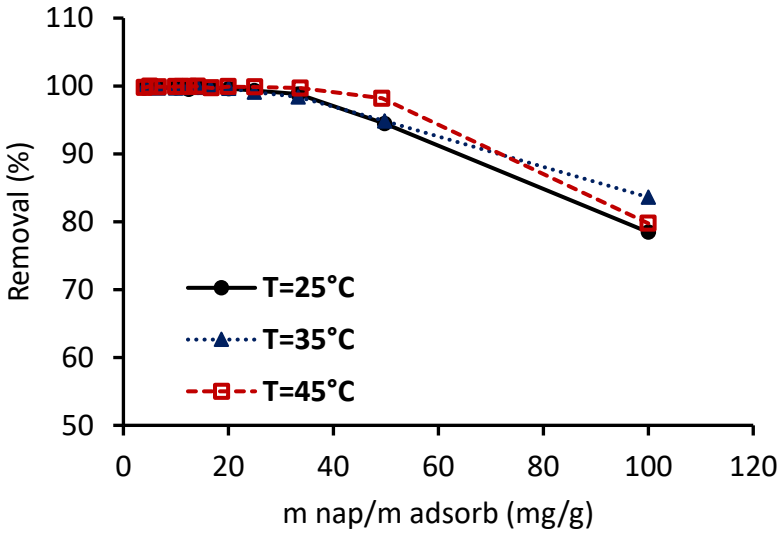


**Figure 8** – Comparison of removal percentage of naproxen in 25, 35 and 45°C with Adsorbent 3 with 20 mg $L^{-1}$ solution and pH 4.4.

Even if the adsorption potential is approximately the same, i.e., it has a high potential for naproxen removal, Figure 9 confirm the measurements of the quantity of naproxen adsorbed adapted with the models of Langmuir and Freundlich demonstrating that temperature influences naproxen adsorption showing that how higher the concentration of naproxen in the solution is, higher will be the adsorption. Is demonstrated in the range of 0.00 to 1.00 g/L that the temperature of 45° C

demonstrates a higher adsorption power of the lower concentrations. Similar events were demonstrated in the Lach and Szymonik study (2019) that when analyzing 3 different types of activated carbon (ROW 08 Supra. WG-12 and F-300) both adsorbents were more effective at higher temperatures (20, 30 and 40°C). This phenomenon is due that the higher the temperature. the greater the mobility of the molecules, then increasing the affinity of adsorbate molecules with the adsorbent surface.

Thes assays at 35°C were the ones that obtained the best results, this also indicates that temperatures above 35°C no longer exist a linear increase in adsorption and may even negatively interfere in adsorption. It is noticeable that for Lach and Szymonik study (2019), although there is a better adsorption to 40°C, the difference to 35°C is tiny and nonlinear. For experimental convenience, the temperature of 25°C was used as standard for sequential studies.

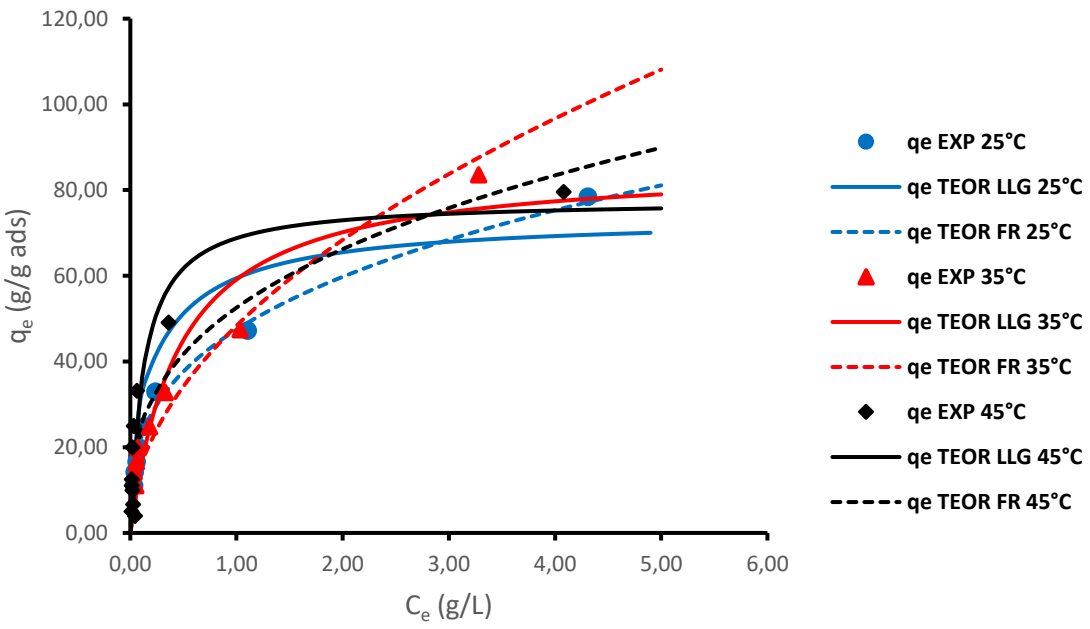


**Figure 9** – Comparison of Adsorption on model of Langmuir and Freundlich on different temperatures with 20 mg $L^{-1}$ solution and pH 4.4.

### 4.3.3. pH

The influence of pH on adsorption assays is very clear. We can note that comparing pHs 4.44, 5.51 and 7.44 the results show a reduction in naproxen adsorption capacity as the concentration increases to 10mg adsorbent in all assays. This happens because coal reaches the adsorption limit, not having enough pores to interact with naproxen, making it impossible for a greater adsorption because it is already saturated with naproxen (See Fig. 10).

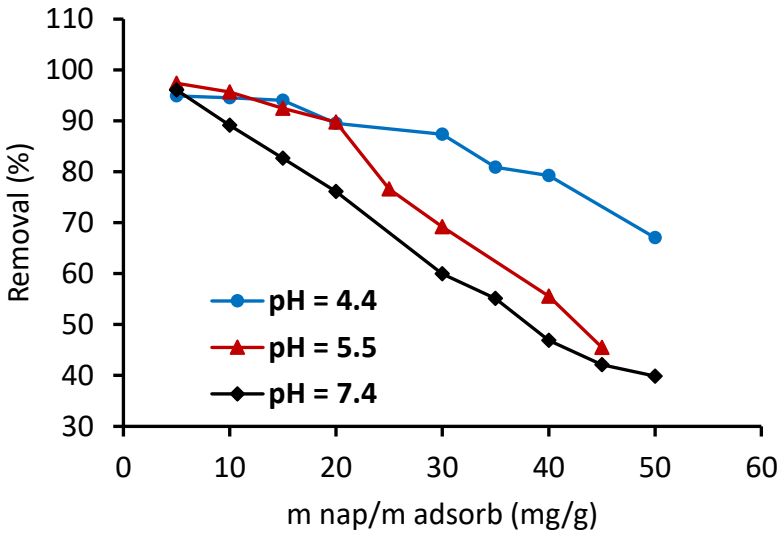


**Figure 10** – Comparison of removal percentage of naproxen with pH of 4.44, 5.51 and 7.41 with Adsorbent 3.

Fig. 10 confirms the previous observations since pH 4.44 allows the better performance. Increasing the pH promotes a decrease in the adsorption capacity of the activated carbons. For small concentrations, the measurements with solution of 1 to 4 mg/L of naproxen for pH 4.44 and 5.51 have similar performance. However, as it is necessary to base the sample with KOH, the natural pH of the 4.44 solution demonstrates a better option for the removal of small concentrations because it does not need to spend other materials. However, it is important to target water in the appropriate pH range for human consumption (6.5 and 8.5) requiring a future correction for human digestion.

The results are in accordance with what was demonstrated by Lach and Szymonik (2019), in which their results also indicate a better performance for the solution with lower pH. The decrease in adsorption may be related to the competitiveness of sodium naproxen anions and $OH^-$ ions has a direct influence on the electrostatic attraction between these two groups that are also present on the surface of activated carbon. The dissociation of weak basic groups on the surface of activated carbon is commonly observed in alkaline solutions leading to an electrostatic repulsion between naproxen and adsorbent indicating why alkaline solutions lose their adsorption capacity compared to acid solutions. In acid solutions. the dissociation of basic functional groups is used in an electrostatic attraction increasing the affinity of adsorbate with adsorbent (Lach and Szymonik. 2019).

Figure 11 confirms that Naproxen is better adsorbed when it is in the pH 4.4 range eliminating the doubt that pH 4.4 and 5.5 have similar behaviors. It is also observed that the Langmuir Model satisfies the behavior of the pH curve well than Freundlich with a $R^2$ = 0.9862, 0.9847 and 0.9790 for pH 4.4, 5.5, and 7.4 respectively (See Tab. 19).

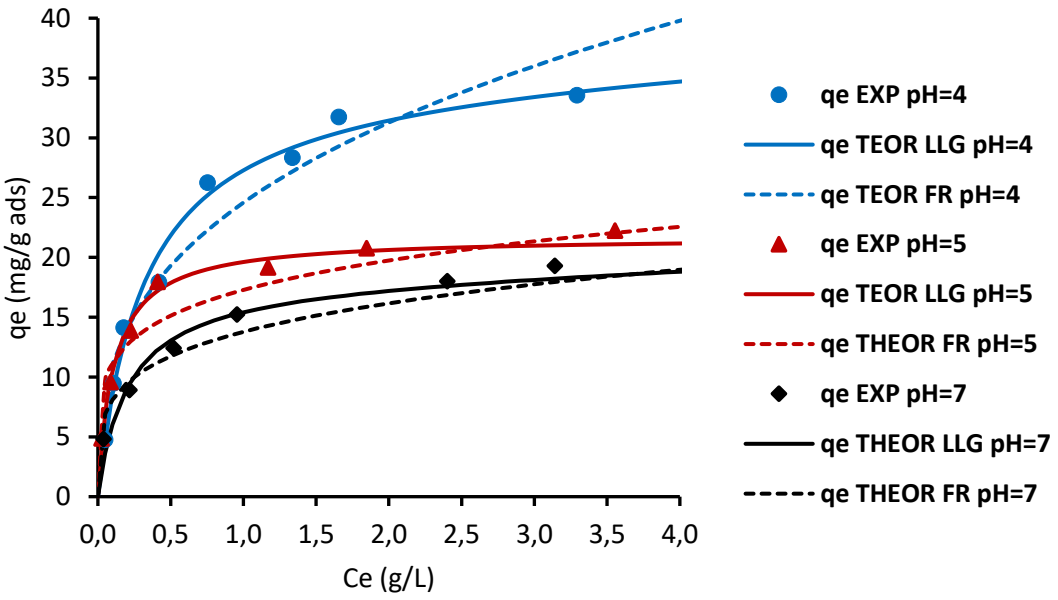


**Figure 11** – Comparison of Adsorption Models on the effect of pHs.

### 4.3.4. Comparison between the adsorbent materials

Adsorbent 3 (550°C + $H_2SO_4$), which is the main adsorbent of this study. demonstrates an excellent potential for naproxen reduction. removing more than 94% of the pollutant from a solution with the ratio of five mg of naproxen for each gram of adsorbent. In a more concentrated solution, it is noted that the removal potential reaches its limit close to 70% removal, due to all pores being already saturated and without ability to remove more naproxen (See Fig. 12).

It was expected that adsorbent 1 (without activation) had the slightest removal of naproxen from the solution, this is justified by the fact that there is no large volume of pores because it does not go through any type of activation, neither chemical nor thermal (fig 112). However. even if it is the worst-case scenario of the adsorbents studied, it is worth mentioning that adsorbent 1 can adsorption naproxen naturally, removing approximately 20% of the naproxen, but its saturation is too fast and as already mentioned, it is not efficient.

When only thermally activated, adsorbent 2 performs better than adsorbent 1, removing 75% of naproxen in a 1 ppm solution that is 3.5 times more than adsorbent 1. Its worst-case scenario is that it also has a fast saturation when the solution is very concentrated. that already at 10 ppm the solution had the ability to remove only 30% of naproxen. The absence of chemical activation besides not assisting in the process of producing coal pores leaves coal without a washing process and may carry some impurities that sulfuric acid is able to digest (See Fig. 12).

Adsorbent 4 (pyrolyzed) shows an unexpected performance. This adsorbent was anticipated to have a better performance compared to adsorbent 3 by undergoing another type of thermal processing in an inert environment. But as shown in Figure 6. both adsorbent 3 and adsorbent 4 have similar performances. This is because chemical and thermal activation (550°c) was enough to produce more than 80% of the micropores (See Fig. 12).

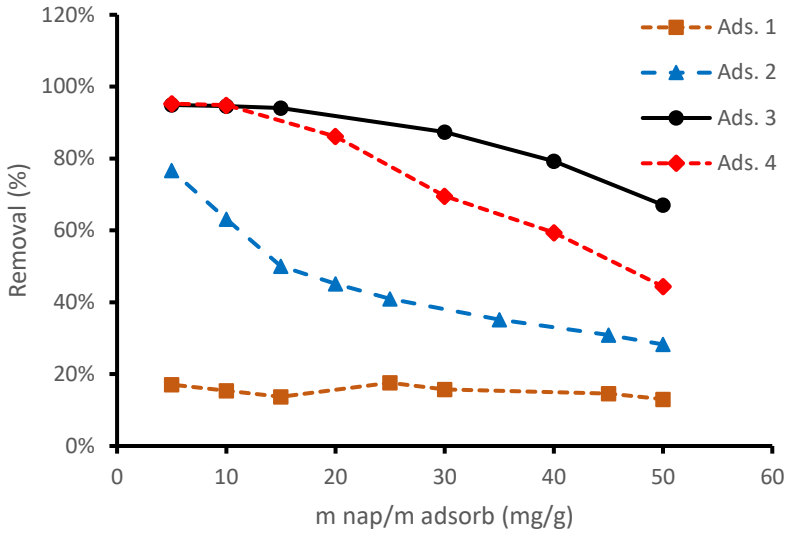


**Figure 12** – Comparison of each removal capacity between **Adsorbent 1, 2, 3 and 4** in a ration of mass of naproxen and mass of adsorbent.

Analyzing the ability to remove and the equilibrium concentration, the result is as already explained: the worst performance is adsorbent 1; adsorbent 2 performs better because it has thermal activation; and adsorbents 3 and 4 are at the top as the most effective confirming that adsorbent 3 is the most effective for removing the pollutant. Adsorbent 4 that went through all 3 activation processes also obtained good removal results, but the excess of treatment may have led to an attrition of the material making it impossible for it to have $q_e$ as high as Adsorbent 3. Another point that reinforces the benefits of adsorbent 3 is that it does not need to go through another process as rigorous and expensive as pyrolysis and still producing great results.

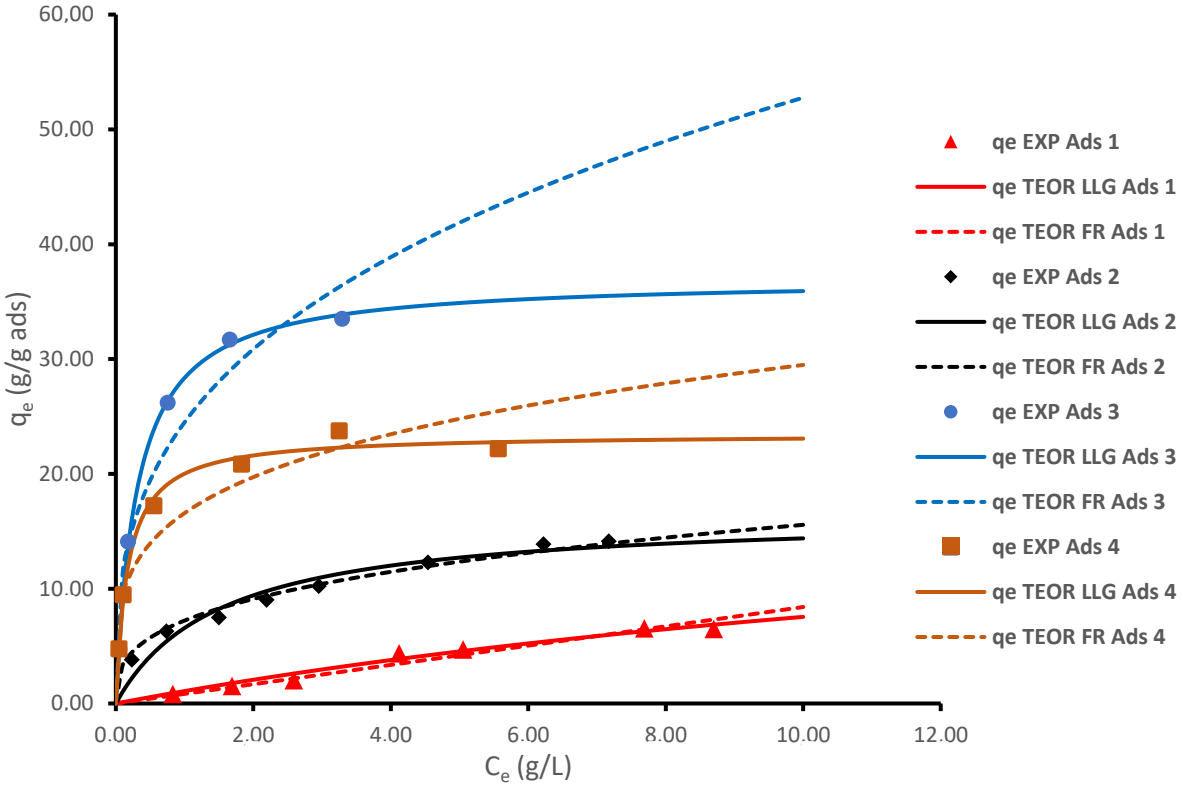


**Figure 13** – Comparison of the yield of each adsorbent on Langmuir and Freundlich models.

## 4.4. Modelling of the equilibrium adsorption isotherms

Table 18 and 19 presents the Langmuir and Freundlich coefficient values for this study. The conditions presented in each result are divided into two: Condition 1 is the method of analysis used in experiments related to temperatures. and the Condition 2 are the experiments related to pH and the other adsorbents that have different parameters that can be observed in chapters 3.6.2 and 3.6.3.

Langmuir is the adsorption model that better explains the experimental points in condition 2 and the Freundlich is better to explain the experimental points in Condition 1. Using the $q_m$ parameter, for temperature, we observed the que was explained in Figure 9, in which the temperature at 35°C has the highest maximum adsorption capacity ($q_m$ = 86.2401 mg $g^{-1}$ ads). For pH and Adsorbents measurements, the pH that best had the maximum amount of adsorption was pH 4.5 ($q_m$ = 37.01 mg $g^{-1}$ ads) which is the same $q_m$ value for adsorbent 3, highlighting as the best Adsorbent studied (See Tab. 19). Similar results were found in a biosorbent derived from peanut shells with $q_m$ = 55.1 ± 1.42 mg $g^{-1}$ ads to 25°C (Tomul *et al*., 2021). For Lach and Szymonik

(2019), although adsorbents have similar behaviors, the amounts of $q_m$ for the three commercial adsorbents are out of the data of this study ($q_m$ = 144.10 mg $g^{-1}$ ads; 116.55 mg $g^{-1}$ ads; 123.90 mg $g^{-1}$ ads for F-300, Row 08 Supra and WG-12, respectively).

**Table 18 -** Coefficients of the Langmuir and Freundlich models for this work on temp. and pH.

| | | **Condition 1** | | | **Condition 2** | | |
|---|---|---|---|---|---|---|---|
| **Activated Carbon** | **Parameter** | **pH 4.50** | | | **pH 5.5** | **pH 7.5** | |
| | | **T=45°C** | **T=35°C** | **T=25°C** | | | |
| **Langmuir** | | | | | | | |
| **Adsorbent 1** | **$q_m$** (mg $g^{-1}$ ads) | 77.6770 | 86.2401 | 73.7290 | 37.01 | 21.74 | 18.00 |
| | **$K_L$** (L g-1) | 7.7283 | 2.1808 | 3.7848 | 3.2776 | 9.236 | 4.998 |
| | **$R^2$** | 0.8799 | 0.9241 | 0.9283 | 0.9989 | 0.9847 | 0.9790 |
| **Freundlich** | | | | | | | |
| **Adsorbent 1** | **n** | 3.00 | 2.00 | 3.00 | 3.00 | 5.20 | 4.30 |
| | **$K_f$** (L $g^{-1}$) | 52.55848 | 48.34675 | 47.4302 | 24.4889 | 17.279 | 13.780 |
| | **$R^2$** | 0.8579 | 0.9908 | 0.9905 | 0.9327 | 0.8527 | 0.9488 |

**Table 19 -** Coefficients of the Langmuir and Freundlich models for this work in each adsorbent.

| | | **Condition 2** | | | |
|---|---|---|---|---|---|
| **Adsorption Model** | **Parameter** | **pH 4.50** | | | |
| | | **T=25°C** | | | |
| | | **Adsorbent 1** | **Adsorbent 2** | **Adsorbent 3** | **Adsorbent 4** |
| **Langmuir** | **$q_m$** (mg $g^{-1}$ ads) | 22.4153 | 16.56 | 37.01 | 23.46 |
| | **$K_L$** (L g-1) | 0.0507 | 0.6587 | 3.2776 | 5.7923 |
| | **$R^2$** | 0.9755 | 0.9565 | 0.9989 | 0.9869 |
| **Freundlich** | **n** | 3.0000 | 3.00 | 3.00 | 4.00 |
| | **$K_f$** (L $g^{-1}$) | 24.4889 | 7.2229 | 24.4889 | 16.5804 |
| | **$R^2$** | 0.9327 | 0.9944 | 0.9327 | 0.8876 |

## 5. CONCLUSIONS

As discussed, naproxen is a non-steroidal anti-inflammatory drug that enters the group of emerging micropollutants that can bring health complications with their long-term undue ingestion. Its monitoring proves to be possible and quantifiable as well as its removal.

A careful literature review was made to the point of removing studies that assisted this study on quantification and removal of the drug from this study. Naproxen quantification was performed using the HPLC-UVis Varian ProStar with a wavelength of 224 nm that results in a linear calibration for adsorbent 3 (main adsorbent studied) with an $R^2 = 0.9976$.

The tests with time as a parameter demonstrate that for 250 and 50 mg of Adsorbent 3, it is possible to remove approximately 100% in 10 and 60 minutes respectively demonstrating the great efficiency of the adsorbent.

The adsorption is different for different temperatures, the higher the temperature the higher the amount of naproxen adsorbed due to the higher degree of agitation of the molecules, but temperatures above 35°C the adsorption increase is no longer linear, leaving the 35°C tests with better maximum adsorption capacity ($q_m$ = 86.2401 mg $g^{-1}$ ads) Unlike temperature, the pH has the opposite effect in which the increase in the pH of the solution negatively interferes with the amount of adsorbent adsorbed by coal ($q_m$ = 37.01 mg $g^{-1}$ ads; 21.74 mg $g^{-1}$ ads and 18.00 mg $g^{-1}$ ads for pH 4.5, 5.5 and 7.5 respectively) .

The study of each adsorbent points out that even without treatment (Adsorbent 1), the only crushed 0.25 mm olive stone has a small adsorption potential ($q_m$ = 22.41 mg $g^{-1}$ ads). Adsorbent 2 which is only carbonized has a higher adsorption power by undergoing a thermal activation ($q_m$ = 16.56 mg $g^{-1}$ ads). The studied characteristics of Adsorbent 3 and Adsorbent 4 are similar due to an optimal pore opening in the chemical activation process carbonization proven by the results of Quantachrome ($V_{mic}/V_{Total}$ = 84% for Ads 3 and 92% for Ads 4) and the very low moisture and ash rate (7.68 % and 0.52 %). This fact makes it unnecessary for the pyrolysis that Adsorbent 4 suffered since it is necessary to go through an extra step in the activation process

and use an advanced process with additional cost that is pyrolysis proving that Adsorbent 3 is the best option.

The studies of pH, temperature, and comparison of the adsorbents are justified by the Freundlich and Langmuir models in which the first better justifies the temperature tests while the other better justifies the pH and adsorbent comparison by having the same parameters.

Compared to other adsorbents found, the olive stone presents lower performances in its maximum naproxen adsorption capacity. However, this does not indicate that it should not be studied and used since even if it showed lower capacity than others, it still present excellent results in adsorption assays with high removal capacities. Its use is also feasible as a reduction of the excess of the olive stone produced and because its treatment is low cost.

## 6. SUGGESTION OF FUTURE WORKS

Within the line of the tests already performed, it can also be understood how adsorbent 3 behaves in the optimum operating conditions resulting, i.e., pH 4.4 to 35°C in Condition 2 (varying the concentration of the naproxen solution from 1 to 10). Other operating conditions can also be studied as lower temperatures, which by an incubator limit could not be performed, and also studies of more acidic pHs as well as the incorporation of an adsorbent kinetics study as well.

In Brazil, sugarcane is an extremely abundant grass popularly known as a source of biofuel and biomass and its bagasse is already known to have adsorptive properties. This brings a range of options for the use of this material that can also be studied as activated charcoal prepared according to this methodology and evaluate the removal of naproxen under the same conditions of this study.

In Bragança there is a great abundance of cherry, which indicates a potential study to follow the line of research of this work. Little information was found about the cherry pit, which indicates a new environment to explore. Walnut peel is also a possibility of study that unlike cherry is already an adsorptive material that can be found more easily in some literatures, but the relationship of adsorption with Naproxen were not found in either of the two materials.

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