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Identification and quantification of pesticides in aqueous matrices and removal using olive pit based adsorbents

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ABSTRACT

The widespread use of pesticides in agriculture raises serious environmental and public health concerns. These chemical compounds, persistent in the environment, have the potential to contaminate soils, groundwater, and bodies of water, even at minimal concentrations. Conventional water treatment techniques do not allow for complete elimination of pesticides, highlighting the urgency for more effective remediation methods. This study proposes the development and characterization of adsorbents derived from olive pit for the removal of three pesticides (acetochlor, dimethoate, and heptachlor). Evaluating the capacity of these adsorbents for pesticide removal aims to provide sustainable and effective solutions to mitigate environmental pesticide contamination.

The methodology of this work was divided into three parts. The first consisted of the preparation and characterization of adsorbents derived from olive pit, producing two activated carbons: one by chemical activation with phosphoric acid, H_3PO_4, called CA, and the other by physical activation in a muffle furnace at 800°C, named CP. The second part involved the identification and quantification analyses of pesticides by GC-MS, also utilizing solid-phase microextraction (SPME) technique to select the best extraction fiber for the mentioned pesticides. The third part involved the study of adsorption kinetics at three different temperatures (25°C, 35°C, and 45°C) over 24 hours. Pseudo-first-order (PFO) and pseudo-second-order (PSO) models were fitted to the experimental values, as well as adsorption isotherm models, namely Freundlich, Langmuir, and Radke. Furthermore, activation energy and adsorption equilibrium were analyzed to better understand the pesticide removal process.

According to the obtained results, the acidic charcoal achieved a higher carbonization yield, 59.19%, while the physical charcoal obtained 19.40%. Additionally, the acidic charcoal exhibited a higher specific surface area with values of 488.7 for CA and only 379.2 m^2/g for CP, and underwent fewer changes in terms of functional groups analyzed by FTIR compared to physically activated charcoal. The best fiber for SPME extraction of pesticides was the blue PDMS/DVB(+OC) (Polydimethylsiloxane/ Divinylbenzene) which better identified dimethoate. Physically activated charcoal proved effective in removing heptachlor, achieving 99% removal in 300 minutes and requiring only 15 mg of adsorbent for 10 ppm of pollutant, while using the same concentration of acetochlor, a removal rate of 98% was achieved, requiring 30 mg of adsorbent in 300 min. The kinetic study results were better fitted to the pseudo-second-order model, with better results observed at 25°C and an equilibrium time of 5 hours; the Radke model allowed for better fitting to the equilibrium isotherms for both pesticides.

It was observed that the carbons have great removal potential, and in the future, new conditions can be applied to study the potential of the carbons, as well as the mixture of pesticides.

Keywords: Adsorption; olive pit activated carbon; GC-MS; SPME; pesticides.

RESUMO

O uso generalizado de pesticidas na agricultura levanta sérias preocupações ambientais e de saúde pública. Esses compostos químicos, persistentes no meio ambiente, têm potencial para contaminar solos, lençóis freáticos e corpos d'água, mesmo em concentrações mínimas. As técnicas convencionais de tratamento de água não permitem a eliminação completa dos pesticidas, o que destaca a urgência de métodos de remediação mais eficazes. Este estudo propõe o desenvolvimento e caracterização de adsorventes derivados de caroço de azeitona para remoção de três pesticidas (acetocloro, dimetoato e heptacloro). A avaliação da capacidade destes adsorventes para a remoção de pesticidas visa oferecer soluções sustentáveis e eficazes para mitigar a contaminação ambiental por pesticidas.

A metodologia deste trabalho foi dividida em 3 partes. A primeira consistiu na preparação e caracterização de adsorventes derivados do caroço de azeitona, tendo sido produzidos dois carvões ativados: um por ativação química com ácido fosfórico, H_3PO_4, denominado CA e o outro por ativação física, em mufla a 800°C, denominado CP. Na segunda parte foram realizadas as análises de identificação e quantificação dos pesticidas por GC-MS, utilizando também a técnica de microextração em fase sólida (SPME) para a escolha da melhor fibra de extração dos pesticidas mencionados. A terceira parte envolveu o estudo da cinética de adsorção, em três temperatura diferentes (25°C, 35°C e 45°C), ao longo de 24 horas. Os modelos de pseudo primeira ordem (PFO) e pseudo segunda ordem (PSO) foram ajustados aos valores experimentais, assim como os modelos de isotermas de adsorção, nomeadamente Freundlich, Langmuir e Radke. Além disso, a energia de ativação e o equilíbrio de adsorção foram analisados para entender melhor o processo de remoção dos pesticidas.

De acordo com os resultados obtidos verificou-se que o carvão ácido obteve maior rendimento de carbonização, 59.19%, enquanto o físico obteve 19.40% , também maior área superficial com valores de 488.7 para o CA e apenas 379.2 m^2 /g para CP, e sofreu menos alterações no que se refere aos grupos funcionais analisados por FTIR, relativamente ao carvão ativado fisicamente. A melhor fibra para extração SPME dos peticidas foi a azul PDMS/DVB(+OC) (Polydimethylsiloxane/ Divinylbenzene) que identificou melhor o dimetoato. O carvão ativado fisicamente mostrou ser eficaz na remoção do heptacloro, com uma remoção de 99% em 300 minutos e necessitando apenas de15 mg de adsorvente para 10 ppm de poluente, enquanto usando a mesma concentração de acetocloro, foi possível obter uma taxa de remoção de 98%, precisando de 30 mg de adsorvente em 300 min. Os resultados do estudo cinético foram ajustados melhor a pseudo segunda ordem, e foram atribuídos melhores resultados a 25°C e com um tempo de equilíbrio de 5 horas; o modelo de Radke permitiu um melhor ajuste às isotermas de equilíbrio para ambos pesticidas.

Foi observado que os carvões têm grande potencial de remoção, e no futuro podem ser aplicadas novas condições para estudo do potencial dos carvões, assim como a mistura de pesticidas.

Palavras chave: Adsorção; carvão ativado de caroço de azeitona; GC-MS; SPME; pesticidas.

ZUSAMMENFASSUNG

Die weit verbreitete Verwendung von Pestiziden in der Landwirtschaft wirft ernsthafte Umwelt- und öffentliche Gesundheitsbedenken auf. Diese chemischen Verbindungen, die in der Umwelt persistent sind, haben das Potenzial, Böden, Grundwasser und Gewässer zu kontaminieren, selbst in minimalen Konzentrationen. Konventionelle Wasseraufbereitungstechniken ermöglichen keine vollständige Eliminierung von Pestiziden, was die Dringlichkeit effektiverer Sanierungsmethoden verdeutlicht. Diese Studie schlägt die Entwicklung und Charakterisierung von Adsorbentien aus Olivenkernen zur Entfernung von drei Pestiziden (Acetochlor, Dimethoate und Heptachlor). Die Bewertung der Kapazität dieser Adsorbentien zur Pestizidentfernung zielt darauf ab, nachhaltige und wirksame Lösungen zur Minderung der Umweltbelastung durch Pestizide anzubieten.

Die Methodik dieser Arbeit wurde in 3 Teile unterteilt. Der erste bestand aus der Herstellung und Charakterisierung von Adsorbentien aus Olivenkernen, wobei zwei Aktivkohlen hergestellt wurden: eine durch chemische Aktivierung mit Phosphorsäure, H_3PO_4, bezeichnet als CA, und die andere durch physikalische Aktivierung in einem Muffelofen bei 800°C, bezeichnet als CP. Im zweiten Teil wurden Identifikations- und Quantifizierungsanalysen von Pestiziden mittels GC-MS durchgeführt, wobei auch die Technik der Festphasenmikroextraktion (SPME) verwendet wurde, um die beste Extraktionsfaser für die genannten Pestizide auszuwählen. Der dritte Teil umfasste die Untersuchung der Adsorptionskinetik bei drei verschiedenen Temperaturen (25°C, 35°C und 45°C) über 24 Stunden. Pseudo-erste-Ordnungs- (PFO) und pseudo-zweite-Ordnungs- (PSO) Kinematikmodelle wurden an die experimentellen Werte angepasst, ebenso wie Adsorptionsisothermenmodelle, nämlich Freundlich, Langmuir und Radke. Zusätzlich wurden Aktivierungsenergie und Adsorptionsgleichgewicht analysiert, um den Prozess der Pestizidentfernung besser zu verstehen.

Nach den erhaltenen Ergebnissen wurde festgestellt, dass die säureaktivierte Kohle einen höheren Carbonisierungsausbeute mit einem Wert von 59,19% aufwies, während die physikalisch aktivierte Kohle 19,40% erreichte. Die säureaktivierte Kohle zeigte auch eine größere spezifische Oberfläche mit Werten von 488,7 für CA im Vergleich zu nur 379,2 m^2/g für CP und unterlag weniger Veränderungen bezüglich der funktionellen Gruppen, die mittels FTIR analysiert wurden, im Vergleich zu physikalisch aktiver Kohle. Die beste Faser für die SPME-Extraktion von Pestiziden war das blaue PDMS/DVB(+OC) (Polydimethylsiloxan/Divinylbenzol), das Dimethoat besser identifizierte. Physikalisch aktivierte Kohle erwies sich als wirksam bei der Entfernung von Heptachlor, mit einer Entfernungsrate von 99% in 300 Minuten und benötigte nur 15 mg Adsorbens für 10 ppm Schadstoff, während säureaktivierte Kohle eine 98% ige Entfernungsrate erreichte und 30 mg Adsorbens in 300 Minuten bei gleicher Schadstoffkonzentration für Acetochlor benötigte. Die Kinetik passte besser zum Pseudo-zweiten-Ordnungs-Modell, und bessere Ergebnisse wurden bei 25°C mit einer Ausgleichszeit von 5 Stunden festgestellt; Gleichgewichtsisothermen für beide Pestizide passten besser zum Radke-Modell.

Es wurde festgestellt, dass die Kohlen ein großes Entfernungspotenzial haben und in Zukunft neue Bedingungen für die Untersuchung des Potenzials der Kohlen sowie die Mischung von Pestiziden angewendet werden können.

Stichwörter: Adsorption; Aktivkohle aus Olivenkernen; GC-MS; SPME; Pestizide.

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LIST OF ABBREVIATIONS

ANVISA	Agência Nacional de Vigilância Sanitária
ASE	Accelerated Solvent Extraction
CA	Acid coal
CARB	Carbamates
CE	Capillary electrophoresis
CP	Physical coal
CPE	Cloud point extraction
DDP	Dichlorodiphenyltrichloroethane
EC	European commission
EU	European Union
ELISA	Enzyme-linked immunosorbent assay
EMP's	Emerging micro-pollutants;
GC	Gas chromatography
GPC	Gel permeation chromatography
HPLC	High performance liquid chromatography
IBAMA	Instituto Brasileiro do Meio Ambiente e dos Recursos Naturais Renováveis
IMS	Ion mobility spectrometry
INE	Instituto Nacional de Estatística
LC	Liquid chromatography
LLE	Liquid–liquid extraction
LPME	Liquid phase microextraction
MAE	Microwave-assisted extraction
MAPA	Ministério da Agricultura, Pecuária e Abastecimento
MEKC	Micellar electrokinetic chromatography
MRL	Maximum residue limits
MSPD	Matrix solid-phase dispersion

OC	Organochlorines
OP	Organophosphates
PDO	Protected Designation of Origin
POPs	persistent organic pollutants
PPPs	Plant Protection Products
PYR	Pyrethroids
QuEChERS	Quick, Easy, Cheap, Effective, Rugged, and Safe
SBSE	Stir-bar-sportive extraction
SFE	Supercritical fluid extraction
SPE	Solid-phase extraction
SPI	Spinosad
SPME	Solid-phase microextraction
WWTP	Wastewater treatment plant effluents

1. INTRODUCTION

The region of Trás-os-Montes, in the north of Portugal where the Polytechnic Institute of Bragança is located, is known for being a producer of olive oil and chestnuts. There is a lot of cultivation of olive and chestnut trees, in addition to the vineyards that are in great abundance across the country. For example, according to Instituto Nacional de Estatística (INE), which classifies the regions by agricultural regions that are supplied with olives in Portugal, the Trás-os-Montes region occupies second place in the ranking below only Alentejo, and with a production of 49,937 tons in the year 2022.

One of the insects that has been reducing the productivity of the production of these cultivars is the olive fly, the *Bactrocera oleae*. An option to control this pest in crops and maintain productivity is the use of pesticides and that is why in recent years traces of pesticides have been found in food and water regularly. It is necessary to use a lot of agrochemicals to eliminate pests and prepare the place for the production of cultivars that will serve as food or material to produce other products.

The questioning of the use of these micropollutants is due to the contaminants that are caused, that is, there is a huge environmental impact due to their use, because once applied to the soil, for example, this product can contaminate the soil and all that biota, it can percolate and end up in aqueous matrices. This can be caused by some natural means as rain or anthropically as the removal of riparian forests that are responsible for not letting much waste reach water bodies [1]. This excessive use of pesticides has many environmental impacts, such as soil and water pollution, the selection of resistant organisms and consequences associated with this like the need for increased concentrations and/or application frequency, as well as the substitution with more toxic products. It also affects non-target organisms and human health [2].

Pesticides are widely sold all over the world, and they also have several restrictions, that is, restrictions that are determined by country or by economic bloc, as is the situation in the European Union. For example, the EU is responsible for establishing the maximum amount of pesticides that are allowed in drinking water, because even if there is wastewater treatment, conventional treatments do not remove these micropollutants. There is a diverse amount of pesticides that are used in different parts of the world and it is worth mentioning that there are countries that prohibit and/or ban the use of some pesticides and in others not, so it is important to know the region that is being highlighted and which are the allowed and the laws that are in force [3].

An alternative to reduce contamination at the source and related environmental impacts of pesticides is sustainable agricultural crop management. There are also sustainable remediation methods that can be applied and seek to use active ingredients from natural and recycled sources, in other words, it is trying to carry out environmental compensation, looking for methods that do not generate more waste and that are effective, there are many forms of conventional removals that end up generating other waste and seeking a sustainable solution is seen as the technology of the future [2].

In order to identify pesticides in water, it is necessary to collect the water and subsequently analyze it. The concentrations that are found in nature are very low and it is often necessary to concentrate the sample. In order for there to be a process of recognizing pesticides and their concentrations, an extraction process must be carried out, which can vary according to the pesticide to be analyzed, its physical and chemical properties, such as solubility in water.

Knowing how to quantify pesticides it is possible to apply removal methods that due to the lack of them in the wastewater treatment plant effluents (WWTP) are being studied and developed by others that are capable of removing and meeting the parameters of legislation. Adsorption stands out as a method of removal where natural and artificial materials can be used as adsorbents.

This transformation not only tackles waste management but also underscores the importance of circular economy practices. By converting what was once discarded into a useful material, the olive pit serves as a prime example of how sustainable technologies can mitigate environmental impact while promoting resource efficiency. Such initiatives highlight the potential for industries to adopt eco-friendly solutions that contribute to a greener future. The use of adsorbents produced from olive pits has already been tested and proven to remove pollutants such as estrogens, according to the study by Milani, E. (2023).

Based on research on sustainable practices and the use of olive pits as an ecological solution, this study aims to address the urgent issue of pesticide contamination in water bodies. By employing activated carbon derived from olive pits as an adsorbent, the research seeks to evaluate the effectiveness of removing three specific pesticides - acetochlor, dimethoate, and heptachlor - from aqueous environments. Through a comprehensive approach encompassing production, characterization, and charcoal adsorption experiments, this work aims to contribute to the development of sustainable remediation methods for pesticide removal, aligning with objectives of environmental preservation and resource efficiency.

1.1 OBJECTIVES

The purpose of this work is to evaluate the levels of three pesticides, acetochlor, dimethoate and heptachlor, and its removal from water bodies. The work consists of several stages:

First: use the olive pit as a natural source for the production of charcoal that will be used as adsorbent, with physical and chemical activation, seeking the ideal for adsorption tests of pesticides;

Second: characterize the produced activated carbons by determining pHpzc, acid and basic sites, FTIR, superficial area, volume of micropores, among others;

Third: perform adsorption experiments, studying adsorption isotherms and adsorption kinetics, with the different activated carbons and pesticides. For this, it is necessary to perform the extraction of compounds using the SPME method (solid-phase microextraction) and the analysis using gas chromatography- mass spectrometry (GC-MS), which will be used to identify, quantify and analyze the removal of three pesticides.

2. LITERATURE REVIEW

2.1 EMERGING MICROPOLLUTANTS

Nowadays, the world has been alarmed by the crescent number of emerging pollutants due to the great development of the industries, the exponential growth of the population and consequently urbanisation and agriculture. The aquatic entities and human health are suffering several consequences because of the major toxic effects these pollutants can provide like endocrine disruption, disruption of the production of blood cells, bioaccumulation, cytotoxicity, and chemo-sensitization [1].

The micropollutants are toxic, organic and/or mineral substances, with persistent and bioaccumulative properties that can cause environmental impacts, is understood as an expanding array of emerging pollutants, including steroid hormones, personal care products whose growth has been high in recent years, pharmaceutically active residues, agricultural emissions, detergents, another's industrial chemicals and other toxic substances. Most micropollutants originate from hospital, domestic, agricultural, industrial activities and can be detected in aqueous systems. The environmental impacts associated with micropollutants can come in different ways, but normally through soil and water contamination, but in industries and urban areas they also end up presenting atmospheric pollution, it is highlighted that agricultural areas are capable of contributing in all ways. towards environmental impacts. These chemicals can be natural or synthetic and they belong to the family of contaminants of emerging concern forming the so-called emerging micropollutants (EMPs) and they are present in sewage at low concentrations due to the continuous release produced by human activities [1,2].

Factors such as dependence on chemical products, the non-degradability of most micropollutants and the unbridled growth of the population may increase the level of micropollutants in the future through oil spills, wastewater, industrial and municipal effluents, as there is a limitation for traditional wastewater treatment stations and industrial and municipal effluents, so we do not have a high level of security for the supply of water, making it difficult to consume and use it for other purposes, and agrochemicals are gaining relevance today due to the constant appearance of their residues in water and at relevant concentration levels [3,5].

2.1.2 Pesticides

Pesticides are substances or mixtures of substances that may be chemical, natural or synthetic that are used in the control, prevention and destruction of weeds, pests, diseases and unwanted animals that interfere with the processes of production, transport, storage, agricultural products, wood or animal feed and highlighting that this term does not include fertilizers and additives. The fact is that molecular targets of pesticides are often shared between pest and non-target species, including humans [6].

During the 1970 years, a revolution in pest control began due to the increasing development of pesticides based on toxic heavy metals, such as arsenic, mercury, copper and lead. Due to its effectiveness against a large number of pest species and using low dosages, dichlorodiphenyltrichloroethane (DDT) but due to its high toxicity, long half-life and bioaccumulation capacity, it was banned. Then we have a wide variety of synthetic pesticides that were produced to supply the lack of what had been banned and we have organophosphates and pyrethroids, which are still toxic to the environment.

This toxicity can be evaluated according to the toxicological classification, which is a system that evaluates the potential of a chemical substance to cause harm to human health. This classification is initially based on studies that investigate the adverse effects of a substance on different organs and systems of the human body.

Next, we have dangerousness, which refers to the ability of a chemical product, in this case pesticides, to cause damage to the environment and safety, in addition to the direct effects on human health, and specifying environmental dangerousness we have the potential of a substance to cause damage to aquatic, terrestrial or atmospheric ecosystems and the ability of a substance to remain in the environment for long periods of time and accumulate in the tissues of living organisms, resulting in long-term adverse effects, that is, bioaccumulation[6,7] .

Around 2 million tons of pesticides are being used to combat weeds, pests and insects every year worldwide [7]. The main pesticide-consuming countries are China, the United States of America, Canada, India, Brazil, Argentina, France, Italy and Japan [9]. In Portugal just in 2020 around 9.7 thousand tons were sold, 1.6% lower than the previous year [8(INE)]. In Brazil, the consumption of pesticides has been higher than 300 thousand tons per year of these commercial products. Expressed in the quantity of active-ingredients, there is a consumption of 130 thousand tons in the country, which presents an increase of around 700% in the last forty years while the agricultural area increased by 78% in the same period [9].

Pesticides is considered a term that encompasses numerous groups, that is, there is a conventional classification based on the target species being herbicides, insecticides that dominate 47.5% and fungicides with 29.5% of pesticide consumption in the world, but there are still groups such as garden chemicals, household disinfectants and rodenticides that are used to destroy and protect from pests [7,10].

According to the analysis of the sales structure of Portugal's, Instituto Nacional de Estatísticas (INE), the group of fungicides stands out, representing in 2020 about 66.0% of the total sales volume (58.5% in 2019), followed by herbicides with 24.7 % (22.5% in 2019), in third place the group of insecticides and acaricides with 4.3% (8.2% in 2019), as shown in Figure 1 below.

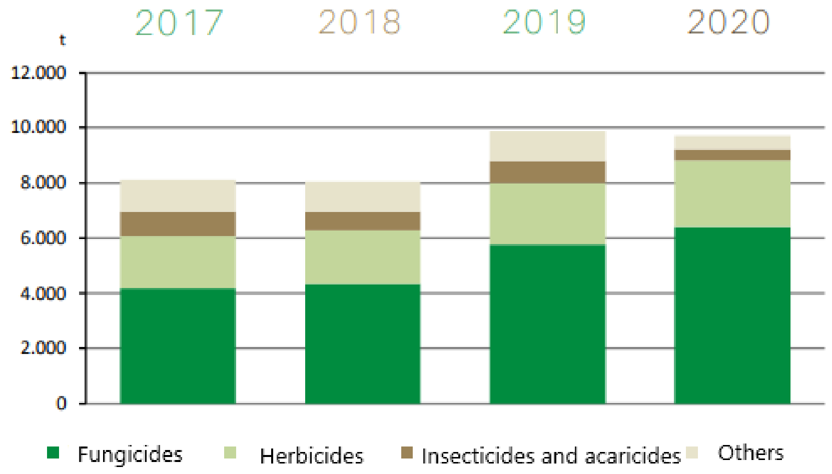

Figure 1. Sale of plant protection products, by type of function (2017-2020).

Source: INE (2021) [8]

Pesticides vary in their chemical and physical compositions from one class to another, so it is important that there is a characterization based on their properties and thus study the groups in particular. A synthetic pesticide is named after a chemical that was made by man and does not exist in nature, its classifications depend on its use. In addition to synthetics, there is also another class called biopesticides, which are natural, and derived from living organisms. Biopesticides are divided into three major groups: biochemical pesticides, microbial pesticides, and plant incorporated protectants [10].

2.1.2.1 Herbicides

Herbicides are pesticides used directly or indirectly to eliminate weeds, that is, some undesirable plants and thus increase crop productivity. Herbicides can have different characteristics in relation to their environmental influences, their mode of application and their physical properties, considering that they are in natural conditions [11,12].

As agriculture advances, there is also an advance in the growing number of applications of herbicides, and consequently, there is an increasing concern about their effects related to the environment. Their prolonged use considerably increases the risk of accumulation and retention, which may be in the soil, crops, surface and groundwater, as herbicides can easily reach water courses due to runoff from agricultural land and crop spraying. When there is exposure over a long period of time, there may be an accumulation and/or transformation of these compounds in the environment, thus affecting aquatic ecosystems, all wildlife and also human health, deriving serious damage related to the nervous, immune, cardiovascular and reproductive systems. Soon they are understood as participants in the degradation of the ecosystem, mainly in regions where commercial agriculture is practised [11,14]. For example, acetochlor is a type widely used in plantations, mainly in crops such as corn, soybeans, cotton and sorghum.

- **Acetochlor**

This is one of the most used pesticides to control annual grasses and broadleaf weeds, which are one of the main problems for agriculture. Due to its wide use, this herbicide is constantly found in the soil and in aqueous matrices all over the world, as it is also endowed with high solubility and low degradation rate. One of the concerns with non-target species is that acetochlor may disrupt the enantioselective thyroid in zebrafish larval embryos and induce oxidative stress and antioxidant activities in human liver carcinoma cell lines. The indiscriminate use of herbicides, especially acetochlor, can lead to the degradation of natural habitats and the loss of biodiversity due to the destruction of non-target plants and the organisms that depend on them, can leach into the soil and reach water sources, resulting in the contamination of aqueous matrices [13].

Below in Figure 2 and Table 1, are presented the structural formula of the acetochlor and some chemical physical and toxicological characteristics, respectively.

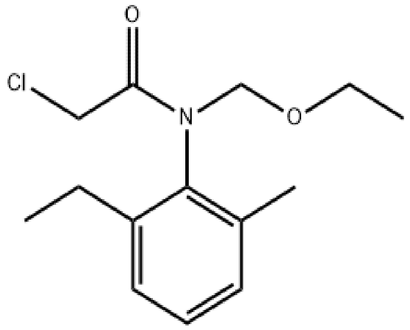

Figure 2 - Molecular structural form of acetochlor.

Source: Adapted from WHO [15]

Table 1- Chemical, physical and toxicological characteristics of acetochlor.

Characteristic	Information
Molecular formula	$C_{14}H_{20}ClNO_2$
CAS RN	34256-82-1
Molar mass (g. mol^{-1})	269.77
Specific mass (g.cm^{-3})	1.1
Boiling point (ºC)	391.5
Solubility in water (mg/L)	222.8
Stability	Photolytically stable in aqueous solution at 25°C
Risk code	Toxic in contact with skin; Toxic by ingestion; Harmful (Xn), Dangerous to environment (N)
Acute toxicity	Moderate toxicity (Class II)
Physical state	Solid
Odour	Aromatic

Colour	Light white

Source: European chemical agency [14] and WHO (2015) [15]

2.1.2.3 Insecticides

This group is used specifically for insects, and is currently being very relevant due to the large number of infectious diseases that are being transmitted by insects, such as dengue, yellow fever, chikungunya and zika, and also parasites such as malaria, trypanosomiasis and leishmaniasis, as well as evidencing a major public health problem [16]. Another great importance of insecticides is their use in agriculture due to the attack of insects on the cultivars, thus harming an entire crop. With all the need for global production and the different types of pests that attack the population, it is necessary to have control of them. At the end of the 19th century the first insecticides were commercialized and since then several others have been analyzed and studied, with that we have some classes of pesticides, namely, organochlorines (OCL); organophosphates (OP); carbamates (CARB); pyrethroids (PYR); and spinosad (SPI) [17,18,19].

Chemical insecticides are classified into four types that depend on the source, namely, carbamate, organophosphate, organochlorine and pyrethroid [11].

Figure 3 below shows a diagram with classification of insecticides:

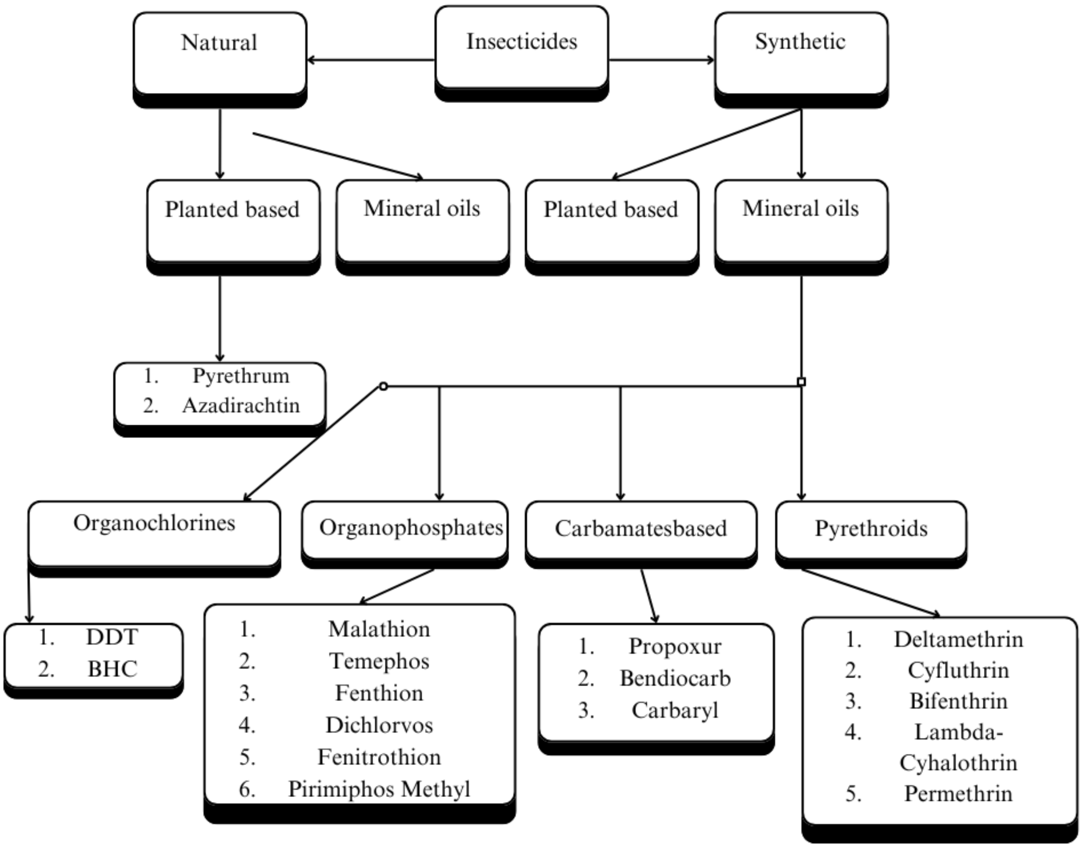

Figure 3 - Insecticides classification.

Source: Adapted from Rajveer Kaur, *et al.* (2019) [20]

- **Dimethoate**

Dimethoate is an organophosphate insecticide with direct action, that is, when in contact with a body it is converted into an active metabolite and has systemic action. It is widely used for a broad range of insects in agriculture and also for the control of flies. This pesticide was introduced on the market in 1956 and is widely used and produced in several countries. Dimethoate is known to be harmful to bees, which play a critical role in plant pollination. Exposure to this pesticide can contribute to the decline of bee populations, which in turn affects food production, and continued use of dimethoate can also lead to the development of resistance in pest populations, making control more difficult. challenging and requiring the use of higher doses of the product; it is a type of pesticide that is considered toxic to humans, as a result of exposure the signs and symptoms develop after latent exposure, and may continue to increase after exposure has ceased [21].

Below the Figure 4 and Table 2, present the structural formula of the dimethoate and some chemical, physical and toxicological characteristics, respectively:

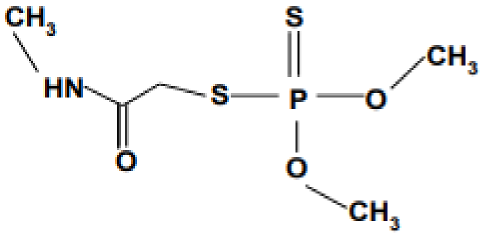

Figure 4 - Molecular structural form of dimethoate.
Source: Adapted from WHO [21]

Table 2- Chemical, physical and toxicological characteristics of dimethoate.

Characteristic	Information
Molecular formula	$C_5H_{12}NO_3PS_2$
CAS RN	60-51-5
Molar mass ($g.mol^{-1}$)	229.2574
Specific mass ($g.cm^{-3}$)	1.304
Melting point (ºC)	52-52.5
Boiling point (ºC/ 0.1 mmHg)	117
Solubility in water	Slightly soluble (2.5 g/ 100 mL)
Stability	Relatively stable in aqueous medium (pH 2-7)
Risk code	Toxic in contact with skin; Toxic by ingestion. Xn: Harmful
Acute toxicity	Moderate toxicity (Class II)
Physical state	Solid
Odour	Mercaptan
Colour	White

Source: WHO, 1998 [21]

- **Heptachlor**

Heptachlor is an insecticide used to control some pests in cultivated or uncultivated soils, such as ants, caterpillars, insect larvae, termites, beetles and other insects. It is present as an impurity in the pesticide chlordane and has a variation which is heptachlor epoxide which is not produced commercially, but is obtained from the oxidation of heptachlor. That is, as heptachlor is very persistent in the soil, it ends up being converted to epoxide, which is a form that degrades more slowly, and thus manages to be more persistent than the initial insecticide. Both heptachlor and its epoxide form absorb very strongly in sediments and both are bio concentrated in aquatic and terrestrial organisms. Heptachlor is part of the list of persistent organic pollutants (POPs) of the Stockholm Convention, which is an international treaty that aims to eliminate these pollutants more safely and limit their production and use; many countries have already restricted the use of this product and others have prohibited it, as is the case in Brazil [22].

Below at Figure 5 and Table 3, are presented the structural formula of the heptachlor and some chemical, physical and toxicological characteristics, respectively:

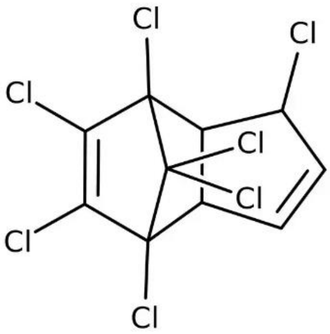

Figure 5 - Molecular structural form of heptachlor.

Source: Adapted from WHO [23]

Table 3- Chemical, physical and toxicological characteristics of heptachlor.

Characteristics	**Information**
Molecular formula	$C_{10}H_5Cl_7$
CAS RN	76-44-8
Molar mass ($g.mol^{-1}$)	373.3
Specific mass (g/cm^3)	1.6
Melting point (°C)	95-96
Boiling point (ºC/ 0.1 mmHg)	160
Solubility in water	Virtually insoluble in water (0.056 mg/L) but fairly

	soluble in organic solvents, e.g., ethanol (45 g/L), xylene (1020 g/L), acetone (750 g/L), benzene (1060 g/L).
Stability	Relatively stable in aqueous medium (pH 2-7)
Risk code	toxic by inhaling dust, by absorption and by ingestion.
Acute toxicity	Moderate toxicity (Class II)
Physical state	Solid
Odour	Camphor (mothballs)
Colour	White and copper colour

Source: WHO [23]

2.1.3 Environmental damage caused by pesticides

In Portugal, in the region of Trás-os-Montes, there is a higher incidence of the production of some crops, such as vineyards and chestnut trees, among which the production of olive oil stands out, with great economic, social and landscape potential. For agriculture, the use of pesticides is very important to help protect cultivars, like in this region in Portugal, especially in these crops, and consequently the pesticide being used is responsible for environmental damage [24,25].

The olive crop has a pest all over the world that often compromises the quality of the oil, and then the olive fly, *Bactrocera oleae*, is responsible for compromising production and with harmfulness documented for a long time in the Mediterranean region, this is a species of monophagous and carpophagous tephritid that attacks the fruits of different subspecies of *Olea europaea L*., with the fly's oviposition on the surface of the fruit and then the damage caused by the feeding of the larva [26]. Therefore, there is a need to control this pest, for which chemical insecticides are used, among them the use of organophosphates, such as dimethoate and fenthion, is known, since the side effects on beneficial insects are known [27].

The exacerbated use of pesticides can lead to many problems for the environment and human health, as it causes the development of cross-resistance and multi-resistance in target insect populations, that is, they adapt to what is being inserted in their environment and this causes an imbalance in the environment and may become an aggravating case in public health [27].

Pesticides can lead to the development of resistance in target populations of insects, target plants and pathogens. This occurs when organisms exposed to pesticides survive and then reproduce, thereby transmitting resistance characteristics to their offspring. In addition to the simple resistance that is best known, there is the development of cross-resistance in organisms, where resistance to one type of pesticide confers resistance to other pesticides with similar modes of action. Over time, this can make the pesticides less effective, requiring higher doses or the use of more potent pesticides. This can result in the need to use a variety of pesticides, increasing the risk of negative impacts on the environment and human health. Excessive use of pesticides can disrupt natural ecosystems, killing not only pests but also beneficial organisms such as pollinators and natural predators. This can lead to an ecological imbalance, causing undesirable changes in biodiversity and ecosystem structure. Furthermore, the risks that these agrochemicals pose to health are very large, especially for farmers, rural workers who deal directly with these chemicals, but also the population closest to rural areas who suffer from the direct effects of contamination. Pesticide exposure can be associated with a range of health problems, including respiratory illnesses, dermatitis, neurological disorders, and even cancer in severe cases [28, 29, 30].

The excessive use of pesticides is one of the main reasons for making sustainable agriculture more difficult; the soil and water matrices close to these agricultural areas also suffer from contamination, that is, the ecological factors associated are the use of pesticides, as well as values of a possible increase in temperature due to the evaporation of these contaminants. Sustainability would reduce environmental impacts as it reduces the use of pesticides and consequently the contamination of air, soil and water [29,30].

One of the ecosystems most affected by pesticides contamination is the aquatic one, as there are many chances for these compounds to reach surface and groundwater, especially in places with greater agricultural activity. That is, supply water and when it is for irrigation because it has direct contact with food and non-target species. These pesticides that later appear in the riverside ecosystems also impact the biological communities present there, and what was evidenced can occur in direct or indirect contact. Pesticides enter the environment through point sources such as manufacturing sites, storage, during transport, industrial and municipal discharges, and through diffuse sources such as agricultural runoff and manure that occur when water moves across the surface or through the soil, and removes from it the pesticides that have been percolated, and consequently are transported and deposited in aqueous matrices. Therefore, the contamination of aquatic resources is due to diffuse sources, that is, after the use of pesticides in agricultural uses and due to natural attenuation, such as rain. For this, it is important to use riparian forests that block the passage of contaminants to aqueous matrices such as lakes, reservoirs, rivers, coastal areas or groundwater [31,32]. Figure 6 below exemplifies point and diffuse sources and their paths to aqueous matrices.

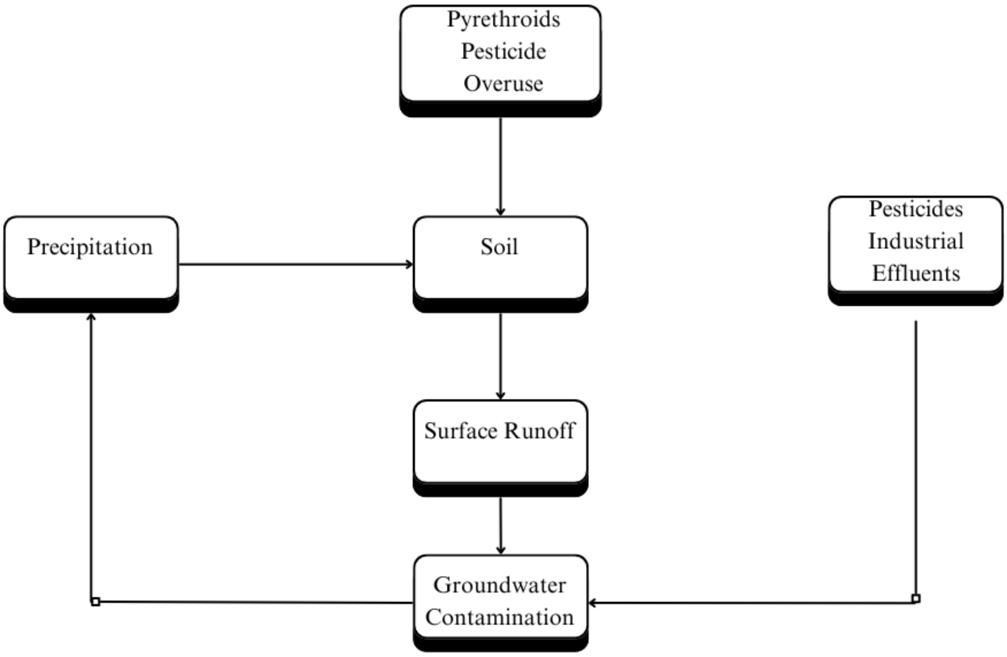

Figure 6: Scheme of the pesticide path from application to aquatic resources

Source: Adapted from A. Ahamad and J. Kumar (2023)

With climate change, there are altered rainfall patterns, and consequently greater impacts are predicted in agricultural regions that do not promote the intensive use of pesticides. With that we have some physical parameters, such as changes in the directions and speed of the winds and in the temperature; the degradation and transformation as chemical and lastly the biological where there are the changes in the microbial activities both in the soil and in the water as stressors that are affecting the environmental distribution and also the toxicity of the pesticides. which are the combined ecotoxicological effects, whether additive, synergistic, potentiating or antagonistic [32].

2.1.4 Legislation and use of pesticides

Even though in recent years there has been greater awareness of the use of pesticides, due to the growing demand for production around the world, it is still necessary to know the limit values that are established by country or by block of countries. That is, it is important to maintain a balance between the risks and benefits of pesticides application [33].

Table 1 above presents the maximum concentration values permitted of some pesticides in water for consumption in Brazil and the European Union.

Table 4 - Minimum requirements for parametric values used to assess the quality of water intended for human consumption.

Pesticide	Maximum limit allowed - Brazil (µg/L)	Maximum limit allowed – European Union (µg/L)
Acetochlor	(-)	0.1
Alachlor	20	0.1
Dimethoate	1.2	0.1
Heptachlor	(-)	0.03
Metolachlor	10	0.1
Terbuthylazine	(-)	0.1

Source: Adapted from Official Journal of the European Union (2020) [33], CONAMA 396/2008[34]. PORTARIA GM/MS Nº 888, DE 4 DE MAIO DE 2021[35].

In the European Union legislation, the concentration values of pesticides are the same for organic insecticides, organic herbicides, organic fungicides, organic nematicides, organic acaricides, organic algicides, organic rodenticides, organic slimicides, related products (inter alia, growth regulators) with 0.10 µg /L as maximum concentration, but in the case of aldrin, dieldrin, heptachlor and heptachlor epoxide, the parametric value shall be 0.030 µg/L, and 0.5 µg/L to 'Pesticides Total', this nomenclature means the sum of all individual pesticides, as defined in the previous row, detected and quantified in the monitoring procedure.

For the placement of Plant Protection Products (PPPs) in the European Union market, the European Commission (EC) defines legislation through Regulation (EC) n° 1107/2009, unacceptable effect on plants, humans or animals and must be convincing. There are also the Maximum Residue Limits (MRL) that are established under regulation, (EC) n° 396/2005 that ensure a higher level of consumer protection, and when an MLR is not explicitly mentioned in the legislation for a given pesticide a default MLR of 0.01 mg/kg is applicable. In Brazil is “the Pesticide Law”, which is regulated by Decree n° 4074/2002, Decree n° 5549/2005, Decree n° 5981/2006, Decree n° 6913/2009, Decree n° 10833/2021 and Decree n° 11,040/2022; all of this occurs through joint action by ANVISA (National Health Surveillance Agency) responsible for assessing the risks of pesticides to human health; IBAMA (Brazilian Institute for the Environment and Renewable Natural Resources), which estimate environmental risks and MAPA (Ministry of Agriculture, Livestock and Supply) which assesses whether pesticides are being efficient for productivity [33,34, 35].

Legislation is present to reduce risks to human health, for this some pesticides still need to be regulated and others need to be reassessed due to their toxicity, mainly in developing countries and with a great focus on agriculture, for example Brazil [34].

2.2 REMOVAL OF PESTICIDES FROM WATER

In conventional water treatment, the technologies that are employed, such as coagulation, flocculation, sedimentation, filtration and disinfection, are relatively weak in terms of micropollutant removal, and they still have rare regulations to limit discharge in wastewater treatment plants. Therefore, it is important to develop technology that aims to remove pesticides from water that undergoes conventional treatments that exist [24].

2.2.1 Extraction techniques

Due to the need to analyse pesticides, so that risks to human health and a series of environmental damages are reduced, as well as compliance with legislation, there are some methods that can be used for its extraction and quantification. Initially, the traditional ones such as liquid-liquid extraction were widely used, but have been replaced by more expeditious methods because the former are slow, laborious and can also be expensive. Recently, there are some methods that are being adopted and most used because they are more effective, cheaper and agile [36]. The pesticide residues that are present in the environment, mainly in aqueous matrices, are usually found in very low concentrations but still not in the values presented by the legislation. Thus, having to search for more specific methods to be analyzed, they must have a high selectivity and good accuracy and preferably be able to analyse different compounds in a single treatment, thus being known as multi residues [37].

The Table 5 presents the procedures of some extraction methods for pesticides, how it is most used and its greatest successes:

Table 5 - Procedures of some extraction methods.

Extraction methods	About the method
Liquid–liquid extraction (LLE)	Adaptable and compatible with a wide range of instruments, LLE is one of the most well-known and well-established
Accelerated Solvent Extraction (ASE)/Pressurised Liquid Extraction	Successfully applied in the preparation of solid and semi-solid samples
Supercritical fluid extraction (SFE)	Used to extract target analytes from solid materials using supercritical fluid as the extraction solvent
Microwave-assisted extraction (MAE)	Sample matrix analytes are partitioned in the solvent by heating solvents in contact with samples using microwave radiation
Solid-phase extraction (SPE)	It is a very common method for isolating and separating analytes from liquids.
Solid-phase microextraction (SPME)	Used for extracting analytes from gaseous, liquid and solid matrices; simple, fast and solvent-free.
Matrix solid-phase dispersion (MSPD) extraction	Allows extraction and cleaning in the same step, simplifying the method and reducing sample loss and solvent use.
Liquid phase microextraction (LPME)	It is a scaled-down version of liquid-liquid extraction (LLE) that can be used to detect pesticide residues in many matrices.
Stir-bar-sportive extraction (SBSE)	A sample preparation process that extracts and enriches organic components from a liquid sample.
Cloud point extraction (CPE)	The existence of cloud point phenomena and micellar solubilization makes extraction in two aqueous phases possible.
QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe.)	Can extract polar and nonpolar molecules at the same time; a microscale extraction procedure, which is faster, easier and requires less organic solvent; It is a quick and easy LLE replacement.

Source: S. Mandal *et al*. (2023) [36]; W.J. Wei *et al* (2022) [38] and Mantovani (2014) [39]

Of the extraction methods listed, the most commonly used for extracting pesticides from water include liquid-liquid extraction (LLE), , solid-phase microextraction (SPME), and the QuEChERS method. LLE is a well-established and adaptable technique. SPME is a simple, fast and solvent-free technique, being especially useful for the extraction of pesticides in aqueous samples, thus being a quick and effective alternative for this extraction.

2.2.1.1 Solid-phase microextraction (SPME)

The solid-phase microextraction (SPME) is a sample preparation technique for extracting analytes from aqueous matrices, which is simple and fast. This sample preparation method consists of sampling, extraction, isolation and enrichment of the analytes in just one step. SPME has two main steps, the first being the partitioning of the analyte between the extraction phase and the sample matrix, the second being the thermal desorption of the concentrated extract when it is connected to an analytical instrument. The advantages of this technique are that they are free of organic solvents and are easy to handle, sensitive, and may become fully automated. However, it also has some disadvantages, which are due to limitations of use for analysis of polar analytes and with low volatility, but also due to the fact that when working with particulate matter, whether in liquid or solid media, greater care must be taken due to fiber fragility. Currently, there are many registrations of commercially available SPME fibers [38,40]. In Table 6 you can find information about some commercial fibers for SPME.

Table 6 - Fibers used for SPME extraction and their characteristics of use by the Supelco trader.

Fiber core	**Pesticides**	**Bond Type**	**pH range**	**Thickness** (μm	**Operation temperature (°C)**	**Recommended Use**
Polydimethylsiloxane/divinylbenzene	Terbuthylazine, Alachlor, Metolachlor and Heptachlor	Partially Crosslinked	2 - 11	65	200 - 270	GC
Polydimethylsiloxane	-	Bonded/ Non-bonded	2-11 and 2-10	7 and 100	220 - 320 and 200-280	GC/HPLC
Carboxen/Polydimethylsiloxane	Dimethoate	Partially Crosslinked	2 - 11	75	250 - 310	GC

Polyacrylate	Alachlor, Metolachlor and Heptachlor	Partially Crosslinked	2 - 11	85	220 - 300	GC/HPLC

Source: Adapted from Hmida (2020) [41] and Supelco [42]

The device used for this method basically consists of a fused silica fiber coated with a sorbent material that must be selected according to affinity with the analytes and compatibility with the liquid matrix [40].

Another advantage associated with using SPME is that it can be combined with many instruments easily, thus expanding the angle of analyses that can be done and analytes that can be used by this method. It can be used with high performance liquid chromatography (HPLC), supercritical fluid chromatography, ion mobility spectrometry (IMS), and gas chromatography (GC) [36].

2.2.2 Analytical method detection

With a high demand for the detection of pesticide residues, there is the use of many more traditional and many modern techniques, where the advantages and disadvantages of both stand out, which are related to questions such as efficiency in separation, analysis time, sample size and interval of the analyte. So, it may even be advantageous for traditional and modern techniques to work together to obtain better results. Table 7 below shows an example of both techniques.

Table 7 - Procedures of some analytical methods detection.

Analytical method detection	About the method
Gas chromatography (GC)	Primarily separates substances based on their volatilities. Non-polar, volatile and easily vaporized substances can be studied
Liquid chromatography (LC)	For high polarity and non-volatile and/or thermally unstable pesticides, liquid chromatography is used as an analytical and separation technique.
Capillary electrophoresis (CE)	Developed as a strong separation method for complex mixtures.
Micellar electrokinetic chromatography (MEKC)	Robust technique for separating neutral and charged analytes using conventional CE equipment.

Capillary isotachophoresis	Method used in analytical chemistry to selectively separate ionic analytes.
Enzyme-linked immunosorbent assay (ELISA)	Capable of providing high sensitivity and specificity to a targeted pesticide.

Source: S. Mandal *et al*. (2023) [36]

2.2.2.1 Gas chromatography (GC)

Gas chromatography is the most popular chromatography technique and it aims to separate substances according to their volatility. Gas chromatography separates individual compounds and is based on their distribution between the stationary phase (liquid or solid adsorbent) and the mobile phase. There are two general types of gas columns for GC, they are capillary columns and compacted columns. The first type is the most used because it has a high efficiency. GC is preferably used for analysis of thermostable, volatile and semi-volatile, polar and non-polar compounds and for compounds that are easily derivable [2,36].

In gas chromatography there are different types of detectors that are classified by mechanism as well as based on ionization, namely, photoionization (PID), electron capture (EDC), thermal conductivity (TCD), thermionic ionization, barrier discharge, optics: photometric flame, chemiluminescence, atomic emission; and electrochemical: electrolytic conductivity detectors, and one of the most used which is Flame Ionization (FID) [41].

Together with the GC we can have a mass spectrometry where it is possible to measure the mass/charge ratio (m/z) of a series of ions in the gaseous phase. To use the MS detection methodology, steps must be followed, namely, the ionization of the sample and the creation of some ions in the gas phase, separation of the ions according to the m/z ratio, and finally the measurement of the number of ions for each m/z value [41].

2.2.3 Removal techniques

The water treatment plants for supply are not very concerned with the pesticides that are present in the water, but with other parameters such as turbidity. It is important that there is technology capable of removing these micropollutants from the water, and for this reason new studies and new advanced technologies are constantly being developed, as we know that the concentrations of pesticides found in nature are very low. These technologies can be used in surface water, groundwater and wastewater, so we have coagulation-flocculation, reverse osmosis, nanofiltration, bioremediation, heterogeneous photocatalysis, chemical treatments and electrochemical methods combined with filtration, and also adsorption [24].

Below in the table there are some studies carried out on the extraction of pesticides and their analysis methods, essential for the removal stage.

Table 8 - Extraction techniques and analytical methods applied to acetochlor, dimethoate and heptachlor.

Pesticides	Analytical Method	Extraction Technique	Reference(s)
Acetochlor	SPE/SPME	GC-ECD	43
Dimethoate	SPE/SPME	GC-MS	44, 45, 46
Heptachlor	SPE/SPME	GC-ECD or GC-MS	47, 48, 49

2.2.3.1 Adsorption

Due to the low efficiency of wastewater treatments carried out by Wastewater Treatment Stations (WWTPs), other technologies are being used to achieve greater success in the treatment of micropollutants, among which adsorption stands out. This technique demonstrates a removal efficiency ranging from 52% to 100% for a dose range of 5 to 20 mg/L. Adsorption is considered a superior and promising methodology due to its simplicity and flexibility, in addition to being an ecological, sustainable, economically viable and technologically advanced solution. Different adsorbent materials, such as activated carbon, zeolites and modified biomass, can be used to remove pollutants, allowing the process to be adapted to different types of contaminants and treatment conditions [50].

The sustainable nature of adsorption is due to the fact that many of the materials are regenerable and reusable, which minimizes environmental impact and reduces the need for constant waste disposal. Furthermore, the simplicity of the process contributes to its economic viability, making it more accessible compared to other advanced treatment technologies. Implementing adsorption technologies in existing WWTPs can be a crucial step towards modernizing these systems, allowing for efficient integration into current treatment processes and a significant improvement in contaminant removal. Thus, adsorption offers a practical and efficient solution to improve the quality of treated water, contributing to environmental sustainability and the protection of water resources [50].

Recently, various adsorbent materials, such as activated carbon, zeolites and modified biomass, have been successfully used to remove pesticides from water. These materials are not only effective in adsorbing contaminants, but they are also regenerable and reusable, which reduces environmental impact and the need for waste disposal. The integration of adsorption technologies into modern WWTPs can significantly improve treatment quality, providing more efficient removal of pesticides and other pollutants. With its ability to adapt to different contaminants and treatment conditions, adsorption represents a practical and effective solution to improve water purification, promoting environmental sustainability and the protection of water resources. The table 9 bellow explain some research about adsorption.

Table 9 - Adsorption studies using olive pits as adsorbent and/or pesticides as pollutants.

Analytical adsorption	About the method
Removal of estrogens from water using olive pit	Activated carbon was used through the olive pit to remove estrogens, where a competition study was also carried out
Purification of glycerol from waste cooking oils	Physically activated charcoal from olive pits was used to remove glycerol using kinetic and isotherm studies.
Use of ball-milled powdered activated carbon (BPAC) for removal of organic pesticides in conventional drinking water treatment process	This study examined the adsorption kinetics, adsorption thermal dynamics, and removal efficiency for six organic pesticides using the ball-milled PAC (BPAC) with varying particle sizes
Carbon materials on pesticides removal and extraction based determination from polluted water	The characteristics, properties, functional strategies, and applications are detailedly presented, and these carbon materials based various solid-phase extraction (SPE) technologies for removal or determination of pesticides

Source: Adapted from Milani (2023) [4], Smolich (2024) [51], Li et al. (2024) [52] and Li W. (2024) [53].

The use of activated carbon derived from olive pits for the removal of estrogens from water has proven effective. This study not only confirmed the capacity of activated carbon to adsorb estrogens but also conducted a competition analysis to evaluate the efficiency of the process under different conditions. Additionally, physically activated carbon derived from olive pits was utilized in the purification of glycerol from waste cooking oils, employing kinetic and isotherm studies to better understand the adsorption process and optimize glycerol removal [4,51].

Another study investigated the use of ball-milled powdered activated carbon (BPAC) for the removal of organic pesticides in conventional drinking water treatment processes. This study detailed the adsorption kinetics, adsorption thermal dynamics, and removal efficiency for six organic pesticides, varying the particle sizes of BPAC. Furthermore, the characteristics, properties, functional strategies, and applications of various carbon materials were presented concerning pesticide removal and solid-phase extraction (SPE) technologies used for this purpose, highlighting the efficacy and versatility of carbon materials in the determination and removal of pesticides from polluted waters [52,53].

3. MATERIALS AND METHODS

This chapter refers to the materials and methodologies used in the experimental work. The research was conducted at the Laboratory of Analytical Chemistry and the Laboratory of Chemical Processes, both located at the School of Technology and Management, in the Polytechnic Institute of Bragança. The materials utilized are cited bellow:

- Sodium chloride +99.5%; Panreac.
- Sodium hydroxide +98%; Panreac.
- HCl with a concentration of 1.2 mol/L, Honeywell.
- KBr; Honeywell.
- Methanol +99.9%; Honeywell.
- Heptachlor, acetochlor and dimethoate were prepared, the agrochemicals were analytical standards with high-purity (98%), and were supplied by Sigma-Aldrich (Merck, Darmstadt, Germany).

3.1 OLIVE PIT

The olive pit used to produce the activated carbon was provided by the Santo Amaro house, it comes from the thread extraction process and is of the species *Olea europea*, with practically zero percentage of oils.

3.1.1 Adsorbent preparation

Initially, the olive pit residue received was crushed in the ZM 200 mill, shown in Figure 7 below.

Figure 7 - Grinding Equipment
Source: Author, 2023.

3.1.1.1 Granulometry

After grinding the dry olive pits, the particle size distribution was assessed using sieves with mesh sizes of 40, 50, 100, and 200, as the grinding process may not produce particles of uniform size. The equipment was placed on a vibrating base for 10 minutes to facilitate the separation process, followed by allowing the mixture to settle to ensure that no particles remained suspended in the solution. This method ensures a more accurate determination of the particle size distribution, which is crucial for subsequent processes and analyses.

To calculate the Sauter diameter, equation 1 below was employed, and this diameter is attributed by the volume/surface ratio, being more accurate than the weighted average of the masses retained in each sieve.

$$Ds = \frac{1}{\sum_{i=1}^{n} \frac{X_i}{D_i}} \tag{1}$$

Where the Ds is the Sauter diameter, the X_i is the frequency distribution and the D_i is the diameter held in each sieve (μm).

3.1.1.2 Coal activation

The production of charcoal by chemical activation was carried out by acid activation of powdered olive pit with concentrated H_3PO_4 and called as CA, activation was carried out in a 1:1:2 ratio (adsorbent, acid and water, respectively – mass proportion) and physical activation just in the muffle and called as CP; Activations were based on Milani research, 2023 [4]. The Figure 8 bellow shows a diagram of the process.

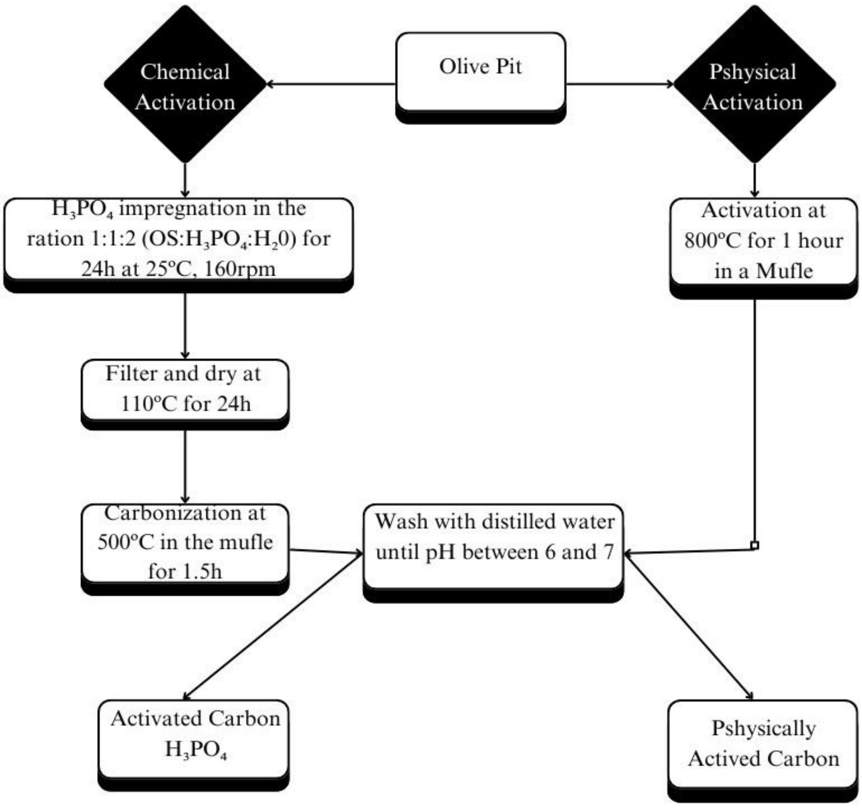

Figure 8 - Scheme of the physical and acid activation process of carbon.
Source: Author, 2024.

The physically process of activation was carried out just at 800°C in a muffle for 1 hours, afer this the coal was washed until pH between 6 and 7, and dry for 24 h with 25°C.

The activation process for the CA was carried out for 24 hours, at 25 °C and 160 rpm for impregnation to occur, then filtration was carried out in order to remove excess water from the coals. After this impregnation process, the charcoal was placed in an oven at 110 °C for 24 hours to dry. Succeeding the activation process, the samples were carbonized as follows: they were placed in crucibles with lids and an internal diameter of 3.9 cm, a height of 5.6 cm and a thickness of 3 mm, in a muffle furnace with a heating rate of 10 °C min^{-1} up to 500 °C per 1.5 hours.

To obtain an activated carbon with pH between 6.0 and 7.0, the coal was washed with solutions of NaOH and HCl 0.02 mol L^{-1} and distilled water. After washing, they were dried for 24 hours in an oven at a temperature of 110 °C. Once the charcoal was dry, it was macerated to form a powder and stored in a jar.

3.1.2 Adsorbent Characterisation

3.1.2.1 Moisture and ash

For the moisture and ash test, triplicates were carried out, where in each replicate, 1 gram of the olive pit was weighed before grinding on an analytical scale, and subsequently taken to the oven where they remained for 24 hours at 110ºC. After this time, were removed and remained in a desiccator until reaching room temperature, then the samples were weighed again and the percentage of humidity following equation 2 below.

$$W\ (\%) = \frac{Wet\ weight - Dry\ weight}{Wet\ weight} x100 \tag{2}$$

To calculate the ash content, the same sample was used after weighing, and placed in a muffle furnace at a temperature of 800ºC for 2 hours. After this period, the samples were kept in a desiccator until they reached room temperature and were then weighed on an analytical balance. The ash content of the samples was calculated according to equation 3:

$$A\ (\%) = \frac{Ash\ weight}{Dry\ weight} x100 \tag{3}$$

3.1.2.2 Carbonization Yield

To determine the carbonization yield, equation 4 was used, where Mi is the mass of the olive pit before carbonization and M_f is the mass after carbonization.

$$CY(\%) = \frac{M_f}{M_i} x100 \tag{4}$$

3.1.2.3 Point of Zero Charge

The point of zero charge (pH_{PZC}) refers to the pH at which a material becomes electrically neutral, that is, it has no net positive or negative charge. Above pH_{PZC}, the surface or material has a net negative charge due to the presence of ionizable functional groups that ionise to release negative ions. Below pH_{PZC}, the surface or material has a net positive charge due to protonation of functional groups, resulting in the release of positive ions [4].

The tests performed were carried out in triplicate. To determine pH_{PZC}, an adaptation of the batch system equilibrium method by Rovani (2015) was used. Eleven Erlenmeyer flasks were prepared containing 25 mL of a 0.01 mol L^{-1} NaCl solution, with the pH adjusted from 2 to 12 using NaOH and HCl solutions, both at 0.02 mol L^{-1}. In each Erlenmeyer flask, 150 mg of adsorbent were added and taken to the shaker incubator for a period of 24 hours at 25ºC and shaken at 160 rpm.

The initial pH (pH_i) and final pH (pH_f) after 24 hours were measured with a pH meter. The pH_{PZC} was determined from a pH variation curve ($\Delta pH = pH_f - pH_i$) as a function of pH_i, finding the intercept point of the abscissa with Y equal to zero.

3.1.2.4 Quantification of surface acidic and basic functional groups

Acidic and basic sites refer to specific regions on a solid surface where acid-base interactions occur. Acidic sites are those sites that have the ability to donate protons (hydrogen ions) or accept pairs of electrons from a base; basic sites are the regions that have the capacity to receive protons or donate pairs of electrons to an acid, they are important because in a porous material they can be crucial for specific chemical reactions, such as the adsorption reaction.

For this analysis, the Batista *et al*. (2022) [54] methodology was used: for the determination of basic sites, 300 mg of adsorbent was placed into an Erlenmeyer and 50 mL of 0.02 mol/L HCl solution was added and taken to a shaker incubator for a period of 24 hours at temperature 25ºC and 160 rpm. After this process, the suspension was filtered and a 10 mL aliquot was removed, titrated with 0.02 mol/L NaOH and phenolphthalein as indicator. 10 mL of the HCl solution without addition of adsorbent were also titrated with NaOH (0.02 mol L^{-1}), this sample being the blank. To calculate the basic sites, equation 5 below was used.

$$Q_B = \frac{5(V_B - V_T)M}{m} x100 \tag{5}$$

Where Q_B is the number of basic groups (mmol g^{-1}), V_B is the volume of NaOH in liters needed to titrate HCl without adsorbent, V_T is the volume of NaOH spent in liters to titrate the filtered suspension, M is the concentration of NaOH solution (mol L^{-1}) and m is the mass of adsorbent used in grams.

For the determination of acidic sites, 300 mg of adsorbent were placed into an Erlenmeyer, 50 mL of 0.02 mol/L NaOH solution was added and placed in a shaker incubator for a period of 24 hours at a temperature of 25ºC and 160 rpm. After this process, the suspension was filtered and a 10 mL aliquot was removed, 0.02 mol/L HCl was added in excess, titrated with 0.02 mol/L NaOH and phenolphthalein as indicator. To calculate the basic sites, equation 6 below was used.

$$Q_A = \frac{5(V_B - V_T)M}{m} x100 \tag{6}$$

Where Q_A is the number of acidic groups (mmol g^{-1}), V_B is the volume of NaOH in liters spent to titrate the NaOH with excess HCl without adsorbent, V_T is the volume of NaOH spent in liters to titrate the filtered suspension, M is the concentration of the NaOH solution (mol L^{-1}) and m is the mass of adsorbent used in grams.

3.1.2.5 Fourier-transform infrared spectroscopy (FTIR)

It is an analytical technique used to identify and analyze the chemical composition of organic and inorganic materials. The sample is exposed to infrared radiation over a wide range of frequencies. The molecules present in the sample absorb this radiation at specific frequencies, which are characteristic of the chemical bonds present in the molecules. The precursor sample (olive pit residue) is prepared for FTIR analysis in tablet form. This preparation involves mixing the material with KBr in a mass ratio of 1:100, followed by pressing the mixture into a mold under pressure. The tablets are carefully removed from the mold. After preparation, the tablets are stored in appropriate conditions until analysis, visually checking their integrity. Each tablet is identified and then analyzed in the spectrum between 4000 and 500 cm^{-1}.

3.1.2.6 Thermogravimetric analysis

The objective of thermogravimetric analysis (TGA) is to investigate the variation in mass of a substance as a function of temperature, under controlled atmospheric conditions. This can reveal important information about the composition, thermal stability, reactivity, and other aspects of the material under study.

The sample was placed in a ceramic crucible, and this analysis was conducted in an atmosphere of synthetic air composed of 21% oxygen and 79% nitrogen, with a flow rate of 100 mL per minute, where heating occurred at a rate of 10°C per minute, ranging from 40 to 900°C.

The analyses were carried out at the Apucarana Multiuser Laboratory Chemical Engineer, Dr. Postgraduate Program in Chemical Engineering - PPGEQ-AP Federal Technological University of Paraná – UTFPR, Street Marcílio Dias, 635 - Apucarana - Paraná – Brazil.

3.1.2.7 Textural properties

To carry out the analysis, acid and physical coals were initially subjected to desorption and drying of the adsorbent for 24 hours in a nitrogen atmosphere. Subsequently, the adsorbents were examined to determine their surface area, porosity, and average pore diameter using a volumetric adsorption analyzer at a temperature of -196.0 °C. The collected data were then adjusted using the Brunauer-Emmett-Teller (B.E.T.) mathematical model to obtain some textural properties, including specific surface area, pore volume, and average pore diameter.

The analyses were carried out at the Apucarana Multiuser Laboratory Chemical Engineer, Dr. Postgraduate Program in Chemical Engineering - PPGEQ-AP Federal Technological University of Paraná – UTFPR, Street Marcílio Dias, 635 - Apucarana - Paraná – Brazil.

3.2 REMOVAL BY ADSORPTION

For the identification and quantification analysis of pesticides, a Shimadzu GC-MS system, specifically the QP2020 model, was employed. This system was outfitted with an AOC-20i autosampler and utilized a Rxi-5ms Low Bleed capillary column provided by Restek (Bellefonte, USA), measuring 30 meters in length with an inner diameter of 0.25 mm and a film thickness of 0.25 µm. The GC-MS utilized is shown in the Figure 9.

Figure 9 - Gas chromatography - mass spectrometry equipment utilized.
Source: Author, 2023.

3.2.1 Analysis of pesticides by GC-MS

The mother solutions of each isolated pesticide were prepared in 100 mL volumetric flasks, using methanol as solvent. After, these solutions were transferred to a 100 mL bottle for later use. In Table 10 below we can see the final concentrations.

Table 10 - Concentration of individual stock solutions.

Pesticides	Concentration (mg/L)
Acetochlor	1000
Dimethoate	502
Heptachlor	480

Source: Author, 2023.

For the calibration curve, concentrations ranging from 0.5 ppm to 22 ppm were initially used for a mixture of the three pesticides and also for each pesticide alone. To make the dilutions, 10 mL volumetric flasks were used and a 1000 µL volumetric pipette was used to pipette the solutions, following their respective ratios to achieve the desired concentration. Then, we topped up the flask with methanol to complete the process. Immediately afterwards, approximately 4 mL were pipetted into 4 mL vials for GC-MS reading.

For the analysis of compounds using GC-MS, we followed the methodology established by Ferroni (2021) [2], which employed a gas chromatograph (GC) coupled to a mass spectrometer (MS). The chromatograph was set with an initial oven temperature of 120 °C and an injector temperature of 250 °C. Samples were injected at a volume of 2 µL in split mode 1:10. The mass spectrometer operated in FullScan mode, with a mass-to-charge ratio (m/z) scanning range from 35 to 450. The ion trap temperature was maintained at 200 °C, while the transfer line temperature was adjusted to 270 °C.

3.2.2 Analysis of pesticides by GC-MS using SPME extraction

For the preparation of dilutions for SPME extraction, sodium chloride and analytical-grade HCl were utilized. The analytical balance used for mass measurements was an ADA 210/C, ±0.0002 g, Adam Equipment.

To analyze the choice of the best fiber using SPME extraction, the solution was initially prepared with a mixture of the three pesticides. The solution was made at a concentration of 5 ppm of each pollutant and 6.25% of NaCl so that SPME could be performed and the fibers would not be damaged. 1.25 g of NaCl were weighed in a watch glass using an analytical balance, according to Figure 10 above, and placed in a beaker together with 10 mL of ultrapure water and solubilized while stirring in a mechanical stirrer. 40 µL of the solution containing 5 ppm pesticide mixture was pipetted into a 25 mL Erlenmeyer flask, then the solution with solubilized NaCl was added and completed with ultrapure water.

The pH was then corrected with a 1 mol/L HCl solution to obtain a pH between 2.5 and 3. Using the digital pH meter equipment, the solution was corrected to a pH of 3.03.

With the solution prepared, 3 mL of this solution was added to four vials with 4 mL, which were then identified and stored in a refrigerator. The fibers that will be used were initially prepared for extraction, in total 4 fibers are used, where each fiber has the color according to its coating, also shown in Table 11 below together with its core and type of assembly.

Table 11 - Type of fiber coating and its core according to color

Hub description	Fiber Coating	Fiber core/Assembly type
Red	PDMS (Polydimethylsiloxane)	Fused Silica/SS
Black	CAR/PDMS (Carboxen/Polydimethylsiloxane)	Fused Silica/SS
Blue	PDMS/DVB(+OC) (Polydimethylsiloxane/ Divinylbenzene)	Fused Silica/SS
White	Polyacrylate	Fused Silica/SS

Source: Author, 2023.

In the Table 11 above is available the specifications of each fiber according to colour, with the information provided we can relate it to Table 12 below which demonstrates characteristics of the fibers.

Table 12 - Thickness and pH range for each fiber in SPME

Fiber Coating	Film Thickness	pH
PDMS	100	2-10
CAR/PDMS	All	2-11
PDMS/DVB(+OC)	65 (+10)	2-11

Polyacrylate	85	2-11

Source: Author, 2023.

The fibers above were initially activated to carry out the extractions, each one was activated according to its activation temperature during the period suggested by the supplier, Table 12 above, and table 13 below in the GC-MS.

Table 13 - Temperature and conditioning guidelines for SPME.

Fiber Coating	**Maximum Temperature** (°C)	**Recommended Operating Temperature** (°C)	**Conditioning Temperature** (°C)	**Conditioning Time (h)**
PDMS	280	200-280	250	0.5
CAR/PDMS	320	250-310	300	0.5
PDMS/DVB (+OC)	270	200-270	250	0.5
Polyacrylate	300	220-280	280	0.5

Source: Author, 2023.

With the SPME solutions prepared and stored, we place each fiber individually in the syringe, placing it in a syringe holder and bathing it for 1 hour in a mechanical shaker at a temperature of 60ºC and rotation speed of 4. For this bath, the fiber needle in the syringe pierces the vial with the solution and remains at a minimum distance from the solution and then the fiber is exposed as shown in Figure 10 below.

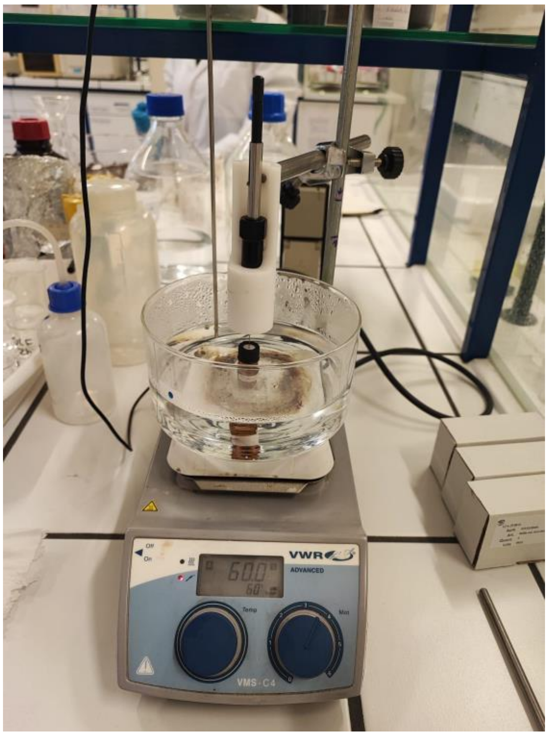

Figure 10 - Solution extraction in SPME
Source: Author, 2023.

After 1 hour, the fiber was collected from extraction and inserted into the GC-MS for analysis. For this analysis, it was necessary to remove the equipment rack to perform direct insertion. The fiber is exposed after the needle is inserted into the GC-MS and remains for 4 minutes, the time needed for the fiber to be cleaned and the compound to be absorbed by the equipment, and after another 13 minutes the entire reading will be complete. Next in Figure 12 we can see the GC-MS without the rack for SPME analysis using the fibers.

Figure 11 - GC-MS without the rack.
Source: Author, 2023.

3.3 REMOVAL OF PESTICIDES

The adsorption study was used to evaluate the removal of acetochlor, dimethoate and heptachlor from water samples. For these analyses, solutions were prepared with ultrapure water and the stock solution mentioned previously in Table 9 was used. To evaluate the removal (%) and adsorption capacity (mg/g) which corresponds to milligram (mg) of adsorbate per gram (g) of adsorbent, equations 7 and 8 below were used.

$$R(\%) = \frac{C_i - C_f}{C_i} x100 \tag{7}$$

$$q = \frac{(C_i - C_f)V}{m} x100 \tag{8}$$

Where C_i is the initial concentration in mg/L, C_f is the final concentration after adsorption in mg/L, V is the adsorption volume in liters and m is the mass of adsorbent in grams.

To determine the error, was utilized RSS value on the adjustments made, equation 9 below is used.

$$RSS = \sum_{i=1}^{n}(y_i - \hat{y}_i)^2 \tag{9}$$

Where n is the number of experimental points, y_i is the value of q found according to the experiments and $\hat{y}_i$ is the value of q predicted by the model.

Using equations 6, 7 and 8 above, you can calculate the percentage of removal, the adsorption capacity and the error in relation to the adjustments made. From this it is possible to carry out kinetic analyses.

3.3.1 Kinetics

The kinetic tests occurred with two different activated carbons: one using physically activated carbon (CF) and heptachlor as pollutant and the second using acidic carbon (CA) and the acetochlor as pollutant. For both tests, 50 mL of each pesticide solution was used at a concentration of 10 ppm and in duplicate.

For the kinetic test using CF as adsorbent and heptachlor as pollutant, the time was varied from 0.5 to 24 hours, with 7 points (0.5, 1, 2, 4, 5, 6, 8 and 24 hours), using 30 mg of the adsorbent at temperatures of 25 °C, 35°C and 45°C and agitation in 160 rpm. For the CA kinetic test with acetochlor, the time was varied in the same proportion of points, but we changed from 8 hours to 7 hours, the other parameters are the same as the previous test.

To treat the data arising from the kinetic tests, equations 10, 11 and 12 below were used, aiming to adjust the pseudo-first order, pseudo-second order to the experimental data.

$$q_t = q_e[1 - e^{(-k_1 t)}] \tag{10}$$

$$q_t = \frac{q_e^2 k_2 t}{k_2(q_e)t + 1} \tag{11}$$

Where q_t is the amount of adsorbate adsorbed by the adsorbent (mg g^{-1}) at any time, q_e is the amount of adsorbate adsorbed by the adsorbent (mg g^{-1}) at equilibrium, k_1 is the pseudo - first order constant (min^{-1}), k_2 is the pseudo-second order constant (g mg^{-1} min^{-1}), t is the contact time in minutes.

3.3.1.1 Activation energy

The activation energy is the minimum energy that molecules must have to start a chemical reaction. The higher the activation energy, the slower the reaction. The methodology of Hussain *et al*. [55] was used which used the Arrhenius postulate where its linearized form is demonstrated in Equation 12.

$$ln\, k = -\frac{Ea}{RT} + ln\, A \qquad (12)$$

Where E_a is the activation energy in J mol^{-1}, R is the ideal gas constant with a value of 8.314 J mol^{-1} K^{-1}, T is the temperature in K, A is a pre-exponential factor and k is the kinetic constant reaction rate in g mol^{-1} min^{-1}.

3.3.2 Isotherms

3.3.2.1 Adsorption equilibrium

The adsorption equilibrium study was carried out by varying the mass of adsorbent between 5 and 35 mg. In total there were 7 points, being 5, 10, 15, 20, 25, 30 and 35 mg of adsorbent for CA and CF, with 50 mL of solution at a concentration of 10 ppm of each pesticide. The removal of heptachlor was carried out using the CF, and Acetochlor using the CA, both with a duration of 5 hours and a temperature of 25 °C.

Freundlich, Langmuir and Radke isotherms models were used to fit the experimental data, and according to the experimental data we have graphs of adsorption capacity at equilibrium (q_e) and residual pesticide concentration at equilibrium (C_e). Next, we have equations 13, 14 and 15 responsible for the adjustment.

$$q_e = K_f C_e^{\frac{1}{n}} \tag{13}$$

$$q_e = \frac{Q_{max} K_L C_e}{1 + K_L C_e} \tag{14}$$

$$q_e = \frac{(ab(Ce^m))}{(a + b(Ce^{(m^{-1})}))} \tag{15}$$

Where q_e is the amount of adsorbate adsorbed by the adsorbent ($mg^{-1}\ g^{-1}$) at equilibrium, C_e is the residual pesticide concentration at equilibrium (mg L^{-1}), KF is the Freundlich equilibrium constant (mg $g^{-1}\ L^{-\frac{1}{n}}$), n is the dimensionless exponent of the Freundlich equation, KL is the Langmuir equilibrium constant (L mg^{-1}) and Q_{max} is the maximum adsorption capacity of the adsorbent (mg L^{-1}) ; a represents the adsorption equilibrium constant, which reflects the affinity between the adsorbate and the adsorbent (L/kg), b refers to the parameter that describes non-ideality in adsorption [(mol/kg)/(mol/kg)/(mol/L)^m] and m represents the slope of the adsorption isotherm at low concentrations.

4. RESULTS AND DISCUSSION

Regarding coal, the careful analysis of its physical, chemical and structural characteristics allows evaluating the adsorption capacity, textural properties, that is, critical factors that determine its efficiency.

4.1 HUMIDITY AND ASH

For this research, results of 14.62% humidity and 1.29% ash were obtained. Humidity (w) is the water content present in the materials, and its determination is extremely important because in organic materials with high humidity it can promote the proliferation of bacteria in the product, altering the characteristics of the raw material. Determination of ash (A) content specifies the amount of inorganic matter that is contained in the material. Table 14 below exemplifies the values found for humidity and ash in this work compared with other results found in other research work.

Table 14 - Results for moisture and ash content for olive pits and their respective errors.

W%	A%	Author
7.4 ± 0.36	0.92 ± 0.12	Biron (2016) [56]
12.13 ± 0.08	1.09 ± 0.08	Milani (2023) [4]
14.62 ± 0.13	1.29± 0.38	This research (2024)

The results for this research are similar to those of the previous ones, with a good standard, that is, in terms of humidity, we have material with slightly more moisture, and proportionality in terms of ash is maintained.

4.2 GRANULOMETRY

The sample was subjected to sieving processes, subsequently, the masses of particles retained by the equipment were recorded at different times, thus allowing the determination of the granulometric distribution of the material. The results for these analyses are in the Table 15 bellow.

Table 15 - Results for particle size distribution.

Mesh	Diameter (µm)	Retained mass (g)	Pass accumulated	Retained accumulated
40	420	0.17	99.2%	0.8%
50	297	0.25	97.9%	2.1%
100	149	3.96	78.1%	21%
200	74	6.45	45.9%	54.1%
Bottom	-	9.19	0%	100%

Source: Author, 2023.

The Sauter diameter found for this material using the equation 1 was 0.174 mm or 174 μm. This is the value of the average diameter of the olive pit sample submitted for analysis. A fine particle, the smaller the particle size, the greater the surface area

4.3 CARBONIZATION YIELD

The table presents the results of the carbonization yield of activated carbon prepared from olive pits using two different activation processes: a physical process (CP) and an acidic activation process (CA) with phosphoric acid (H_3PO_4). Carbonization yield is expressed as the percentage of the mass of activated carbon obtained after the carbonization process relative to the initial solid mass, indicating how much activated carbon is produced from a certain mass of olive pits.

Table 16 - Physical and acid coal results for carbonization yield.

Activation	%Carbonization yield
Physical Carbon	19.40 ± 0.90
Acid Carbon	59.19 ± 0.95

Source: Author, 2024.

It can be seen that there is a large difference between the percentage of carbonization of physical coal in relation to acid coal, that is, the percentage presented for acid coal of 59.19% is about 3 times greater than that of physical coal which is 19.40%. Corroborating previous studies by [56] which states a higher carbonization rate for charcoals from activated materials in an acidic environment with around 35.96%, the physical one being 25.5%. It can be associated with more efficient dehydration, protection against volatilization and greater formation of a porous structure due to the action of the applied acid

4.4 POINT OF ZERO CHARGE

For adsorption tests, the adsorption capacity is closely linked to the surface charge of the materials present on the pore walls. This charge, in turn, is significantly influenced by nanoscale confinement within the mesopores. A fundamental concept related to surface charge is the point of zero charge (PZC). This point represents the condition in which the net electric charge density on a surface is zero. PZC is generally defined by the pH of the solution at which the surface charge becomes neutral [57]. The point of zero charge founded for the CA was 2.55 and 7.24 for the CP, these results reflect the activation methods, the acid activation with H_3PO_4 got acid character and the physical got a basic character.

For example, Jacobson *et al*. (2022) [57] presents studies related to mesoporous silicas, where the surface charge increases due to factors such as ionic diffusion and the curvature of the pore throats. In carbon materials, the geometry of the mesopores plays a crucial role in determining the surface charge, thus affecting the flow of ions in nanochannels.

Zero charge point analyzes (pHpzc) were carried out for CP and CA coals. In Figures 12 and 13 below, we have a representation of the pH behavior of these materials and their respective neutral charge points.

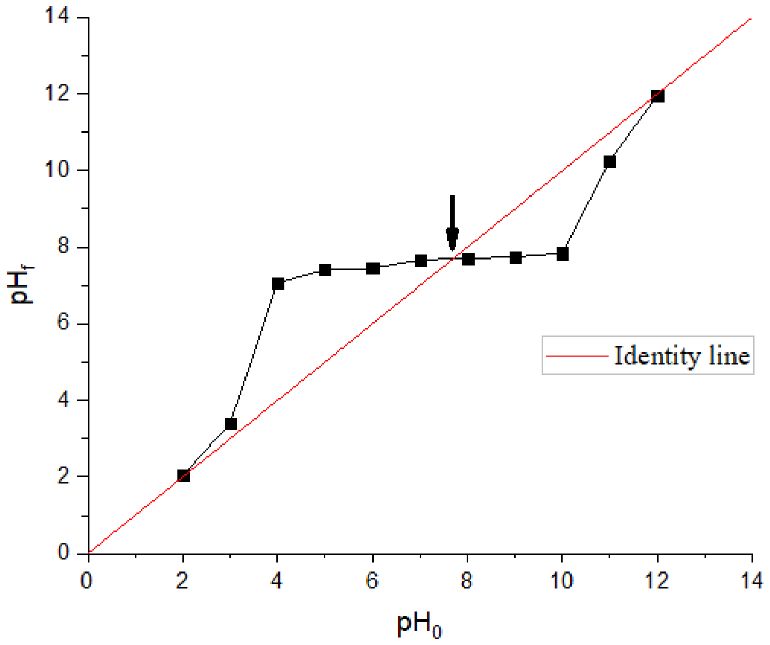

Figure 12 - pHpzc graph for physical coal

Source: Author, 2024.

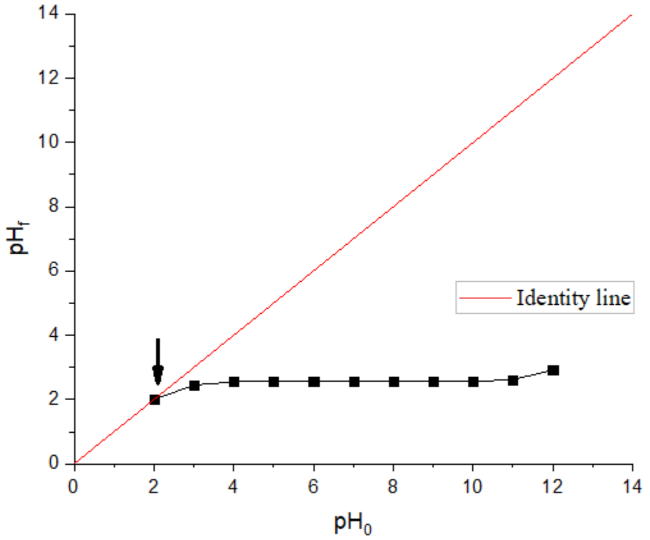

Figure 13 - pHpzc graph for acid coal

Source: Author,2024.

The physical coal obtained a PZC value of 7.24, closer to neutral pH, due to this coal being only carbonized at 800°C and not having any chemical activation agent and located at the point on the graph where an arrow is noted, the CA which was activated with H_3PO_4 had its PZC value of 2.55 considered acidic, the expected values are slightly lower than the results obtained by other researches, as can be seen below in Table 17.

Table 17 - pHpzc values for some activation methods.

Biomaterial	**Activation**	**pH_{PZC}**	**Author**
Olive Pit	H_3PO_4	3.88 ± 0.38	[58]
Olive Pit	H_3PO_4	3.84 ± 0.05	[4]
Olive Pit	H_3PO_4	2.55 ± 0.01	This research
Olive Pit	800°C	7.71 ± 0.19	[58]
Olive Pit	800°C	8.64 ± 0.02	[4]
Olive Pit	800°C	8.91±0.47	[52]
Olive Pit	800°C	7.24±0.34	This research

Table 17 above makes a comparison of the pHpzc found for activated carbons under the same conditions, and presents the point of zero charge value below in relation to the same acid activation carried out in other research, now considering physically activated carbon, close values were obtained for [58] in the same activation. The values also show similarity with the form of activation, that is, an acidic activated carbon has a point of zero charge with a more acidic rate and the physically activated one has a more neutral character as it is the same as the natural material, that is, as no there are chemical changes in its form and only physical transformations, the pH is not affected as much. The pH values may be associated with lower values due to the final washing process, which is assigned an ideal range of 6 to 7. The acid charcoal was closer to 6, while the physical one was closer to 7. Below the neutral charge point the charges will be positive due to the presence of H^+ and above they will be negative due to the presence of OH^-, so if my pollutant is negatively charged, a lower pH of the phpzc is recommended to have a greater electrostatic attraction and thus make stronger adsorption as well

4.5 QUANTIFICATION OF SURFACE ACIDIC AND BASIC FUNCTIONAL GROUPS

Quantifying surface acidic and basic functional groups is pivotal in understanding adsorption phenomena as it delineates adsorbate-surface interactions, influences surface reactivity and catalysis, determines adsorption capacity, and guides surface modification strategies.

The point of zero charge (PZC) is intimately related to the quantification of surface acidic and basic functional groups, as it provides crucial information about the surface's charge behavior in different pH environments. Determining the PZC involves understanding the balance between acidic and basic functional groups on the surface.

Table 18 - Results obtained for the acidic and basic sites of the activated carbons.

Activated Carbon	Acid sites (mmol/g)	Basic sites (mmol/g)
CP	0.39 ± 0.05	0.48 ± 0.03
CA	11.20 ± 0.13	2.53 ± 0.08

The table 18 above compares acid and basic sites for two types of activated carbon: CP, derived from olive pit through physical activation, exhibits lower acid and basic sites (0.39

± 0.049 mmol/g and 0.48 ± 0.032 mmol/g, respectively), while CA, an acid-activated carbon, shows significantly higher values for both, basic (2.53 ± 0.080 mmol/g) and specially acid sites (11.20 ± 0.126 mmol/g), indicating its suitability for applications requiring heightened surface reactivity.

The high values related to acidic sites can be attributed to acid activation, that is, the use of the acidic chemical component for the production of charcoal.

Quantifying these groups allows for the precise estimation of the PZC, enabling predictions about the surface charge under varying pH conditions. This knowledge is vital for optimizing adsorption processes, controlling surface reactivity, and designing materials tailored to specific applications where adsorption phenomena are significant.

In the realm of adsorption, the number of active sites aligns with the surface area, notably the micropore volume, which holds primary sway over the overall surface area. Thus, adsorbents boasting larger surface areas hold apparent advantages in adsorption processes. Moreover, surface groups introduce a spectrum of charges positive, neutral, or negative across the surface, rendering it capable of attracting adsorbing species, thereby enhancing its efficacy in capturing target substances [59].

4.6 FOURIER-TRANSFORM INFRARED SPECTROSCOPY (FTIR)

In further investigating the composition of the adsorbent's surface, Fourier Transform Infrared Spectroscopy (FTIR) analysis was employed. This comparative analysis aids in understanding how the surface chemistry of the adsorbent evolves during the carbonization process, ultimately impacting its adsorption properties.

Below is the Figure 14 showing the results obtained for the analysis of these functional groups for CP and CA.

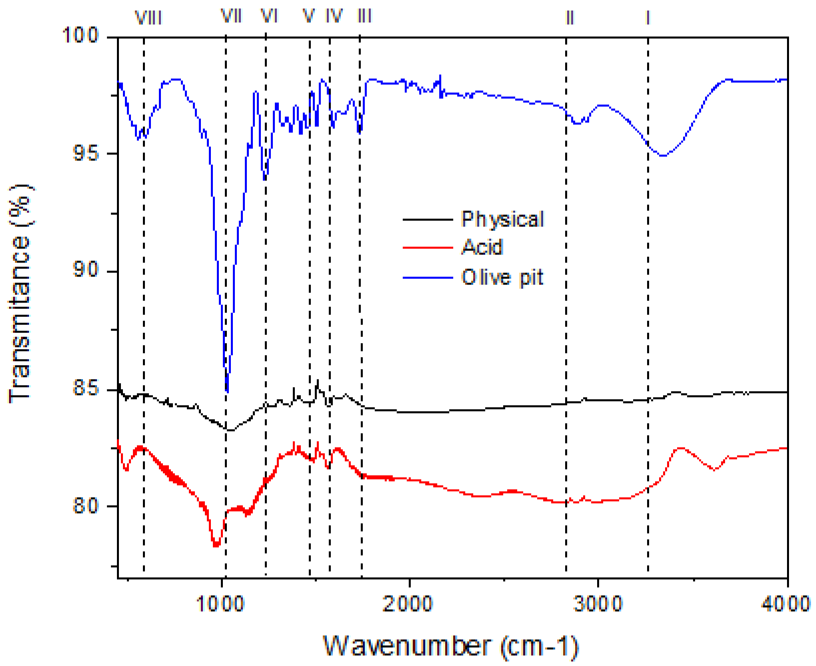

Figure 14 - FTIR graph for olive pit in natura and the activated coals.

Source: Author, 2023.

This graph shows the results for CP and CA where we have the transmittance by wavenumber, within this result we can observe the bands that correspond to those observed in the spectra and the respective functional groups identified, in Table 19 below it is detailed this information.

Table 19 - Identification of the wave number and associated functional groups for CA, CP, and the raw material.

Peak number	Wavenumber	Functional group	Reference
I	3336	O — H (Alcohol and phenols)	[60]
II	2783	H — C	[61]
III	1732	C = O (phenolic hydroxyl)	[61]
IV	1594	C=C (aromatic bond)	[60]
V	1475	C — O (ester)	[60]
VI	1233	O — C (ester)	[62]
VII	1028	O — C (ether)	[60]
VIII	493	C — H (cyclic amides)	[60]

Table 19 presents the functional groups highlighted by the FTIR analysis carried out for the two coals and the material and natural. This way you can see the changes that occur in groups according to activation.

This analytical technique allows for the comparison of functional groups present before and after carbonization. FTIR provides valuable insights into the chemical composition of materials by analyzing the absorption of infrared light by molecular bonds by examining the FTIR spectra, one can identify changes in functional groups, which can shed light on the structural transformations occurring during carbonization.

For the comparation between the olive pit and the activated coals, initially, it is noteworthy the decrease in the cyclic amide group in the activated carbons compared to olive pit in its natural form. This decline is more pronounced in the physically activated charcoal, suggesting a breaking or modification of amide bonds during the activation process.

Furthermore, there was a significant reduction in the presence of the ether group in the activated carbons compared to the original material. This decrease can be attributed to the breaking of ether bonds during the activation process, resulting in a change in the chemical structure of the activated charcoal.

Although the aromatic groups did not show drastic changes, slight alterations in the carbon-hydrogen bonds associated with these functional groups were observed after activation [61].

Lastly, the alcohol and phenol groups exhibited considerable variations, especially in the physically activated carbons. This suggests modifications in the chemical bonds of these hydroxyl groups during activation, resulting in a change in the presence and structure of these functional groups in the activated carbons [60].

These differences highlight the significant impact of the activation process on the rearrangement of chemical bonds and the presence of different functional groups in the structure of activated carbons, providing important insights for their application.

4.7 THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis (TGA) is an analytical tool utilized to examine the pyrolytic degradation composition of heterogeneous biomass. This method holds considerable importance owing to the kinetic factors involved in understanding the pyrolytic decomposition of biomass. By scrutinizing the changes in mass as temperature increases, TGA provides valuable insights into the thermal stability, composition, and physical properties of biomass materials. Additionally, derivative thermogravimetric analysis (DTGA) further enhances the understanding by revealing specific decomposition processes or chemical reactions occurring at different temperature ranges. Therefore, the application of TGA and DTGA aids significantly in unraveling the complex nature of biomass pyrolysis, thereby facilitating advancements in various fields such as renewable energy production and sustainable resource utilization [63].

Figures 15 and 16 bellow show the results for each coal.

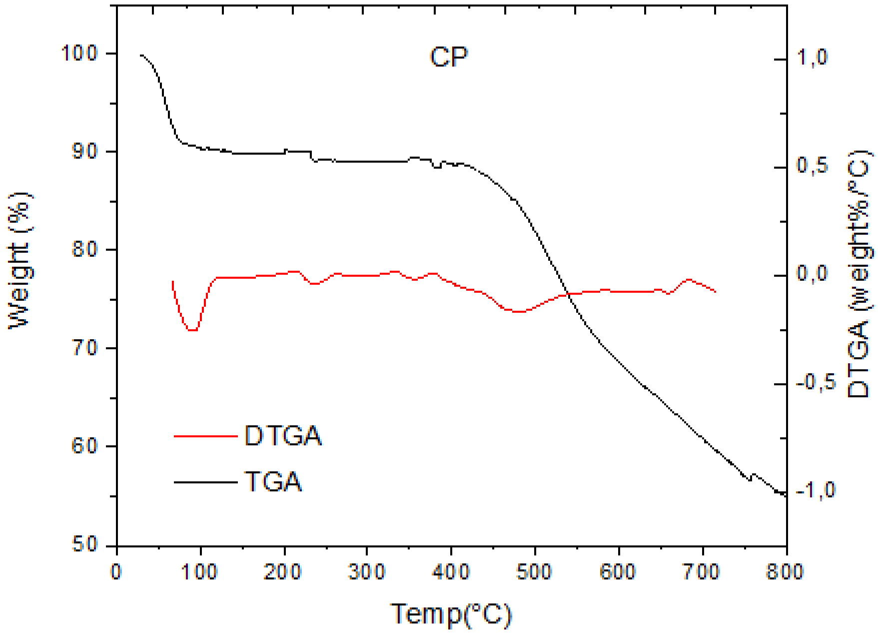

Figure 15 - Thermogravimetry for physical coal.

Source: Author, 2024.

Initially, up to 100°C, this physical coal experience a decrease in mass as moisture is expelled. Following this, as the temperature approaches between 200°C and 300°C, a devolatilization process commences, predominantly decomposing cellulose and hemicellulose [64,65]. After this point, the other decrease between 400°C and 700°C and the decrease in mass observed may be attributed to the thermal decomposition of lignin present in the activated carbon derived from olive pit. Lignin, a complex polymeric component, can decompose into volatile gases and carbonization products at high temperatures, thereby contributing to the mass loss recorded in thermogravimetry [66].

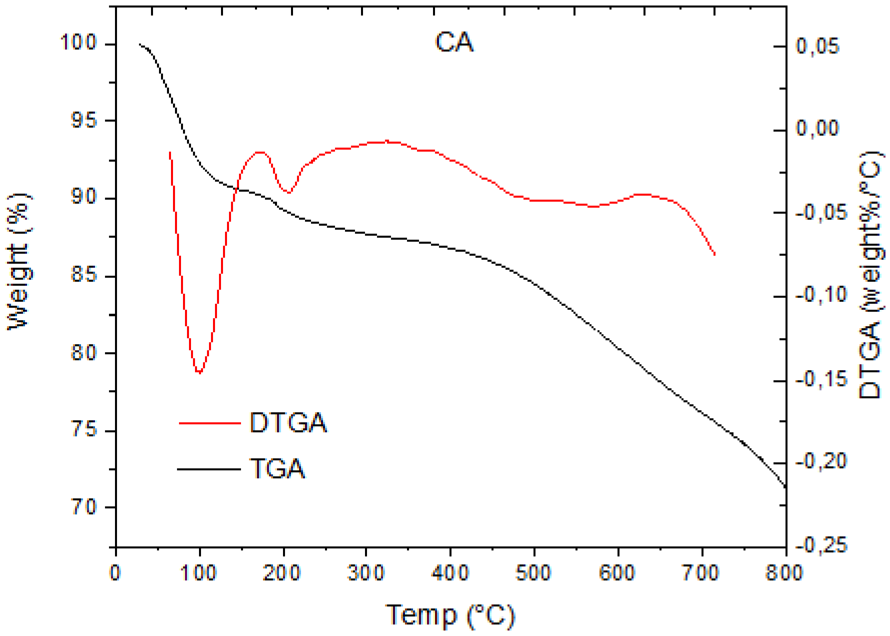

Figure 16 - Thermogravimetry for acid coal.

Source: Author, 2024.

In this analysis, we have the same parameters for loss as the physical charcoal presented above, but there is a noticeable higher loss in mass compared to the physical one. The acid activation with H_3PO_4 can cause a greater removal of mineral impurities and a higher creation of porosity in the charcoal structure, leading to increased moisture adsorption and consequently greater mass loss at lower temperatures. Additionally, the alteration in the material's chemical structure during acid activation may result in a different thermal decomposition at higher temperatures, explaining the higher mass loss observed after 400 degrees [67].

4.8 TEXTURAL PROPERTIES

Among adsorbent materials, activated carbons stand out as unique and versatile substances due to their considerable surface area, microporous structure and diversity of adsorption effects, in addition to having high adsorption capacity and surface reactivity. However, the phenomenon of adsorption on activated carbon is highly complex, influenced by a range of factors ranging from the chemical composition to the textural properties of the material [68].

Surface oxygen complexes are particularly relevant and prevalent, playing a fundamental role in the physicochemical and surface properties of carbons. The relationship between surface group (SG) content and adsorption properties has been the subject of theoretical and experimental study in porous carbons [68], especially in activated carbon and soot particles, the authors also state that previous studies on the Influence of surface groups such as COOH and OH have suggested that dispersive interactions with the π cloud of activated carbon play a significant role in the adsorption process, mainly leading to physisorption of the substrates of interest onto the carbon surface. It is important to note that these studies generally focus only on the protonated form of these surface groups, failing to consider the influence of pH on these chemical species [68].

Table 20 – Some textural properties of CP and CA.

Activation carbon	**Surface area (m^2 /g)**	**Micropore area (m^2 /g)**	**Micropore volume (cc/g)**	**Pore volume (cc/g)**	**Pore diameter (nm)**
CA	488.7383	362.949	0.194684	0.2030	1.1318
CP	379.256	354.168	0.190393	0.1891	1.1194

The table above presents the results obtained for the parameters of surface area, micropore area and volume, pore volume, and average pore diameter.

The CA sample displays a significantly larger surface area compared to CP (488.7383 m^2/g versus 379.256 m^2/g). This suggests that the CA sample possesses a more developed porous structure, providing a larger area for adsorption interactions. Similarly, the micropore area of CA is also greater than that of CP (362.949 m^2/g versus 354.168 m^2/g), indicating a small difference proportion of micropores in CA's porous structure. The total pore volume and micropore volume are slightly higher for the CA sample compared to CP (0.2030 cc/g versus 0.1891 cc/g for total pore volume and 0.194684 cc/g versus 0.190393 cc/g for micropore volume). This suggests that the CA sample has slightly higher porosity, especially concerning micropores, which are crucial for the selective adsorption of specific-sized molecules. The average pore diameter is similar for both samples, with values close to 1.12 nm. This suggests that both samples have a predominantly similar pore size distribution. Overall, the results indicate that the CA sample possesses a more developed porous structure, with larger surface area and micropore area compared to CP. This may make CA more effective in adsorption applications, especially when size-selective molecule adsorption is important.

Furthermore, characterization contributes to the development of more effective activation methods, ensuring that they meet the specific requirements of each application. Therefore, understanding the properties of activated carbon through characterization is essential to optimizing its performance, promoting more efficient and sustainable solutions to diverse environmental and industrial challenges.

4.9 ANALYSIS OF PESTICIDES BY GC-MS WITHOUT EXTRACTION

In this regard, we have the identification of pesticides in the GC-MS where the signal time of the substance that was used is the same as that obtained by Ferroni (2021) [2] and also identified by the target ions selected; in Table 21 below these points are mentioned.

Table 21 - Identification of the elution order and signal intensity (TIC) for each pesticide and the target ions.

Elution order	Pesticide	Retention time (min)	Target ions
1	Dimethoate	10.012	65, 100 and 272;
2	Acetochlor	12.684	59, 146 and 223;
3	Heptachlor	13.056	87 and 125.

Ferroni (2021) [2], determined the ions based on the mass spectrum obtained from the individual analysis of each pesticide. The evaluation focused on identifying the most abundant ions and those that stood out for each compound. Figure 17 bellow shows one identification of the heptachlor signals.

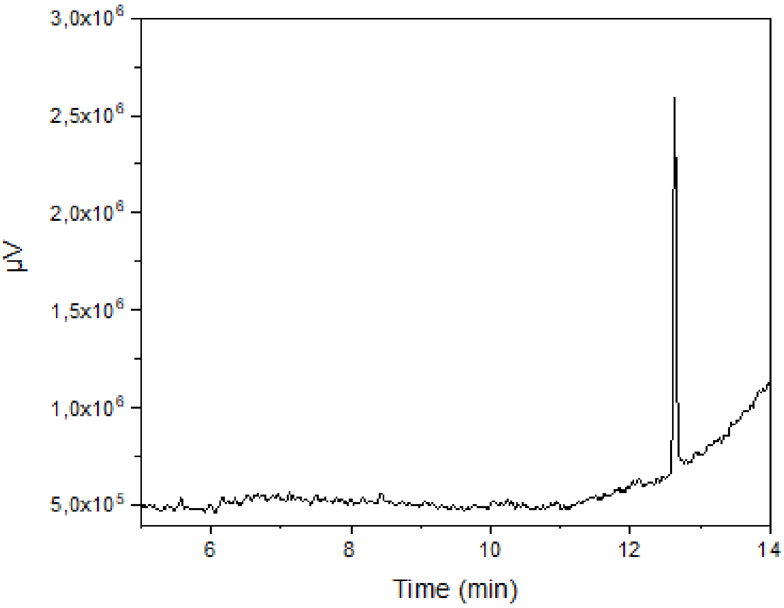

Figure 17 - Heptachlor signal identification on the chromatogram.

Source: Author, 2024.

It was possible to obtain the calibration curve for pesticides in the same way. For this, they were analyzed with a slightly higher concentrations in order to obtain better results and to serve as a basis later.

In the figures below we have the calibration curves for dimethoate, acetochlor and heptachlor with concentrations from 8 till 22 ppm.

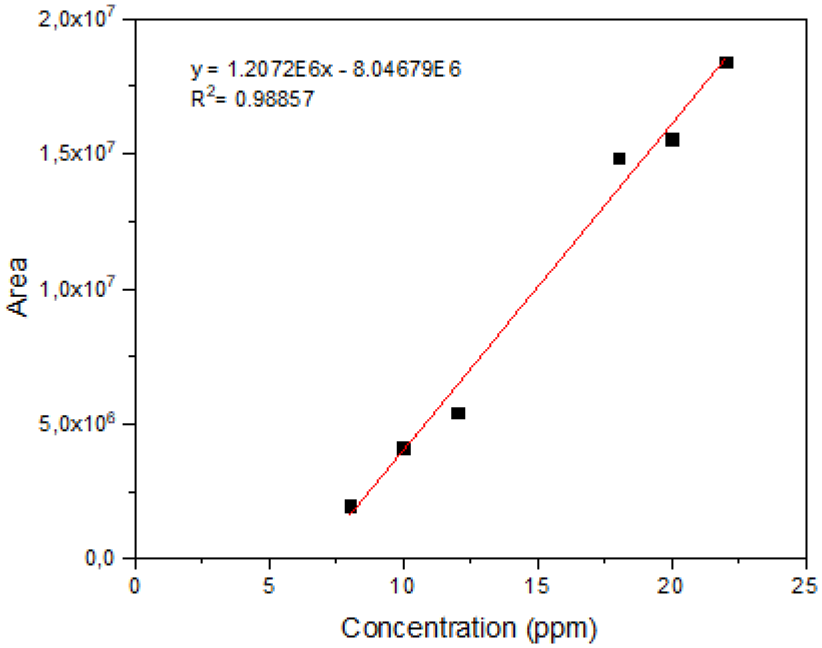

Figure 18 – Dimethoate Calibration curve.

Source: Author, 2024.

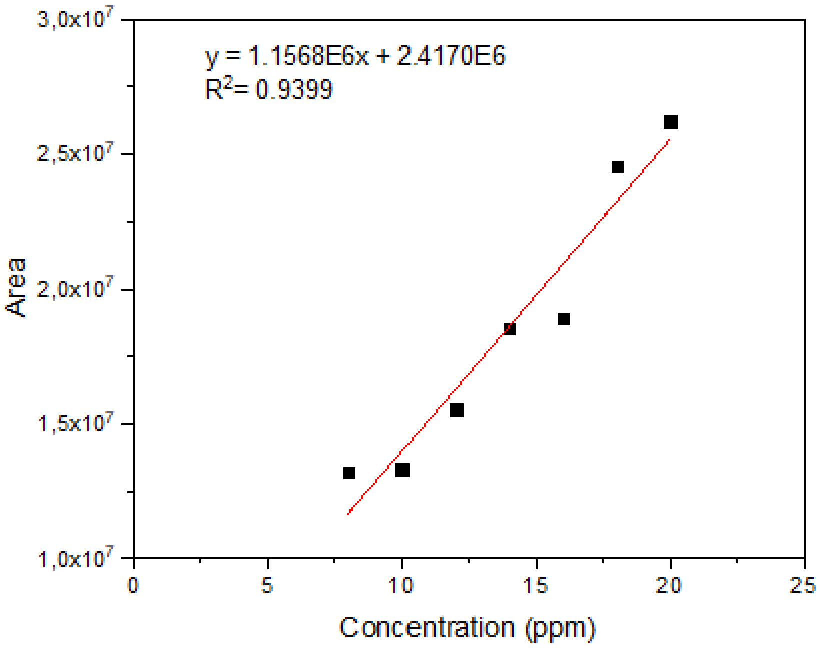

Figure 19 - Acetochlor calibration curve.

Source: Author, 2024.

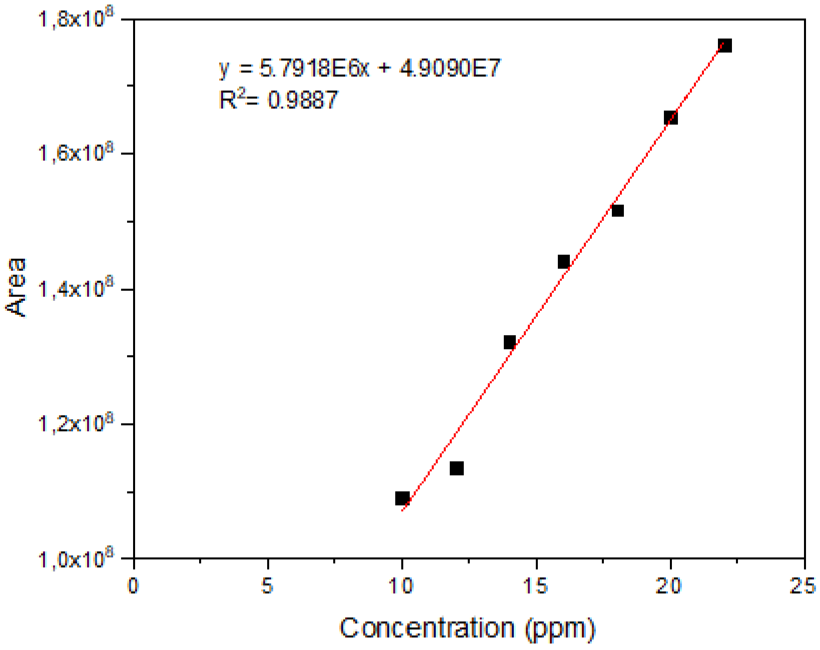

Figure 20 – Heptachlor calibration curve.

Source: Author, 2024.

In these results, two points was removed from the dimethoate curve, and one point for acetochlor and heptachlor for better adjustment and was observed more assertive values for acetochlor and heptachlor, but dimethoate still presents difficulties in identifying and quantifying. Therefore, we decided to carry out the adsorption experiments only with acetochlor and heptachlor, the same ones in the figures above have a more aligned behavior and with a smaller error.

Performing an 8-point pesticide calibration curve in GC-MS is essential to ensure the accuracy and reliability of measurements in this analytical method. The calibration matrix must correspond as closely as possible to the clinical sample matrix, avoiding distortions caused by differences between them. This ensures that the signal-concentration relationship is conserved, minimizing biased measurements. Significant differences in matrix between calibrators and clinical samples can lead to matrix effects, where the signal-concentration relationship is not conserved. An 8-point calibration curve allows for better assessment and mitigation of these effects, ensuring more reliable results [69].

Furthermore, increasing the number of calibration points reduces uncertainty in estimated parameters, leading to more accurate results in pesticide quantification. Assessment of the linearity of instrument response over the pesticide concentration range is also possible with an 8-point calibration curve. This is crucial to avoid under- or overestimation of pesticide concentrations in the sample. Additionally, performing a multi-point calibration curve allows you to verify quality control performance and monitor the stability of the analytical method over time, ensuring consistent results [69].

The equation of the straight line, in this context, is a mathematical representation of the relationship between the signal detected by the instrument (y) and the concentration of the pesticide in the sample (x). This equation is used to calculate the unknown pesticide concentration in a sample based on the signal measured by the instrument. The equation of the line is generally expressed in the form:

$$y = mx + b \tag{17}$$

Where y is the signal detected by the instrument, x is the concentration of the pesticide in the sample, m is the slope of the straight line, which represents the analytical sensitivity of the instrument, that is, how much the instrument signal changes in response to a unit change in pesticide concentration, b is the intercept of the line, which represents the instrument signal when the pesticide concentration is zero.

Therefore, when plotting the points of the calibration curve (signal vs. concentration), the equation of the straight line is fitted to the experimental data to calculate the values of m and b. Once the equation of the straight line is determined, you can use this equation to calculate the unknown concentration of pesticide in a sample based on the signal measured by the instrument [69,70].

To do this, it is necessary to rearrange the equation of the straight line as described in equation 14 below.

$$x = \frac{y - b}{m} \tag{18}$$

This equation allows calculating the pesticide concentration in the sample using the signal measured by the instrument and the parameters of the straight line determined by the calibration curve. Therefore, this equation of the straight line describes the relationship between the instrument signal and the pesticide concentration, allowing the precise quantification of dimethoate, acetochlor and heptachlor in samples analyzed by GC-MS [69,70].

4.10 ANALYSIS OF PESTICIDES BY GC-MS USING SPME EXTRACTION

A first analysis was carried out at 100 ppb, after these analyzes it was noted that it was difficult to find the signal of some pesticides and especially dimethoate, so the extraction was carried out again with a concentration of 5 ppm to find a better signal and thus which fiber would be ideal for possible future analyses. For this we have the results in Figure 21 below:

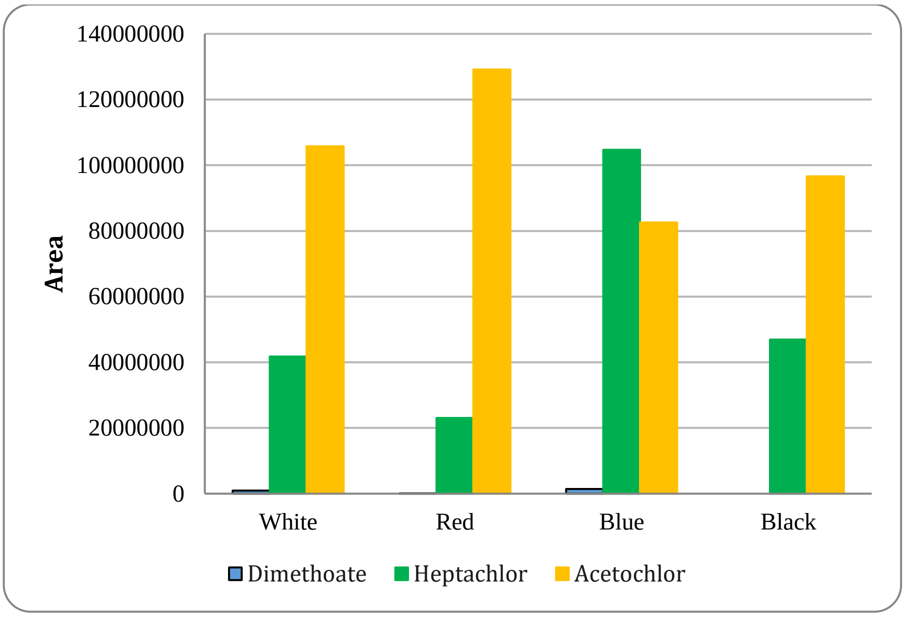

Figure 21 - Comparison between the areas found for the three pesticides in each fiber.

Source: Author, 2024

According to the graph obtained by comparing the fiber area results, we can already see that the blue one is the one that highlights the presence of dimethoate the most, this fiber is the PDMS/DVB(+OC) (Polydimethylsiloxane/ Divinylbenzene) and have the core of Fused Silica/SS and your pH rage is between 2-11; In accordance with this, we have table 22 where we can see the area results obtained for the extraction in each fiber.

Table 22 - Values of identified areas of each pesticide in the following fibers tested

Pesticides	**White (Area)**	**Red (Area)**	**Blue (Area)**	**Black (Area)**
Dimethoate	900995	15877	1430112	0
Heptachlor	41744303	23043664	104679106	46947346
Acetochlor	105739315	129141525	82625214	96633523

Source: Author, 2024

It can be seen that the area of dimethoate is greater in the blue fiber, in addition, the blue fiber highlights a better relationship of area values for the other two pesticides, heptachlor and acetochlor. In the black fiber there was no presence of dimethoate and in the red and white the area values are relatively low. Therefore, the blue fiber becomes the best for SPME extraction of the three pesticides presented.

4.11 KINETIC STUDIES

For the kinetic analyses, three temperatures were chosen being 25°C, 35°C and 45°C to identify which was best suited for the removal of heptachlor and acetochlor, and separate kinetics experiments were carried out for each pesticide and each with one charcoal. In addition to changing the temperature, samples were carried out at 8 time points (30, 60, 120, 240, 300, 360, 420 and 1440 minutes); This means that the CP study was carried out with acetochlor at different times, as was the CA study with Heptachlor.

4.11.1 Removal of heptachlor using physical coal

The assays were conducted and as the aliquots were removed, analyzes to quantify the pollutant was carried out in GC-MS. With the initial area value of the solution that was prepared and the values obtained through measurement according to the time mentioned above, it was possible to calculate the heptachlor removal rate with CP. Figure 22 below exemplifies the percentage of removal obtained for this analysis.

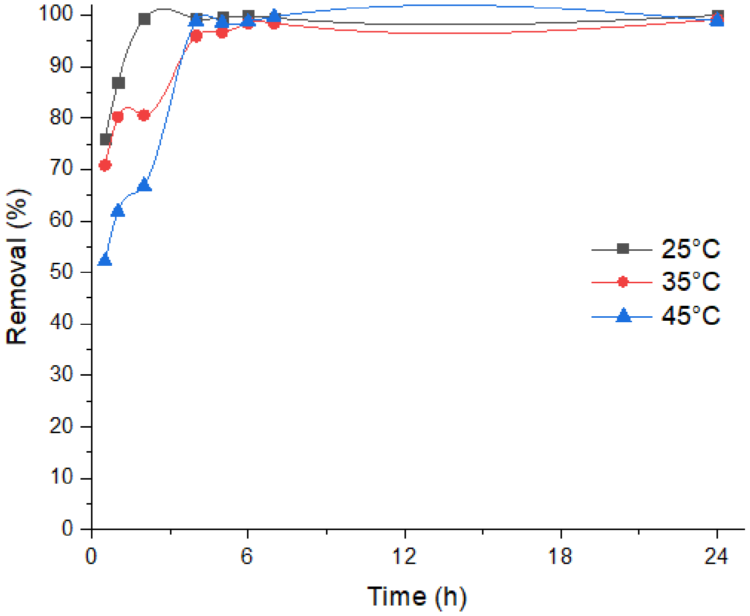

Figure 22 - Comparison between removal of heptachlor in three different temperatures.

Source: Author, 2024

The Figure 22 above shows a faster growth in the removal rate at 25°C, that is, this temperature allows greater removal in shorter times. At temperatures of 35°C and 45°C, removal becomes a little slower. It can be seen that the time in which the removal percentage reaches equilibrium at 25°C is faster than at other temperatures, this confirmation can be better seen in Table 23 below.

Table 23 - Removal (%) for heptachlor in each temperature using CP.

Time (h)	% removal - 25° C	% removal - 35° C	% removal - 45° C
0.5	75.98	70.84	52.19
1	87.00	80.25	61.94
2	99.28	80.58	66.83
4	99.33	96.00	98.79
5	99.56	96.72	98.55
6	99.84	98.47	98.77
8	99.49	98.49	99.69
24	99.99	99.16	98.92

Source: Author, 2024

The values obtained for the temperature of 25°C present very relevant removal percentages since we see it approaching 100% within a period of 2 hours. Taking into account the removal at 25°C, 35° and 45°C, the equilibrium time adopted for this analysis was 5 hours and after 6 hours the removal values was really similar, thus guaranteeing an affirmation of the removal of heptachlor with CP.

The pH of the solutions was measured during the kinetic tests in order to know what impact the removal using this activated carbon would have on the solution after the time elapsed, thus, the pH values for the heptachlor solution 10 ppm, values between 5.5 and 6 were obtained; The values for the solution + coal were between 6.5 and 7.5 and only the ultrapure water in contact with the coal was 6.8 to 7.2.

In the Figures 23, 24 and 25 bellow, the fitting for pseudo first order and pseudo second order to the experimental data is presented, at temperatures of 25°C, 35°C and 45°C, respectively.

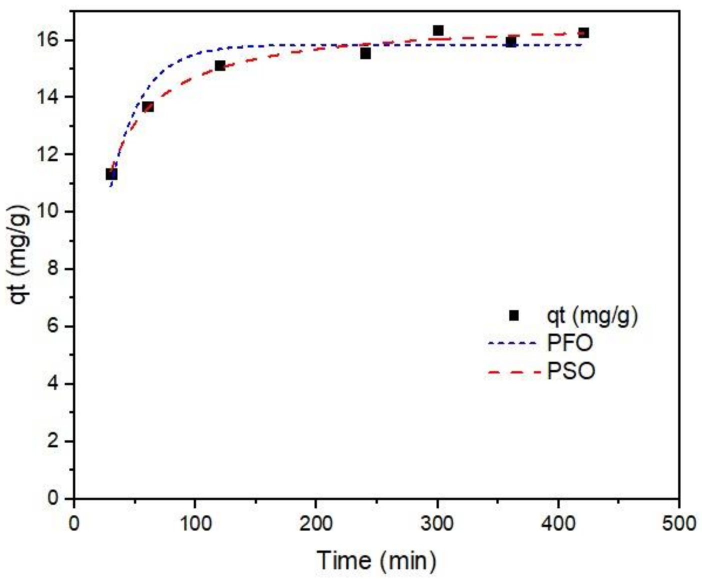

Figure 23 – Fitting of the qt value as a function of time for the first and second pseudo-order kinetics for heptachlor at 25°C.

Source: Author, 2024

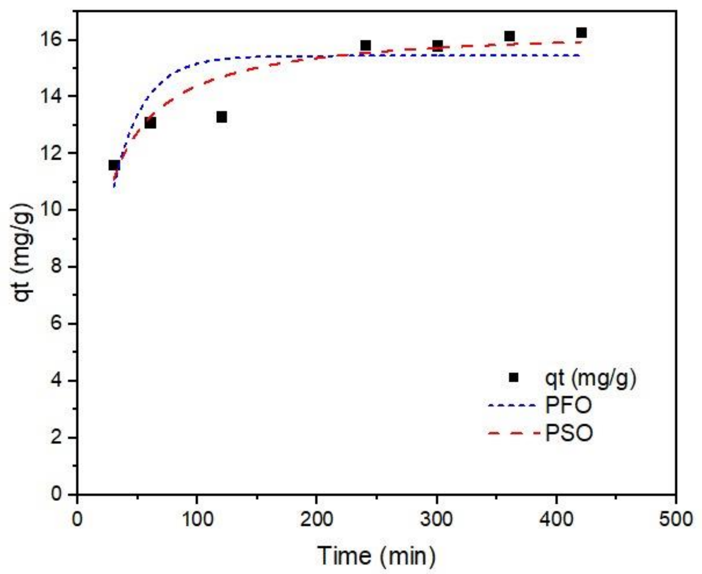

Figure 24 – Fitting of the qt value as a function of time for the first and second pseudo-order kinetics for heptachlor at 35°C.

Source: Author, 2024

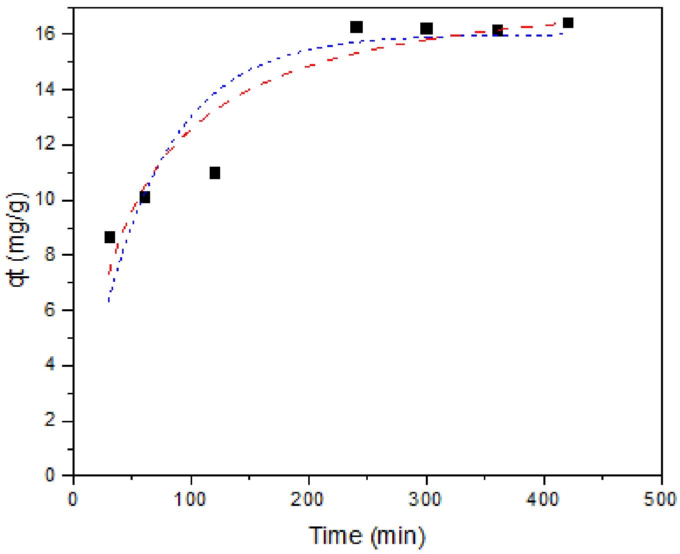

Figure 25 - Fitting of the qt value as a function of time for the first and second pseudo-order kinetics for heptachlor at 45°C.

Source: Author, 2024

The figures above show the adjustment for PFO and PSO of the kinetics performed; it can be seen better alignment in the distribution of points for removal at 25 °C. Regarding the adjustments, a better adjustment for the pseudo second order can be seen in all the graphs above, only the 45°C one showing a similarity between both adjustments. In Table 24 below we have the parameters found for both adjustments.

Table 24 - The pseudo-first and pseudo-second order parameters were determined for kinetic studies conducted at temperatures of 25°C, 35°C, and 45°C, focusing on the adsorption of heptachlor using activated carbon with acid treatment.

	Pseudo First Order			**Pseudo Second Order**		
T (°C)	**k1**	**Qe (mg/g)**	**Error**	**k2**	**Qe (mg/g)**	**Error**
25	0.039 ± 0.003	15.85 ± 0.24	1.386	0.0040 ± 0.0003	16.79 ± 0.144	0.266
35	0.040 ± 0.008	15.45 ± 0.53	7.040	0.0040 ± 9.7566	16.48 ± 0.44	2.520
45	0.018 ± 0.003	16 ± 0.89	14.347	0.0012 ± 0.0004	18.16 ± 1.11	8.082

The analysis of heptachlor removal kinetics data using the pseudo first order (PFO) and pseudo second order (PSO) models demonstrated that the fit was more accurate for the pseudo second order model at all temperatures investigated. This indicates that the heptachlor removal kinetics is more appropriately represented by a second-order process, where the removal rate is proportional to the square of the pollutant concentration and the adsorption capacity of the adsorbent. Especially at 25°C, a more consistent alignment of the removal points with the pseudo-second order model was observed, indicating its particular effectiveness at this temperature [71,72, 73].

The parameters obtained for the pseudo-second order model exhibited consistent rate constant (k2) values and a high agreement between the amount of heptachlor adsorbed experimentally (Qe) and the values predicted by the model. Therefore, the results suggest that the heptachlor removal process is sensitive to temperature, with kinetics that best fit the pseudo-second order model under all temperature conditions evaluated.

4.11.2 Removal of acetochlor using acid coal

For the acetochlor kinetic tests, the tests were carried out in the same form as the CP previously, the data obtained for the percentage of removal of this pesticide is shown in the Figure 26.

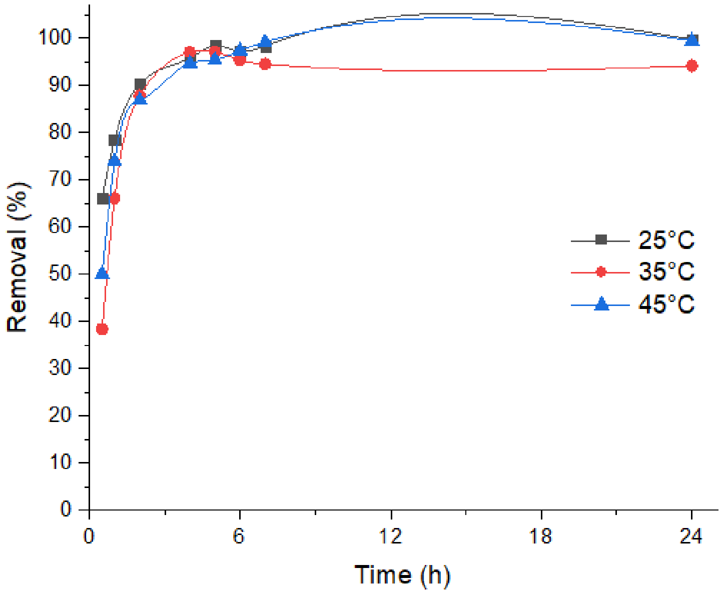

Figure 26 - Comparison between removal of acetochlor in three different temperatures.

Source: Author, 2024

It can be seen from the graph provided in Figure 26 above that acetochlor has a good removal rate, approaching 100% at all temperatures. In this case, the temperature of 25°C stands out for presenting higher removal percentages even in shorter times, that is, as can be seen, the first point already starts with a higher removal than the other two temperatures, in addition it is possible to see a balance in removal from the 4-hour point where differences in removal rates are minimal and reaching better efficiency at the 5-hour point. This difference can be seen better in Table 25 below.

Table 25 - Removal (%) for acetochlor in each temperature using CA.

Time (h)	% removal - 25° C	% removal - 35° C	% removal - 45° C
0.5	66.08	38.43	49.98
1	78.50	66.03	73.98
2	90.28	87.81	86.80
4	95.79	97.01	94.67
5	98.38	97.11	95.38
6	97.18	95.31	97.39
8	98.36	94.50	99.17
24	99.72	94.14	99.47

Source: Author, 2024

Here, the best values obtained for removal at 25°C can also be seen more visibly in the data, with 98.38% for 25°C, 97.11% for 35°C and 95.38% for 45°C.

For these removal analyses, pH values were measured in the solution water before and after the period of contact with the coal. Initially, pH values were obtained for ultrapure water between 6.5 and 8, while ultrapure water in contact with the solution was between 5.5 and 6.5; ultrapure water with the solution plus charcoal after removal between 2.6 and 3 and only ultrapure water plus charcoal obtained pH values between 2.6 and 3.5. In other words, CA leaves the pH lower after removal.

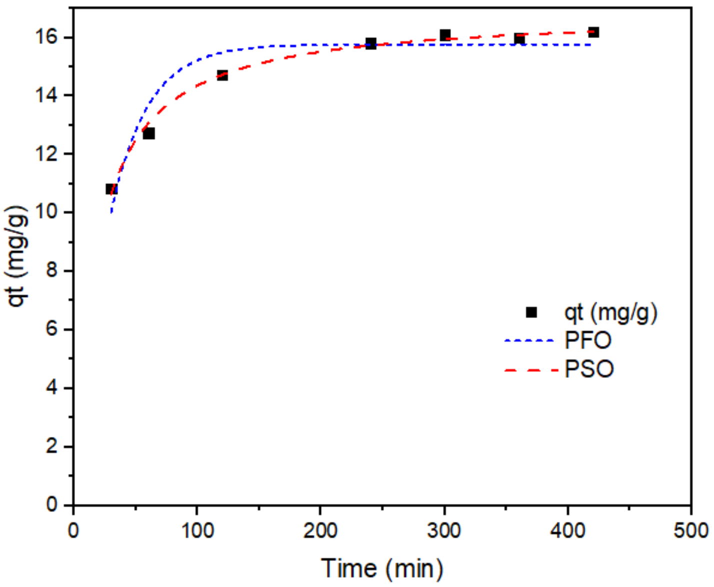

Figure 27 - Fitting of the qt value as a function of time for the first and second pseudo-order kinetics for Acetochlor at 25°C.

Source: Author, 2024

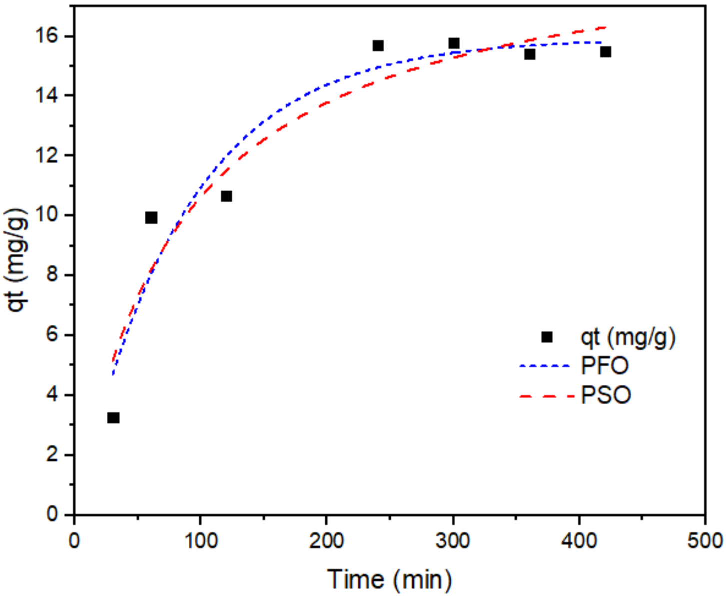

Figure 28 - Fitting of the qt value as a function of time for the first and second pseudo-order kinetics for Acetochlor at 35°C.

Source: Author, 2024

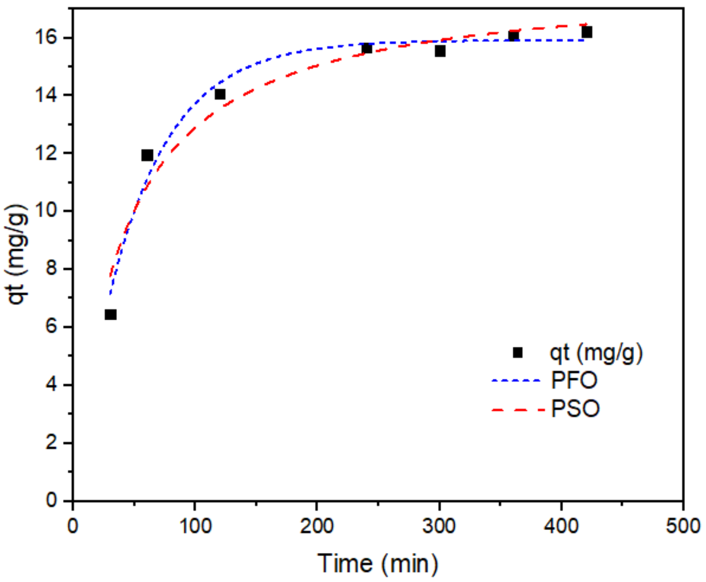

Figure 29 - Fitting of the qt value as a function of time for the first and second pseudo-order kinetics for Acetochlor at 45°C.

Source: Author, 2024

For the graphs above, a better adjustment of the pseudo second order at a temperature of 25 degrees and that of the first order at a temperature of 35 and 45 degrees can be visibly perceived, where the adjustment better follows the experimental points. Table 26 below presents the values obtained for the PFO and PSO adjustment parameters with the experimental kinetic.

Table 26 - The pseudo-first and pseudo-second order parameters were determined for kinetic studies conducted at temperatures of 25°C, 35°C, and 45°C, focusing on the adsorption of acetochlor using activated carbon with physical treatment.

	Pseudo First Order			**Pseudo Second Order**		
T (°C)	**k1**	**Qe (mg/g)**	**Error**	**k2**	**Qe (mg/g)**	**Error**
25	0.0337 ± 0.0037	15.77 ± 0.323	2.484	0.0030 ± 1.9563	16.87 ± 0.12	0.182
35	0.01166 ± 0.0022	15.93 ± 0.819	8.429	0.0006 ± 0.0002	19.54 ± 1.84	10.071
45	0.0198 ± 0.0015	15.92 ± 0.285	1.615	0.0014 ± 0.0003	18.02 ± 0.69	3.441

Analysis of adsorption kinetic data for the pesticide acetochlor using physically treated activated carbon revealed some interesting trends. The graphs showed that the pseudo second order model had a more accurate fit at 25°C, while the pseudo first order model was more appropriate at 35°C and 45°C, where the fits better followed the experimental points, this suggests that acetochlor adsorption kinetics is influenced by temperature, with different models being more suitable in different temperature ranges. In the given table, the parameters of pseudo first order (PFO) and pseudo second order (PSO) models have been presented. The values of rate constant (k) and amount adsorbed at equilibrium (Qe) varied with the temperature and the kinetic model used. Specifically, it was observed that the k2 values for the PSO model were higher at 25°C compared to 35°C and 45°C, suggesting faster adsorption at this temperature [71,72,73,74].

The error values for both models were relatively low, indicating a good fit to the experimental data at all temperatures tested. In summary, the results highlight the importance of temperature in the adsorption kinetics of acetochlor using physically treated activated carbon, with different kinetic models offering better fit under different temperature conditions.

4.12 ACTIVATION ENERGY

The process of determining activation energy often involves employing the Arrhenius equation, which describes the relationship between reaction rate and temperature. By linearizing this equation (13), researchers can extrapolate activation energy values. In this context, Table 27 likely presents these activation energy values alongside other pertinent data.

Table 27 - Activation energy values for pseudo-first and pseudo-second order specified for CP and CA.

Activade carbon	**1° Order**		**2° Order**	
	Energy of activation	**R^2**	**Energy of activation**	**R^2**
CA	-39.81	0.53	-75.33	0.57
CP	-41.33	0.69	-139.44	0.57

This comprehensive approach allows for a more nuanced understanding of the energetics involved in the adsorption phenomenon.

we see activation energy values for both pseudo-first and pseudo-second order kinetics for adsorption onto different adsorbents (CA and CP). Interestingly, for both adsorbents, the activation energy for the pseudo-second order model is considerably higher than that of the pseudo-first order model. This indicates that the adsorption process on these adsorbents involves a higher energy barrier for the pseudo-second order kinetics compared to the pseudo-first order kinetics, which revealed adsorption occurred spontaneously [75].

Moreover, examining the R^2 coefficients, we observe variations in the goodness of fit for different adsorbents and kinetic models. For example, for adsorbent CA, the R^2 value is higher for the pseudo-second order model (0.57) compared to the pseudo-first order model (0.53), suggesting a better fit of the pseudo-second order model to the experimental data. Conversely, for adsorbent CP, the R^2 values are similar for both kinetic models.

The activation energy values provided in Table 27 for pseudo-first and pseudo-second order kinetics offer insights into the adsorption mechanisms, particularly regarding chemisorption. Higher activation energy values, such as those observed for CA (-39.81 for first order and -75.33 for second order) and CP (-41.33 for first order and -139.44 for second order), suggest the likelihood of chemisorption processes. These elevated energies indicate a significant energy barrier for the formation of chemical bonds between the adsorbate and adsorbent, indicative of chemisorption, which involves the formation of strong chemical bonds. Therefore, the observed activation energy values support the hypothesis of chemisorption being the predominant adsorption mechanism in this context [76].

Overall, these results imply that the adsorption process onto different adsorbents can exhibit varying energetics and kinetics, with the pseudo-second order model generally providing a better description of the experimental data, particularly when considering the activation energy and goodness of fit.

4.13 ADSORPTION EQUILIBRIUM

4.13.1 Heptachlor with CP Isotherm

The pesticide removals were quantified in GC-MS at 25°C and after 5 hours in contact with different masses of adsorbent (5, 10, 15, 20, 25, 30 and 35 mg), with this temperature and time being the same. previously defined in the removal analyzes according to temperature and time, they can be seen in figure 30 below in percentage of removal.

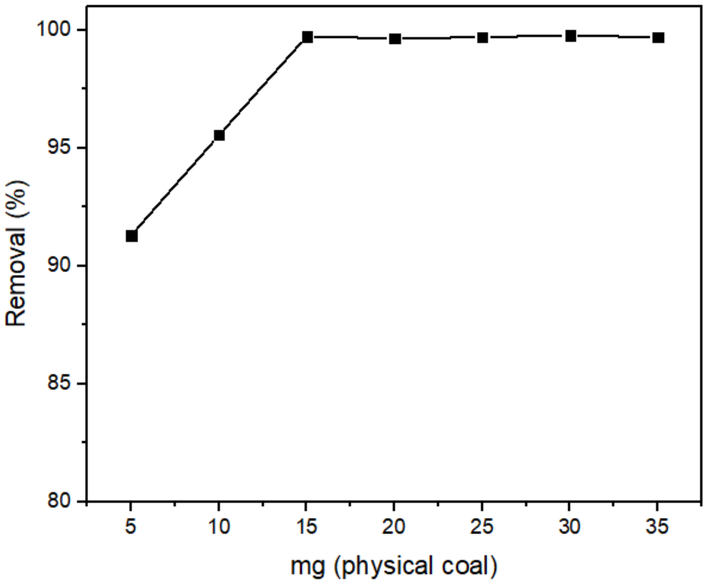

Figure 30 - Removal percentage curve for CP adsorbent mass variation

Source: Author, 2024

The results highlight that removal equilibrium was achieved with a mass of 15 mg of CP, indicating the efficiency of the adsorbent. Moreover, the maintenance of the removal rate post-equilibrium underscores the stability of the adsorption process. The close to 100% removal signifies the complete efficacy of CP in eliminating the pesticide from the initial 10 ppm sample, which is pivotal for effective purification of contaminated water. These findings strongly suggest that CP could be a promising option for remediating pesticide-contaminated waters.

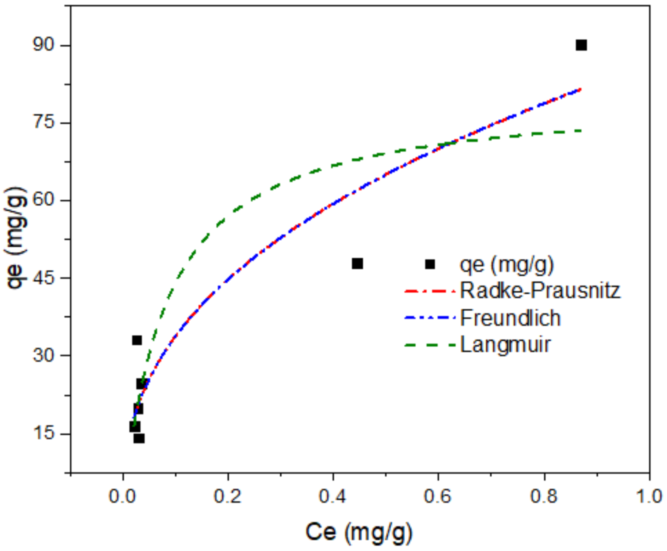

Figure 31 - Graph of qe as a function of the Ce for the Radke, Freundlich and Langmuir isotherms adjust of heptachlor with CP at 25°C.
Source: Author, 2024

The analysis of isothermal curves for heptachlor adsorption involved evaluating three models: Radke-Prausnitz, Freundlich, and Langmuir. Figure 31 demonstrated that the Radke model offered the best fit for the variation in adsorbent mass at the same temperature and time [77]. Furthermore, Table 28 compared the adjusts obtained for each adjustment at 25°C in 5 hours, showing comparable adjust for the Freundlich and Radke-Prausnitz models, slightly lower for the Langmuir model.

Table 28 - Comparison of the errors obtained for each adjustment to the heptachlor isotherm at 25°C in 5 hours

Method	RSS
Freundlich	509.433
Langmuir	915.750
Radke-Prausnitz	509.436

This highlights the significance of selecting the most suitable model for describing adsorption behavior. Even with both have the same fit at the figure 31 and the table 28, the preference for the Radke model, supported by the potential applicability in accurately characterizing heptachlor and almost all pesticides adsorption.

The Radke-Prausnitz model is often preferred in describing pesticide adsorption due to its ability to capture complex adsorption behaviors. This is attributed to the model's flexibility in its mathematical formulation; it considers the heterogeneity of the adsorbent surface, which is crucial when dealing with pesticide adsorption, given the variation in interaction between pesticides and active sites on the adsorbent surface; The Radke-Prausnitz isotherm model is commonly utilized in adsorption systems characterized by low concentrations of the adsorbate and the model is also capable of describing non-ideal interactions between pesticides and the adsorbent, taking into account factors such as van der Waals, electrostatic, and dipole-dipole interactions, which play a significant role in pesticide adsorption. This makes it a preferred choice for studies on pesticide adsorption and in the search for effective methods of environmental contamination remediation [78,79].

4.13.1 Acetochlor with CP Isotherm

The same procedure used for the heptachlor isotherm was carried out with acetochlor, the same temperature and period of 5 hours was used in accordance with the results obtained and presented in the kinetics in topic 4.11.2. Figure 32 below better exemplifies the results obtained for the removal of acetochlor using the previously defined CA, temperature and equilibrium time.

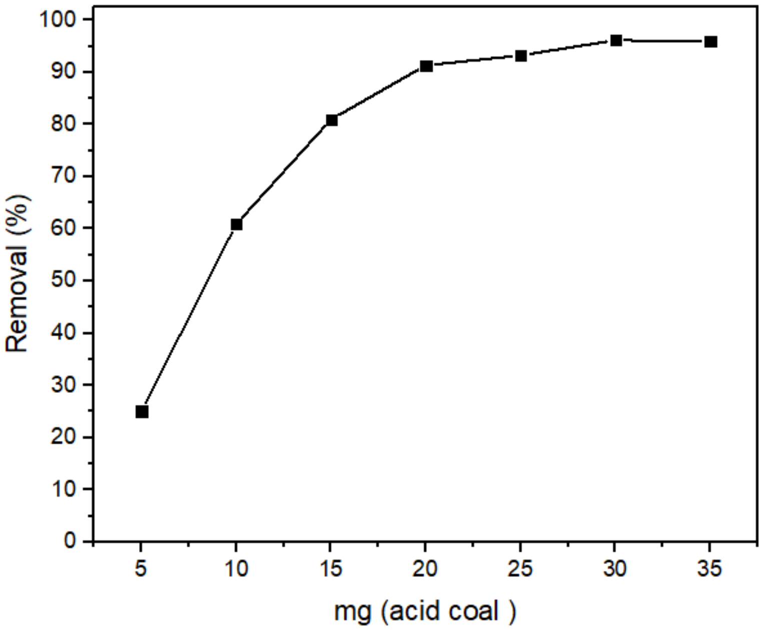

Figure 32 - Removal percentage curve for CA adsorbent mass variation.

Source: Author, 2024

The increased removal of acetochlor with acid charcoal as the adsorbent mass increases highlights the significance of dosage optimization in enhancing treatment efficiency. Attaining equilibrium after 20 mg of adsorbent signifies a critical threshold for effective removal, with further dosage augmentation, particularly at the 30 mg point, yielding the most favorable outcome. This observation underscores the importance of meticulous adsorbent selection and dosage determination to maximize removal efficiency in water treatment applications

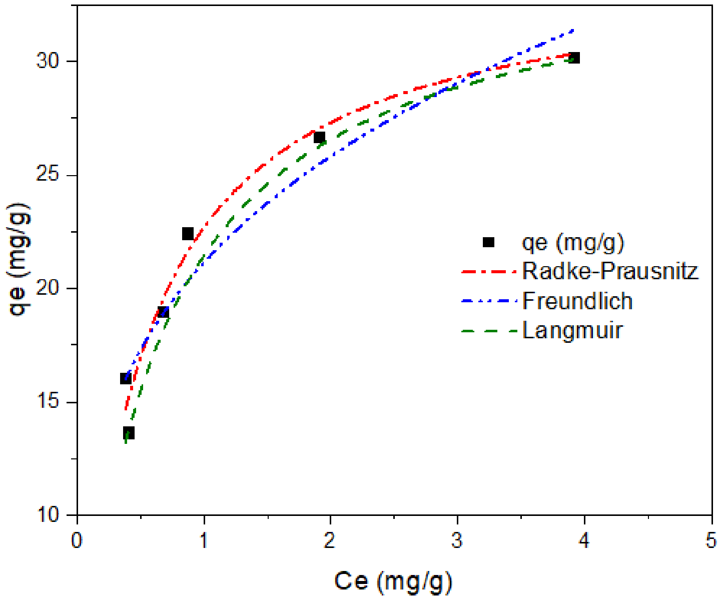

Figure 33 - Graph of Ce as a function of the qe for the Radke, Freundlich and Langmuir isotherms adjust of acetochlor with CA.

Source: Author, 2024

Figure 33 above presents the adjustments more in accordance with the experimental points than figure 31, this is due to the % of removals having an increasing increase as the adsorbent mass increased, different from heptachlor with physical carbon which there was an exponential increase right at the beginning and it became saturated. For this graph above, the best fit was that of Radke [77]. Table 29 exemplify the results for this analysis about the adjustment.

Table 29 - Comparison of the errors obtained for each adjustment to the acetochlor isotherm at 25°C in 5 hours.

Method	RSS
Freundlich	14.551
Langmuir	624.627
Radke-Prausnitz	5.426

Table 29 compares the errors obtained for each adjustment to the acetochlor isotherm at 25°C in 5 hours. The values presented represent the quality of the fit of the models to the experimental data, with the closer to 1, the better the fit. It is observed that all methods - Freundlich, Langmuir, and Radke-Prausnitz - resulted in error values relatively different and Radke have the best position [77,79].

Andrunik (2021) says that the results obtained by various researchers indicate that the type of pesticide may have an essential influence on the shape of the adsorption isotherm [80].

Properly comparing experimental data with adjustments is fundamental to determine which model best fits the studied system. This comparison allows for selecting the most appropriate model, providing an accurate description of the phenomenon of interest; It facilitates assessing the fit quality and interpreting the results, ensuring that the conclusions drawn from the data are robust and reliable [81].

5. FINAL CONSIDERATIONS AND CONCLUSIONS

The study of using olive pits as an alternative for wastewater treatment has been gaining increasing momentum and impact in the realm of analysis worldwide. In other words, the utilization of natural materials as potential sources for pollutant removal, particularly micropollutants, is being increasingly explored. The use of olive pits as a source material for activated carbon production offers several significant environmental benefits in removing micropollutants from water. Firstly, olive pits are an abundant by-product of the olive oil industry, meaning their utilization reduces the amount of organic waste disposed of, thereby contributing to environmental impact reduction. Activated carbon produced from olive pits possesses effective adsorptive properties capable of removing a wide variety of micropollutants from water, including pesticides, pharmaceuticals, and estrogens, thus enhancing water quality and safeguarding human and environmental health. Therefore, the use of olive pits as a raw material for activated carbon production not only provides a sustainable solution for agricultural waste management but also plays a crucial role in mitigating water pollution and promoting environmental sustainability.

The use of olive pit carbon for pesticides removal was divided into two parts: the characterization of the carbon and the removal of pesticides in water. The initial studies focused on specific parameters of the olive pit, the primary material for the prepared adsorbent. Determining parameters such as moisture and ash content is crucial as they impact product characteristics. Results of this research was 14.62 ± 0.13 for moisture and 1.29± 0.38 for ash, being aligned with previous studies, indicating slightly higher moisture content in the olive pits. Granulometry analysis provided insights into particle size distribution, with the Sauter diameter of 0.174 mm revealing the average size of the sample.

The carbonization process yielded significantly different results for physically activated and acid-activated charcoal, with the latter showing a substantially higher carbonization yield. This discrepancy between 19.40% for CP and 59.19% for CA underscores the importance of considering activation methods in production processes, with acid activation proving more efficient in this regard.

Additionally, the determination of the point of zero charge (PZC) elucidated surface charge behavior, essential for understanding adsorption mechanisms where in the physical activation was provided the pH in 7.24±0.34 and the acid activation pH in 2.55 ± 0.01. Moreover, the quantification of surface acidic and basic functional groups further elucidated adsorption phenomena, providing crucial insights into adsorbate-surface interactions and guiding material design strategies. Fourier-transform infrared spectroscopy (FTIR) analysis allowed for a comprehensive examination of functional groups present in the adsorbents, highlighting changes in surface chemistry post-carbonization. Thermogravimetric analysis (TGA) examines weight changes in materials with temperature. TGA of olive pit-derived activated carbon showed distinct degradation patterns for physically and acid-activated charcoal. Physically activated charcoal exhibited moisture expulsion and cellulose/hemicellulose decomposition, while acid-activated charcoal had higher mass loss due to increased porosity and altered chemical structure from acid activation.

These findings underscore the potential of olive pits as a sustainable raw material for activated carbon production, with implications for wastewater treatment and environmental remediation efforts. By leveraging natural materials and optimizing production processes, significant strides can be made towards mitigating water pollution and promoting environmental sustainability.

For water removal application, natural concentrations of pesticides are much lower, necessitating extraction. This study utilized SPME extraction, identifying the best fiber for dimethoate, acetochlor, and heptachlor removal. The blue fiber PDMS/DVB (+OC) (Polydimethylsiloxane/Divinylbenzene) and Fused Silica/SS showed the best results, capable of extracting and identifying all three pesticides.

Due to difficulties in identifying and quantifying dimethoate, it wasn't included in the removal part. Eight points were tested at different temperatures (25°C, 35°C, and 45°C) for pesticide removal. Physical charcoal achieved 99.56% removal for heptachlor at 25°C in 5 hours, while acid charcoal attained 98.38% removal for acetochlor, demonstrating high efficiency nearing 100%. Operating at 25°C is crucial as it's considered ambient temperature, minimizing additional energy usage, especially from non-renewable sources.

Different masses were tested for the adsorbent, with 15 mg sufficient for heptachlor removal and double (30 mg) for acetochlor. Acid charcoal rendered water acidic post-removal, while physical coal kept neutrality, enhancing treatment efficiency and reducing costs and environmental impact.

The removal efficiency of acetochlor was 98.38% using acid-activated charcoal, while heptachlor achieved a higher removal rate of 99.56% with physically activated charcoal. Despite both achieving high efficacy, physically activated charcoal required a lower adsorbent mass and maintained water neutrality post-removal, potentially offering cost and environmental advantages over acid-activated charcoal.

In conclusion, olive pit-derived activated charcoal, particularly physical charcoal, exhibits high removal potential, achieving comparable results with less charcoal than acid charcoal. Maintaining neutral pH post-treatment simplifies subsequent processes, optimizing treatment systems and reducing environmental impacts

This study highlights the potential of utilizing olive pits as a sustainable raw material for activated carbon production, contributing to several objectives of the United Nations' Sustainable Development Goals (SDGs). Firstly, by repurposing olive pits, a by-product of the olive oil industry, this research addresses SDG 12 (Responsible Consumption and Production) by reducing organic waste and promoting circular economy practices. Furthermore, the use of activated carbon derived from olive pits aids in achieving SDG 6 (Clean Water and Sanitation) by effectively removing pesticides and other micropollutants from water, thus enhancing water quality and safeguarding human health. Additionally, the optimization of production processes and the utilization of natural materials align with SDG 9 (Industry, Innovation, and Infrastructure) by promoting sustainable industrialization and fostering innovation in wastewater treatment technologies. By leveraging these approaches, significant strides can be made towards mitigating water pollution and promoting environmental sustainability, contributing to the broader global agenda for sustainable development.

6. FUTURE WORKS

Future steps should involve:

- Study pesticide mixture removal in both coal using the parameters identified.
- Study the removal using SPME extraction with the results obtained before.
- Apply the results in tests to real samples.
- Study the impact of the activate coal obtained from olive pit at the toxicology from the water after the removal by the ecotoxicology studies

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ANEXOS

Equipment to measure pH
Source: Author, 2024.

Gas chromatography - mass spectrometry equipment utilized.
Source: Author, 2024.

XXVII ENCONTRO LUSO GALEGO DE QUÍMICA

22-24 NOVEMBRO 2023

PORTO, PORTUGAL

Colegio Oficial de Químicos de Galicia

ASOCIACION DE QUIMICOS DE GALICIA

Sociedade Portuguesa de Química

CERTIFICADO DE APRESENTAÇÃO

Por este meio certifica-se que

Tairone Cesar da Silva Pereira Junior

apresentou o trabalho

Removal of pesticides from water using activated carbon obtained from olive pit

Tairone Cesar da Silva Pereira Junior, Maisa Saldanha Pinheiro, Cristhiane Rohde, Ana Queiroz, Paulo Brito, António Ribeiro

no XXVII Encontro Luso Galego de Química, organizado pela Delegação do Porto da SPQ e pelo Colégio Oficial de Químicos da Galiza (COLQUIGA), realizado na Fundação Dr. António Cupertino de Miranda, de 22 a 24 novembro 2023.

A Comissão Organizadora

Joaquim Luís Faria

Removal of pesticides from water using activated carbon obtained from olive pit

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Currently, there is rampant population growth that requires a proportional increase in food production. In this context, the use of pesticides to improve agricultural productivity stands out. The global annual consumption is about 2 million tons; for example, in Portugal alone in 2020, 9.7 thousand tons were used to combat weeds, pests, pathogens, and other undesirable organisms [1]. This excessive use of pesticides has many environmental impacts, such as soil and water pollution, the selection of resistant organisms, the need for increased concentrations and/or application frequency, as well as the substitution with more toxic products. It also affects non-target organisms and human health. An alternative to reduce contamination at the source and related environmental impacts of pesticides is sustainable agricultural crop management [2]. There are also sustainable remediation methods that can be applied and seek to use active ingredients from natural and recycled sources. In this work, we aim to use the olive pit as a precursor for the production of an adsorbent charcoal for the removal of pesticides such as acetochlor, heptachlor, and dimethoate from aquatic bodies [2]. Based on effective results in removing pharmaceuticals from aqueous effluents and purifying biodiesel with the same material, it was decided to produce charcoal using both physical and chemical activation methods to optimize a removal process, which may include pesticides [3,4].

Charcoal was produced with acid activation by impregnating it with orthophosphoric acid (H_3PO_4) for 24 hours at 25ºC on a mechanical stirrer at 160 rpm. It was then filtered through a porous filter using a vacuum pump and dried in an oven at 110ºC. It was carbonized in a muffle furnace at 500ºC for 1.5 hours and then washed with distilled water until reaching a pH between 6 and 7. The same process was applied to basic activation using potassium hydroxide (KOH). Physical activation was done directly in a muffle furnace at 800ºC, then by washing until reaching a pH between 6 and 7 [3,4]. Table 1 provides some data related to the charcoal preparation conditions. One of the objectives of this work is to achieve the highest efficiency in removing pesticides from water using the activated charcoal obtained from olive pit. The expected results involve charcoal that can retain the highest amount of the studied pesticides on its surface area.

Table 1. Activated carbon preparation conditions.

Activation	Reagents	Temperature (°C)	Time (h)
Physical	-	800	1
Acid	H_3PO_4	500	1.5
Basic	KOH	750	2

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