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ABID SARRA

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Valorization of a byproduct (olive stones) from agriculture

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Dr. Smail TERCHI	**MOHAMED BOUDIAF UNIVERSITY -M'SILA**	**Chairman**
Pr. Hadi DEBIH	**MOHAMED BOUDIAF UNIVERSITY -M'SILA**	**Rapporter**
Pr. Abdelbaki REFFAS	**MOHAMED BOUDIAF UNIVERSITY -M'SILA**	**Examiner**
Dr. Mokhtar DJEHICHE	**MOHAMED BOUDIAF UNIVERSITY -M'SILA**	**Examiner**

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بسم الله الرحمن الرحيم

Dedications

I extend my heartfelt gratitude to ALLAH Almighty, to whom I turn for guidance and support in all my endeavors. I dedicate this work to my beloved parents, who have selflessly loved, sacrificed, and supported me throughout my academic journey. I am deeply grateful for their unwavering love and dedication.

I also express my sincere appreciation to my brother, Abdou, and my sisters, Aya and Hiba, for their unwavering support and encouragement. To my friends, I am grateful for the memories and experiences we have shared, which have enriched my life.

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Summary. Humic acids, particularly Suwannee River fulvic acid (SRFA), play a significant role in the environmental behavior of organic pollutants by influencing their mobility and bioavailability. Adsorption, a surface phenomenon involving physical or chemical interactions, is a method of valorizing olive stones, which shows excellent potential for removing organic pollutants from polluted water. This study examines the characterization and potential applications of olive stones biomass from the M'Sila region in Algeria as a biosorbent for organic matter (SRFA). XRD and FTIR analyses reveal the presence of cellulose, hemicellulose, and lignin in olive stones, interactions with SRFA leading to changes in peak intensity. TGA analysis was performed on a sample containing 36% SRFA adsorbed on olive stones, while UV-Visible spectroscopy revealed an average adsorption of 58% SRFA on olive stones. The study concludes that olive pomace has potential as a biosorbent for SRFA, and that further treatments can enhance its adsorption capacity. The type of interaction between O.S /SRFA in our case is likely electrostatic.

Key words: ***Biomass; Interactions MO/MI; Adsorption; Contaminants; Valorisation.***

ملخص: _ الأحماض الدبالية، ولا سيما حمض الفولفيك لنهر سواني (SRFA)، دورًا مهمًا في السلوك البيئي للملوثات العضوية من خلال التأثير على حركيتها وتوافرها البيولوجي. ويُعد الامتزاز، وهو ظاهرة سطحية تنطوي على تفاعلات فيزيائية أو كيميائية، طريقة لتثمين ثفل الزيتون، الذي يُظهر إمكانات ممتازة لإزالة الملوثات العضوية من المياه الملوثة. تبحث هذه الدراسة في التوصيف والتطبيقات المحتملة للكتلة الحيوية لثفل الزيتون من منطقة المسيلة في الجزائر كمادة ماصة حيوية للمواد العضوية (SRFA). تكشف تحاليل XRD وتحليلات FTIR عن وجود السليلوز والهيميسليلوز واللجنين في ثفل الزيتون، والتفاعلات مع SRFA مما يؤدي إلى تغيرات في شدة الذروة. تم إجراء تحليل TGA على عينة تحتوي على 36% من SRFA الممتز على ثفل الزيتون، بينما كشف التحليل الطيفي بالأشعة فوق البنفسجية المرئية عن متوسط امتزاز 58% من SRFA على ثفل الزيتون. وخلصت الدراسة إلى أن ثفل الزيتون لديه القدرة على استخدام ثفل الزيتون كمادة ماصة حيوية ل SRFA، وأن المزيد من المعالجات يمكن أن تعزز قدرته على الامتزاز. ومن المرجح أن يكون نوع التفاعل بين المواد العضوية الثابتة/ SRFA في حالتنا هو تفاعل كهروستاتيكي.

الكلمات المفاتيح: ***Biomass*** الكتلة الحيوية: ***Interactions*** تفاعلات MO/MI؛ الامتزاز؛ الملوثات؛ إزالة التلوث. التثمين.

R***ésumé.*** Les acides humiques, en particulier l'acide fulvique de la rivière Suwannee (SRFA), jouent un rôle important dans le comportement environnemental des polluants organiques en influençant leur mobilité et leur biodisponibilité. L'adsorption, un phénomène de surface impliquant des interactions physiques ou chimiques, est une méthode de valorisation des grignons d'olive montrant un excellent potentiel pour éliminer les polluants organiques des eaux polluées. Cette étude examine la caractérisation et les applications potentielles de la biomasse des grignons d'olive de la région de M'Sila en Algérie en tant que biosorbant de la matière organique (l'acide fulvique de la rivière Suwannee, SRFA). Les analyses XRD et FTIR révèlent la présence de cellulose, d'hémicellulose et de lignine dans les grignons d'olive, les interactions avec l'acide fulvique de la rivière Suwannee entraînant des changements dans l'intensité des pics. L'analyse TGA a été réalisée sur un échantillon contenant 36% d'acide fulvique de la (SRFA) adsorbé sur des résidus d'olive, tandis que la spectroscopie UV-Visible a révélé une adsorption moyenne de 58% d'acide fulvique de la rivière Suwannee sur les résidus d'olive. L'étude conclut que les grignons d'olive présentent un potentiel en tant que biosorbant pour les SRFA, et que des traitements supplémentaires peuvent améliorer leur capacité d'adsorption. Le type d'interaction O.S.SRFA dans notre cas est probablement électrostatique.

Mots clés : ***Biomasse : Interactions M.O./M.I. ; Adsorption ; Contaminants ; Dépollution. Valorisation.***

General introduction

All living beings, including humans and the environment, interact with each other in various ways, and a dynamic equilibrium exists between them, which evolves over time. Human development and activities have significantly altered the natural environment over centuries, from agriculture to industrialization, global warming, and pollution. This has led to the creation of environmental problems that persist across generations. The primary consequences include decreased water quality and increased pollution [1].

Water pollution poses a significant threat to both the environment and human lives. The effects of pollutants can vary depending on their type and source. For instance, heavy metals, dyes, and certain organic pollutants have been identified as carcinogens.

Organic pollutants encompass a vast array of compounds with varying degrees of toxicity. Some of the most concerning organic pollutants that pose significant threats to aquatic organisms, plants, and humans include dyes, pharmaceuticals derived from plants and animals, personal care product wastes, and petroleum-based organic pollutants [2].

Fulvic acids, particularly Suwannee River fulvic acid (SRFA), can play a significant role in the environmental behavior of organic pollutants. Fulvic acids, being part of dissolved organic matter, can impact the mobility and bioavailability of pollutants in natural systems. The charges of humic and fulvic particles are crucial in binding with pollutants, affecting their aggregation and bioavailability. The size and charge of humic and fulvic acids are essential factors in determining their environmental impact [3].

In the study of the role of fulvic acid composition in the photosensitized degradation of aquatic contaminants, it was found that fulvic acids can contribute to the degradation of organic pollutants to a certain extent [4]. Additionally, the association between SRFA and various concentrations of cationic surfactants has been investigated, shedding light on the organization of fulvic acid and its interactions [5]. Thus, the interaction of fulvic acids, especially SRFA, with organic pollutants is a complex process influenced by factors like size, charge, and composition, ultimately affecting the behavior and fate of pollutants in natural environments.

Therefore, it is important to emphasize the need for the implementation of appropriate treatments to reduce this type of pollution. In general, water treatment involves a range of diverse and complex techniques that wastewater treatment plants are increasingly struggling to control at reasonable costs. It is, therefore, particularly wise to develop an economical process to carry out the depollution of industrial waters laden with various pollutants.

Various methods have been proposed for treating wastewater containing organic pollutants, based on principles such as precipitation and coagulation, chemical oxidation, sedimentation, filtration, adsorption, and ion exchange, etc. Adsorption is currently widely used for the removal of both organic and inorganic micropollutants from aqueous solutions. Adsorption is a surface phenomenon where molecules from a fluid phase transfer to a solid surface, resulting in an interface layer. This process involves two types of interactions: physical and chemical. The adsorption process is usually reversible, with the reverse process being desorption [6].

Adsorption on olive stones has been a topic of interest in environmental research as a potential treatment method for contaminated water. Olive stones have shown excellent potential as an adsorbent material for the removal of organic pollutants such as dyes and phenols from wastewater. Activated carbon produced from olive stones has also been investigated for the adsorption of aqueous phenol solutions, showing high adsorption capacities and good agreement with adsorption models [7].

The significant quantity of olive stones generated annually in Algeria presents a valuable opportunity for valorization into various products, contributing to the economic and environmental sustainability of the olive industry. The valorization of olive stone is not only economically beneficial but also environmentally friendly, as it reduces waste and promotes a more circular economy in the olive industry. By utilizing olive stones, Algeria can reduce its environmental footprint while generating additional revenue streams and creating new opportunities for local industries [8]. Researchers and industries should explore innovative ways to transform this agricultural by-product into valuable commodities, fostering a more sustainable and profitable olive sector in Algeria.

This work focuses on the valorization of olive stones for its use in the depollution of waters contaminated by organic matter. In this context, we have chosen a biomass-derived material (by-product), olive stone. The adsorption tests were conducted in contact with SRFA (Suwannee River Fulvic Acid) from the Suwannee River (USA).

In the first part **(Chapter I)**, we will provide a summary of the main scientific events related to the valorization of olive-based biomass. Additionally, we will present a theoretical study on humic acids and particularly fulvic acid.

The second **(chapter II)** describes the experimental methodology followed for the preparation of adsorbent materials, as well as the characterization techniques.

The third **(chapter III)** is devoted to the presentation of the different experimental results obtained as well as their discussion.

A general **conclusion** summarizes the main results obtained during this work and perspective.

Chapter I

I.- Bibliographic review (previous work and issues)

I.1.- Lignocellulosic biomass

I.1.1-General

Lignocellulosic biomass, a plentiful and sustainable plant-derived resource, consists primarily of polysaccharides (cellulose and hemicelluloses) and an aromatic polymer (lignin). This biomass holds significant promise as a substitute for fossil fuels in the production of second-generation biofuels and various bio-based chemicals and materials, all while safeguarding global food security. It encompasses agricultural byproducts like cereal straw and bagasse, forest leftovers such as pine, as well as specific crops and rapidly regenerating plants like miscanthus, switchgrass, and poplar [9].

The forefront of industrial utilization of lignocellulosic biomass is instrumental in establishing a circular bioeconomy, characterized by cutting-edge design and manufacturing techniques that promote industrial waste recovery and reuse beyond the realms of biofuel and biochemical production [10].

I.1.2- Structure and composition

The fundamental structure of lignocellulosic biomass primarily consists of cellulose, hemicellulose, and lignin, along with minor components like extractives, pectin, protein, and metal or ash. Cellulose and hemicellulose, both polymeric carbohydrates, release various hexose and pentose sugars upon hydrolysis, while lignin, a three-dimensional methoxylated polyphenolic compound, predominantly envelops cellulose and hemicellulose, thereby impeding their depolymerization during biomass hydrolysis. The proportions of these constituents vary across species, with hardwood biomass containing more cellulose than softwood biomass, and agricultural feedstocks having greater hemicellulose content compared to hardwood. Additionally, agricultural residues and grass typically have lower lignin content than softwood and hardwood biomass. These polymers are connected through various bonds, forming heteromatrix structures whose complexity and rigidity depend on the composition of lignocellulosic constituents, which is primarily influenced by the type, species, and origin of the biomass [11].

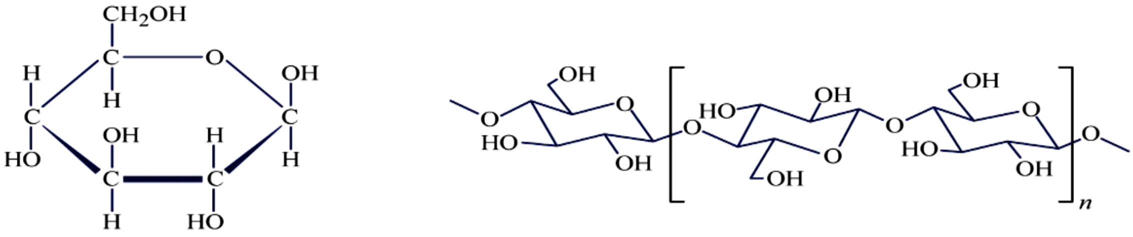
Table I.1. Chemical composition of different lignocellulosic biomass

Forest feedstocks	Cellulose	Hemicellulose	Lignin
Hardwood			
Bamboo	43	23.1	26.2
Aspen	49	18.2	25.6
Poplar	49.7	12.3	16.4
Eucalypt wood	43.4	15.3	25.5
Oak	41.3	28	24.3
Softwood			
Pine wood	42	14.7	26.3
Sprice	18.5	4.6	50.6
Douglas fir	40.9	18.41	29.30

Cellulose, hemicellulose, and lignin collectively provide essential adaptations crucial for plant survival, such as structural strength, water resistance, and protection against microbial degradation. These attributes make lignocellulosic biomass a widely available and enduring raw material for construction and as a basic fuel source. Yet, the distinct chemical composition of these polymers within the matrix indicates a vast potential for utilizing lignocellulose in the production of high-value products like transportation fuels, bioplastics, and innovative materials [12].

I.1.2.1- Cellulose

Cellulose is a complex carbohydrate made up of 3,000 or more glucose units, making it the most abundant naturally occurring organic compound. It accounts for approximately 33% of all vegetable matter, with 90% of cotton and 50% of wood being cellulose. Although humans cannot digest cellulose, it serves as a food source for herbivorous animals like cows and horses, as they retain it long enough for microorganisms in their digestive tract to break it down. Protozoans in the gut of insects like termites also digest cellulose. Cellulose is of significant economic importance as it is processed to produce paper and fibers, and chemically modified to create substances used in the production of various items such as plastics, photographic films, and rayon. Cellulose derivatives also have uses as adhesives, explosives, thickening agents for foods, and in moisture-proof coatings [13].



glucose cellulose

Figure I. 1 Cellulose

With the exception of hemicellulose and lignin, cellulose exhibits consistent structural characteristics across various types of lignocellulosic biomass. It serves as a primary structural component in plant cell walls, characterized by a generic formula of **$(C_6H_{12}O_5)_n$.** The length and polymerization degree of cellulose chains can vary depending on the specific lignocellulosic biomass. Comprised of glucose subunits linked by β-1,4-glycosidic bonds, cellulose forms a linear homopolymer held together by both inter- and intramolecular hydrogen bonds, facilitating their arrangement into microfibrils. Due to the bonding of hydroxyl groups, cellulose polymers are insoluble in water, creating a hydrophobic environment. Cellulose typically exists in two forms: crystalline, which constitutes the majority of its structure, and amorphous, where a smaller fraction of disordered chains is present [11].

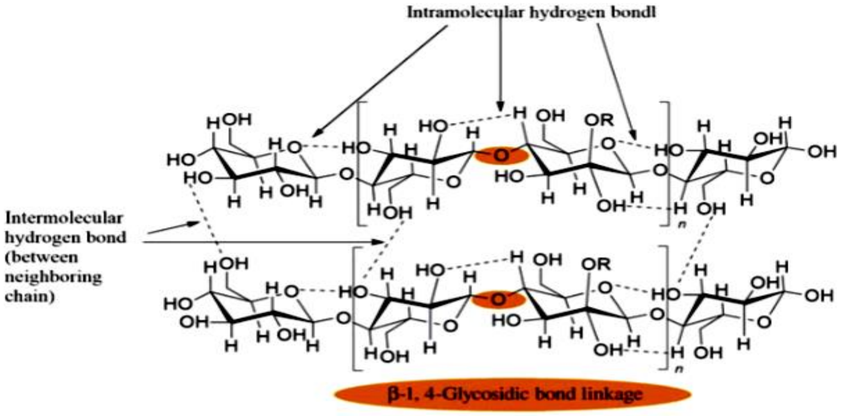


Figure I. 2 Chemical structure of cellulose chains.

I.1.2.2- hemicellulose

Hemicellulose refers to cell wall polysaccharides that have a strong affinity for cellulose microfibrils through hydrogen bonds and Van der Waals forces. It is a heterogeneous group of plant-derived polysaccharides that includes D-xylose, D-mannose, D-galactose, L-arabinose, D-galactose, and 4-O-methyl-D-glucuronic acid. Hemicellulose is used in the production of alcohol through fermentation, sorbitol by reduction, and has applications in food, toothpaste, cosmetics, explosive manufacturing, and papermaking. Pentose of hemicellulose is used to produce feed yeast, furoic acid, xylose, and xylitol. Xylooligosaccharides, a degradation product of hemicellulose, are widely used in functional food and pharmaceutical fields due to their unique physical and chemical properties and physiological functions.

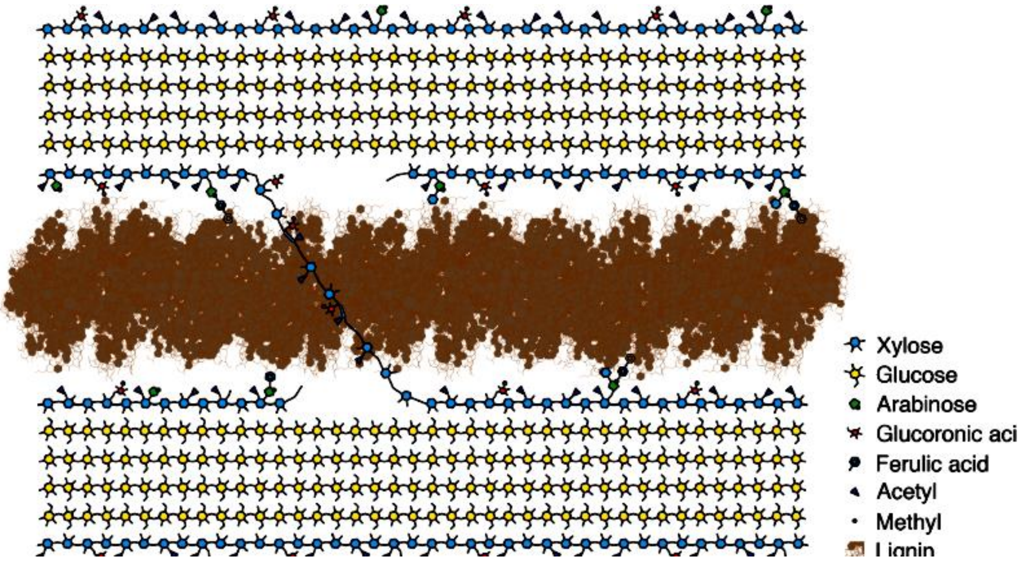


Figure I.3. Hemicellulose-cellulose network in the cell wall of grasses.

The hemicellulose molecules (glucuronoarabinoxylan), shown in blue, can bind to sections of the cellulose microfibril (shown in yellow) through hydrogen bonding. The hemicellulose molecules can span two or more cellulose microfibrils, tethering them together.

Hemicellulose is extracted from various plant sources and locations, resulting in different structures and molecular compositions. The hemicellulose from different biomass species, such as hardwood, softwood, and gramineous plants, have distinct chemical structures. For instance, the hemicellulose in the secondary wall of hardwood cells are primarily glucuronoxylan or 4-O-methyl-glucuronoxylan with some acetyl groups, while the hemicelluloses in softwood cells are mainly galactose glucose mannan or O-ethyl-galactose glucose mannan. The structures of hemicellulose also vary within different parts of the same raw material. Additionally, different raw materials and extraction methods can lead to different types and contents of side chains in the obtained hemicelluloses. Wheat straw is an important biomass raw material for the extraction of hemicellulose, and recent research has focused on the hemicellulose from wheat straw [14].

I.1.2.3- Lignin

Lignin, a complex organic polymer rich in oxygen, is a fundamental component of wood alongside cellulose. While it ranks second to cellulose in Earth's organic abundance, its industrial applications beyond fuel are limited. Found predominantly in the cell walls of wood, lignin constitutes 24–35% of the oven-dry weight of softwoods and 17–25% of hardwoods.

As a phenolic compound characterized by an aromatic ring with an attached -OH group, lignin is a blend of three intricate polymeric compounds. The composition of these monomers varies depending on whether the lignin originates from gymnosperms, woody angiosperms, or grasses. Lignin contributes to the structural integrity and rigidity of plant cell walls, aiding plants in resisting gravitational forces. It also acts as a waterproofing agent, facilitating water transport in xylem tissues and possesses antifungal properties, swiftly forming a protective barrier against fungal intrusion following injury.

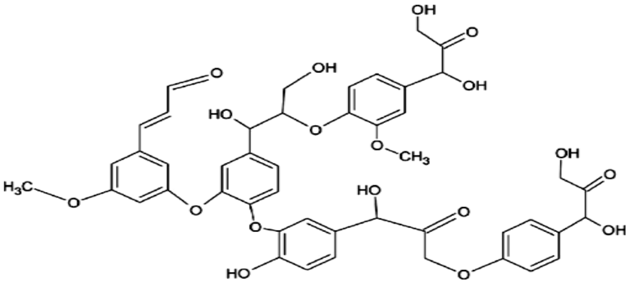


Figure I. 4 Chemical structure of lignin.

In paper production, lignin is extracted from wood pulp using agents like sulfur dioxide, sodium sulfide, or sodium hydroxide. Its industrial applications include serving as a binder for particleboard, a soil conditioner, a component of phenolic resins, and an adhesive for linoleum. Additionally, lignin is utilized in the production of vanillin (synthetic vanilla) and dimethyl sulfoxide [15].

I.1.2.4- Pectin

Pectin is a water-soluble carbohydrate found in the cell walls and intercellular tissues of certain plants. It aids in maintaining the adhesion of adjacent cells in plant fruits. During the ripening process, the precursor substance protopectin is converted to pectin, which becomes more water-soluble and helps maintain firmness and shape. Overripe fruits lose their shape and soften due to the breakdown of pectin into simple, completely water-soluble sugars.

Commercially, pectin is valued for its ability to form a thick gel-like solution, making it suitable for producing jellies, jams, and marmalades. Its thickening properties are also useful in the confectionery, pharmaceutical, and textile industries. Pectic substances, a group of associated polysaccharides, can be extracted with hot water or dilute acids, with citrus fruit peels and apple pomace being the primary commercial sources.

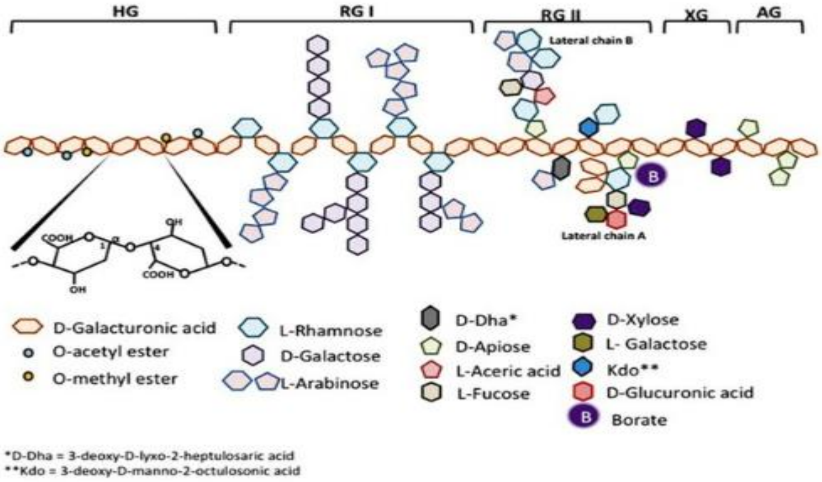


Figure I.5. Schematic representation of pectin structure. AG, arabinogalactan; HG, homogalacturonan; RG, rhamnogalacturonan; XG, xylogalacturonan.

Pectin has several health benefits for humans, including reducing low-density lipoprotein (LDL) levels to lower cholesterol, slowing food passage through the intestine to alleviate diarrhea, and activating cell death pathways in cancer cells, suggesting a potential role in cancer prevention. [16].

Pectin, with its straightforward and cytocompatible gelling properties, has recently emerged as a valuable material for various biomedical applications, such as drug delivery, gene delivery, wound healing, and tissue engineering [17].

I.1.2.5- Extractables

Extractable substances are small molecules found within the porous structure of wood that can be dissolved in common organic solvents (such as hexane, dichloromethane, acetone, toluene/ethanol, methanol) or water, hence their name. These substances, primarily consisting of secondary metabolites, are not essential for tree growth and can possess either lipophilic or hydrophilic characteristics. The content and composition of extractables vary based on factors like wood species, tree part studied, age, location, harvest time, and storage duration. They play a significant role in determining wood properties like color, odor, natural durability against biological degradation, acoustic features, and can impact various processing methods like adhesion, finishing, and pulping.

Extractables can be extracted using different techniques such as hot extraction with a Soxhlet apparatus, accelerated extraction systems like Dionex, maceration, or steam distillation. These compounds exhibit a wide range of structures and can be classified into three main groups: Terpenes and Terpenoids, Waxes and Fats, Phenolic compounds [18].

I.1.3- Ligno-cellulose and its valorization

Lignocellulosic biomass, a renewable and abundant raw material, has an annual global production of approximately 181.5 billion tons, with only around 8 billion tons currently utilized.[19]. Lignocellulosic biomass, a resourceful and abundant material, comprises plants and their byproducts, including agricultural and paper mill waste. This biomass is a rich source of three of the most plentiful natural polymers on Earth: cellulose, lignin, and hemicellulose. These polymers can be harnessed for the production of bioplastics, with or without functionalization, or for the creation of chemical compounds. The potential applications of lignocellulosic biomass are vast, offering sustainable and environmentally friendly alternatives to traditional materials and processes. The versatility of this biomass, coupled with advancements in biotechnology and materials science, presents exciting opportunities for the development of innovative products and solutions [20].

Cellulose, lignin, and hemicellulose are the primary constituents of lignocellulosic biomass derived from natural plants, known for their abundance, renewability, biodegradability, and biocompatibility. These properties position them as valuable resources for various commercial applications, suggesting the potential to decrease society's reliance on fossil fuels with effective management. However, the inherent low solubility and processability of natural lignocellulosic materials restrict their practical utilization. Therefore, pretreatment processes are typically necessary to enhance their solubility and processability, enabling their subsequent use as a sustainable energy source or renewable resource [21].

Numerous approaches have been investigated to address the substantial volumes of lignocellulosic residues generated, focusing on enhancing their reuse and recycling[22]. Limarta et al. have conducted notable research on the efficient depolymerization of lignin through diverse catalytic methods, such as utilizing a carbon-supported ruthenium catalyst in ethanol/formic acid or a combination of metallic catalysts and bases in supercritical ethanol [23]. Bijoya Devi et al. have explored innovative ways to enhance the value of various lignocellulosic wastes, particularly by utilizing them in cultivating fungi for mushroom production and other valuable by-products [24]. Additionally, Karadirek and Okkay have devised a statistical model for producing activated carbon from spent mushroom compost [25]. Kim et al. have pioneered the pyrolysis of Kraft lignin in a rotary kiln reactor to prevent carbon agglomeration, while Trinh et al. have introduced effective pretreatment strategies to optimize bioethanol production and concentration through pervaporation [26].

Numerous investigations focus on the production of biofuels from lignocellulosic waste, highlighting its potential as a valuable resource beyond energy generation. Furthermore, lignocellulosic waste has demonstrated its suitability as a feedstock for chemical production, expanding its applications in various industries. The concept of a comprehensive biorefinery, derived from forest residues, is also gaining traction in the literature, aiming to establish a circular bioeconomy that maximizes the utilization and value of these renewable resources [27].

In the era of a circular economy, the conventional management of lignocellulosic waste, which primarily involves grinding and compacting to reduce costs but not environmental impact, is becoming outdated and less cost-effective. Alternatively, recycling lignocellulosic waste as a byproduct or through composting, energy valorization, biofuel production, glucose and other high-value products synthesis, and the creation of biopolymers, biocomposites, nanofibers, and nanoparticles, are increasingly recognized as viable and sustainable options that align with the principles of a circular economy.

The development of processes to convert lignocellulose into valuable chemicals, polymers, and energy is crucial for maximizing the utilization of renewable resources. Renewable sources, including lignocellulosic biomass, are poised to replace traditional fossil fuels and the chemicals derived from them, as they do not compete with food production. This shift towards renewable sources is essential for reducing our reliance on non-renewable resources and promoting a more sustainable and environmentally friendly economy [28].

I.1.4-Olive sector: Between production and co-products

The cultivation and production of olive oil have been a long-standing practice in the Mediterranean region for over 7000 years, with a growing global demand due to its high dietetic and nutritional value. Approximately 750 million olive trees exist worldwide, with 98% located in the Mediterranean region, where more than 97% of olive oil is produced. Spain, Italy, and Greece are the leading olive oil producers, followed by Turkey, Tunisia, and other countries like Portugal, Morocco, and Algeria.

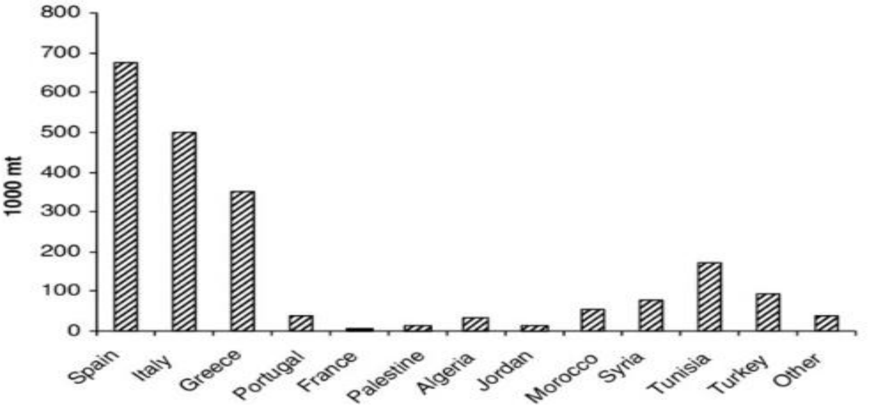


Figure I. 6. Olive oil-producing countries (International Olive Oil Council, 2004).

The traditional press extraction method and the continuous three-phase decanter process generate three products: olive oil (20%), a wet solid waste (30%) known as "crude olive cake" or "olive husk," and an aqueous waste (50%) referred to as "olive mill wastewater" or "olive mill effluent" or "alpechin." Crude olive cake, a mixture of olive pulp and stones, can be processed in seed oil factories to extract the remaining oil, used as solid fuels, animal feed supplements, or returned to olive groves as mulch. However, the profitability of seed oil production is being questioned, and the disposal of crude olive cake is adequately addressed by one of these alternatives.

In contrast, the treatment and disposal of olive mill wastewater (OMWW) present a more complex challenge. Despite attempts for over 50 years, particularly in major olive oil-producing countries, an environmentally friendly and economically viable solution has yet to be widely adopted [29].

I.1.4.1- Impact of olive residues

Over the past few years, the olive industry has experienced significant growth, leading to an increase in the production of olive products and, consequently, a rise in by-product generation. These by-products, including olive leaves, olive black water, and olive pomace, can have detrimental environmental impacts if not managed properly during olive oil processing [30].

The organic load in olive mill wastewater is considered one of the highest of all concentrated effluents, being 100-150times higher than the organic load of domestic waste-water. during the extraction of olive oil, whether through continuous or discontinuous processes, wastewater is produced, which is a mixture of water from the olive fruit and water used for washing the fruit. This wastewater is acidic and contains high levels of total suspended solids (TSS), total dissolved solids (TDS), phenols, and other organic matter.

The organic content of OMW is characterized by high chemical oxygen demand (COD), biochemical oxygen demand (BOD), and fat, oil, and grease (FOG) concentrations.OMW contains toxic organic materials such as sugars, tannins, polyphenols, polyalcohols, pectins, proteins, and lipids. The ecological stabilization and detoxification of OMW's effects are challenging and often ineffective due to the high load of toxic organic compounds. Improper discharge of OMW can disrupt biological activities in domestic wastewater ponds, causing a strong and unpleasant odor due to aerobic digestion in open-air systems and posing a threat to surface and groundwater.

The disposal of OMW during the olive harvest season can lead to serious environmental problems. In addition to wastewater generation, a significant amount of solid waste is also produced, highlighting the environmental concerns associated with olive oil production [31].

I.1.4.2- Valorization of olive by-products

The cultivation of olive trees and the production of olive oil result in significant quantities of solid waste, including olive tree pruning (OTP), olive leaves (OL), olive stones

(O.S.), and liquid effluents like olive stones (O.S.), olive oil mill wastewaters (OOMW), and olive mill waste (OMW), depending on the oil extraction methods employed. Historically viewed as challenging waste materials with environmental implications, olive by-products are now being reevaluated and acknowledged for their potential as sources of high-value compounds such as phenols and antioxidants. These compounds can be repurposed as natural additives in the food, cosmetic, and pharmaceutical industries [32].

Past research investigating the utilization of olive by-products in animal nutrition has demonstrated promising economic advantages and the potential for alternative feed sources. Findings indicate that incorporating olive industry by-products into broiler diets at specific levels does not adversely impact growth performance parameters, although higher levels may have negative effects [30].

I.1.5 – Olive stones. A valuable by-product

I.1.5.1- General

Olive stones, also known as olive cake or olive husk, is the solid residue generated after olive oil extraction. It is one of the most plentiful agroindustrial by-products in the Mediterranean region, consisting of a lignocellulosic matrix (cellulose, hemicelluloses, and lignin) with phenolic compounds, uronic acids, and oily residues. The quantity and physicochemical properties of these residues **(olive stones)** vary depending on the extraction method used. Historically, traditional pressing has been employed for centuries with only minor modifications, while centrifugation (two and three-phase systems) has become more prevalent in the olive oil industry over the last few decades. The choice of extraction method significantly impacts the amount and characteristics of olive pomace produced[33].

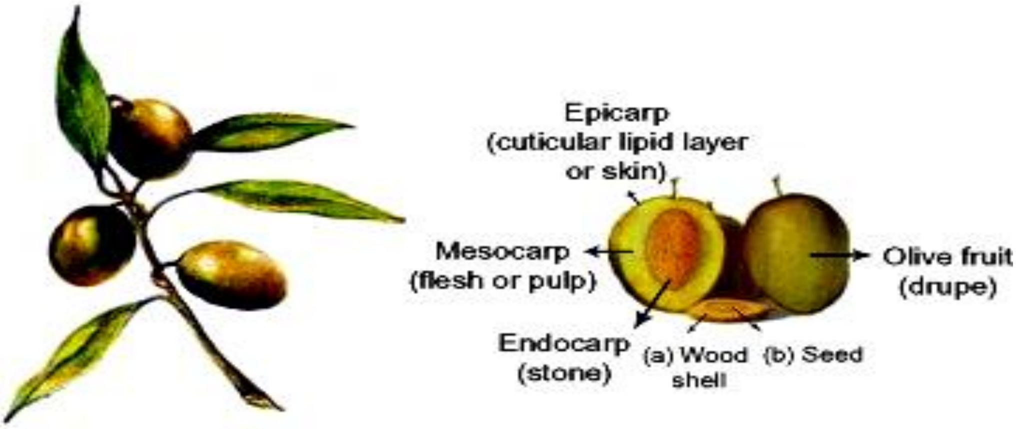


Figure I. 7. Cross section of olive fruit.

I.1.5.2- Composition of olive stone. Chemical and mineral composition of olive stones

Olive stone is a solid byproduct comprising residual skin, pulp fragments, and traces of oil from the olive oil extraction process [34]. **Table 2** provides a summary of the proximate composition of raw material olive pomace, revealing that the primary components are polysaccharides, accounting for 35.1% of the total. These polysaccharides are primarily composed of hemicellulose (approximately 19%, with xylose and arabinose monosaccharides being the main constituents) and cellulose (16.2%, as glucose). Lignin makes up 31.7% of the olive pomace composition, with 20.5% being Klason lignin and 11.2% acid-soluble lignin. Water and ethanol-soluble extractives account for 25.2% of the total olive pomace waste, while fat and protein content represent 12.1% and 5.7%, respectively. The inorganic fraction (ashes) accounts for 4.6% of the olive pomace composition, with potassium (2798.4 mg/kg), calcium (352.0 mg/kg), and magnesium (145.4 mg/kg) being the most prominent minerals[35].

Table I.2. Chemical composition of olive stones.

Proximate Composition (g/100 g Dry OP)		**Mineral Element (mg / g Dry OP)**	
Cellulose	16.16 ±0.78	Potassium	2798.44 ±29.64
Hemicellulose	18.96 ±1.79	Calcium	352.03 ±23.01
Xylose	15.32 ±0.45	Magnesium	145.41 ±16.54
Arabinose	3.64 ±0.2	Iron	12.24 ± 2.71
Acetyl group	3.75 ± 0.73	Sodium	16.42 ±0.67
Lignin	31.69 ±1.4	Aluminum	16.93 ±2.08
Insoluble	20.47 ±1.31	Manganese	1.56±0.22
Soluble	11.22 ± 0.13	Zinc	2.92 ± 0.36
Protein	5.66 ±0.31	Copper	2.73 ± 0.29
Fat	12.06 ±0.79	Boron	4.02 ±0.52
Ashes	4.35 ± 0.22	Barium	0.18 ±0.03
Total extractives	25.23 ±1.88		

Microbiological Characteristics

The microbial community of olive stones (O.S.) has been found to be comparable to that of other oil by-products, such as olive mill waste water (OMWW), and consists of both bacteria and yeasts. Vivas et al. identified Proteobacteria as the dominant bacterial group, followed by Actinobacteria (Streptomyces), Firmicutes (Staphylococcus), and Acidobacteria. Additionally, members of Hydrocarboniphaga, Pseudoxanthomonas, and Stenotrophomonas (Gammaproteobacteria) were detected, with Comamonas (Betaproteobacteria) being the primary microbial group. Firmicutes were found to be the most prevalent and diverse bacterial group in the olive pomace microbiome, as determined by amplification of the internal transcribed spacers between the 16S and 23S rRNA genes (ITS-PCR) and 16S rRNA sequencing. The fungal population in olive pomace appears to be significantly influenced by the olive cultivar [36].

I.1.5.3- Different sectors for valorizing olive stones

Olive stones, a byproduct of the olive industry, offers numerous valorization opportunities, including:

- Oil extraction: Solvent extraction allows recovery of at least 6% of residual oil, often referred to as "olive oil."

- Fertilizer use: Olive pomace can be utilized as a fertilizer, enriching soil with organic matter.

- Aromatic compound production: Thermophilic and filamentous fungi fermentation of olives in solid medium generates a variety of compounds for agrifood, cosmetic, and pharmaceutical applications. Anaerobic fermentation of cow manure with olive pomace produces methane (57-65% of biogas), used for water heating and electricity production.

- Wastewater and vegetable water treatment: Olive stones biosorption of heavy metals and phenols offers an alternative to expensive and inefficient conventional methods.

- Lightweight building material: Olive stones can be used as a pore-forming additive in clay brick manufacturing, providing good insulation characteristics.

- Bioactive peptide extraction: Olive stones contains bioactive peptides with potential health benefits.

- Probiotic biomass production: Fermented olive stones can generate probiotic biomass, supporting gut health.

- Orchard fuel: Olive stones can replace traditional orchard fuels, reducing greenhouse gas emissions.

- Gasification process: Olive stones can be used in gasification, an alternative to combustion, for energy production.

- Diabetes treatment: Olive stones are recommended as a remedy for diabetes management.

- Hydrocarbon-based bacteria source: Olive stones can be used as physical oil sorbent and a biological source for hydrocarbon-based bacteria, aiding in bioremediation.

- Livestock feed: Sifted spent olive pomace, without stones, is easy to preserve and has better nutritional value, serving as food reserves during scarcity [33].

I.2- Organic Matter

I.2.1- Fulvic acid from the Suwannee River (SRFA, USA).

The Okefenokee Swamp, a vast wetland in southeastern Georgia, is the origin of the Suwannee River, which flows southwesterly from the swamp into the Gulf of Mexico.

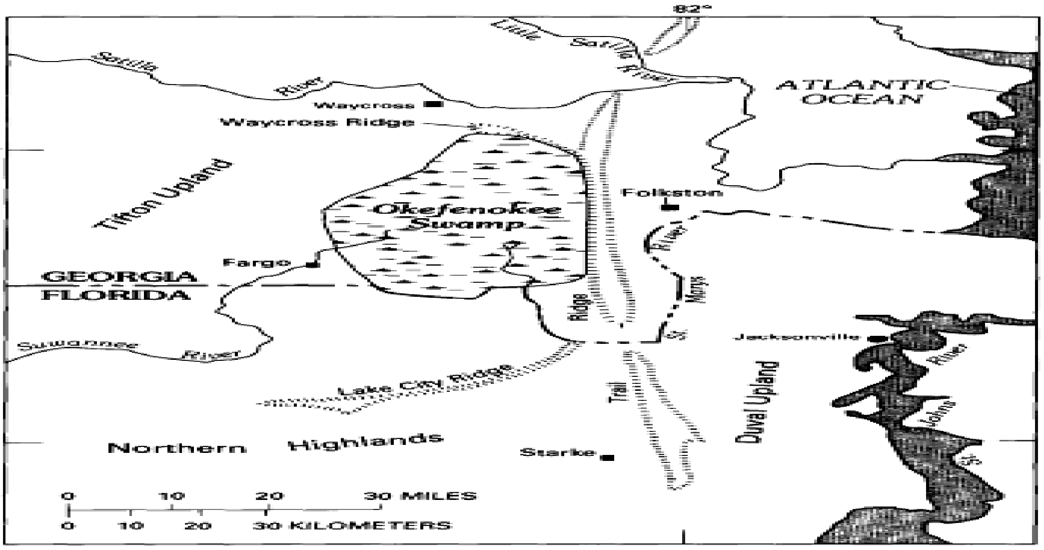


Figure I. 8. Location of the Okefenokee Swamp, Suwannee River, St. Marys River, Trail Ridge, and other physiographic features of southeastern Georgia and northeastern Florida.

The St. Marys River's course to the ocean is influenced by several geographic factors, causing it to flow south from the wetland along the western edge of Trail Ridge, then eastward through a gap in Trail Ridge. The river then moves nearly north for 50 km along the eastern edge of Trail Ridge before turning east to the Atlantic Ocean.

Three notable aspects of the Suwannee River's water quality are its acidity (pH of 4), low concentration of dissolved inorganic solids (specific conductance ranging from 30 to 60 µS/cm), and high concentration of dissolved organic substances, particularly fulvic acids. The water's acidity is due to organic acids produced during the anaerobic decomposition of plant litter and peat in the Okefenokee Swamp [37] .

I.2.2- Structure and composition

The Suwannee River stands out due to its consistently brown-colored water stretching from its origin in the Okefenokee Swamp to its estuary in the Gulf of Mexico. This large river's uniqueness is further highlighted by its location in a sandy region and its year-round consistent discharge. For several decades, the river's brown color has been attributed to the presence of organic matter, with both colloidal and dissolved organic constituents bound to various metal ions and oxides. [37].

Suwannee River fulvic acid (SRFA) is a well-studied aquatic humic substance, accounting for 66% of the dissolved organic carbon concentration in the Suwannee River. SRFA has been extensively fractionated and characterized using various techniques. Normal-phase fractionation on silica gel yielded seven fractions (Si-1 to Si-7) eluted with solvents of increasing polarity. Additionally, reverse-phase fractionation on XAD-8 resin produced 18 subfractions, which were analyzed by infrared spectroscopy. These studies have provided valuable insights into the composition and structure of SRFA, making it a useful model compound for understanding the properties and interactions of aquatic humic substances [38].

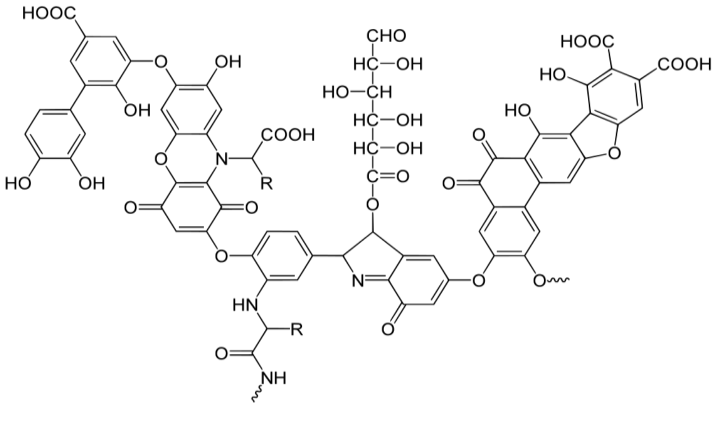


Figure I. 9. Humic substances (fulvic and humic acids)

Chapter II

In this chapter, we present the equipments, as well as the experimental and analytical methods specific to each technique for evaluating the capability of olive pomace to adsorb organic matter (SRFA).

II.1. Materials preparation

In this work, we have used olive kernels (NO) as adsorbents. These materials are prepared using the following process:

a) Washing process

The olive kernels are washed multiple times with tap water to remove dust and adhering impurities, as well as water-soluble substances, until clear washing water is obtained. Subsequently, they are rinsed with distilled water for further purification.

The olive kernels are exposed to hydrogen peroxide for 48 hours to eliminate residual oils and organic matter. Subsequently, they are washed several times with distilled water for further purification.

b) Drying process

The drying of the materials was carried out using solar energy and also in an oven, at temperatures between 50 and 60°C, to prevent any potential alteration of the physicochemical properties of the materials.

c) The grinding process

The grinding process was conducted to achieve homogeneous materials for laboratory studies, resulting in small-sized grains, typically less than 2 mm in size.

d) Sieving

The particle sizes used for adsorption tests were isolated using a sieve with a mesh size corresponding to a diameter of 90µm. Only the grains that pass through the 0.315mm mesh sieve were considered for the adsorption tests.

II.2 Materials Used

-Laboratory glassware: graduated cylinders, funnels, beakers, pipettes, test tubes, measuring cylinders.

-Balance, stirrers.

-pH Meter (HANNA Instrument 211).

II.3 SRFA adsorption on Olive stone (O.S.)

100 mg of olive stones fine particles with a diameter less than 80 µm (Φ<80 µm) were mixed with 20 mL of an SRFA solution at a concentration of 200 mg/L SRFA. The experiments were carried out at an average pH of 4.57, based on previous tests indicating that the optimal adsorption of anionic compounds like SRFA onto adsorbents such as olive pomace occurs in an acidic environment with a pH around 5. The mixture was stirred for 6 hours and then allowed to settle. The liquid above the sediment was collected for UV/Visible measurements. The solid residue (SRFA-O.S.) was dried overnight at 60 °C, ground, and sieved to particles smaller than 2 µm. The olive stones and SRFA-O.S. samples were analyzed using **XRD; FTIR; UV/Visible spectroscopy, SEM and TGA/DTG.**

II.4 analysis methods

II.4.1 UV-Vis Spectroscopy

The SFRA solution and the supernatant obtained after the contact of Olive stones with SRFA were analyzed using a UV/Visible Shimadzu 1800 spectrophotometer device.

In UV-Vis spectroscopy, the wavelength is commonly denoted in nanometers. The UV range typically spans from 100 to 400 nm, while the visible range extends from around 400 to 800 nm. As per the equations, shorter wavelength radiation possesses higher energy, and in UV-Vis spectroscopy, the low-wavelength UV light exhibits the greatest energy.

At times, this high energy level can lead to undesired photochemical reactions when analyzing samples that are light-sensitive.

Figure II.1. UV/Visible Shimadzu 1800 spectrophotometer device

When light interacts with a sample, either by passing through it or being reflected from it, the amount of light absorbed is the difference between the incident radiation (I_o) and the transmitted radiation (I). This amount of absorbed light is quantified as absorbance. Transmittance, on the other hand, refers to the light that passes through the sample. It is typically expressed as a fraction of 1 or as a percentage, and is defined as follows:

$$\mathbf{T = I / I_o \; ; \quad or \quad \%T = I/I_o \times 100}$$

Where:

– I: is the intensity of the transmitted light

– I_o: is the intensity of the incident light

Absorbance is defined as follows: $\mathbf{A = -\log_{10}(T)}$

Where A: is the absorbance and T: is the transmittance

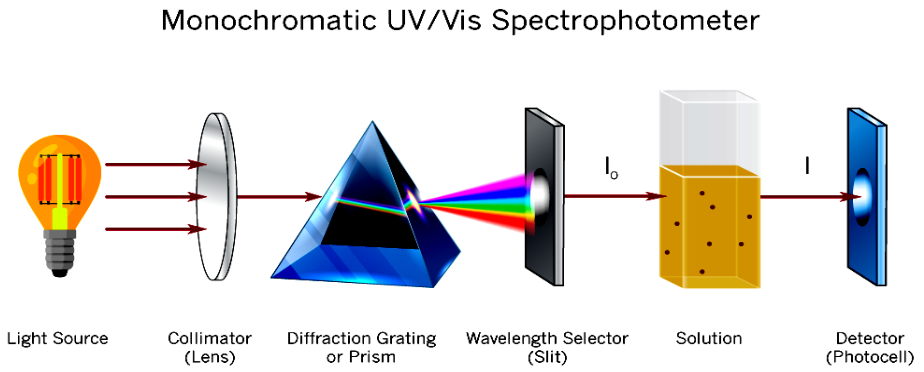


Figure II.2. The optical setup of a monochromatic UV/Vis spectrophotometer

In most cases, absorbance values are preferred because the correlation between absorbance and both concentration and path length tends to be linear, making it suitable for various applications.

II.4.2 UV-Vis Spectrophotometer work

Ultraviolet-visible (UV-Vis) spectrophotometers utilize a light source to illuminate samples with light spanning the ultraviolet and visible wavelength ranges, typically from 190 to 900 nm. These instruments then measure the light that is absorbed, transmitted, or reflected by the sample at each specific wavelength. Some UV-Vis spectrophotometers even have an extended wavelength range, reaching into the near-infrared (NIR) region from 800 to 3200 nm.

It is feasible to ascertain the chemical or physical properties of the sample. Typically, it is achievable to:

-Identify molecules within a solid or liquid sample

-Establish the concentration of a specific molecule in a solution

-Describe the absorbance or transmittance across a liquid or solid over various wavelengths

-Assess the reflectance characteristics of a surface or determine the color of a material

-Investigate chemical reactions or biological processes [39].

II.4.2 X-Ray Diffraction

In the provided experiment, a Philips PW1710 diffractometer with a Cu anticathode (Cu Kα wavelength (λ) of 1.54 Å) was used. The data were recorded in reflection mode 2θ, with a diffraction angle range from 5° to 80°, steps of 0.02°, an acquisition time of 10 s, and a low rotation speed (0.001°.s-1).

X-ray diffraction (XRD) is an effective technique for determining the crystal structure of materials. It can detect crystalline materials with crystal domains greater than 3-5 nm and is used to characterize bulk crystal structure and chemical phase composition.

X-rays are a form of electromagnetic radiation with wavelengths ranging from 0.01 to 0.7 nm, which is comparable to the spacings between lattice planes in crystals. The spacing between atoms in metals typically ranges from 0.2 to 0.3 nm. When an incident beam of X-rays interacts with a target atom, the X-ray photons are scattered in different directions. Elastic scattering occurs when there is no change in energy between the incident photon and the scattered photon, while inelastic scattering involves the scattered photon losing energy.

These scattered waves may superimpose, and when the waves are in phase, constructive interference occurs. If the waves are out of phase, destructive interference occurs. Atoms in crystal planes form a periodic array of coherent scatterers. Diffraction from different planes of atoms produces a diffraction pattern that contains information about the atomic arrangement within the crystal.

II.4.2.1 Bragg's Law

Bragg demonstrated that by treating the diffraction from a crystal as reflections from hypothetical planes of atoms within the crystal, an equation could be derived to predict the locations of diffraction maxima in a diffraction pattern. Imagine a pair of parallel X-rays striking a set of horizontal parallel planes, as illustrated in the Figure. Although the parallel rays reach the planes in phase, the lower ray has a greater distance to travel compared to the upper one by the time they are both reflected. Through basic trigonometry, it can be proven that $n\lambda = 2d.\sin\theta$. This Bragg relationship indicates that constructive interference of the waves will only occur when the difference in path length is a multiple of the wavelength, λ.

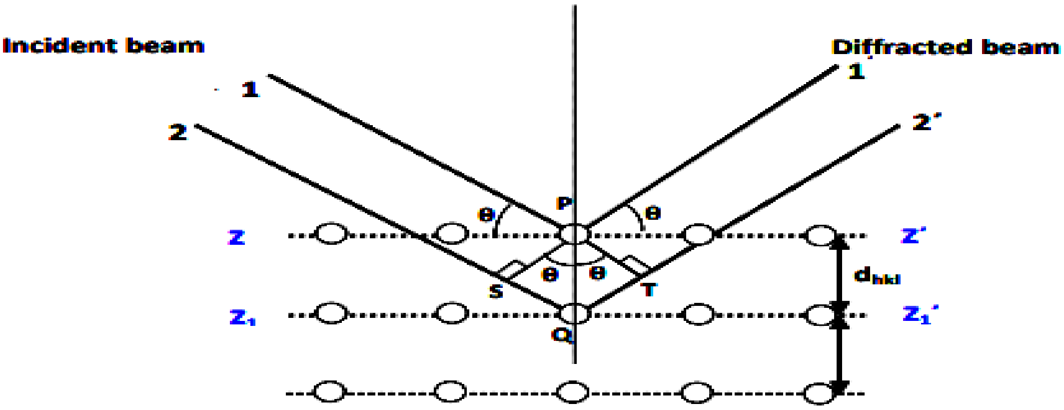


Figure II.3. Braggs analysis for X-ray diffraction

II.4.2.2 Working principle and Instrumentation

The instrument known as an X-ray diffractometer utilizes a single wavelength X-ray beam to analyze specimens. By continuously adjusting the incident angle of the X-ray beam, a diffraction intensity spectrum versus the angle between the incident and diffracted beams is recorded. The primary components of the diffractometer include:

-X-ray Tube: the source of X-rays

-Incident-beam optics: to prepare the X-ray beam before it reaches the sample

-Goniometer: the platform that supports and moves the sample, optics, detector, and/or tube

-Sample holder

-Receiving-side optics: to prepare the X-ray beam after interacting with the sample

-Detector: to quantify the number of X-rays scattered by the sample

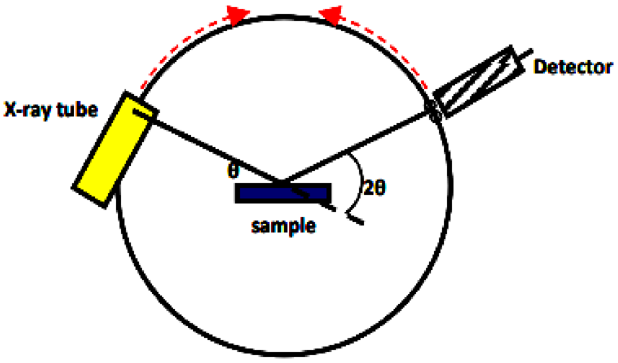


Figure II.4. Basic components of X-ray diffractometer

II.4.2.3 Strengths

• Powerful and rapid technique for identifying unknown minerals, typically taking less than 20 minutes.

• In the majority of instances, it offers a clear and definitive identification of the mineral.

• Only minimal sample preparation is necessary.

• XRD instruments are readily accessible.

• Interpreting the data is relatively simple.

II.4.2.4 Limitations

-Homogeneous and single-phase materials provide the most accurate identification of unknown samples.

-Access to a standard reference file containing the d-spacings and hkl values of inorganic compounds is necessary.

-A minimum of a few tenths of a gram of material, ground into a fine powder, is required for analysis.

-For mixed materials, the detection limit is approximately 2% of the sample.

-Indexing patterns for non-isometric crystal systems can be complicated when determining unit cell dimensions.

-Peak overlap may occur, worsening at higher diffraction angles [40].

II.4.3 Infrared spectroscopy Fourier transform (FTIR)

FTIR spectra were acquired using an FTIR-8400 Fourier transform SHIMADZU spectrophotometer. Each spectrum was generated by recording fifty scans with a spectral resolution of 4 cm-1 in transmission mode within the range of 400 to 4000 cm^{-1}.

FT-IR, short for Fourier Transform InfraRed, is the preferred method for infrared spectroscopy. In this analytical technique, infrared radiation is passed through a sample. The sample absorbs some of the infrared radiation while the rest is transmitted through. The resulting spectrum reflects the molecular absorption and transmission, essentially creating a unique molecular fingerprint of the sample. Just like fingerprints, no two distinct molecular structures produce the same infrared spectrum, making infrared spectroscopy valuable for various types of analyses.

FT-IR spectrometry was developed to address the limitations of dispersive instruments, particularly the slow scanning process. To overcome this challenge, a method was devised to simultaneously measure all infrared frequencies instead of individually scanning each one. This solution involved using a simple optical device known as an interferometer. The interferometer generates a distinct signal that encapsulates all infrared frequencies within it. This signal can be rapidly measured, typically within a second or so, significantly reducing the time required per sample to just a few seconds instead of several minutes.

Figure II.5. Shimadzu FTIR-8400S Spectrometer

II.4.3.1. The Sample Analysis Process

The normal instrumental process is as follows:

The typical process in an FTIR spectrometer is as follows:

1.The Source emits infrared energy from a glowing black-body source. This beam passes through an aperture that controls the amount of energy presented to the sample and ultimately to the detector.

2.The Interferometer receives the beam, where the "spectral encoding" occurs. The resulting interferogram signal then exits the interferometer.

3.The Sample compartment receives the beam, which is either transmitted through or reflected off the sample surface, depending on the analysis type. This is where the sample absorbs specific frequencies of energy that are uniquely characteristic of its composition.

4.The Detector measures the final beam, using specialized detectors designed to measure the interferogram signal.

5.The Computer digitizes the measured signal and performs the Fourier transformation, generating the final infrared spectrum presented to the user for interpretation and further analysis [41].

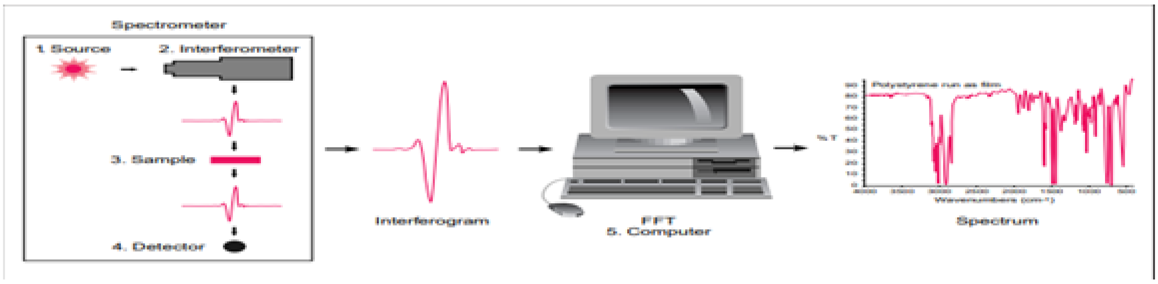


Figure II.6. Analysis Process in an FTIR spectrometer

II.4.4 Thermogravimetric analysis TGA

Thermogravimetric Analysis (TGA) is a method where the mass of a substance is observed concerning temperature or time as the sample undergoes a controlled temperature regimen in a controlled atmosphere. This technique involves monitoring how the weight of a material changes as it is heated, either increasing or decreasing. The study involved obtaining thermogravimetric curves using the Perkin Elmer TGA-7 model, with a heating rate of 10°C/min in air, within a temperature range of 30°C to 800°C under a nitrogen atmosphere with a flow rate of 20 mL/min. Each sample, weighing between 3 to 5 mg, was placed in an alumina crucible and subjected to controlled heating.

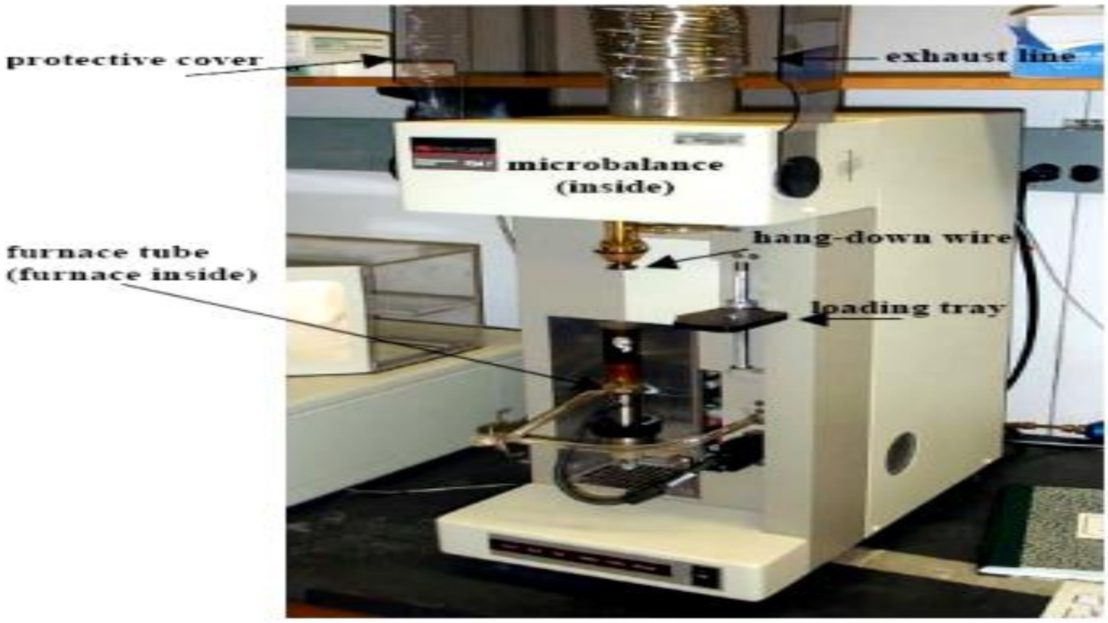


Figure II.7. Perkin Elmer TGA 7 Thermogravimetric Analyzer

Thermogravimetric Analysis (TGA) measures the weight change of a material as it is heated or cooled in a furnace.

A TGA setup includes a sample pan supported by a precision balance, placed in a furnace where the sample is heated or cooled during the experiment. The mass of the sample is continuously monitored throughout the process. A sample purge gas regulates the sample environment, which can be either inert or reactive, flowing over the sample and exiting through an exhaust [42].

II.4.5. Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is a powerful technique for high-resolution imaging and analysis of surface topography and composition. In an SEM, a focused beam of electrons is scanned across the sample, and the interactions between the electrons and the sample are detected and used to construct an image. This technique allows for the visualization of surface features as small as 1-10 nanometers, making it particularly useful for studying the morphology of materials at the nanoscale.

The SEM uses various signals generated by the electron-sample interactions, such as secondary electrons, backscattered electrons, and X-rays, to provide information about the surface. Secondary electrons are most valuable for showing morphology and topography, while backscattered electrons are useful for illustrating contrasts in composition in multiphase samples. X-ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete orbitals of atoms in the sample, and the characteristic X-rays emitted are used for elemental analysis.

SEM analysis is considered non-destructive, as the X-rays generated do not lead to volume loss of the sample, allowing for repeated analysis of the same materials. The SEM instrument consists of an electron source, electron lenses, a sample stage, detectors for various signals, and display/data output devices, all housed in a vacuum system with power supply, cooling system, and vibration-free floor. SEM is widely used in various fields, including materials science, biology, and engineering, to investigate the surface properties and structures of materials, such as the texture of biological samples, the morphology of nanoparticles, and the defects in materials [43].

Chapter III

RESULTS AND DISCUSSION

III.1 Introduction

This chapter presents and discusses the experimental results obtained from the study of adsorption of organic matter (SRFA) as an organic pollutant, on olive stones used as natural adsorbent materials. The experimental program focused on investigating the potential of olive stones as a low-cost, eco-friendly bio-adsorbent for the removal of the fulvic acid (SRFA) from polluted water.

III.2 XRD analyses

The X-ray diffractograms of olive stones samples, both with and without contact with organic matter (SRFA), exhibit several diffraction peaks. Three of these peaks are characteristic of native cellulose, a component of lignocellulosic materials, and are observed at deviation angles of approximately: **2 Ө≈ 17,14° - 17,30° ; 2 Ө≈ 22,13° - 22, 17° and 2 Ө≈ 14,8° 14,9°.**

The last angle is less prominent in both diffractograms. Additionally, the diffractograms of olive stones samples in contact with organic matter (SRFA) and without contact display multiple peaks, with only two corresponding to native cellulose observed at deviation angles of approximately **2 Ө≈ 20,8° and ≈ 4,8°.**

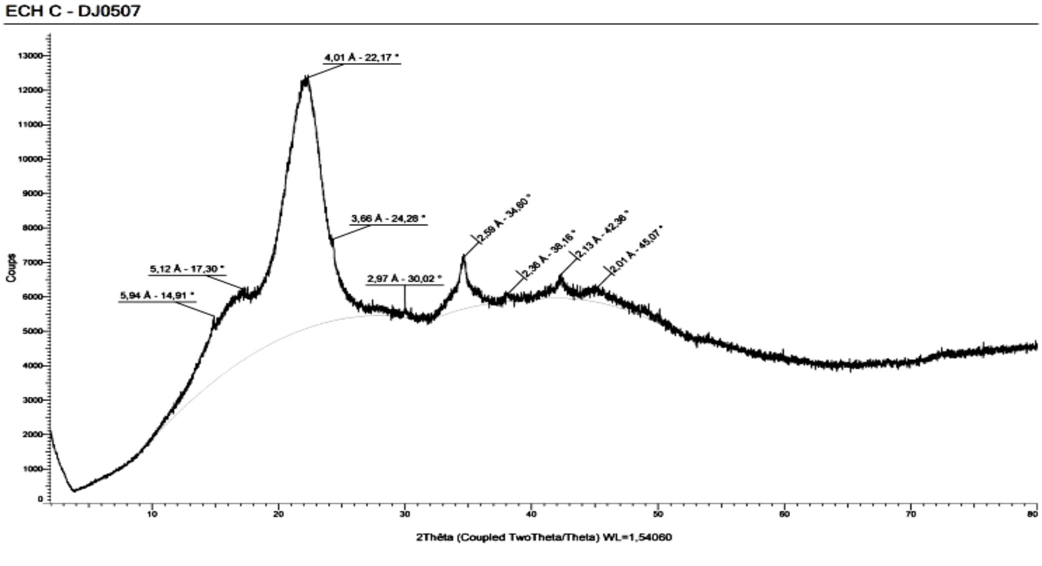


Figure III.1. XRD spectra of olive stones **before** contact with organic matter (ECH C).

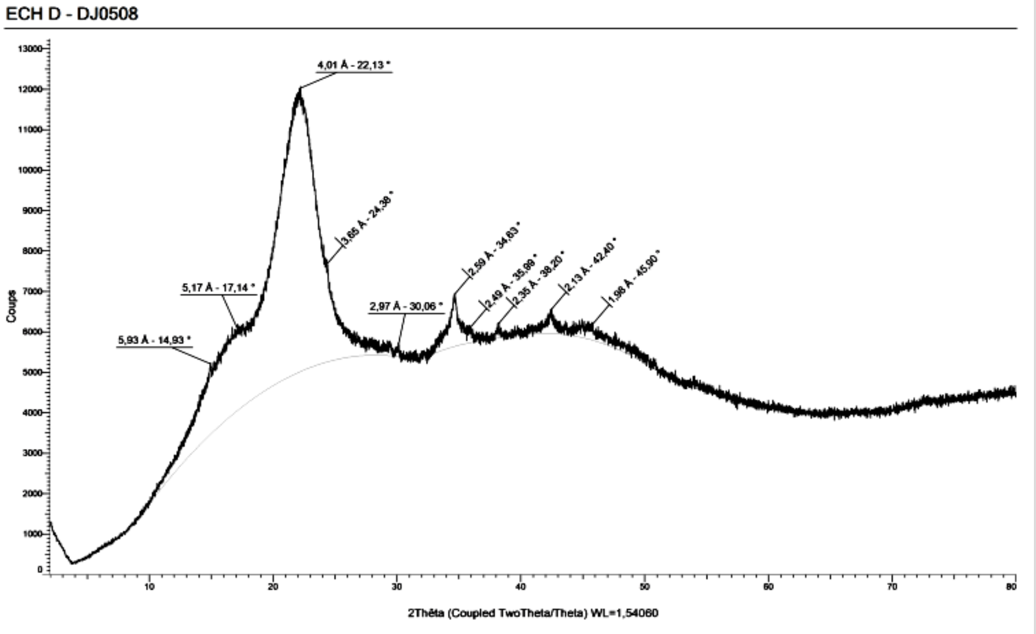


Figure III.2. XRD spectra of olive stone **after** contact with organic matter ((ECH D).

The remaining unidentified peaks correspond to other phases present in these materials. These peaks appear relatively less intense in the samples after contact (SRFA-O.S.) with organic matter compared to those before contact (O.S.).

III.3. Fourier Transform Infra-Red spectroscopy (FTIR)

The FTIR spectra depicted for the two olive pomace samples, before and after contact with the fulvic acid of SRFA, exhibit strong similarities with noticeable differences. A broad band spanning from 3100 to 3700 cm^{-1} is observed in both samples, indicating the stretching of OH bonds. This band is associated with OH vibrations in carboxylic groups, alcohols, or phenols, possibly originating from compounds like cellulose, hemicelluloses, and lignin. Notably, this peak is shifted to lower wave numbers in the SRFA-O.S. sample (peaking at 3252 cm^{-1}) compared to the O.S. sample (peaking at 3338 and 3324 cm^{-1}), suggesting a variation in the molecular structure bearing the -OH group. A faint peak around 3000 cm^{-1} in the SRFA.O.S. sample is linked to C-H stretching in RHC=CHR.

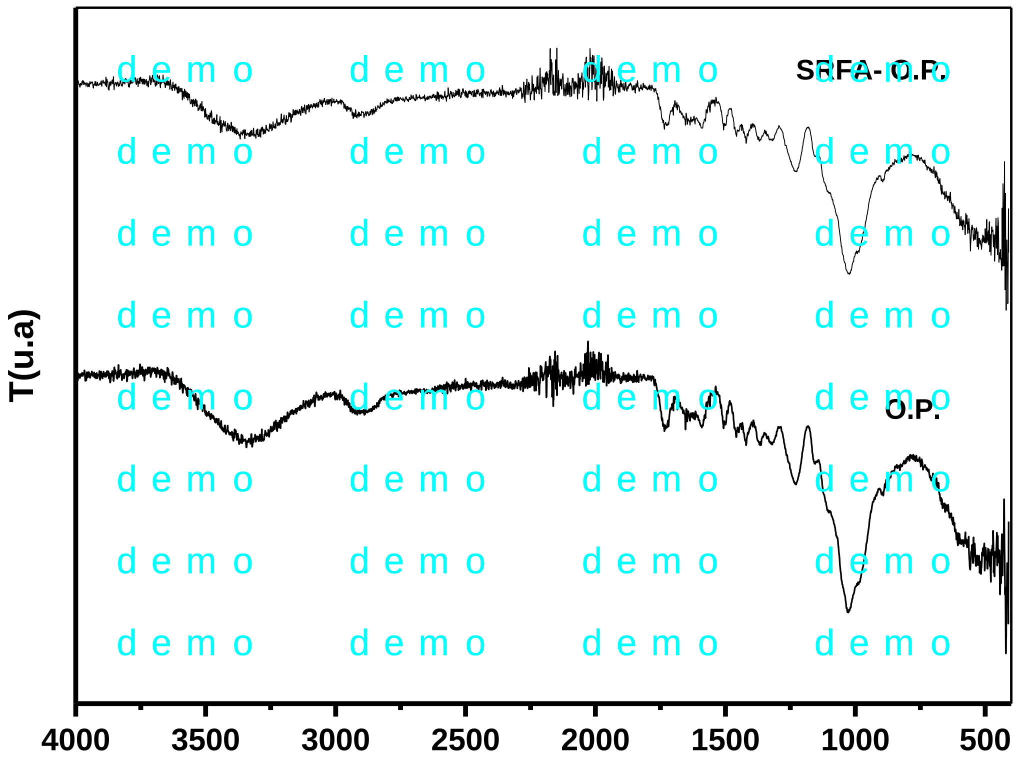


Figure III.3. The FTIR spectra depicted for the two olive stones samples, before and after contact with the fulvic acid of SRFA.

The distinct peaks at approximately 2925 and 2855 cm^{-1} correspond to asymmetric and symmetric -C-H stretching in aliphatic chains. While present in both samples, these peaks are less intense in the O.S. sample. In the range of 1200-2000 cm^{-1}, various peaks attributed to organic compounds are observed, underscoring the intricate structure of the SRFA-O.S. sample. The bands within the 1710-1742 cm^{-1} range are associated with C=O stretching in carbonyl groups of esters and carboxylic groups, showing differences in wave numbers and intensity between the two samples.

The broad band around 1600 cm^{-1} is linked to C=C stretching in alkenes and aromatic compounds, with contributions from C=O stretching in ketones. The band at approximately 1530 cm^{-1} arises from C-N stretching vibrations combined with N-H bending (Amide II band). Peaks within the 1200-1400 cm^{-1} region are attributed to symmetric methyl bending, symmetric -COO- stretching vibration, and C-O stretching in carboxylic acids. The bands spanning 850 to 1200 cm^{-1} are associated with C-O stretching in carboxylic groups of organic molecules, as well as Si-O stretching, particularly from mineral phases.

III.4. UV/Visible Analysis

The absorbance results for the SRFA and the olive stones in contact with the SRFA are presented in **Table III.1**, and the corresponding spectra are shown in **Figure III.4**.

The analysis suggests that olive stones (O.S.) particles, in their natural and untreated state, have the ability to adsorb around 58% of the fulvic acid (SRFA).

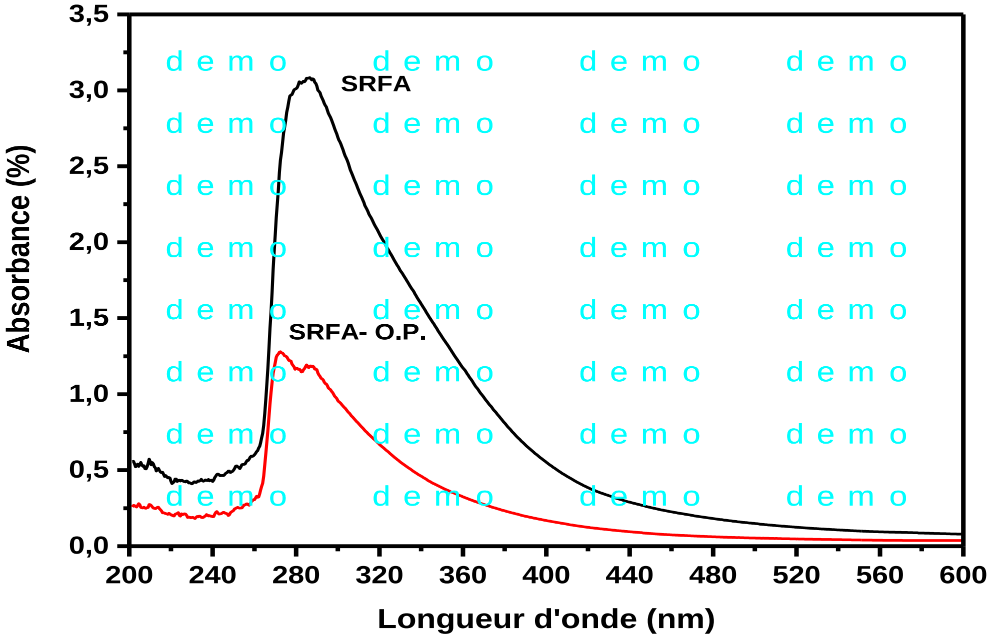


Figure III.4. UV/Visible spectra on SRFA and SRFA - O.S.

This level of adsorption is remarkable, highlighting the substantial capacity of these natural particles to remove contaminants without requiring any artificial treatment or modification.

Table III.1. Results of UV/Visible spectroscopy on SRFA and SRFA -O.S.

Sample	**SRFA**	**SRFA-O.S.**
Absorbance (%)	3,105	1,30
Maximum wavelengh (nm)	285,33	273,62
Residual mass (%)	-	58
Mass adsorbed (%)	-	**~ 58**

III.5 Scanning Electron Microscopy (SEM)

The image of the olive stone (O.S.) particles, at a scale of 10 micrometers, shows a heterogeneous and irregular surface with cavities of varying shapes, sizes, and depths. These cavities likely correspond to the macrofibrils characteristic of lignocellulosic materials, where cellulose chains group together to form microfibrils, which then accumulate to generate macrofibrils.

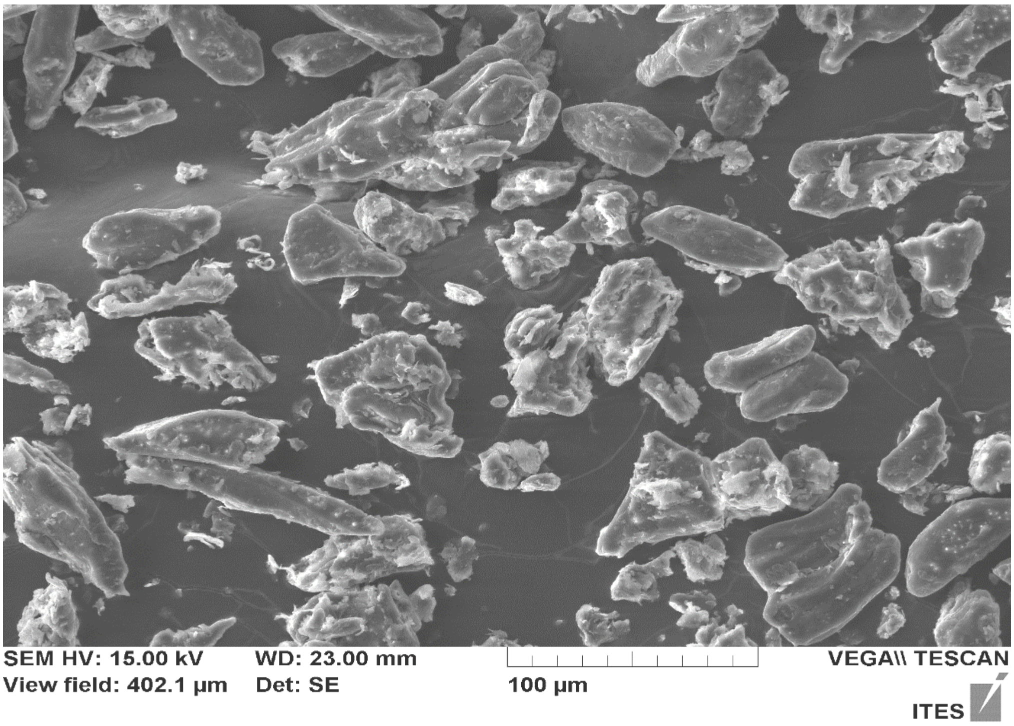


Figure III.5. Olive stone without organic matter

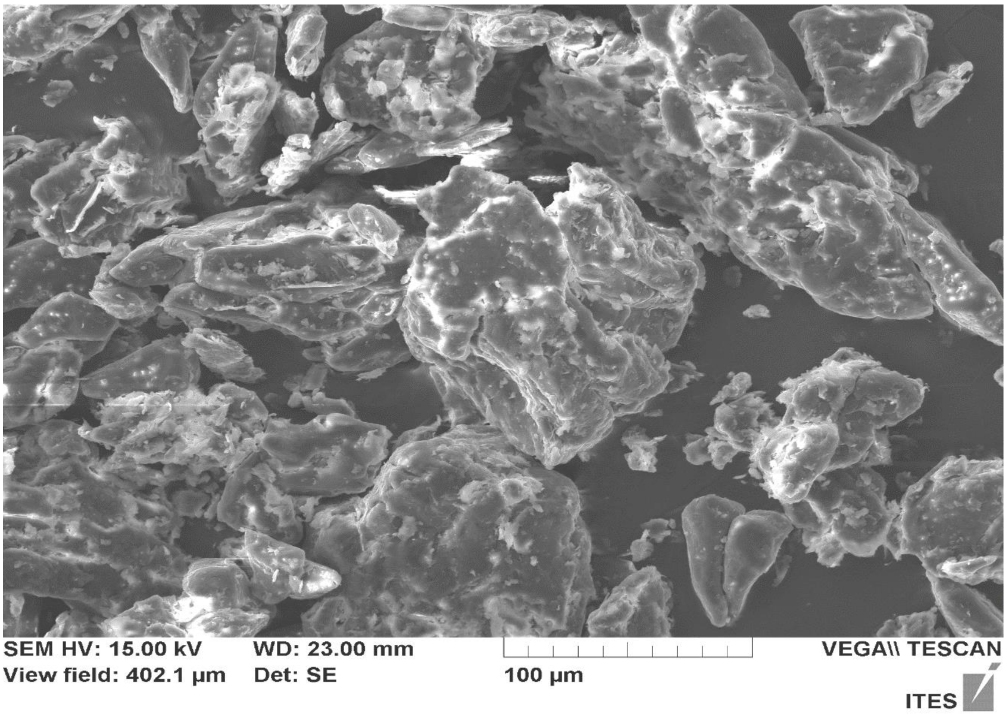


Figure III.6. Olive stone with organic matter

In the case of the SRFA-O.S. sample (O.S. in contact with SRFA fulvic acid), the particle surface resembles that of the O.S. sample but with shallower cavities. This observation confirms the adsorption of organic matter molecules by the O.S.

III.6. Thermogravimetric analysis TGA

The thermal properties were investigated through thermogravimetric analysis in the temperature range of 30 to 800°C. Thermogravimetric curves were generated using a Perkin Elmer TGA-7 ATG analysis equipment with a heating rate of 10°C/min in air, within the temperature range of 400 to 800°C under a nitrogen atmosphere with a flow rate of 20 mL/min. Each sample, weighing between 3 to 5 mg, was measured in an alumina crucible and subjected to controlled heating.

For olive stones, a small weight loss peak of 20% due to water loss is observed from room temperature to 220°C. Between 250 to 475°C, a weight loss peak attributed to hemicellulose and lignin is prominent. The highest weight loss peak for olive stone occurs at 375°C, primarily associated with cellulose and lignin decomposition. The thermal analysis suggests that the volatiles are mainly from cellulose pyrolysis. The presence of broad or less intense peaks in olive stones indicates lower cellulose content.

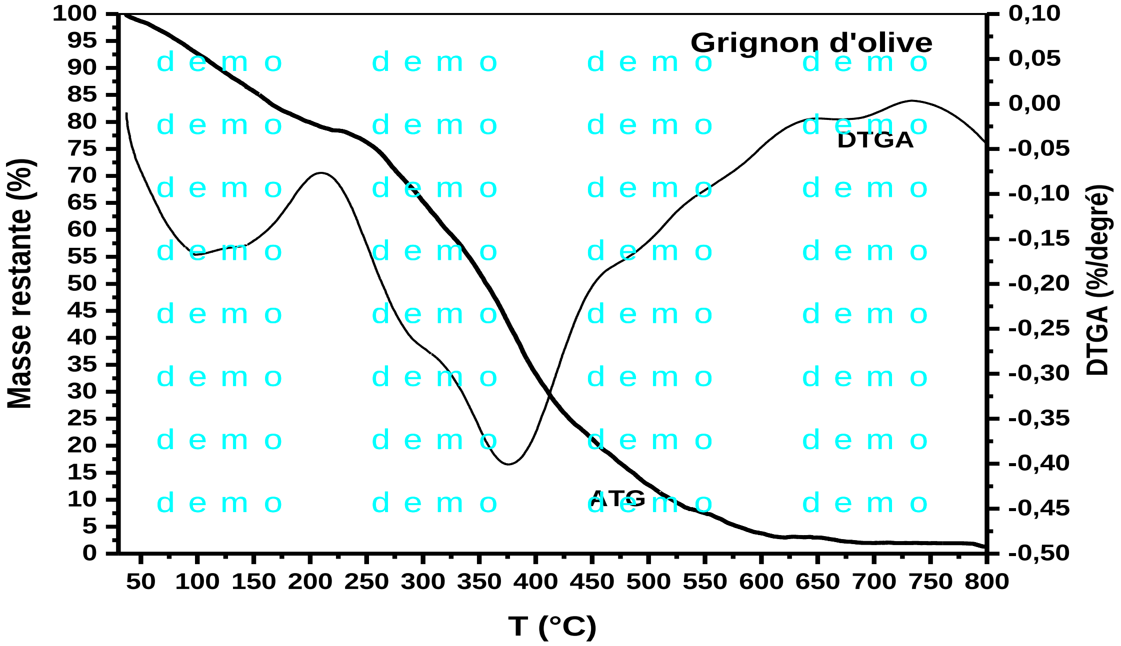


Figure III.7. TGA and DTG spectra of olive stones only**.**

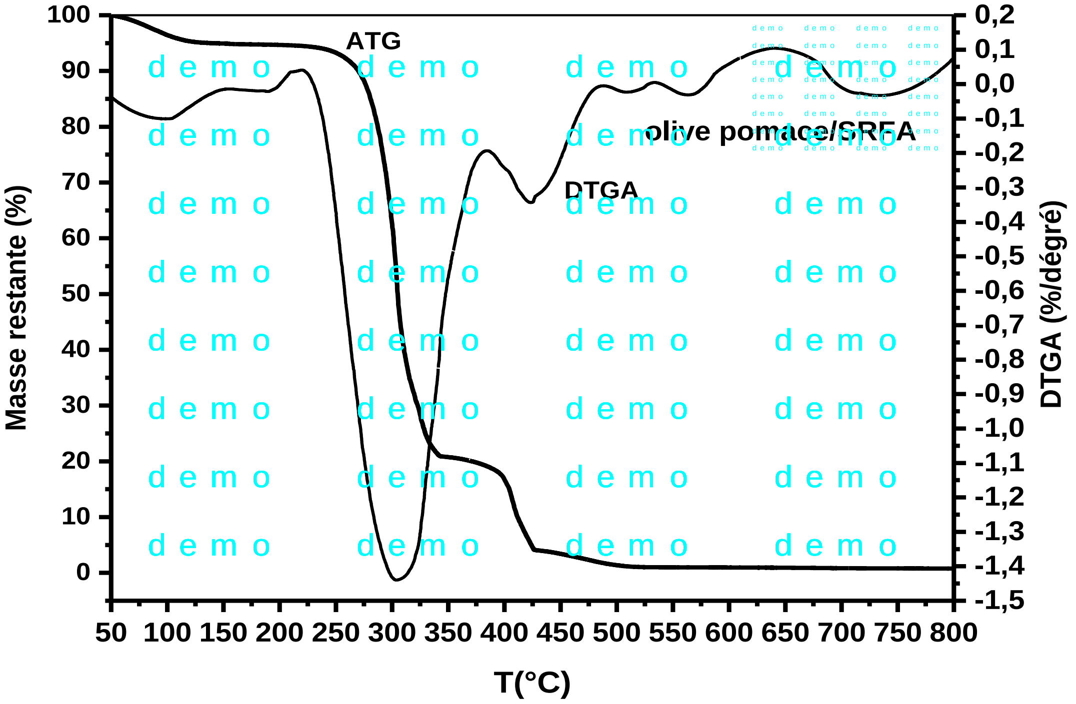


Figure III.8. TGA and DTG spectra of olive stone with organic matter.

Carbonization initiates after 500°C, with pyrolysis nearly complete at this stage. Consequently, the curve of olive stone beyond 500°C tends to exhibit a smoother trend. The thermal stability of olive pomace is comparatively better than other agricultural by-products, such as pistachio shells with a maximum pyrolysis temperature of 318°C, lower than almond shells at 375°C.

The table below summarizes the mass loss calculations at various temperature intervals, detailing the results of the ATG/DTGA analyses of olive stone before and after contact with SRFA.

Table III.2. The results of the ATG/DTGA analyses of olive pomace before and after contact with SRFA

	Desorption of water			**Combustion of organicmatter**			**Adsorbed mass**	**OH loss**		
	T(°C)	**Mass(%)**	**Max.(°C)**	**T(°C)**	**Masse (%)**	**Max.(°C)**		**T(°C)**	**Masse (%)**	**Max (°C)**
O.S.	32-220	20,00	120	**250-475**	**75**	**375**	**~35,38**	650-750	5,00	670
SRFA- O.S.	37-150	5	100	230-580	**76**	300		-	-	-

After adsorption, the surface of the solid becomes more hydrophobic, suggesting an affinity between certain fractions of the organic matter and the chosen solids.

We note that there is a concordance between the values found by the ATG technique and the UV/Vis technique, which confirms that our sample, olive pomace, can be used as a biosorbent. **(Table III.3.).**

Table III.3. The ATG/UV results converge shown the amount of SRFA organic matter adsorbed.

	Temperature range (°C)	**Mass loss (%)**	**Adsorbed quantity (%) ATG/DTG**	**Adsorbed quantity (%) UV/Visible**
O.S.	250-475	**74,5**	**~ 36%**	**~ 58%**
SRFA – O.S.	230-580	**76**		

The ATG/UV results converge, as shown in the table below detailing the amount of SRFA organic matter adsorbed.

Surface modifications such as acid treatment or chaffing can be used to improve the adsorbed quantity or % adsorption of the organic material (fulvic acid) contained in the SRFA.

General conclusion

This study investigates the characterization and potential applications of olive stones biomass from the M'Sila region (Northeast Algeria) as a biosorbent, focusing on its interaction with Suwannee River Fulvic Acid (SRFA).

X-ray Diffraction (XRD) analyses reveal well-defined peaks corresponding to lignin, cellulose, and hemicellulose in the olive stone, with cellulose showing high crystallinity.

The SRFA-modified olive pomace exhibits changes in peak intensity, suggesting a partial reduction of cellulose and hemicellulose, possibly due to the insertion of SRFA fractions. Fourier Transform Infra-Red (FTIR) spectra confirm the presence of cellulose, hemicellulose, and lignin in the olive pomace, while interactions with SRFA lead to altered peak intensities, indicating the potential for acid or base treatments to enhance efficiency. UV/Visible analysis shows a decrease in absorbance after contact with SRFA, suggesting adsorption of SRFA onto the olive stone.

Thermogravimetric Analysis (TGA) reveals thermal properties, indicating a loss of water content, decomposition of hemicellulose and lignin, and enhanced thermal stability compared to other nut olive stone. After SRFA adsorption, the surfaces become hydrophobic, indicating an affinity between organic matter fractions and solids.

The TGA analysis was performed on a sample containing 36% SRFA adsorbed on olive pomace, while the UV-Visible spectroscopy revealed an average adsorption of 58% SRFA on the olive stone. In conclusion, the olive stones demonstrates potential as a biosorbent for SRFA, and further physicochemical treatments can enhance its adsorption capacity.

The interactions between fulvic acid in organic matter and biomass are thought to be electrostatic. We propose to follow this work with an in-depth study, namely, carrying out chemical or thermal treatments to optimize the adsorption capacity of the olive stones.

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