

FIRAT UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
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**SYNTHESIS AND CHARACTERIZATION OF ACTIVATED
CARBON FROM OLIVE SEEDS**

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Master's Thesis

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Division of Analytical Chemistry

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Department of Chemistry

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THESIS APPROVAL

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I hereby declare that I wrote this Master's Thesis titled “Synthesis and Characterization of Activated Carbon from Olive Seeds ” in consistent with the thesis writing guide of the Graduate School of Natural and Applied Sciences, Firat University. I also declare that all information in it is correct, that I acted according to scientific ethics in producing and presenting the findings, cited all the references I used, express all institutions or organizations or persons who supported the thesis financially. I have never used the data and information I provide here in order to get a degree in any way.

27 January 2022

Dlshad Aziz HAMID



PREFACE

Firstly, I have to thank Allah for all the opportunities, help, and energies given to me to finish this thesis. Secondly, I am grateful to my supervisor *Prof. Dr. Mehmet YAMAN* who helped me so much and gives so many opportunities to learn and deal with new categories. He has also guided me on how to do researchs and always encouraged me to work hard and how to be an active team worker. Indeed, I learned a lot from his and his experience which helps me in my next career, I am thankful for all these.

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ABSTRACT

Synthesis and Characterization of Activated Carbon from Olive Seeds

DIshad Aziz HAMID

Master's Thesis

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Activated carbon synthesis has previously been described to include the use of biomasses, like Olive seed. In addition, the use of H₂SO₄ concentration, stirring time, and pyrolysis temperature as chemical activation agents in the synthesis stage has not been studied until now. In this experiment, olive seeds were burned in an inert gas atmosphere to produce activated carbon. It was determined that the active carbons were produced by treatment of H₂SO₄ in the ranges of concentrations from 10% ,25% and, 40%, stirring time between 4-16 hours, and temperatures between 550-650 °C were measured. Conductivity, FTIR, SEM, and BET measurements were used to characterize the adsorbents. In the pre - concentration process, factors including pH, stirring time, and beginning volume was varied for optimisation of analytical parameters. The adsorbent produced using optimal parameters (modified with 40% sulfuric acid, stirred for 16 hours and obtained at 650 °C) was used to determine toxic elements in natural waters at the optimized preconcentration pH conditions (pH 5 for Pb) and 60 minutes of stirring time as the optimum for Pb. Multi-element determinations were made using the ICP - MS technique in these studies. Pb concentrations in natural waters ranged from 1.3 to 2.1 ppb (ng / ml), when pre - concentration techniques were used under optimal conditions. All of the elements examined were determined to be less than the World Health Organization's limit levels.

Keywords: Biowaste, Preconcentration, Solid-phase extraction, Toxic element, ICP-MS.

ÖZET

Zeytin Çekirdeklerinden Aktif Karbonun Sentezi ve Karakterizasyonu

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Zeytin çekirdeği de dahil olmak üzere aktif karbon sentezinde biyoatıkların kullanımı daha önceki çalışmalarda yayınlanmıştır. Ancak sentez aşamasında kimyasal aktivasyon aracı olarak H_2SO_4 konsantrasyonu, karıştırma süresi ve piroliz sıcaklığının optimizasyonu şimdiye kadar araştırılmamıştır. Bu çalışmada, zeytin çekirdeği inert gaz ortamında termal olarak aktif karbona dönüştürülmüştür. Optimizasyon çalışmalarında %10, %25 ve %40 konsantrasyon aralığında H_2SO_4 ile muamele edilerek sentezlenen aktif karbonlar, karıştırma süresi 4-16 saat aralığı ve 550-650 °C arasındaki sıcaklıklar değerlendirildi. Elde edilen adsorbanlar iletkenlik ölçümü, FTIR, SEM ve BET gibi yöntemlerle karakterize edildi. Önderiştirme adımında, analitik parametrelerin optimizasyonu için pH, karıştırma süresi ve başlangıç hacmini içeren koşullar değiştirildi. Optimum parametreler kullanılarak (%40 sülfürik asit ile modifiye edilmiş, 16 saat karıştırılmış ve 650 °C'de elde edilmiş) sentezlenen adsorban, optimize edilmiş zenginleştirme pH koşullarında (Pb için pH 5 ve 60 dakika karıştırma süresi) doğal sularda kurşun elementinin tayini için kullanılmıştır. Ölçümlerde birden fazla elementin aynı anda belirlenebildiği ICP - MS yöntemi kullanılmıştır. Optimum koşullarda zenginleştirme işlemleri uygulanarak doğal sularda Pb konsantrasyonları 1.3-2.1 ppb (ng/mL) aralığında gözlemlenmiştir. Bulunan konsantrasyonlar, çalışılan tüm elementler için Dünya Sağlık Örgütü tarafından izin verilen sınır değerlerin altındaydı.

Anahtar Kelimeler: Biyoatık, Önderiştirme, Toksik element, Katı faz ekstraksiyonu, ICP-MS.

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SYMBOLS AND ABBREVIATIONS

SYMBOLS

°C	Degree Celsius
K	kelvin
Pb	Lead
N ₂	Nitrogen
W	width
Å	Angstrom
ppb	Parts Per billion
ppm	Parts Per Million
g	gram
µg	Microgram
kg	Kilogram
mg	milligram
mL	Milliliter
ng	nanogram
pg	Picogram

ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
FT-IR	Fourier Transform Infrared Spectrophotometer
ICP-MS	Inductively Coupled Plasma-Mass Spectroscopy
AC	activated carbon
ICP	inductively coupled plasma
AES	Atomic Emission Spectroscopy
MS:	mass spectrometry
FAAS	flame atomic absorption spectroscopy
TEM	Transmission Electron Microscope
MW	Microwave
PA	Phosphoric Acid
PAC	powered activated carbon
GAC	granular activated carbon

ACF	activated carbon fiber
SEM	scanning electron microscope
Bs	bamboo steam
EFB	empty fruit branch
CNS	coconut shell
DRFP	Delonix regia fruit pod
BEFB	banana empty fruit branch
GI	gastrointestinal
ED	electro dialysis
ZICNSC	zirconium impregnated cashew nut shell
WHO	world health organization
TC:	tetracycline
PC	paracetamol
GHGs	greenhouse gases
BET:	Brenauere-Emmett-Teller
BJH	Barerett – joyner – Halenda
SRM	standard reference material
ANOVA	a one - way variance – analysis
LOD	Limit of detection
LOQ	Limit of quantification

1. INTRODUCTION

The most commonly used is activated carbon (AC), and an effective adsorbent [1-6]. However, the scope of its application is limited due to its high cost. It has been shown that the use of cheap agricultural waste and for the manufacture of byproducts of AC provides an economical solution to this problem [7, 8]. In water and waste water treatment, the adsorption of organic carbon micropollutants is widely applied and the benefits of such adsorbents are well documented.

Today activated carbon occupies an important place among modern adsorbents as a very versatile and universal material due to its distinctive properties. Activated carbon is of interest in many sectors of the economy and a wide range of industries such as food, pharmaceutical, chemical, mining, vacuum industries oil, nuclear, and automotive. Many of these uses place significant demands on the chemical nature and surface properties of these adsorbed carbons [9]. The surface of pores accessible for macromolecule adsorption determines its characteristics. The porosity depends on both the precursor and the type of activation. Activated carbon precursors are carbon-rich organic materials for example charcoal, wood, and lignite. The availability, affordability, and purity of precursors are all important requirements, but the production method and intended application of the result are also significant. Agricultural waste is a very important raw material for two reasons: renewable resources and cheap materials [10].

AC is most commonly used as an adsorbent for purification and separation processes on an industrial scale, In catalytic processes, as a catalyst or catalyst carrier, and materials used as electrodes in electrochemical devices, and because of its large specific surface area related to the dispersion pore size, processes, chemical structure of the surface is varied, and the surface has a reasonably excellent mechanical property [11]. As a result, the demand for AC is rising rapidly. However, the price of activated carbon prevents it from being widely used. Activated carbon manufacturing at a lower cost has therefore become increasingly popular.

Materials having a high carbon concentration, but lower inorganic carbon concentration, are typically used to make activated carbon, which is costly. Recent experiments on cheaper and more commonly accessible precursors, such as agricultural by-products or waste, have helped to lower the price of AC. Activated carbon may be made from agricultural waste products since they are readily available and inexpensive to get. As a result of its high adsorption process and mechanical robustness, they may be utilized to make activated carbon [12].

Activated carbon may be made from a variety of materials, including bamboo [13], bagasse [14], cherry kernel [15] olive kernel [16], oil-palm kernel [17], nutshells [18] apricot kernel [19], walnut shells [14], groundnut shells [20], pine cone [21], acorn shells [22], coffee husks [23] palm shell [24], peanut shells [25, 26], coconut shells [27], tobacco residues [28], cotton stalk [29], tea industry waste [30]. Active carbon may be generated by both physical and chemical activation. The

two forms of physical activation are activated and carbonized, respectively. An inert atmosphere is used to carbonize raw material before activating it with steam or CO_2 at high temperatures. Chemical activation is the process of treating raw materials with an activating reagent before heating them in an inert environment. Alkalies are among the chemicals that are employed in chemical activation (sodium hydroxide, K_2CO_3 , potassium hydroxide, and Na_2CO_3), salts of alkaline earth metals such as zinc chloride and aluminum chloride (phosphoric acid and sulfuric acid). pyrolytic degradation is inhibited and gum formation is prevented by the use of these chemicals.

In the case of chemical activation, of particular interest is the effect of potassium hydroxide and zinc chloride on the carbonization of intermediates, and particularly Zinc chloride is a chemical agent frequently employed in the manufacture of AC [31, 32]. however, a large number of publications have been written on how to make activated carbon cheaper, Deiana et al. 2009, have published several studies on chemical activation of agricultural wastes and products in recent years [33], who conducted only one study of the production of AC from chemical H_3PO_4 grape stalks. As nuclear energy interests continue to grow.

Toxic levels of lead have continued to rise in recent years. Human health has been put at risk by the inadequate elimination of Heavy metals from soil and water, which is especially dangerous because of its poisonous nature, accumulation, and persistence in the environment. A quick and sensitive technique for the correct determination of lead must thus be developed. Preconcentration techniques are employed often because of limits in sensitivities of ICP-AES and flame AAS [34]. In contrast, to trace metals like copper, cadmium, lead, nickel [35], lead sensitivity is very low in FAAS because of the formation to trace lead measurements [36]. It is possible to employ the enriched material as an absorbent or remover, depending on the adsorbent's capability and cost. [37].

Many different methods have been used for this purpose, such as ion exchange, chemical precipitation, membrane separation, and adsorption strategies [38]. Among these methods, the most promising is the adsorption method. Adsorbents may be made from a wide variety of materials, many of which are readily available, inexpensive, efficient, and environmentally friendly properties are of great importance in their selection [39]. The high surface areas, great porosity, well-developed interior pore structures, and a broad range of functional groups have been commonly utilized in preconcentration & removal processes as an adsorbent for activated carbon (AC) [40]. AC may be manufactured from agricultural biowastes to minimize the costs of AC preparation [41]. The olive shell can also be investigated among other agricultural bio sorbents since its food crops are widely cultivated and consumed worldwide [42]. The chemical activation procedure for AC preparation is very low at $500\text{--}800^\circ\text{C}$ in comparison to physical activations and the production process produces greater carbon outputs [43]. Suitable heat or pre- and post-chemical treatments

may alter the characteristics of the functional groups in the surface of AC to increase its adsorption capacity [44]. The benefits of acidic treatment include cost-efficiency, operational simplicity, and energy conservation. There was extensive usage of sulfuric, citric, phosphoric, and similar acid nonoxidizing [45]. In short, chemically modified biological waste is a candidate because it offers relatively fast separation and the highest enrichment ratios achievable at low cost [38]. In this investigation, the high adsorption capacity of AC was first obtained using Olive seed as raw material after modification with H_2SO_4 separately and pyrolysis at 600 °C. Lead (Pb) in model solutions at the level of ng / ml.

Objective of Thesis

1. Synthesis of AC from olive seed biowaste after chemical modification and pyrolysis.
2. To determine the concentrations of Pb in drink water or water pollutant, Elazig.

2. LITERATURE REVIEW

In this research, AC is one of the most commonly utilized adsorbents in many industrial applications due to its adsorption capacity. The production of AC from olive shells and the quality of the products were investigated.

2.1. History of Activated Carbon and Present-Day Applications

Since ancient times, it has known the useful properties of activated carbon. It dates back to around 1500 BC when the Egyptians used coal as an adsorbent and a purifying agent for medicinal purposes. It was found around 420 BC that Hippocrates dusted the wounds to remove their fragrance with the powdered charcoal. Old Hindu societies purified the water with charcoal filtration [46]. The first Swedish chemist to observe the adsorption on charcoal in 1773 was Karl Wilhelm Scheele. Several years later, activated carbons started to be used as coloring agents for syrup in the sugar industry. At the beginning of the 20th century, Germany was the first factory to manufacture activated carbon for use in Germany's sugar refining sector.

In the early 1900s, several additional plants were produced to primarily decolonize activated carbons. I employed carbon activation in gas masks to defend against dangerous gasses and vapors during World War. Color-controlling devices for the controls of air pollution, industrial and automotive emissions, chemical purification, and electrodes in batteries are being employed to remove the colors from pharmaceutical and food items. Global carbon production is 500,000 tons per annum [47]. 80% is for applications in liquid phases and 20% for applications in solid phases [46].

2.2. Types of Carbon Materials

All carbon compound materials have a unique connection with and with other elements. The primary allotropic carbon forms [5] are classed as diamond, graphite, and fullerenes. Carbon atoms can be hybridized in many ways. Diamond a cubic 3D structure is formed in which each carbon atom links with 4 other carbon atoms via sp^3 connections. The duration of the connection is 154 pm. Diamond is the hardest material with the greatest heat capacity and melting temperature, as well as the biggest atomic density of any solid substance known to date. Graphite is a mineral that is composed of hexagonal layers in which atoms are connected by sp^2 σ and delocalized π bonding with the nearby carbon atoms. Graphite has a thermal conductivity even higher than diamond and has excellent conductivity. Fullerene: they are three-dimensional carbon structures that are twisted to form an empty cage of 60 (C_{60}) or more carbon atoms between carbon atoms. This results in an intermediate $sp^{2+\epsilon}$ shape between sp^2 and sp^3 [48] due to a re-hybridization. Most carbons have

allotropic shapes, that is to say, a sp^2 -based structure. The graphite allotropic form may be divided into graphite carbons and non-graphite carbons [49] based on the degree of crystallographic order in the third direction (C-direction).

Furthermore, the non-graphitizable carbons are divided into graphitizable and non-graphitizable carbons. This is a "non-graphitic carbon which can be changed into graphite carbon after graphitizing" whereas it is a "non-graphitic carbon that cannot be converted by high-temperature conversion into graphite carbon. The size of carbons varies dependent on different structures, and a vast range of different structures lead to a large number of different carbon kinds. Figure 2.1 shows a diagram of several of these carbon structures [50].

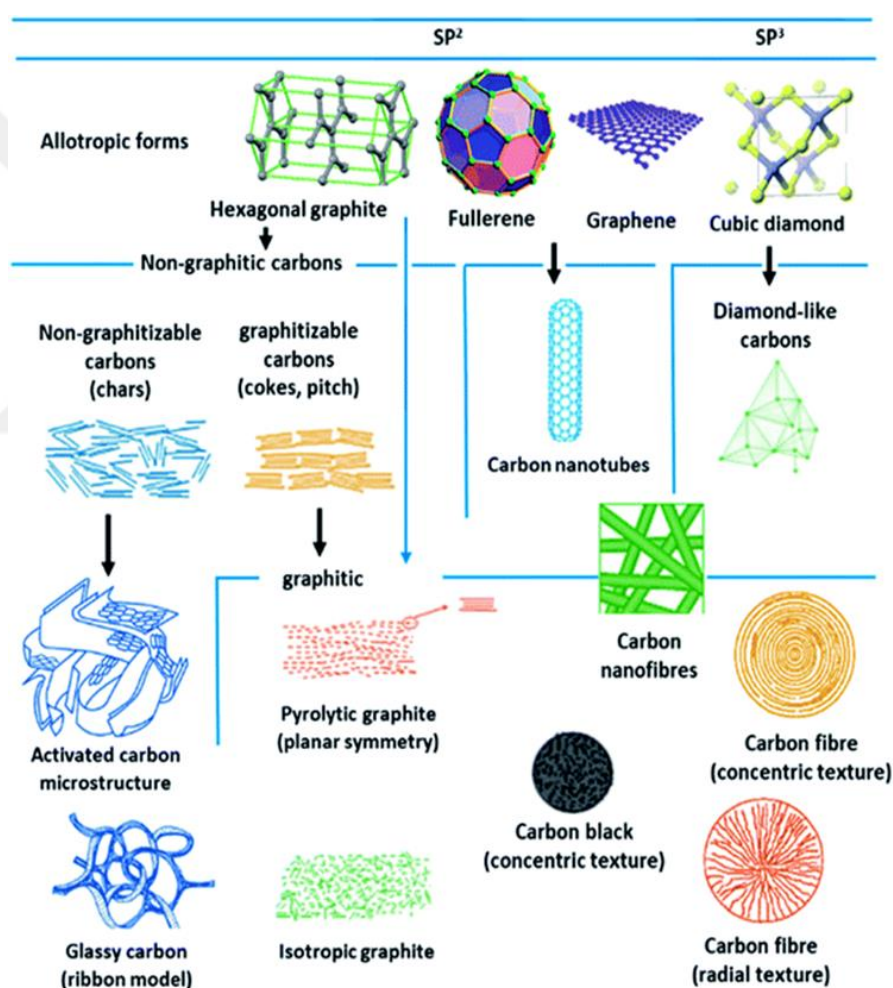


Figure 2.1. Main allotropic carbon forms and some carbon structures derived from them [50]

2.3. Definition and Properties

Activated carbon is the non-graphitical microcrystalline carbon form. The X-ray carbon analyzes indicate a structure that is considerably more unordered than graphite with crystallites of just a few thick layers and a breadth of less than 10 nm [51]. The gaps within the activated carbon

crystallites are the micropore structure with a wide $250 \text{ m}^2/\text{g}$ - $2500 \text{ m}^2/\text{g}$ internal surface. It can preferably absorb organic molecules and other non-polar chemicals from gas or liquid streams due to the chemical structure of activated carbon.

Due to these characteristics, they have been used over many decades to purify gases, separate gas mixtures, clean exhausted air, especially solvent recovery, heavy metal removal and the decolorization of solutions, and water purification. Carbonate adsorbents have been more widely used in solving environmental problems relating to water purification and air pollution removal. [52]. Adsorption removes impurity from gases and liquids using activated carbon. Adsorption is a word that defines the existence of a material at an interface between a liquid and a substance that is higher than that present in the fluid. Figure 2.2 shows the pore structure of activated carbon (TEM).

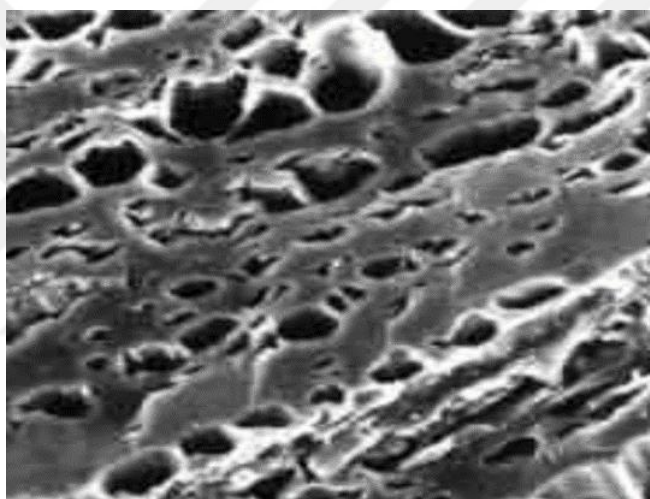


Figure 2.2. Pore Structure of Activated Carbon (TEM) [53]

Chemisorption or physical adsorption is considered the adsorption process. Physical adsorption, weak van der Waals forces hold impurities on the surface of carbon while the forces are relatively strong in chemisorption, adsorption happens on active surface sites. The effectiveness of carbon, therefore, depends on the accessible area of the carbon, as well as on the presence of active places on the surface where there may be chemisorption. (The presence of active sites on the surface is crucial not for physical adsorption). The porous structure and chemical composition of the AC depends on the raw materials used for their synthesis and on the technique of activation. This is why activated carbon surfaces or pore volumes can vary widely between different types.

2.4. Preparation of Activated Carbon

Two main steps are supported for synthesizing AC. The first is carbonation, the second is activation. The carbonization is carried out in the inert atmosphere by pyrolysis/gasification to

produce biochar [54]. At this stage, the composition of the carbonized material was generated by the thermal decomposition of the volatile substance [4]. The temperature, the heating rate, the flow rate of N_2 gas, and the residence duration are the main parameters in this step. The produced biochar displays low adsorption capacity so that the volume of a pore, its pore width, and its surface is improved by an activation process[55]. Unorganized carbon was first eliminated during activation, lignin was exposed to activating chemicals and the development of a microporous structure was carried out.

The walls between pores are finally burnt and the pores are expanded to a great extent. This increases intermediate pores and microporosity, reducing microporous volume. Activation can be a procedure for the removal of accumulated tarry compounds from biochar before carbonization or after carbonization, depending on the kind of activation, to improve porosity and to give high ACs with high surface areas [56]. Figure 2.3 shows the basic activation process using biomass for the synthesis of AC.

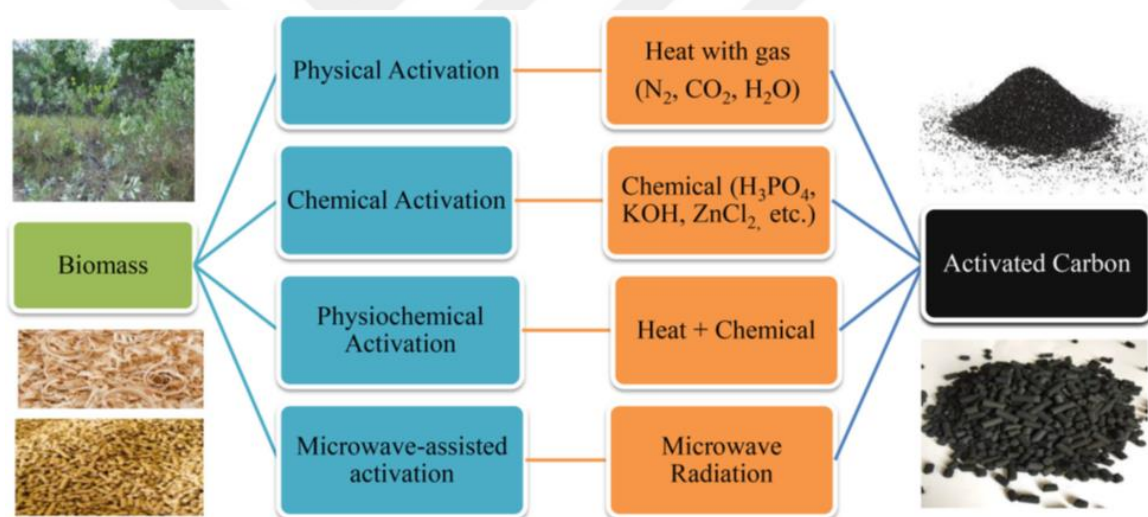


Figure 2.3. Activation processes and their methods [57]

Carbon activation begins with the removal of tarry materials to eliminate accumulated tars which cause pores to be blocked and assist to facilitate the agent for biochar reaction later [58]. Carbon parts are then burned and oxidized by an activating agent in biochar. The two most essential parameters to be taken into consideration for the formation of porous structures are the activation temperature and time. These characteristics have been reported to match the pore volume, however, they are reversed to AC. The first stage in preparing AC is to carbonize biomass, where the high temperature must be checked and limited since activation at high temperatures, may lead to the formation of undesirable chemicals which may occur when the material is thermally degraded [59].

2.4.1. Carbonization/Pyrolysis

The thermal decomposition of an inert atmosphere in an Oven with N₂ purging is the carbonation or pyrolysis of raw material for removing volatile, non-carbon particles such as nitrogen, oxygen & hydrogen and enriches the fixed carbon to create biochar [4]. In the process of decomposition, small pores of precursors start to emerge, leading to the deposition of tarry compounds produced with increasing temperature [60]. This deposition can, in some circumstances, induce a collision of some tarry materials and the breakdown of pores walls that lead to hydrocrack and carbon deposition. Table 2.1 shows a four-stage overview of the carbonization process [61].

Table 2.1 Four stages in the process of carbonization [61]

Stage	Temp (°C)	Type of reaction	Process
1	≤200	Endothermic	Raw materials are first dried to eliminate moisture.
2	170 - 300	Endothermic	Pre-carbonization phase: To create various pyroligneous liquids (acetic acid and methanol) and light tars and non-condensable gases (CO and CO ₂)
3	250 - 300	Exothermic	In the second stage of manufacturing biochar, pyroligneous fluids and light tars are removed in bulk.
4	>300	—	Reduce volatile and non-carbon molecules in biochar to increase their concentration.

Careful selection of parameters is therefore important for the processing and has a significant effect on the quality of the final good product [62]. The temperature of carbonization is extremely important because of the greatest effects on the process, following heating reaction rate, quantity and flow rates of inert gas & finally the residence or hold duration., as shown in Figure 2.4.

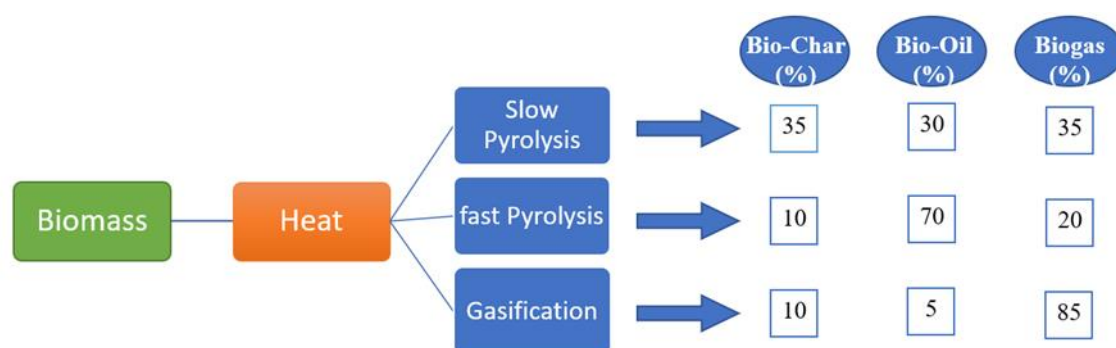


Figure 2.4. Biomass conversion to bio-oil, charcoal, and gas thermo-chemical [57]

Generally, the more volatile species, as well as the increase in carbon content and ash content, are released as the temperature is increased. This decreases biochar production, though [59]. The reduction in yield is considered to be related to the primary breakdown of biomass at high temperatures (devolatilization), and also the secondary breakdown (cracking), of biochar waste. Higher temperatures hence lead to greater biochar quality [57]. Carbonization temperature and carbonization had a significant influence on the performance and reliability of AC, for instance, studied in research carried out by [63].

2.4.2. Physical Activation

Physical activation might be a one- or 2-step procedure [64]. Physical activation is usually the process of double step, where carbonization of the dried materials takes place at 400-700 °C to create biochar and then activation with oxidizing gases such as air, steam, carbon dioxide, and its mixes [65]. For a certain burn-off at a high temperature of around 800 -1100°C [66], the carbonized biochar has generally smaller than 300 m²/g of surface area [67]. The pores closed by tarry compounds are assigned to these low surfaces and adsorption capacity, which may be eliminated by activation [58].

Carbonization and activation take place concurrently in a single-stage process where the temperature of 600 - 800°C is maintained [68]. In a single-step procedure, a specified temperature is used to carbonize the dried sample, similar to the dual-stage technique; however, AC can be further heated for a specified time simply by converting inert gas to gas oxidation. Although the method is comparable, the single-stage is far more practicable since it passes the cooling stage following the carbonization process, which can minimize physical stress, electricity generation, costs, and operating time [67]. While widening the narrow pores on the surface of AC, the physical activation also produces new pores, improving the structure's surface area and pore volume [69]. But physical activation tends to produce a relatively small carbon yield and activation carbon quality compared to chemical activation because of greater activation temperatures and a longer period of activation [64].

The exothermal character of the reactions which might lead both to excessive burns on the internal as well as on the outside of the biochar, which could lead to lower yield, makes Air (oxygen) less suitable to activate the agent [61]. Steam & Carbon dioxide appear to produce the same maximum area of BET, both of which react to carbon, providing maximum areas of 1000 m²/g and greater values. Although the techniques are identical they are slightly different in mechanism and reaction [70]. It was stated that water molecules may spread to pores of AC more quickly due to the tinier size of water than Carbon dioxide, and so provide a faster reaction to this than carbon by CO₂ and therefore to create new pores [71].

Stearns react 4 times more quickly with carbon than CO₂ at a near activation temperature [67]. Therefore, AC may reach a high surface area in a short time through steam activation [72]. Activating CO₂ priorities, the creation of new pores over the expansion of narrow pores whereas activating steam favors the expansion of the micropores to create mesopores and macropores at a standard heating rate from the beginning of the activation process. This guarantees a wider dispersion of pores in the resultant ACs [59]. Even with a greater activation rate, microporous and mesoporous structures for steam activation and CO₂ activation respectively would lead to higher percentages [66]. In certain situations, CO₂ activation seems to be a better alternative, because the activation process is cleaner, easier to handle, since gas is sustained and stabilized even at high temperatures up to 800 degrees Celsius, due to its slow reactions [73].

2.4.3. Chemical activation

A single step or a double step process might be a chemical activation. Except for the carbonization step both methods are similar [59]. There is no carbonization during the single-stage process and the primary step is to activate the dried sample by reacting with dehydrate substances such as NaOH, KOH, ZnCl₂, and H₃PO₄ [74]. Biochar is formed by heating the dried material to between 400 and 600 degrees Celsius before chemical activation is carried out in the double-stage procedure [64]. Three kinds of chemical activation can be used: (i) activation in basic, (ii) active in acid, and (iii) activation in neutral [75].

Depending on the type of surface area, various precursors have varied effects, pores, and yields according to the type of dehydration agent used [76]. Basic bio-activation with alkaline metal hydroxides like KOH and NaOH yields in general very high surface ACs of up to 2000 m²/g. Alkaline hydroxides of metals can be used, however, are restricted by precursor types. In a study from [77], the metal alkaline hydroxides have been reported to be used in the dual-stage procedure generally because they work with charcoal more efficiently. Carbonization of precursor includes several pores that may be used for dehydration and react to a high surface and high porous carbons and ACs. Carbonization of precursor [59], metal alkaline hydroxides may not penetrate precursors because the porous of the raw materials is not apparent [78]. Impregnation alone is not enough to create porous AC, and therefore chemical activation will need a two-stage in a research study, for instance [79].

Surface area activates with 280 m²/g and 660 m²/g are reported to be activated with interacting with rice husk by NaOH. Biochar are also known to be significantly more sensitive to KOH activation, which can help generate surface high-quality ACs [80]. The most often utilized activator is H₃PO₄ among the activators. This might be because it is less economically advantageous than acidic activation due to the increased costs. Activation with H₃PO₄ acids as a cheaper method might result in a greater yield [75]. Alterations the total amount of micropores and mesopores that

results in substantial surface changes, porosity, and final products reactivity [81] Another research was done by [82, 83] on the impacts of H_3PO_4 and ZnCl_2 on the textural characteristics of the acidic activation and neutral activation of the oil palm shell. The area of the surface and the pore volume produced with acidic activation have been observed to be greater than the neutral activation. Differences in the textural characteristics were explained since H_3PO_4 had a greater rate of activation at 8.86 percent burn-off per hour and ZnCl_2 had a 22 percent burn-off/hour [82]. However, metal alkali hydroxides and acids as activators are less preferred in environmental terms, because they are hazardous, corrosive, toxic, and are likely to cause an explosion when precautionary measures are needed.

More dependable dehydrating agents the likes of K_2CO_3 are thus used for single-stage activating to create activated carbons and reduce the issue of acidic and basic chemicals which contribute to waste disposal [66]. In comparison to physical activation, chemicals activation is a better alternative in terms of surface evolution, micropores, greater carbon output. because of lower temperatures of activation and shorter activation time it is economically viable [75]. Therefore, their drawback is that chemicals are remaining on charcoal and a further washing step needs to be eliminated [78] or physical activation of AC followed (physiochemical activation) [66].

2.4.4. Physiochemical activation

In addition to chemical activation and physical activation, physiochemical activation can concurrently be used to activate [84] . There are two ways for producing physiochemical activation ACs: (I) chemical treatment after carbonization (post-carbonization) and (ii) chemical treatment before carbonization (pre-carbonization) [66]. In the case of oxidizing and carbonizing gas in the inert atmosphere, and then in a physical activation at increased temperatures between 600-850 °C, the first approach is a carbonizing process that is followed by impregnation of biochar.[67], although precursors to chemical treatment and physical activation are present in the second technique [85, 86] The chemical activation sequence of that procedure affects the quality and textural characteristics of the ACs produced.

The pore locking action of the dehydrating agent explains the lower surfaces of the post-carbonized sample [87]. Accordingly, the blocking might be removed by physical activation. Moreover [84], Explained that a physiochemical activation may be applied if a dehydration agent is on biochar's surface after washing the pores blocking stage. A further physical activation stage to improve the porosity of biochar is therefore required [88].

Several research comparing procedures physiochemical and chemical activation shows that dual-stage activation generates ACs with varied yet improved texture and quality properties [89]. It stated the well-developed pores structures, which are dispersed equally, created by physiochemical activation. In another research, they report that the surface area in Phosphoric acid

and Carbon dioxide activation and Carbon dioxide single activation altered within a range of 1035-1653 m²/g and 554-1213 m²/g respectively, including just a Carbon dioxide activation of 2 hours more optimal hold duration (7 h). Dual step activation They state (5 h) [82]. In addition, AC surface area was also reported as 632 m²/g with a pore volume of 0.26 cm³/g, as a result of sole CO₂ activation [86]. Tseng et al. [90], also, noted in their study is that only micropore structures are produced on the surface when carbons are treated with KOH. While the ratio of macropores to mesopores rises when heated treated with carbon dioxide gas for physiochemical activation. This improves the porosity ratio and mass transfers to improve adsorption capacities [91].

2.4.5. Microwave-assisted activation

Microwave (MW), because of its best qualities such as selective, fast, evenly distributed, and volumetric heating, as well as indirect interactions between the heated foundation and the heated materials and rapid and precise regulators, was a realistic substitution to the conservative approach to the production of activated carbon [92]. Procuring configuration, MW radiation strength, activated duration, precursor characteristics, the interactions between MW and chemical substances are the main working restrictions of microwave activation [64]. With Microwave heating, the energy is readily warped by dipole and ion transmission from within the molecules to heat. In contrast, when high-frequency voltage is supplied, The applied force is connected to the dipolar time or the dipole moment time of the atoms [93]. A high-temperature gradient thus proceeds from the inside of the example molecule to its cold outside, making it more operational and efficient [94].

MW activation is a mix of chemical and/or physical activation that can generate activated carbon of better Quality in one stage [95] or two-stage [96]. As indicated in Figure 2.5. The two principal processes for one stage activation of the microwave using a reactor are carbonization and activation [97]. The advantage of this activation is that by a simple procedure, AC is provided with a steady process. Dual-stage activation of the microwave consists of the charred and activated biochar under the microwave radiation system [98]. Biomass sources are needed for the BET surface area in this process, radiation power, runtime, and additives [64]. MW Activation is an exceptionally versatile method for the production, distribution, and textural characteristics of ACs [99].

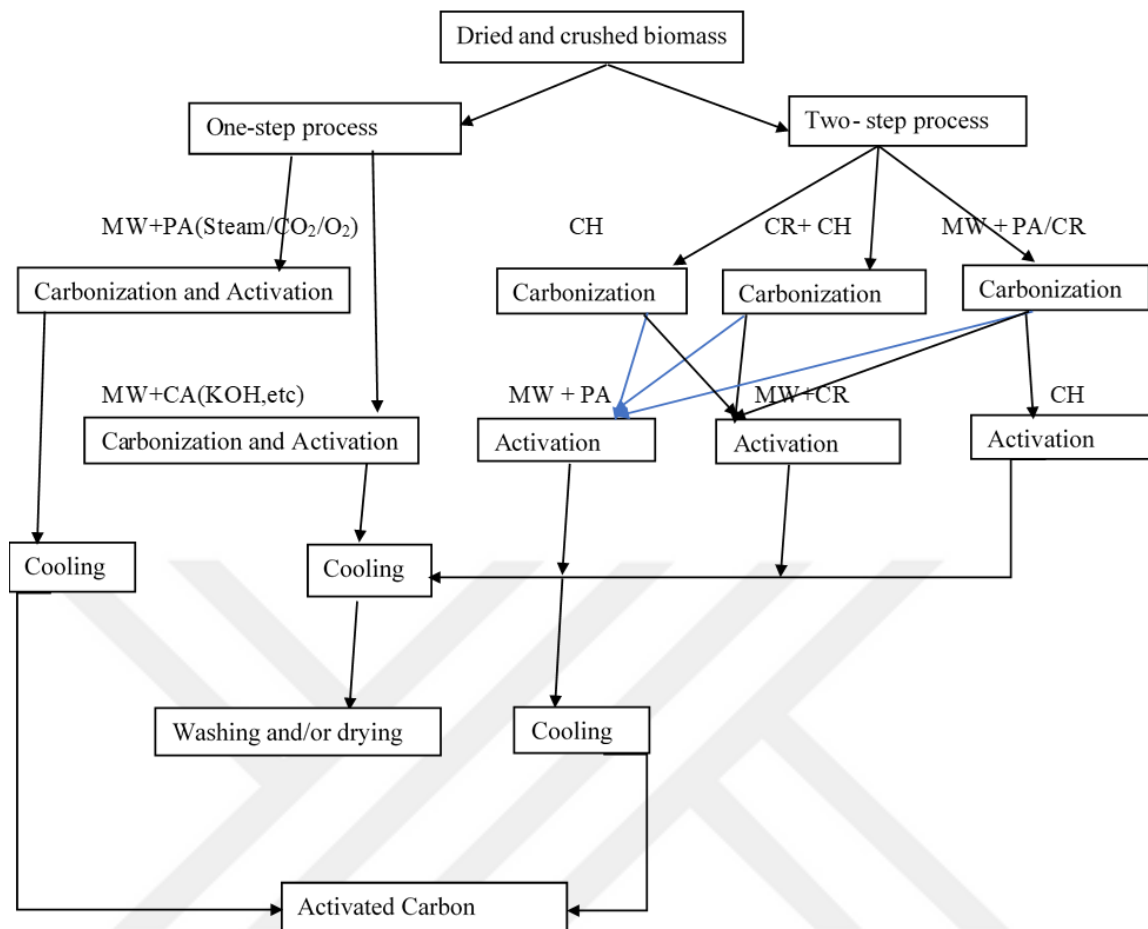


Figure 2.5. AC Preparation Schematic diagram from Microwave Biomass (MW) [64]

2.5. Structure of Activated Carbon

The capacity of the AC adsorption is strongly dependent on the carbon structure.

2.5.1. Porous structure

The high adsorption capacity of the ACs has strongly to do with porous properties such as the distribution of surface, size pores, and pore volume. All ACs have a porous structure that contains up to 15% ash content of minerals [100]. This porous structure was created during the carbonization that produced AC, and further expanded during activation by removing gaps of tar with other carbonated material between the elementary crystallites.

The shape of pores and the pore volume depend mainly on the nature of raw materials and the processes of activation. The process of activation eliminates disordered carbon by exposure the crystallites to the active ingredients which cause the porous structure to form. There are many different kinds of pores of activated carbon and pores can vary greatly in size and structure. Active carbons are connected to pores varying in size from a few nanometers to several thousand

nanometers. a classical pores categorization according to their mean width (w), that is the distance between the slit pore walls or the cylindrical pore radius, recognized by the International Union of Pure and Applied Chemistry (IUPAC).

Table 2.2 summarizes the proposals made by [101] and recognized by the International Union of Pure and Applied Chemistry (IUPAC).

Table 2.2 Pores classification based on their width (IUPAC, 1972)

Type of pores	Width (w)
Micropores	$< 2 \text{ nm}$ ($20 \text{ \AA}$)
Mesopores	$2 - 50 \text{ nm}$ ($20 - 500 \text{ \AA}$)
Macropores	$> 50 \text{ nm}$ ($> 500 \text{ \AA}$)

As the effective radius is less than two nm, micropores are adsorbed by volume filling and capillary condensation is not present. Micropores often have a pore size of 0.15 to $0.70 \text{ cm}^3/\text{g}$ and make up around 95% of the whole area of the activated carbon [102]. It has been categorized as being possible to divide the micropores into 2 overlapping microporous areas such as ultra-microporous (with efficient pores smaller than 0.7nm) and super-micropores (having radii of 0.7 to 2 nm). General adsorption of gases and vapors and to a little extent the small-angle x-ray method characterizes the microporous structure of the adsorber [103].

Mesopores, also called transitional pores, are between 2 and 50 nm wide. The mesopore surface area is no more than 5% of the overall area and its volume is between 0.1 to $0.2 \text{ cm}^3/\text{g}$. However, it is feasible to increase mesopores with a volume of between 0.2 and $0.65 \text{ cm}^3/\text{g}$ with a surface area of $200 \text{ m}^2/\text{g}$ by using specific techniques. The characteristic features of mesopore include adsorption-desorption hysteresis, and capillary condensation [104]. In addition to their adsorption contribution, mesopores work as conductors leading the adsorbate molecule into the micropore network. Figure 2.6 shows a typical distribution of pore size of activated carbon. Mesopores are often characterized by adsorption-desorption gas isotherms, mercury porosimetry, and electron microscopy [105].

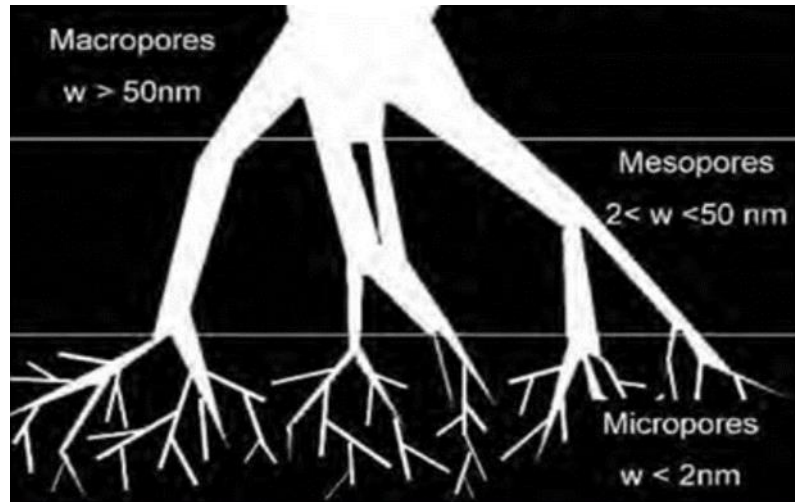


Figure 2.6. Structure of activated carbon pores as seen in an image

Pores with effective radii of greater than 50 nm, often between 500 and 2000 nm, are called microporous. Macropores contribute extremely little and do not surpass $0.5 \text{ m}^2/\text{g}$ and 0.2 to $0.4 \text{ cm}^3/\text{g}$ accordingly to overall surface area and pore volume. Therefore, macropores are not of major significance in the adsorption process but work as transport routes for the adsorption into mesopores and micropores [106].

2.5.2. Crystalline Structure

During the carbonization process, Active carbons are forming their microcrystalline structure. About the interlayer distance, the crystalline structure of ACs differed from the graphite. Interlayer spacing in ACs varies from 0.34nm to 0.35nm , which in the case of graphite is 0.335nm . A graphite's structure approximates closely the base structural unit of AC. Figure 2.7 shows the graphite crystal consists of layers of hexagons united with the weak van der Waals forces.

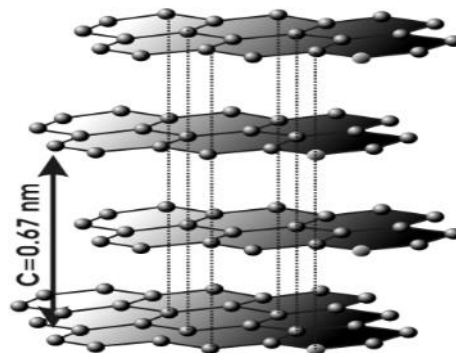


Figure 2.7. Graphite layered structure

Much of the study proposes a modified carbon graphite structure. Free valences have been produced due to the continuous bonding breakdown of micro crystallites during the carbonizing process. Moreover, processing parameters and contaminants impact the development of vacancies (pores) in the structure microcrystalline [107]. Active carbons are divided into two categories based on the graphitizing capability: graphitizing and non-graphitization. Carbon graphitizing has a huge number of parallel graphite layers. Due to the poor linkage between the neighboring micro crystallites, the carbon produced was sensitive and had a reduced developed porous structure. Due to tight linkages between crystallites and a highly developed microporous structure, the non-graphitizing carbons is hard [108]. The development of a non-graphitizing structure with strong links is encouraged either by the presence of oxygen in the initial raw material or by hydrogen inefficiency. In Figure 2.8, the schematic representations of graphitizing and non-graphitizing carbon structures are presented.



Figure 2.8. Scheme representation of AC structure: (a) graphitized carbon, and (b) non-graphitized carbon [109]

2.5.3. Chemical Structure

Structure of chemicals of an AC surface, in addition to its porous and crystalline structure. While its porous shape determines the adsorption capacity of AC, it is significantly controlled by a relatively small number of chemical binding hetero-atoms (mainly oxygen and hydrogen) [46]. The change in the configuration of electron clouds in the backbone chain leads to unpaid electrons and invalids that affect the adsorption of ACs primarily for polar compounds. ACs are always linked with substantial oxygen and hydrogen quantities [110]. And additional heteroatoms such as sulfur, halogens, and nitrogen [111]. These raw material-derived heteroatoms are present in AC structures during the process of carbonization or during activation, they may be chemically bound to the surface [69].

Much study reveals that heteroatoms are linked in a defective position to the carbon atom on the edges and corners or to C-X surface compounds known as surface groups or surface complexes at defect positions to form C - O, C-H, C-sulfide, and C-X surface compounds [46]. The influence of carbon surface chemistry on aromatic adsorption was thoroughly investigated [106], etc. aquatic

phase. Numerous research has focused on the impact of surface chemistry in the field of catalyst dispersion or catalyst activity [106]. Oxygen is by far the most significant heteroatom that affects the comportment, electrical and wettability, and catalytical characteristics of carbon [112]. The presence of oxygen on the carbon surface as functional groups was researched extensively. Oxidation treatments for carbon, in general, obtain oxygen-containing functionalities [113].

2.6. Classification of Activated Carbon

activated carbons are complex products, and the rating is difficult based on their ways of preparation, physical properties, and surface properties. However, the total particulate size categorization divides active carbon into powdered activated carbon (PAC), granular activated carbon (GAC), and activated carbon fibers (ACFs) [106].

2.6.1. Powdered Activated Carbon (PAC)

The PAC can be added to the water in various places of the water process with a tiny particle size to allow time to adsorb and then to sediment or filtrate PAC [114]. PAC consists of crushed or carbon ground particles so that 95% to 100% of the particle passes through a 0.279mm specified sieve as per (AWWA) American wastewater associated. The typical PAC particle size is between 15 and 25 μ m. PAC has a variety of applications in both drinking and wastewater treatments. The PAC is mainly used to treat compounds of smell and taste and to treat low pesticide concentration and other organic micro-pollutants.

2.6.2. Granular Activated Carbon (GAC)

The form of the GAC has often crushed charcoal or shell granules, GAC particles are between 0.2 and 5 mm in size. GAC is indicated as a mesh for application of the liquid phase, for example, 8/20, 20/40 or 8/30 and 4/6, 4/8, or 4/10 for application of the steam phase. For liquid-phase adsorption, particle sizes of 12/42 Mesh are advantageous. In drinking water and wastes as an advanced process, GAC filters are commonly utilized in the purification process, in particular in removing hazardous organic compounds [115]

2.6.3. Activated carbon fibers

ACFs are carbonated carbons that are then heat-treated in an oxidizing environment. In 1970, ACF was created utilizing a predecessor of viscose rayon consisting mostly of cellulose [116]. The precursors for the production of ACF were subsequently thermoset polymers such as saran or phenolic resins [117]. An excellent predecessor of ACF should be non-graphitic and non-

graphitizable isotropic carbon fiber. Since the late 1980s interest has still been focused on producing ACFs from, so many cheap predecessors [106].

2.7. Factors Affecting the Production of Activated Carbon: -

Many factors affect the production of AC such as:

2.7.1. Raw material

Most carbon-rich organic compounds which do not fuse when carbonized can be utilized as a raw material for the production of AC [118]. There are numerous factors in the choice of raw material for the production of porous carbon (Table 2.3 and 2.4).

- i. a high concentration of carbon.
- ii. Inorganic content is low (i.e. low ash).
- iii. High density and sufficient volatile content.
- iv. Countries' capacity to maintain a stable supply.
- v. The potential range of activation.
- vi. Low-cost raw materials.
- vii. Low degradation upon storage.[114]

2.7.2. Temperature

Temperature impacts the characteristics of the activated carbon generated, especially the ultimate activation temperature. Usually performed at temperatures exceeding 8000 °C in the Steam and CO₂ combination for commercial AC. Activated temperatures, as indicated by numerous authors, greatly impact the output of AC and also the activated carbon surface. The temperature was as low as 2000 °C and as high as 11000 °C [114].

2.7.3. Activation Time

The activation time also impacts the carbonization process and characteristics of AC in addition to the activation temperature. The activation time usually utilized for the coconuts and balm shell is 1-3 hours from the previous research. With the time rising, the percentage of yield gradually increased. This result is perhaps because the organic components are volatilized with raw materials, which leads to activated carbon production [114].

2.8. Textural Morphology of AC Derived from Different Agricultural Waste Materials under SEM

A scanning electron microscope (SEM) is an essential tool to study the morphology of the resultant activated textured surface.

Table 2.3 Chemical activation conditions and characteristics of the activated carbon

Starting material	Activation condition	S _{BET} (m ² /g)	V _{mic} (cm ³ /g)	V _t (cm ³ /g)	Pore size (nm)	Ref.
Cotton stalk	H ₃ PO ₄	1720	0.71	0.89	-	[58]
Wood apple outer shell	ZnCl ₂	794	-	0.47	-	[119]
Hazelnut shell	ZnCl ₂	647	-	0.35	34.0	[120]
Apricot stone	ZnCl ₂	814	-	0.43	34.0	[120]
Coir pith	ZnCl ₂	910	0.13	0.36	1.60	[121]
Palm kernel shell	KOH	217	0.11	0.12	-	[58]
Bagasse	ZnCl ₂	923	-	0.53	0.80	[122]
Rice husk	ZnCl ₂	927	-	0.56	0.80	[122]
Cocoa pod husk	KOH	490	-	0.24	2.0	[123]
Cocoa pod husk	K ₂ CO ₃	615	-	0.31	2.0	[123]
Cocoa pod husk	ZnCl ₂	780	-	0.58	2.9	[123]
Acacia mangim wood	KOH	5.25	-	0.015	11.79	[124]
Hazelnut bagasse	KOH	1642	0.60	0.96	-	[125]
Hazelnut bagasse	ZnCl ₂	1489	0.45	0.93	-	[125]
Bamboo	KOH	1533	-	0.5	-	[126]
Durian shell	H ₃ PO ₄	1024	0.21	0.35	2.5	[58]

Table 2.4. Physical activation conditions and characteristics of the activated carbon

Starting material	Activation condition	S _{BET} (m ² /g)	V _{mic} (cm ³ /g)	V _t (cm ³ /g)	Pore size (nm)	Ref.
Pistachio-nut shell	CO ₂ , 900 1C/30 min	778.1	0.22	0.47	-	[127]
Sugarcane bagasse	Steam, 900 1C/2 h	320	-	0.17	2.1	[128]
Peanut hull	Steam, 600 1C/2 h	253	0.09	0.22	-	[129]
Almond shell	Steam, 850 1C/30 min	601	0.34	0.37	-	[130]
Walnut shell	Steam, 850 1C/30 min	792	0.44	0.52	-	[130]
Almond tree pruning	Steam, 850 1C/30 min	1080	0.57	0.95	-	[131]
Olive stone	Steam, 850 1C/30 min	813	0.45	0.55	-	[132]
Coconut shell	CO ₂ , 600 1C/2 h	1700	0.88	1.14	2.7	[133]
Coconut shell	Steam, 1000 1C/120 min	1926	0.93	1.26	2.6	[27]

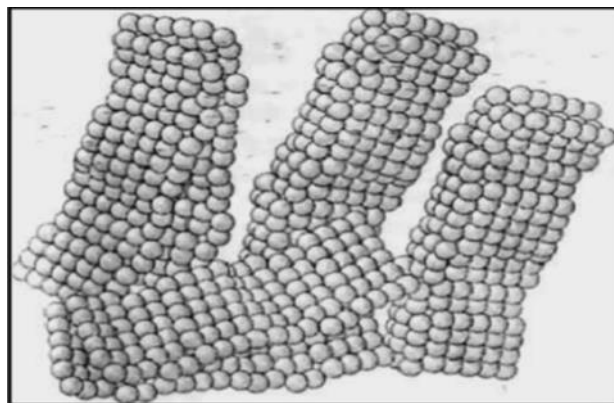


Figure 2.9. Microporous carbon is depicted in this model [36]

Porosity characteristics of AC of various kinds of agricultural wastes usually suggest that the variance in cellulose and lignin content in initial substances could impact the porous carbon structure. Higher content of Lignin and cellulose produces macropore and micropore activated carbons correspondingly [134]. Figure 2.9 shows the model of microporous carbon. The textures of the activated carbon may generally be determined by several factors, including experimental conditions, initial materials, kinds of activation, and kinds of materials agents, as well as their impregnation or concentration ratios.

2.8.1. Starting material of biomass

Research has indicated that its starting material for biomass is the most important factor influencing the texture of AC. Various biomass would generate varied morphology of texture, though with similar kinds of treatments [16] reported that the carbon texture and development of porosity are heavily impacted by the property of the beginning material. Two distinct biomasses, i.e., Olive Pits and walnut shells were studied. This one has a homogenous carbon structure, while the latter has coarser carbon textures with heterogeneous surfaces. The investigation revealed that the exterior surface properties for both biomasses at varied concentrations of chemical activating agents (KOH) were not significantly affected as shown in Figure 2.10 (a) and (b) [135, 136]. Activated carbon synthesized from rice husk by physicochemical activation and chemical activation correspondingly.

Research also demonstrated that both distinct activation types created a homogeneous distribution of pore structure [137]. Also observed was that various raw materials created the various morphological texture of the surface. They synthesized activated carbon made of 3 different biomasses; bamboo stem (BS), oil palm empty fruit bunch (EFB), and coconut shell (CNS) using (KOH) under the N_2 atmosphere. However, all ACs displayed uneven cavities and cracks and tiny pits which spread over the surface owing to intense interactions with chemical agents as seen in Figure 2.10. (c)–(e) [138].

Two distinct types of hulls of seed were investigated; A chemical activation (phosphoric acid) at 400 °C was obtained by branchiostegal eumycota (BESH) and *Prosopis Africana* (PASH). It has been shown that both active carbon surface morphology depends on the material beginning. The surface of both precursors was smooth and pore evolutions following chemical activations were illustrated in Table 2.3 [139] characterized coir pith AC NaOH and H₃PO₄, which discovered the two types of activated carbons to have channels such as the fragmented and pitted structures on the surface [140]. The activated carbons were produced using several kinds of activating agents were originated from the *Jatropha* husk (H₂SO₄, HNO₃, HCl, H₃PO₄, H₂SO₄+ H₂O₂, H₂SO₄+(NH₄)₂S₂O₈, NaOH, and ZnCl₂). All the micrographs were generally revealed honeycomb similar structures but with varied pores [141]. Activated carbon has been produced from two distinct forms of biomass: walnut shell and almond shell using orthophosphoric acid, which exhibited grooves, cracks, and regularly smaller pores, respectively, for the morphology of the surface for both almond and walnut shell.

2.8.2. Types of Activating Agents

Admiral et al. [125] two distinct chemical agents, Zinc Chloride, and potassium hydroxide from hazelnut bagasse were producing activated carbon. Images of the resultant activated carbon are shown in Figure 2.10 (a) and (b) and Figure 2.11.

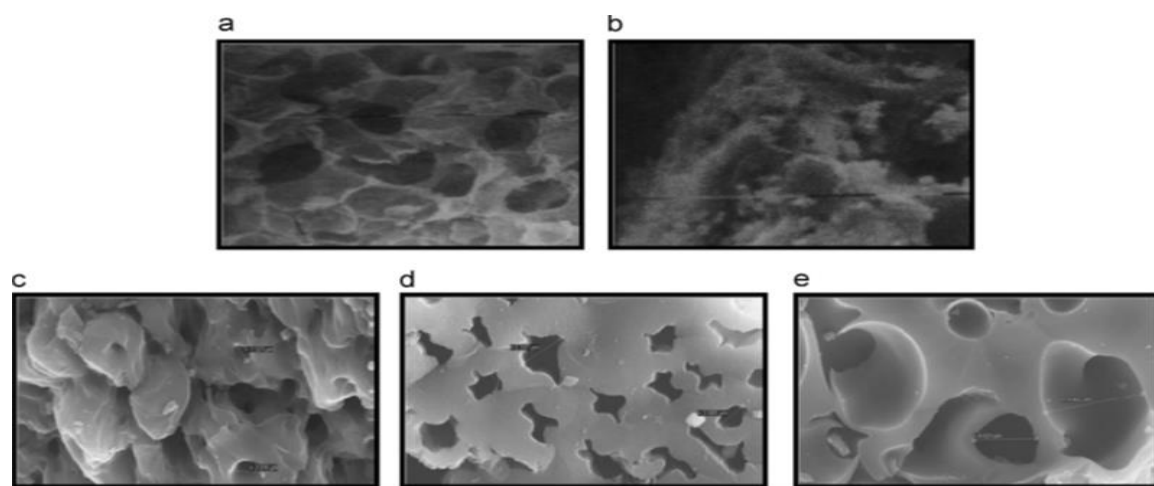


Figure 2.10. SEM of activated carbon of (a) walnut shell (b) olive pit [16], (c) oil palm fruit bunch, (d) coconut shell, and (e) bamboo stem [137]

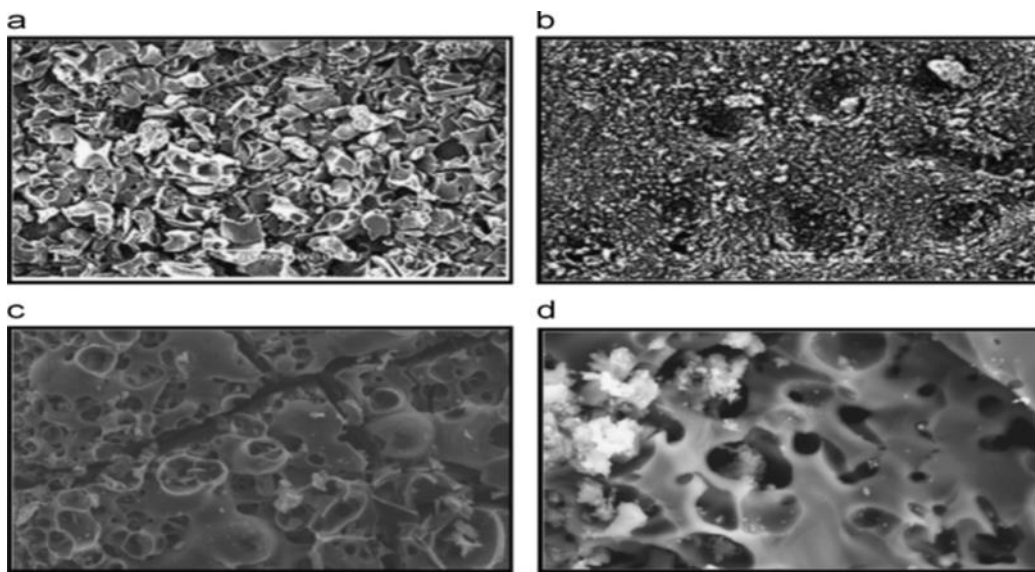


Figure 2.11. Scanning electron microscopy of (a) ZnCl_2 activated carbon, (b) KOH activated carbon [125], (c) K_2CO_3 activated carbon and (d) ZnCl_2 activated carbon [142]

They discovered that various active agents may create the varied surface texture of the AC morphology. The AC of ZnCl_2 owing to their evaporation during carbonization was discovered in several cavities. However, KOH activated carbon outside surface was more smooth with many small pores scattered [143]. Activated carbon produced from the pulp of oak cups with two chemical activators Zinc Chloride and H_3PO_4 was also investigated.

In morphology, the activated carbon of ZnCl_2 was seen by scanning electron microscopy to be full of cavities whereas the exterior structure was intact for activated carbon of H_3PO_4 [142]. Activated carbon produced by utilizing K_2CO_3 and ZnCl_2 as activating agents from kernel palm shells with chemical activations. SEM examination shows that the active carbon from ZnCl_2 has well distinct pores and cavities as seen in Figure 2.11(c) and (d). Due to fast pore growth and the creation of too many cavities and cracks, the distribution by pores of activated Carbon deriving from K_2CO_3 was non-uniform. However, the cleaner and smoother surfaces of both activated carbons are compared to their raw materials. Sugimura et al. [16] characterized AC from *Delonix regia* fruit pod (DRFP) and banana empty fruit bunch (BEFB) with both H_3PO_4 and KOH. Results indicated that the active carbons treated with both KOH and H_3PO_4 indicated some holes with a broken edge and bigger pores than the size of the pores correspondingly.

2.8.3. Concentration of Chemical Activating Agents

The content or impregnation ratio of the chemical activating agents employed might also affect the porosity growth of activated carbon. Vaisnavara et al. [122] the influence of the H_3PO_4 concentration on nutshell generated active carbon surface morphology was investigated. It showed

that increasing H_3PO_4 influenced porosity growth owing to aggressive assault and fast pore formation in the activated surface at the maximum concentration of H_3PO_4 (80 wt.%) [63]. Also utilized in the research of porosity on AC from pomegranate seeds are the various concentration of ZnCl_2 . Depending upon the impregnation rate and temperatures of the exterior surface of the ACs were varied in pores & size. All activated carbons had cavities and were produced irregularly.

2.8.4. Types of Activations

Williams and Reed [144] investigated the evolution of biomass fiber waste pore structure by physical and chemical activation. Figure 2.12 Shows both physically and chemically treatable activated carbon scanning electron micrographs. The initial investigation revealed that both treatments did not have a significant effect on the surface morphology of the original biomass. However, under increased magnifications, the surface of activated carbon was found to be pitted and cracked but the surface was smoothly activated by chemically activated carbon.

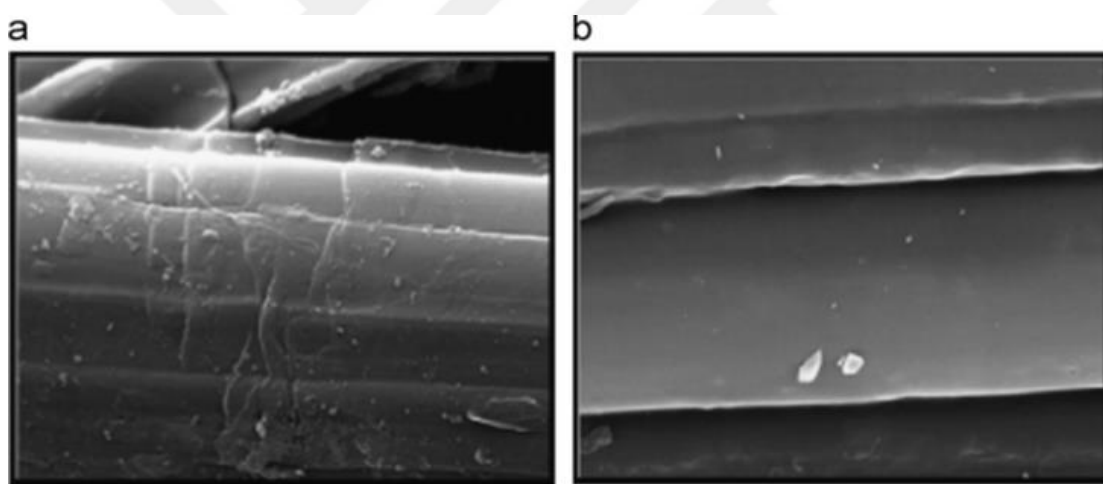


Figure 2.12. Scanning electron microscopy of (a) physically activated carbon and (b) chemically activated carbon [107]

2.9. Heavy Metal Ions

The copper, magnesium, zinc, selenium, cobalt, manganese, chromium cadmium, lead, nickel, mercury, iron, heavy metal ions, and other metals are not biodegradable and in nature accumulate. Heavy metal ions generally have atomic weights between 63.5 and 200.6 and a specific gravity over 5.0 [145]. In the Earth's crusts are found heavy metals also called trace elements because of their occurrence at a very small concentration (ppm and ppb). Heavy metallic contamination is affected by natural events such as weathering and volcanic eruptions. The existence of these heavy metal ions may also occur due to metal corrosion, air deposition, soil erosion, and the re-suspension of sediments.

However, a considerable quantity of these heavy metal ions is collected and presented by human activities such as fertilization, mining, textile, melting, industrial output, domestic and agricultural usage of metals and metal compounds in wastewater [146]. The periodic table allows the division of heavy metals into s-block, p-block, d-block (transition), and f-block (inner-transition). Furthermore, heavy metals may be categorized according to Lewis acid theory into soft, hard, and medium metals [147]. Soft metals are referred to as big particle-sized metals, high polarization, and low oxidation states, whereas hard metals are determined for tiny particles with lower polarization and a strong oxidation state [148]. Medium metals are zero oxidizing.

2.9.1. Heavy metal toxicity

Heavy metals are atomic weight elements between 63.5 to 200.6 and have a specific gravity larger than 5.0. Many heavy metals are health- or environmentally hazardous. Heavy metals including Pb, Cr, Zn, Hg, Se, U, As, Au, Ag, Cd, and Ni in industrial wastewater [149]. Exposure to Pb, Cd, Hg, and As, is the primary health hazard caused by heavy metals (Table 2.5). These metals have been thoroughly investigated and routinely evaluated by international organizations such as the WHO for their impact on human health. Severe metal intoxications can affect central neurological function, cardiovascular and gastrointestinal systems GI, kidney and lung, endocrine glands, liver, and bones. Chronic exposure to heavy metal has been involved in many degenerative illnesses in the same systems, and also can raise the risk of some tumors.

Non-biodegradable pollutants represent a serious environmental and health danger and no secondary technique can be used to remove the waste. Thus, the removal of such refractory pollutants might include tertiary/advanced wastewater treatment methods including adsorption, precipitation, membrane ion exchange, electrolysis, and separation. So far, several effective processes for the removal of heavy metals have been developed Lakherwal, D [150] studied many ways of heavy metal removal, including electrodialysis, chemical precipitation, reverse osmosis, ion exchange, ultrafiltration, floatation, coagulation, nanofiltration, flocculation, etc.

These methods are often efficiently used to remove the majority of the metals from a high or moderate solution. Thus, Chemical operations create enormous quantities of metallic sludge, making it difficult to recover metals. The sludge must also be disposed of further. Moreover, wastewater generally has unacceptable total dissolved solids following these treatments. When used to dilute metal waste or to reduce metal ion concentrations, the procedures are ineffectual or not cost-effective and need a high level of skill; most end-users thus do not utilize them.

However, most of the approaches are expensive and need significant skill; hence, many end-users are not using them. The adsorption method has therefore received broader application because of its relatively low cost, simplicity, adaptability, and resilience. Low-cost, by-product-based

Table 2.5 Heavy metal sources and toxicological effects [151]

Heavy metal	Sources	Effect
Cu	Copper water heaters; Water pipes; copper-powered greens and Frozen copper greens, alcoholic drinks from cooking facilities; water heaters for instant gas; pesticides; fungicides, copper gems; copper cooking pans. Hormone pills.	Nausea/vomiting, Postpartum psychosis, Insomnia, Cystic fibrosis, Arthritis/rheumatoid arthritis; Anemia; Mental disorders, heart problem, Hypertension, Stuttering, Inflammation, and enlargement of the liver, Hyperactivity, Autism Schizophrenia.
Cr	the textile industry and Steel	weakened immune systems, Pulmonary fibrosis, Skin rashes, respiratory problems, hemolysis, acute renal failure, lung cancer, alteration of genetic material, kidney and liver damage.
Ni	zinc base casting, silver refinery effluents, power storage, electrical plating.	Dizziness, nausea and vomiting, chest pain, headache, cancer of lungs, Myocarditis, pulmonary fibrosis, nose and bone, rapid respiration, Encephalopathy, Dermatitis.
Pb	The mining, stainless steel, automotive, battery, and paint industries, Pollutants are caused by increased industrialization.	Motor Neuron Degeneration, Nausea, Headache & vomiting, Encephalopathy, Mental retardation, Learning difficulties, Fatigue, Vertigo, Birth defects, kidney damage, Anorexia, Thyroid dysfunction, Muscle weakness, Hyperactivity, Cirrhosis of the liver, Insomnia, Schizophrenic behavior.
Hg	Industries such as chloro-alkali, oil refinery, paint, battery, pulp and paper, rubber and fertilizer, adhesives for the denture, soft fabric, medicines, pesticides, thermometers, light pipes cosmetics, and high-intensity street-lights, medications.	Minamata disease, Hypertonia – muscle rigidity, Tremors, Cerebral palsy, Nausea Seizures, Loss of hearing or vision, Kidney damage, Birth defects, Chromosome damage, Mental retardation, blindness and deafness, Gingivitis, Tooth loss.
Cd	Nuclear fission plant, pesticide fertilizer, electroplating, Welding, Cd Ni batteries.	bone marrow, Kidney damage, gastrointestinal disorder, cancer, bronchitis,
Zn	plumbing, Refineries, metal Plating, brass manufacture.	Fumes of zinc have a corrosive impact on the skin, damaging the nerve membrane.

adsorbents and industrial solid waste might be utilized to eliminate recalcitrant residues in the synthesized wastewater. The utilization of this material into wastewater treatment adsorbents would

help minimize waste disposal costs. Massive research on the absorption of hazardous waste from industrial wastewater utilizing agricultural waste and industry by-products [152]. Different low-cost adsorbents were examined for technological capability to remove heavy metals from polluted water [153]. Instead of utilizing commercially activated carbon, scientists have been employing cheap, high-adsorption materials such as zeolite, chitosan, and other adsorbents.

2.9.2. Various Conventional Methods of Heavy Metal Removal

Many various methods are used for the removal of heavy metal such as:

2.9.2.1 Adsorption

Adsorption is the accumulation of a gaseous or liquid solute solid or liquid (adsorbent) on a surface, resulting in a molecular or atomic layer (adsorbate). Adsorption occurs naturally in most physical, chemical systems, and biological, and it's commonly utilized in industrial applications including activated charcoal, water filtration, and synthetic resins. Because of its ease and cost efficiency, adsorption is now considered to be one of the best techniques for wastewater treatment [154, 155]. Adsorption is a widely used method for removing metal ions from a variety of industrial effluents [156]. AC is the most commonly utilized adsorbent. It's a porous, amorphous material made up of tiny crystallites with a graphite grid that occurs in tiny pieces or powder form. It can eliminate a wide range of hazardous metals.

AC is one of the most commonly utilized adsorbents for metal ion adsorption [157, 158] clay minerals [159], biomaterials, zeolites, and industrial solid wastes [160]. One source of reduced adsorbents is natural material or specific residue from agricultural or industrial operations. In most cases, these materials are readily available in great amounts locally. As a result, they are cheap and have minimal economic value [161] on a wide range of sorbents, scattered study has previously been done. Bark/tannin-rich substances, chitin/chitosan, lignin, xanthate, dead biomass, seaweed/algae/alginates, ash, zeolite, bone gelatin beads, clay, moss, peat moss, modified wool, iron-oxide-coated sand, and modified cotton are some of the known low-cost sorbents.

2.9.2.2 Chemical precipitation

Chemical precipitation procedures use chemical reagents, which are then separated into clean water by precipitated solids. Metals can be precipitated using coagulants including iron salts lime, alum, and other organic polymers [162]. It reported 80% elimination by Zinc, Copper, and lead and up to 96.2% elimination by a combined hydroxide precipitate and air floatation method of the oil from industrial wastewaters.

2.9.2.3 Ion exchange separation technique

Ion exchange separation is a process in which one ion is substituted for another ion in wastewater. In comparison to the coagulation process, ion exchange produces less sludge [163]. Separation is determined by the chemical property of the ion exchange resin. Resins are divided into two categories: synthetic and natural resins [163]. When compared to natural resin, synthetic resin produces far superior results. Synthetic resin is used to remove arsenic; it is the use of synthetic resin that removes arsenic [164].

Each type of resin is further classified into two categories: cation exchange resin and anion exchange resin. The cation resin is used to remove metals. Many types of research have determined that zeolite has the highest potential for adsorbing metal in wastewater [165]. The structure of zeolites is a crystal composed of silicate and aluminum linked by oxygen bridges. The alkaline charge balancing cations Na^+ , K^+ , Ca^{2+} , and Mg^{2+} are linked electrostatically with Al in zeolites, increasing the ion exchange efficiency [166]. Heavy metals such as Ni, Cd, Cu, Pb, and Zinc are widely removed from industrial water using zeolites resin [167]. Secondary pollution occurs as a result of resin re-formation (recharging), which necessitates the use of reagents, raising the expense of water treatment. Ion exchange is a good choice for low-pollution water. It is usually used in laboratories, although it raises the expense of water treatment on a big scale [163]. Magnetic ion exchange was first utilized as an ion exchange resin in 1995 to eliminate natural materials [168].

2.9.2.4 Electrodialysis

Electro Dialysis (ED) is a membrane technique in which ions are moved through a semi-permeable membrane while being influenced by an electric potential. The membranes are either anion- or cation-selective, which indicates that only positive or negative ions may pass through them. Polyelectrolytes containing negatively charged materials form cation-selective membranes, which reject negative ions while allowing positive ions to pass through [169].

2.9.2.5 Coagulation/ flocculation

Coagulation and flocculation are crucial parts of both drinking water and wastewater treatment. The chemical process that happens when a chemical or coagulant is applied to water is known as coagulation. The coagulant causes the colloidal particles in the water to clump into tiny aggregates known as "flocs". The suspended substance is subsequently attracted to the flocs. Flocculation is a steady, moderate mixing of the water to induce the formation of flocs and their growth to a size that will readily settle out. examines the basic underlying mechanisms in coagulation's elimination of organic pollutants [150]. The effects of starting pH and turbidity, alum and pre-ozonation dosages, and flocculation duration on dissolved organic material elimination during alum coagulation were investigated.

2.9.2.6 Ultrafiltration

Ultrafiltration is a separate method that employs membranes with pore diameters ranging from 0.1 to 0.001 microns. High molecular weight compounds, colloidal solids, and organic and inorganic polymeric molecules are often removed by ultrafiltration. Water and low molecular weight compounds penetrate a membrane while particulates, colloidal particles, and macromolecules are trapped in this pressure-driven filtration process. Although the electrical charge and surface chemistry of the particles or membrane may impact purification effectiveness, size exclusion is the primary removal method [169].

2.9.2.7. Reverse osmosis

Cellophane-like membranes filter pure water from polluted water in the RO process. Reverse osmosis is when pressure is exerted to the concentration surface of the membrane, cleaned water is forced into the dilute side, washing away the refused contaminants from the concentrated side in the refuse water. The remedy of organic-containing wastewater, metal finishing and wastewater from electroplating, municipal wastewater, paper and pulp, textile, mining and petrochemical, radioactive wastewater, and food processing industries and polluted groundwater have all been indicated as applications for Reverse osmosis processes [170-173].

2.10. The Role of Trace Metals in Living Things

Some of the heavy metals in nature taken in high concentration negatively affect their functions. Prolonged exposure to some of these can cause various diseases, up to cancer, or it can be short-term. Although at high concentrations it can result in the death of the more than 40 elements found in human tissues, it is an important metabolic factor in the organism. Those with effects are defined as essential elements. Compounds in various matrices depending on their concentration are divided into three major, minor, and trace components.

Major components; While describing the components with concentrations greater than 0.1%, the minor component; concentrations it is used for concentrations in the range of 0.1 – 100 ppm. Concentrations less than 100 ppm define them as trace components. The term ultra-artifact, which has been used recently, is used for concentrations in the ppb level.

- Elements found at major levels in human tissues are Mg, Cl, Na, Ca, S and P.
- Trace elements (< 100 ppm) can be classified into three groups:
- Required trace elements: Co, Mn, Cr, Cu, Fe, Zn, Se, V.
- Trace elements used for therapeutic purposes but not essential: Li, Pt, Bi, Al, Ga, Au.
- Elements that are both nonessential and toxic: Ni, Cd, Te, Ti, As, Pb, Sb, Hg, Ag [174].

Necessary elements can be used as a necessary component of enzymes with metals in their structure or as an enzyme – they act as activators in metal complexes. Higher than the permissible concentrations of trace elements in living things it has been reported to have undesirable or unidentified effects [175].

Lead from toxic trace elements; biological systems by entering food through the air, soil, and water it is one of the toxic metals that have very harmful effects on the environment and is widely used in industry. The sources that commonly emit Pb today are listed below:

- Drinking water mains pipes (it is gradually replaced by plastic pipes).
- Lead-tin alloy vessels (still in poor countries and rural areas can be used)
- Contribution to gasoline (recently removed).
- Paints containing Pb (until 1940 $\text{Pb}(\text{OH})_2 \cdot 2\text{PbCO}_3$), in the form of wall paints used white oil paint
- Ceramic glazing layer used as an additive to SiO_2 in the form of PbO .
- Metal industry and battery production.
- Soldering of cans used in food packaging.

Lead has a toxic effect on human metabolism by accumulating in the brain, causing changes in blood enzymes. It has also been reported to cause a decrease in IQ value [176]. World Health Organization temporarily tolerated weekly Pb intake by WHO 0.025 mg/kg body weight was determined as [177]. The absorption of lead entering the body orally is in the range of 5-10% in adult humans. It may be 7.5-15% (50% more than adults) in children up to the age of stated [175]. The absorption level of inhaled Pb is between 30-70%. In the case of small-diameter particles, this ratio is even greater.

The potential for lead to accumulate in the body and result in chronic poisoning has increased the interest in the determination of their concentrations in foods and beverages [177, 178]. For this reason, 20 ppb of lead in drinking water is permissible by the World Health Organization (WHO) set as the limit value. Cd, and another toxic trace element, is rust-resistant and soft. used in the metal industry. In addition, various industries such as nickel, silver, copper in forming alloys with metals, in electrical coating works, like soldering and welding, aircraft in the industry, as a neutron scavenger in nuclear reactors, dyes used in glass production, and CdS . it is used as a cathode in pigments such as yellow pigment and dry batteries.

Except for the occupational compulsory intake, the transmission of Cd to humans is mostly through food. Cigarette, Cd is the most important source of purchase. The organs most damaged by cadmium are the kidneys [179, 180]. The weekly temporarily tolerable amount of carcinogenic cadmium World Health It is set at 0.007 mg/kg body weight by the organization. This is the weekly limit to 50 μg cadmium intake [177]. Nickel metal causes allergies in the body, as well as some inorganic nickel derivatives and cancer. It has been reported that there is a potential relationship between [181]. Therefore, Ni in the environment and food there is increasing interest in the

determination of concentrations in samples. While the Ni concentration allowed in drinking water is 50 µg/L in European Union countries, World Health Organization (WHO) has determined this value as 70 µg/L (ppb). At least 2 L per day for an adult considering that he drank water, it is clearly understood how important these determinations are. In Table 2.6, the daily limit concentrations determined by the World Health Organization are given.

Table 2.6. According to WHO, daily intake of toxic trace elements can be ingested through food Concentrations

Toxic Metal Name	Daily limit That can be Obtained through Food amounts (µg/kg)
Cd	7.0
Pb	0.5
As	15
Ni	2.8

The most commonly used analysis methods for the determination of trace metal concentrations are AAS, AES, Methods such as UV – Visible, ICP–MS, and NAA. Of these methods. The sensitivity of AAS, AES, and UV-Visible spectroscopy is at the level of µg/kg or µg/L. Not suitable for appointments. To overcome this disadvantage, preconcentration procedures use remains up-to-date.

2.11. Applications of activated carbon

AC was widely utilized in water purification to remove impurities and toxins because of the restricted water supply [72]. It has been claimed that about 80% of ACS is used in liquid-phase or aqueous solutions worldwide [182]. One of the most important and effective organic and inorganic adsorbents has been proved ACS. The flexibility of the adsorption, surface, and pore structure of AC are the major reasons for its use [183]. The functional group of active carbon surfaces dissociated or retracted ions in solution which generated electric charges when carbons are in contact with an aqueous solution.

The dissociation or attraction strength depends on the solution's pH and the surface properties of the adsorbents [59]. Recently, many scientists recognized the use of green nano-composites for pollutants and contaminants removed from the water, with nano-particle loading technology in ACs to improve the efficiency of adsorption and uptake [184].

Tungsten oxide nanoparticles in this context [185], Zero valent nanoparticles in iron [186], Nanoparticles of iron oxide [187], Nanoparticles and Ag [188]. The ACs utilized largely for the removal of dye and metallic contaminants were loaded to the ACs. The pH of the solution is a major

parameter that determines the density of the surface and the cationic or anionic character of the surface. This means that the low pH solution attracts anions and that it attracts cations at high pH values. Therefore, pH regulation of the solution may be applied to the loaded inorganic groups. Acidic carbons are more suited to cation retention while basic carbons are more efficient for anion elimination [182].

2.11.1. Inorganic Pollutants from Water

In organic Pollutants from water including Metallic and non-Metallic removal.

2.10.1.1 Metallic pollutant removal

Metallic contaminants include heavy metals and metalloids are dangerous and not degradable to water contaminants that are biomagnified in the food chain. Having them around is detrimental and can lead to long-term health and illness impacts in people or other living organisms [189]. In addition, they have tiny and complex structures which are important since they are difficult to eliminate. These pollutants are biomagnifying the bodily accumulated food chain that causes long-term health consequences.

The primary sources of this metal are agricultural and industrial operations, including mining, fertilizer use, electroplating, and automotive production [190]. Many research has shown the usage of ACs to remove metal contaminants in low cost and easy terms [189]. Thus, ACs are commonly utilized in water purification with metals including copper, iron, lead (II), cadmium, and chromium (VI) [191]. The elimination of the metal contaminant from water is immediate due to its tiny size and is loaded in a solution, which generates substantial communication with AC during the electrostatic conduct process of adsorption [192]. Adsorption of AC is affected by a variety of factors, including the interplay between the metal ion and its structure, pH for the solution and zero charge point, porosity and surface area, surface oxygen functionality, and other variables, and ion-size ions with large tapering microporosity volumes (usually 1.0 –1.8 nm) [193].

The adsorbate and adsorbent interact via non-electrostatic forces, as well as electrostatic forces, and dispersive forces between them, and in the adsorption process, these forces play an important role [192]. Acacia mangium AC had a chromium removal effectiveness of 37.16 mg/g, whereas Acacia nilotica Bark AC had a chromium removal rate of 93.1 percent [194]. Pipes, accumulators, and additives in fuels and paints are all made from lead, which is one of the most significant elements in the industrial world. [195]. High levels of lead have been found in residential water pipes because lead is utilized in pipework, and these levels can rise to 2 mg/l or more. According to reports, lead has the potential to accumulate in living organisms and exhibits harmful signs in the human body [78]. It is thus necessary to examine this contaminant to eliminate it from the water. Just Tamarind wood AC in solution pH 10 is employed for lead adsorption in a solution

with an average pH of 5. Tamarind wood AC generated by ZnCl_2 activation has the greatest known surface area of AC at $1322 \text{ m}^2/\text{g}$ [59], and the maximum capacity of 114.8 mg/g was achieved with tropical almond shells AC produced from the CO_2 and steam activation combination [70]. As a result, lead has been reported to be eliminated (100%) by watermelon peel AC and Oil palm shell AC, respectively [196].

2.10.1.2 Non-metallic pollutant removal

Although anion may be helpful and important for humans, the excessive presence of certain anions, like fluorides, molybdates, and phosphates, may be a risk to living organisms and may be deleterious. Millions of individuals have fluorosis caused by high amounts of fluoride in drinking water, particularly in developing countries [197]. For example: [198], Fluoride ions have been accessible using water and excessive (3.24 ppm) and the positive link between the high fluoride levels in water and the fluorosis in children was explained in their report. Likewise, Molybdate is also quickly absorbed in the form of anion by the grassy animal and is found in a food and water chain that may be detrimental to grazing and cancerous to the human body [6, 199, 200]. As a result, continuous monitoring and careful management of anion concentrations are required to keep an appropriate water concentration.

The utilization of agricultural waste coir pith with activation of Zinc Chloride for the elimination of the anion contaminants in H_2O , such as phosphate, thiocyanate, and molybdates, was studied by three distinct research investigations. At a pH of 3.2, the greatest adsorption capacity is $16\text{-}18 \text{ mg/g}$, and for the removal of molybdate and thiocyanate, the ranges are $4\text{-}8$ respectively, whereas for phosphate it shall be relatively low, and 5.1 respectively from $3\text{-}10 \text{ pH}$. They found that, although coir pith may be a low-cost adsorbent, it may be a useful precursor for producing ACs to remove anion contaminants, and chemisorption and ion exchanges on the surface of ACs affect the capacity of adsorption. Sulfur may be removed 52.67 mg/g from water using an AC walnut shell that has a large surface area and $484.25 \text{ m}^2/\text{g}$ capacity for absorption [197]. Cashew nutshell AC and cashew nut AC impregnated with zirconium, both chemically active with H_2SO_4 Compared. Zirconium impregnated Cashew nutshell AC (ZICNSC) improved elimination effectiveness of 80.33% than just cashews nutshell AC (72.67%), which demonstrates the potential of modified fluoride ion removal AC.

2.11.2. Organic pollutants from water

AC Widely used and applied several sector removal Organic Pollutants from water.

2.10.2.1 Color/dye removal

Dyes are widely used and applied in sectors including textiles, cosmetics, paints, and paper products. The textile industry is the primary cause of water contamination from the environmental perspective [201]. 3600 types of dyes used in the industrial sector [202], In the effluent release around 2-20% of the dye are lost for each manufactured [203]. Thus dyes are one of the greatest and heaviest wastewater contaminants [204]. Effluents released by the industries include dyes that are poisonous and carcinogenic to the water of the river and other water resources [4]. Their water presence can decrease aquatic flora and fauna photosynthesis due to deterioration of the marine environment. Furthermore, the ingestion of dyes might be harmful as they induce human body changes [72]. AC has a high potential for removing dyes from the solution of water. The capacity to remove is based on the surface area, pores, AC group and polarity, solubilities and sizes of the dye molecules, and pH and other ions in solution [205].

The conservative approach for steam activation accomplished ACs and the pre-treatment procedure has the adsorption properties of organic chemicals (dye) from (aq) solution with an abundance of mesopores and adsorption ability, particularly for large molecules [206]. Acacia mangium and Acacia nilotica AC have been proved capable of removing various dyes. This can remove 90,5 percent of hazardous textile methyl orange dye [207] and 250 mg/g of methylene blue [208]. It is reported that the most adsorption capacity is over 100 mg/g. The greatest adsorption is derived from the ACs utilized for adsorption of methylene blue derived from AC KOH activated distillers with a high area of 1430 m²/g that can absorb 934.579 mg/g of an aqueous solution of methylene blue. At 55 C at pH 5.8 adsorption was conducted [209].

Ramulus Mori and rice husk with N₂H₉PO₄ are activated for the production of AC for methylene blue adsorption. The surface area was 1061 m²/g and 1154 m²/g at 314.1 mg/g and 129.5 mg/g of adsorption capacity, correspondingly [210]. The date pit has been widely utilized for the manufacture of AC for the elimination of methylene blue, methyl orange, Remazol yellow, and maxilon blue, both with physical and chemical activations. Date pit AC derived from activation by ZnCl₂ performed best for methyl orange adsorption with maximum adsorption found being 434.8 mg/g followed by dates pit AC activated by KOH for the elimination in methylene blue of the adsorption in an aqueous solution of 316.1 mg/g of dyes [4]. AC made of bamboo cane powder demonstrated the ability to remove lanaysn orange from the aqueous solution, with a high adsorption capacity of 2600 mg/g [72]. For malachite green adsorption, ACs generated from B. aethiopum flower and Rambutan peels have been utilized with chemical activation. The findings indicated that the adsorption capabilities were significantly different, when the B. aethiopum flower active carbon adsorbed 48.23 mg/g dye, whereas the peel adsorbed the rambutan 418.6 mg/g dye of aqueous solution [59].

The application for removing dye (methylene blue and rhodamine B) from the aqueous solution was studied using green nano-composites for the Coconut Husk Synthesis and Almond shell using Ag nanoparticles and WO₃ Nanoparticles respectively. Rhodamine B with WO₃/AC has an adsorption capacity high of 1666.67 mg/g value while Ag active carbon eliminated with methylene Blue has a comparatively low value of 240 mg/g. Anfar et al. Found that high value was related to the addition of WO₃ nanoparticles which impacted processes of adsorption for improved adsorption.

This may be compared to active carbon okra waste, which has a capability of 321.5 mg/g adsorption [72]. In contrast, the low value of Ag active carbon adsorption might be explained by Tuan et al. due to nanoparticles that impact very little the adsorption capacity of AC. It was found that nanoparticles do not affect the size, structure, and capacity to adsorb AC. The studies also showed that the surface areas and functional groups of ACs are important for the adsorbate interactions. Furthermore, nanoparticles cannot assist to improve adsorption capability in all situations.

2.10.2.2 Phenolic compounds removal

Phenolic compounds are largely produced by the chemicals and petrochemical industries [211]. These contaminants are extremely poisonous, carcinogenic, and regarded to be a severe danger to aquatic ecosystems and living organisms [211]. The quantity of phenolic compounds in bodies of water has thus been strictly restricted by health and environmental agencies, and these contaminants have priority to be removed [84]. The concentrations of these pollutants in industrial effluents were regulated by EPA (Environmental Protection Agencies) by a maximum of 0.1 mg/L while the maximum allowed concentrations of 0.001 mg/L of phenols were established in the drinkable water at the World Health Organization (WHO) [84].

Surface chemistry is more important than porosity in the adsorption of phenolic compounds by active carbon since the surface functionality increases substantially compared with the pore's arrangement size. The hydroxy group and carboxy of the active carbon have conserved the adsorption of phenol, which increases the attraction of the active carbon to p-p bond water between the active carbon and adsorbent surfaces [59]. Phenol and the phenolic compounds removed by AC retained the mechanism of the donor-acceptor where the electron donor and the solute's aromatic rings accept the surface-oxygen groups [76].

The pH of the solution influences phenol adsorption, where both high and low pH values decrease in the amount of adsorption. The phenols are highly pH-anionic and result in reduced adsorption between the anionic phenol and the carbon surface. The lower pH values in acidic solutions produce protons, which strive to reduce adsorption in carbonyl groups [212]. Bisphenol A adsorption utilizing argan nutshell AC was examined [213]. The maximal capacity of adsorption

at 293 K must be 1250 mg/g. The AC nutshell demonstrated improved adsorption effectiveness compared to commercial ACs. Durian peel is also a precursor utilized for this adsorption.

Moreover, the adsorption effectiveness with durian AC peel found is relatively poor (4.2 mg/g) at a 69 percent removal rate, albeit it lasted one-day adsorption process [87] active carbon for the adsorption of phenols was utilized to get lignocellulosic biomass such as the date pits, the kernel of avocado, kernel rape, baobab, and Acacia seeds. The Phosphoric acid-activated baobab wood activated carbon was the best adsorbent among these active carbons. Maximum adsorption was achieved at 24 h, with an optimum pH of 3 at 50 C [214]. They indicated in their investigation that acid surface functional groups on activated carbons may eliminate AC adsorption efficiency, whereas non-acidic or basic functional groups might improve adsorption. Chemical activation with Phosphoric acid and Potassium hydroxide of date pits AC was used in another study to remove compound phenolics from date pits AC (o-nitrophenol and p-cresol). Basically-treated AC was able to eliminate 322.5 mg/g of phenolic compounds from an aqueous solution, but acid-treated AC was only able to remove 142.9 mg/g [4].

2.10.2.3 Pesticides Removal

In contemporary agriculture, pesticides are necessary, but extensive use of pesticides can impair water quality. The most utilized pesticides in agriculture and gardening are bentazon, carbofuran, and 2,4-dichlorophenoxyacetic acid. They can be seen as hazards to aquatic human health and the environment because of their carcinogenic effects and mutagenicity, and their maximum water concentrations at certain levels. Tap water and potable water allowed concentrations are 0.05 mg/L, 0.09 mg/L, and 0.1 mg/L for bentazone, carbofuran, and 2,4-dichloro-phenoxy acetic acid correspondingly [215]. Based on the results, adsorption has been utilized as one of the most successful methods for separating pesticides from water resources [4].

Adsorption of pesticides through the AC is influenced by the organic material percentage, the continuous flow of the adsorption mechanism, and the carbon doses in the AC [216]. Pesticides were commonly adsorbed on date stones, which were frequently utilized as predecessors [217]. The date stone adsorption AC was investigated with several Drin pesticide kinds such as aldrin, dieldrin, and aqueous solution endrin. The maximum capacity for adsorption in endrin, dieldrin, and aldrin have been obtained at 228.047, 295.305, and 373.228 mg/g, respectively. Aldrin is reported to have the lowest solubility in this experiment and may thus be inferred that the increased adsorption was caused by a reduction in pesticide solubility in water [218]. The adsorption capacity of physiochemically activated date seed active carbons has been studied. The date of seed was handled physiochemical with Potassium hydroxide and Carbon dioxide, and the data obtained were 86.26 mg/g and 137.04 mg/g correspondingly under the same circumstances for adsorption of bentazone

and carbofuran. The differences in molecular adsorption capabilities of smaller carbofuran than bentazone have been explained.

This leads to simple diffusion and fixation on the active carbon surface. In another research, the same experiment was performed and comparable findings were reported: Bentazon 78.13 mg/g with carbofuran 175.4 mg/g. They also included a 2,4-dichlorophenoxy acetic acid adsorption experiment. In this investigation, 175.4 mg/g of pesticides could be removed from an aquatic solution by AC [215]. soya stalks, corn cob, Olive kernel, and rapeseed stalks were physically activated to generate active carbons for the elimination of bromopropylate. This study showed efficiencies of elimination of 90% to 100% for all precursors utilized [219].

2.10.2.4 Pharmaceuticals compounds removal

One of the developing environmental contaminants commonly utilized in human, agricultural, and aquaculture sectors is pharmaceutical compounds. The increased usage of pharmaceutical products has resulted in the continual release into the aquatic ecosystem throughout the years. They may be remained in the water because of their high level of stability and hydrophilicity in bodies of water, and therefore represent a hazard to the ecosystem. Though the pharmaceutical concentration in water is much reduced, it might still have harmful environmental impacts typically at a trace level [220]. The removal of the pharmaceutical chemicals by AC varies according to the bridge procedure, operating conditions, adsorbent kind, precursor kinds, activation method, and adsorbate characteristics (pharmaceutical).

In addition, an essential role in the adsorption of AC carbon is operational techniques such as the adsorbent dosage, adsorbent characteristics, operating temperature, pH solution, ionic capacity, and organic structure [210]. Most researchers have found that Langmuir and Freundlich's isothermal models are regulated by the adsorption of the pharmaceutical compounds' chemical by AC [221]. Kinetic modeling was utilized to evaluate the adsorption process management rate of the carbon surface [222, 223], analyzed the results of several studies that used different precursors to remove ibuprofen from an aqueous solution. The physical and chemical-activated mung bean husk, cork powder, olive stones, and mug wort leaves produce it. Damp cork powder was observed to produce the greatest performance among such materials that we're able to extract ibuprofen from water by 378.1 mg/g. This result may be contrasted with cork powder treated with K_2CO_3 and cork powder activated steam has shown superior. Carbon dioxide-activated olive stones also demonstrated a comparatively higher outcome than the remaining active carbons, with a capacity of 282.6 mg/g adsorption, whereas the other adsorbents had a capacity of less than 200 mg/g. Naproxen elimination can be additionally compared with waste apricot active carbon and olive waste active carbon. Treated $ZnCl_2$ wastes apricot active carbon removed 106.4 mg/g in 1 hours of the pharmaceutical, whereas treated H_3PO_4 wastes AC could only remove 39.5 mg/g following 26

h adsorption. The adsorption of naproxen and ketoprofen was also evaluated to olive waste. Active carbons were evaluated with their adsorption ability using the same treatments for precursors (olive waste) (H_3PO_4).

Olive waste active carbon was shown to have greater adsorption to naproxen (39.5 mg/g) than ketoprofen (24.7 mg/g). Of course, the active carbon olive waste has not been a good absorber for pharmaceutical compounds since it has not produced successful results. The principal paper mill slot active carbon was, however, an adsorbent of 405 mg/g high adsorption capacity for paroxetine [72] and High elimination efficiency of 75. 85, and 84 % correspondingly for SMX, CBZ, and PAR [224]. The quantity of clofibril acid (AC), tetracycline (TC), and paracetamol (PC) may be reduced by 83. 9703, and 84 % by H_3PO_4 activated waste textures (Cotton) active carbon, correspondingly [225]. Another research study found very efficient ranitidine adsorption within 93-99 % of the Lagenaria Vulgaris shell AC with a surface area of 665 m^2/g . In contrast, levofloxacin removals by date stones active carbon ranged between 41.40-97.01% with 100.4 mg /g and cyclamen persicum AC with a surface area of 799-880 m^2/g showed positive adsorption to diclofenac (22.22%) [221].

2.11.3. Other Pollutants from Aqueous Solution

AC may be used to remove a variety of contaminants, including caffeine, aniline, suspended particles, and other substances. Aniline is utilized in isocyanate production as an important component in the petrochemical sector. It is utilized also in the rubber, pesticide, and pharmaceutical sectors for the synthesis of accelerators and antioxidants [105]. Caffeine is an alkaloid that is used in teas, soft drinks, coffees, chocolate, and a few kinds of sweets, as a cardiac, brain, and breathing stimulant. It consumes around 200mg daily per person in general and is metabolized by the human body with approximately 1-10% via urine [226].

ZnCl_2 provides superior results for aniline elimination using apricot stones AC than phosphoric acid, with 147 mg/g and 115 mg/g results with the matching surface area of 1111 and 1382 m^2/g respectively [105]. Durian shell active carbon could eliminate 874 mg/g toluene while orange peel active carbon could eliminate p-nitrotoluene with 20 mg/g and cocoon shell activated carbon can adsorb 212.77 mg/g of benzene and formaldehyde could be eliminated by active carbon coffee residues with 245 mg/g [59].

On the other side, the KOH-activated cocoon shell-activated carbon removed the equivalent surface area of 39 percent of suspended particles of 478 m^2/g and steam-activated bio-sorbent Oil palm mesocarp fiber activated carbon from palm oil mill effluent (POME) with 80.0 %.In addition to it, Potassium hydroxide also adsorbate up to 46.65 and 79.77% of $\text{NH}_3\text{-N}$ sugarcane bagasse active carbon and sea mango active carbon correspondingly [209]. Aceh coffee grinds AC has 56% removed ammonia from activation with HCl [227] and bagasse of sugarcane With the respective

surface area of 692 m²/g at pH 4, AC may extract naphthalene by 119 mg/g [228]. Pineapple leaves active carbon that was activated by 155,5 mg/g of absorbed caffeine with a suitable surface of 1031 m²/g with phosphoric acid [226].

2.11.4. Gas Adsorptions

Besides the liquid materials, AC has also been shown to be efficient in Gas Adsorptions since the combustion of fossil fuels creates greenhouse gases (GHGs). an and environmentally polluted gases, increasing energy demand [195]. AC is among the hopeful solid adsorbents which can be used for NO₂, CH₄, CO₂, H₂S, and H₂ adsorption due to its many benefits, such as moisture-intense ability, easy regeneration, low cost, high gas absorption capabilities in normal atmospheric conditions, a high surface, adequate dissemination of pore sized, good mechanical stabilization and very low energy consumption [229]. H-H, dipole-dipole, and covalent bonding between gasses and functional groups adsorbing the contaminating gas resulted in higher efficiency [230]. The surface area, the adsorption ability, the structure of the carbon micropore and reproducibility, processability of the solution rely on the adsorption by AC the harmfully gas [205]. The adsorption of CO₂ is highly complex for texture characteristics and adsorbent surface groups [231] and the typical adsorption capability by AC is about 5 wt.% (298 K and 0.1 bar). CO₂ adsorption was facilitated by electrostatic communication between the potassium ions of functional groups. [232].

The capacity for CO₂ adsorption has considerably improved to 873 K in heating-temperature correlation. however, Micropore has the largest CO₂ adsorption impact (1 bar) and the pore size has a substantial adsorption influence at lower pressures (below 0.3 bar) [233]. The use of AC in NO₂ adsorption depends on pores, the kind, and the chemical organization of the activated carbon surface structure. Hydrogen sulfide is a colorless, poisonous, odorous, and damaging gas having a threshold of 0.0047 ppm for human and environmental conditions [234].

AC is the most successful and famous method of H₂S removal in which activated carbon is utilized for the elementary usage of hydrogen sulfide gas with dangerous chemicals (Potassium hydroxide and Sodium hydroxide) or oxidative chemicals (Potassium iodide and KMnO₄) [235]. Recently, the elimination of NO_x and SO₂ has become more important because of their toxicity and activated carbons are promising to remove those harmful gases by improving their sorption ability. It has been shown that metal oxides are impregnated with AC to simultaneously eliminate SO₂ and NO_x [236]. sunflower activated carbon grains are better produced than activated carbon almond shells, which are compatible with the corresponding area of 1790 and 862 m²/g respectively for CO₂ gas adsorption, (4.6 mmol/g correspondingly and 2.7 mmol/g).

The activation agents were CO₂ and ZnCl₂ for sunflower seed activated carbon and AC almond shells, with an area near to each other of 870 m² / g. Furthermore, the palm oil shell with a 1213 m² surface can remove CH₄ to 13 cm³/g, while the KOH-activated Agarics fungi can capture

4.7 wt % of H₂ by the amount of 2137 m²/g [59]. Phoenix dactylifera grains AC activated by N₂ have eliminated up to 141,14 mg/g of CO₂. [229] and H₂S was taken out up to 88.8% using AC coconut shell[196]. The walnut shell and plum stone activated carbon shell with values of 66.3 mg/g and 67 mg/g showed almost equal efficacy for the elimination of NO₂ [237]. Oil palm shell activated carbon with surface area 1213, 742,34 and 551,05 m²/g may be activated by ZnCl₂, CO₂, and Na₂CO₃; it is shown to be highly efficient in removing CH₄ and H₂S [66].

2.11.5. Recycling/Regeneration and Handling of AC

AC regeneration or recycling is very important for the protection of the environment and preservation of resources [193]. AC may be recovered when contaminants are eliminated from the used AC and up to 80% can be recycled at high efficiency [238]. When the activated carbons are soft, the particles get smaller, but the hard active carbon may often be recycled since the stiff component is well preserved [76]. The AC is generally recycled and thermally regenerated [239], Steam [212], and chemical [4] process. The steps are as follows:

A. Thermal recycling [240]

- The AC utilized is initially drained.
- The dried activated carbon will be heated to higher temperatures to carbonize the contaminants.
- The activated carbon is then regenerated to keep the hollow pores in the range of temperatures between 700 and 1000C.

B. Steam recycling [212]

- The active carbon filter is continually flushed back with warm water.
- The steam would then be connected and enforced by the AC within the 120-130 C range of temperature to remove contaminants.
- The carbon is finally flushed back to be used again.

C. Chemical recycling [4]

- The adsorbate from AC is utilized to desorb or decompose certain chemical reagents (acidic and alkaline)
- Efficiency is based on the sort of contaminants available for AC.
- When chemicals remove contaminants, reagents must also be eliminated for the regeneration of the activated carbon.

In the handling of activated carbon, while AC contact there is no substantial effect on human health (the "Carbon, activated – Material handling - Flexion Corporation," n.d.). Due to the interaction of activated carbon with eyes, human skin, and breath, only mild irritations might happen. Because unused activated carbon is non-toxic, it may be disposed of in harmless trash. On

the other side, the AC utilized may be characterized by the contaminant and should be disposed of under the relevant rules. In the reusing of the AC, care should be taken. The usage of reactivated activated carbons for drinking water treatment should follow particular standards and regulations [212]. To decrease the number of dust intakes by researchers, ACs with dust treatment should consider the impact of eye protection and dust masks with dust filters. When high vapor concentrations are adsorbed in activated carbon, the temperature could increase, and it may become partly wet with water and/or more air to reduce the concentration ("The Care and Management of AC - WCP Online," n.d). Oxygen reduction can reach hazardous levels in a closed vessel since the wet AC eliminates oxygen effectively from the air. Where humans work in a containing vessel AC, adequate safety and the requirements for less oxygen must be preserved ("Activated Carbon Safe Handling J Desotec," n.d.)



3. MATERIALS AND METHODS

The method that we used in this study is described as follows:

3.1. Devices Used in Measurements

Devices and apparatus used in experimental studies are given below.

Inductively Coupled Plasma-Mass Spectrometer (ICP-MS -Perkin Elmer Elan9000),
Scanning Electron Microscopy (SEM), (JEOL JSM-7001F- Field Emission Scanning Electron)
Microscope and Zeiss Evo Scanning Electron Microscope),
Magnetic Stirrer (VELP Multiposition heating magnetic stirrer),
Fourier Transform Infrared Spectrophotometer (FT-IR - Perkin Elmer),
Pressing Device (Graseby/Specac),
Electronic balance (Gec-Avery),
Centrifuge (NF 200 Core),
pH meter (SCHOTT LabStar Ph),
Distilled Water Device (Millipore Direct-Q),
Oven (M 6040 P Hot Air Sterilizer Laboratory),
BET device (Micromeritics Asap 2020 Surface Area and Porosity Analyzer)
Raman Spectrometer
Different size beaker, straw, flask, flask, measuring cup, funnel, glassware.
Furnace 1200K.

Table 3.1. Conditions applied in the metal determination by ICP-MS

Parameter	Description
ICP-MS	PerkinElmer ELAN 9000 ICP-MS
Nebulizer	Crossflow
Spray Chamber	Ryton, double-pass
RF Power	1000 W
Spray Chamber	1000 W
Plasma gas flow rate	15 L min ⁻¹
Auxiliary gas flow rate	1.0 L min ⁻¹
Carrier gas flow rate	0.9 L min ⁻¹
Sample uptake rate	1.0 ml min ⁻¹
Detector mode	Auto
Integration time	Element –dependent
Internal Standard	IR

3.2. Experimental Parameter

The conditions applied in the measurements with ICP-MS are given in **Table 3.1**. ICP-MS Operating Conditions and Analytical parameters

Integration time Dependent element

Spectra with FT-IR spectrophotometer:

- (1) After the Olive seeds are ground in an herb grinder and sifted through a 270-mesh sieve before chemical modification.
- (2) After chemical modification with different concentrations of H_2SO_4 and

After activation with pyrolysis and HCl, activated carbons synthesized in small mortar by grinding were taken for 3 separate sub-samples of the same sample obtained. SEM of activated carbon obtained under optimum conditions for scanning electron microscopy (SEM). Gold plated applied to images. Obtained by growing at different rates under vacuum power of 15 kW was applied for SEM images.

3.3. Preparation of Related Solutions

To obtain working curves for quantitative analysis, certain concentrations of stock and dilute solutions were prepared. 1000 ppm stock metal solutions: Metal nitrate salts containing 100 mg metal in dilute nitric acid dissolved and made up to 100 mL.

Model solution: Solutions containing 30 ppb Pb.

18% HCl solution: Take 10 mL of 36% concentrated acid with $d=1.19 \text{ g/mL}$ and add it to 20 mL diluted.

0.1 M CH_3COONa : After 2.05g solid CH_3COONa is taken and dissolved in water, 250 diluted to mL.

0.1M CH_3COOH : 0.6 mL of 100% concentrated acid with $Y_d=1.05 \text{ g/mL}$ is taken and added to 100 mL diluted.

Preparation of Buffer Solutions in the pH 3-6 Range

pH 3 buffer: It was prepared by adding 0.1 M HCl to 0.1 M sodium citrate solution and measuring the pH.

pH 4 buffer: Prepared by mixing 10 mL of 0.1 M CH_3COONa with 40 mL of 0.1 M CH_3COOH .

pH 5 buffer: It was prepared by mixing 35 mL of 0.1 M CH_3COONa with 15 mL of 0.1 M CH_3COOH .

pH 6 buffer: Prepared by mixing 47.5 mL of 0.1 M CH_3COONa with 2.5 mL of 0.1 M CH_3COOH .

3.4. Supply of Samples

In this study, Olive seeds were used as a sample. The samples to be analyzed within the scope of the thesis were obtained from the Elazığ. was done as soon as the water samples were taken, nitric acid was added to pH = 2. Thus, the collapse ensured not to occur.

3.5. Activation of Biomass and Adsorbent Synthesis

Oliv seeds were washed with tap water and rinsed with distilled water, and then dried in an oven. After chemical modification with sulfuric acid, pyrolysis was performed. Cellulose with sulfuric acid is envisaged to increase the adsorption by binding sulfonate groups. The steps related to the modification process with sulfuric acid are given in Figure 3.1.

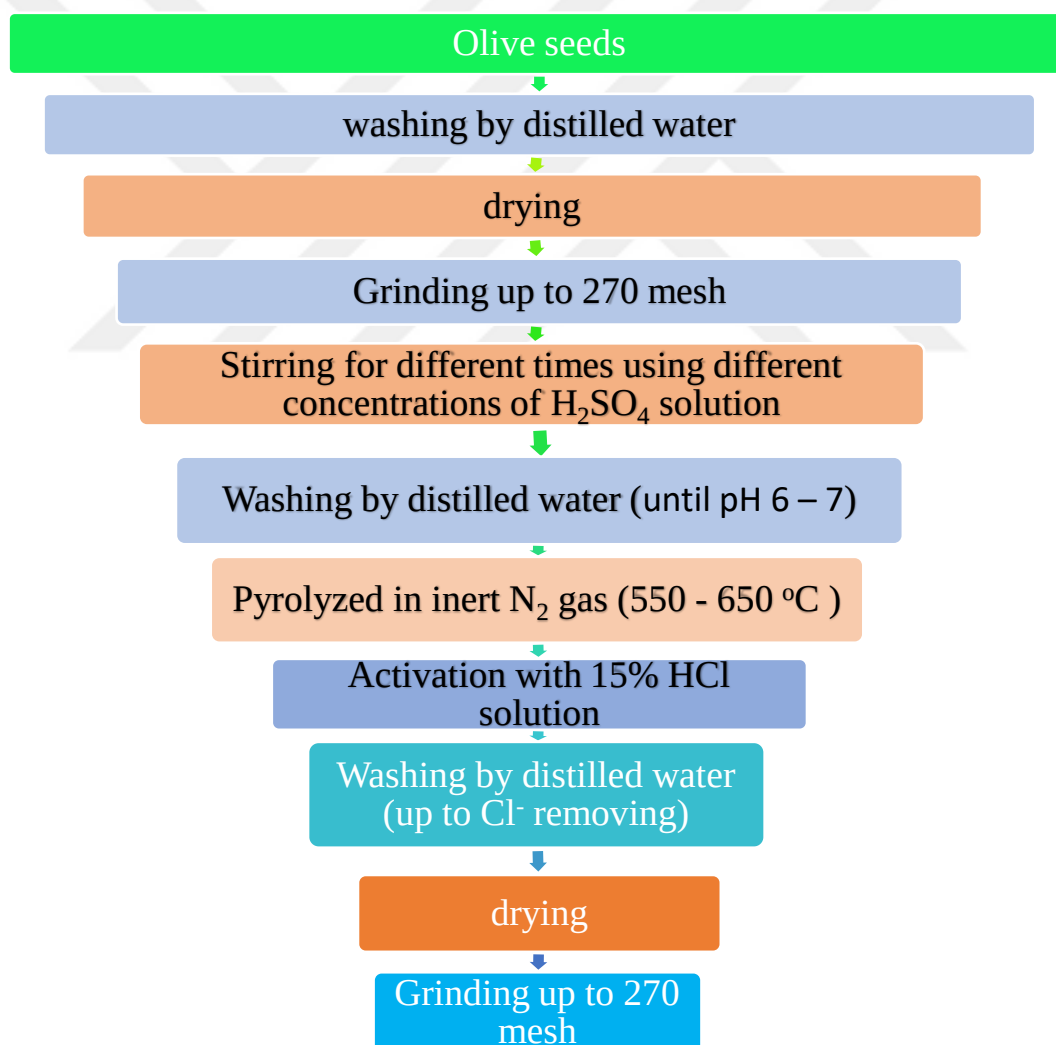


Figure 3.1. Modification of olive seeds with H₂SO₄ and activated carbon production scheme

3.6. Characterization of Biomass

Characterization was done using conductivity, FTIR spectroscopy, SEM, and BET.

3.6.1. Conductivity measurements

Conductivity measurements of ACs obtained at different H_2SO_4 concentrations and different temperatures were made.

3.6.2. Characterization with FTIR

Active synthesized from olive seed samples, raw, after modification, and in the last step. FTIR (Fourier Transform Infrared Spectroscopy), as in Figure 3.2, spectra for the characterization of AC carbon. For this purpose, 10 tons of sample / KBr = 1 / 100 after mixing in a mortar. The disc was formed under pressure [241, 242]. The spectra of the prepared discs were obtained by FTIR spectroscopy in the range of $400\text{-}4000\text{cm}^{-1}$.



Figure 3.2. Fourier Transform Infrared Spectrophotometer (FT-IR - Perkin Elmer)

3.6.3. Characterization of AC with SEM

In this study, the highest conductivity values of the obtained activated carbons were determined for 16 hours. SEM, as in Figure 3.3, images of ACs obtained as a result of Stirring and pyrolysis at $650\text{ }^{\circ}\text{C}$ were taken. To this end, a small amount of sample taken with a special spatula was prepared by coating gold on the disc.



Figure 3.3. Scanning Electron Microscopy (SEM)

3.6.4. Characterization with BET

The highest conductivity measurement was 16 hours of stirring, modification with 25% H_2SO_4 and 0.05 - 0.10 g of the AC obtained at 650°C , the gas adsorbed by placing the sample in the BET device, as in Figure 3.4, BET plots were obtained from the amount and pressure change.

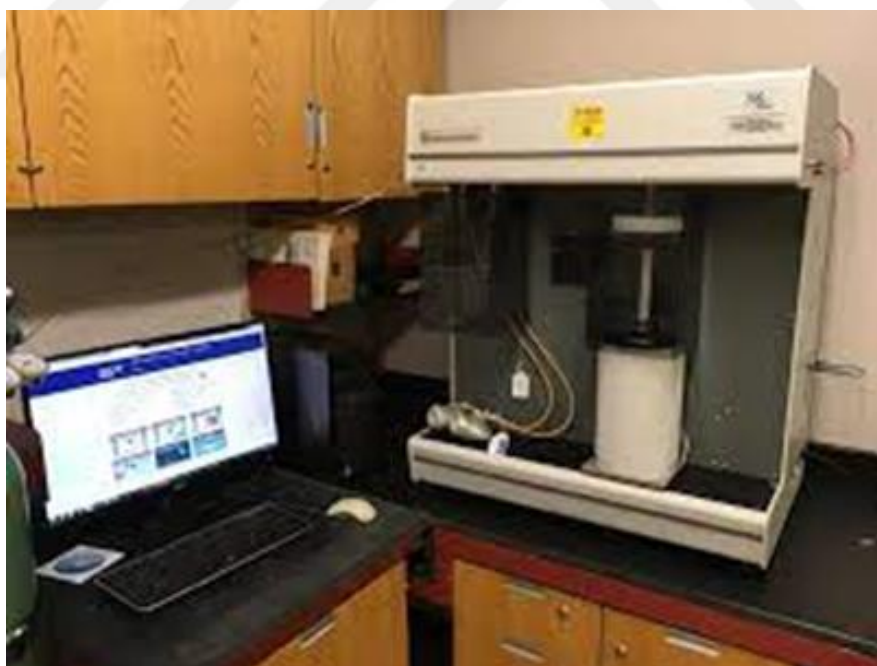


Figure 3.4. BET (Brunauer—Emmet-Teller)

3.7. Determination of Metals by ICP–MS

The ICP – MS, as in Figure 3.5, method was preferred because it provides multi-element analysis. At this stage Using a range of standard solutions (Pb, solutions) in the 10 –1000 ppb range.



Figure 3.5. ICP-MS Instrument

3.8. Optimization Study for Advancement

In the preconcentration process, the adsorbent with the highest conductivity from the obtained activated carbons 0.05 g adsorbent was taken to be used in 150 mL metal solutions of different concentrations. (Pb, solutions) are added and the necessary pH adjustments are made to reach the optimum values the range has been determined.

3.9. Advancement Process

For this purpose, 150 mL model solutions containing 30 ppb Pb were used. (These solutions are hereinafter referred to as model solutions) Add 0.05 g of adsorbent was done. The pH was adjusted to the value to be studied in the range of 3 - 6. Thus, 150 mL of pH adjusted 15 mL of buffer solution was added to the solutions. 30 min preconcentration after the stirring procedure was applied. The process steps are given in Figure 3.6 take 15 - 60 minutes at optimum pH.

Experiments were carried out by stirring in the range (150 mL solution). The preconcentration process steps are as follows.

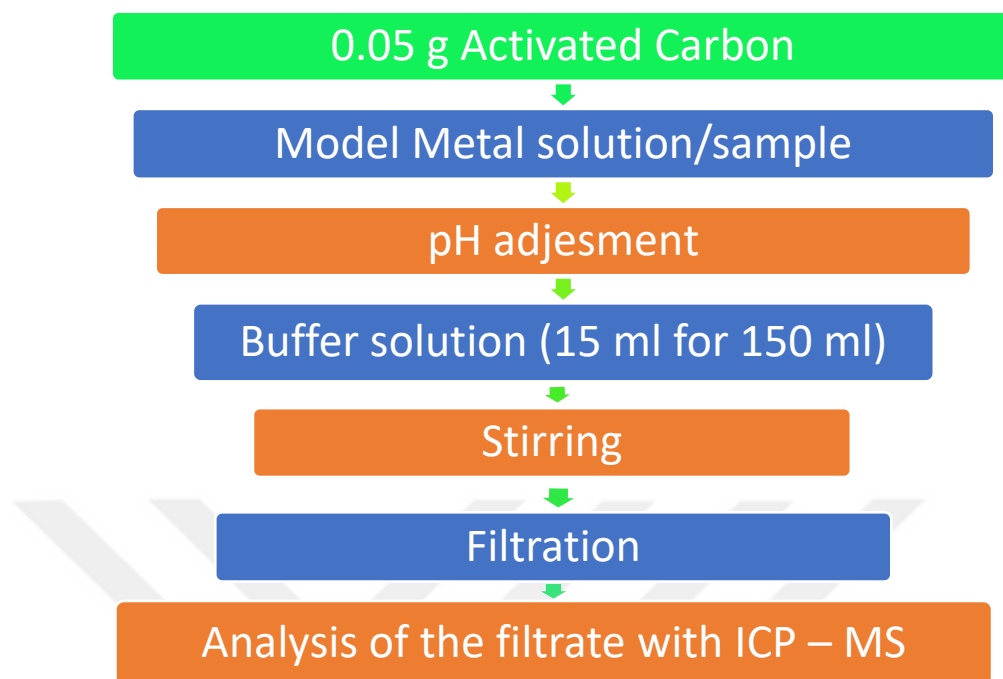


Figure 3.6. Preconcentration process steps for biomass-based activated carbon

3.10. Studies on Finding Optimum Values

In this section, optimization studies of the parameters in the preconcentration step are explained.

3.10.1. Determining the Optimum pH Range

To determine the optimum pH range, 150 mL model solutions are used as optimum 0.05 g of the AC evaluated adsorbent was added. The pH of the solutions (in the range of 3 - 6) was 0.1 M NaOH and adjusted with 0.1 M HCl. The preconcentration process is in Figure 3.6 after the buffer solution is added. steps were applied and clear solutions were analyzed by ICP – MS. containing the optimum values pH - % yield graphs are given in the results section.

3.10.2. Determining stirring Time

To determine the optimum stirring time, 150 mL model solutions were added as optimum. 0.05 g of the AC evaluated adsorbent was added. Solutions adjusted to optimum pH (3.0 for Pb after adding 15 mL of buffer solution, the preconcentration in Figure 3.6 is between 15-60 minutes, process steps were applied. The solutions obtained after preconcentration were analyzed

by ICP – MS was done. The Stirring time depends on the concentration values proportional to the signal read from the ICP-MS plotted against. The results found are given in the findings section.

3.10.3. Effect of Initial Volume on Leading

Together with other parameters found suitable to find the optimum initial volume amount (optimum pH and stirring time) 50 – 100, 150, and 300-mL initial volume solutions by working with the model the metal solutions were subjected to pre-concentration steps. At the end of the process, metal, when the concentrations are determined by ICP – MS, the yield, is sufficient for all volumes studied. Since there is an initial volume of 150 mL in optimization studies, natural water is used. 300 ml samples were preconstituted in the application studies.

The olive seed was obtained in Elazig, Turkey, from a local market. The samples have been properly washed with DW. and dried in an oven over 12 hours at 100 °C. The samples were then crushed using a grinding machine and sieved through a 270 mesh (0.053 mm) sieve. The analytic reagent grades were all the chemicals utilized. A stock solution of lead ion was prepared by dissolving Lead nitrate $Pb(NO_3)_2$ purchased from Merck (Germany) in sulfuric acid and diluting with distilled water. This solution has every day been diluted to ready standard model solutions (10-100 ppb). Additional chemicals such as HNO_3 , H_2SO_4 , HCl , and CH_3COOH/CH_3COONa buffer solutions were prepared from their ultra-pure reagents (Merck). Ultrapure water has been prepared to utilize Millipore Q for all tests.

The infrared spectra were used to determine the AC molecular structure. The spectra have been produced by transmitting by use of potassium bromide (KBr) pellets and evaluated using a Fourier Transform-Infrared Spectrophotometer (FTIR) (Perkin Elmer FTIR-USA) in the region between 400 and 4000 cm^{-1} . An adsorbent morphology was evaluated by the scanning electron microscope (SEM) (Zeiss EVO-MA10). Micromeritics asap 2020 Surface and Porosity Analyzers (Brunauer—Emmet-Teller (BET), and Barrett-Joyner-Halenda (BJH) methods measured the surface area, total pore size, and pore volume distribution analyzes. The pH measurements were performed using the digital pH meter 100 (Cyberskin). For the determination of Lead, inductively coupled plasma-mass spectrometry was used (Perkin Elmer Elan9000).

The instrument-ICP-MS has a LOD and LOQ of respectively 0.02 and 0.06 Pb ng mL^{-1} . SPS-SW2-Surface Water, standard reference material (SRM), was utilized for measuring reliability. 5.0 g of dried Olive shell powders were chemically modified using H_2SO_4 (25%, w/v) as described in Figure 3.7. After washing the modified sample with distilled water up to pH 6, the pyrolysis procedure was followed by heating to 650 °C at an increasing rate of 20 °C min^{-1} and maintaining this temperature for 1 h under N_2 flow protection. Severs studies illustrate that temperatures about 650°C are most acceptable in the acid treatment of agriculture materials to produce optimal characteristics of the AC [243]. Rising the temperature of activation to 650 °C

affects the raw material with the development of porosity. The distilled waters were used to neutralize the sample after activation by HCl of 15% (w/v) for 1 h. (about pH 6). The resulting AC was then dried and utilized for Lead cation adsorption. Add 0.05 g of the active carbon produced to the Lead solution model of 150 mL (30 ppb), adjusting the pH of those solutions to the necessary diluted and base solutions (between 3.0 and 6.0), adding 10 mL of CH₃COOH/CH₃COONa buffer solution. In 15–60 minutes the solutions were stirred. The Lead ions in the filtrate remaining were determined after filtering. The detailed steps of the scheme were shown in Figure 3.7, Figure 3.8. At least three replications were made of each parameter, and the mean was utilized in the tables and figures. Therefore, all statistical computations are based on the triple reading average for every standard solution. A one-way variance analysis (ANOVA) was done in statistical evaluation to examine for each sample of interest the equality of mean values. The SPSS (version 15) statistical program was used for all statistical computations. The Statistical value of $p \leq 0.05$ was considered.

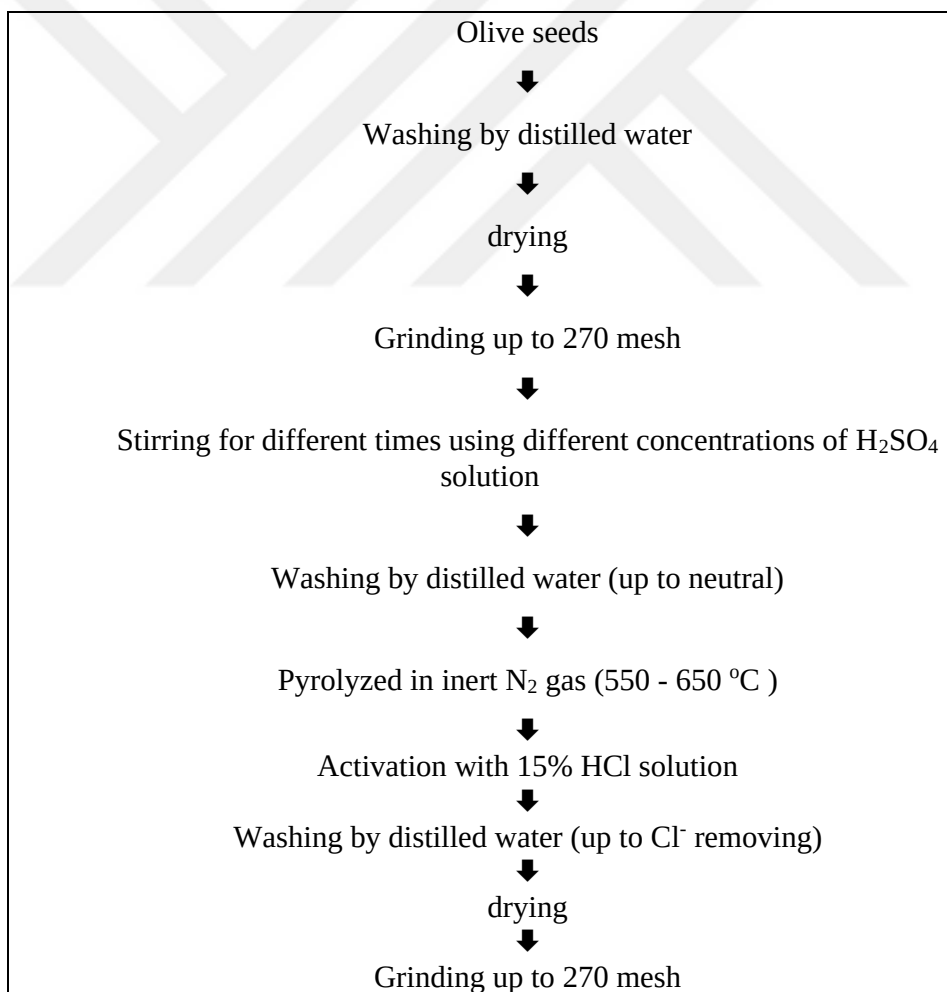


Figure 3.7. Scheme of the activated carbon synthesis

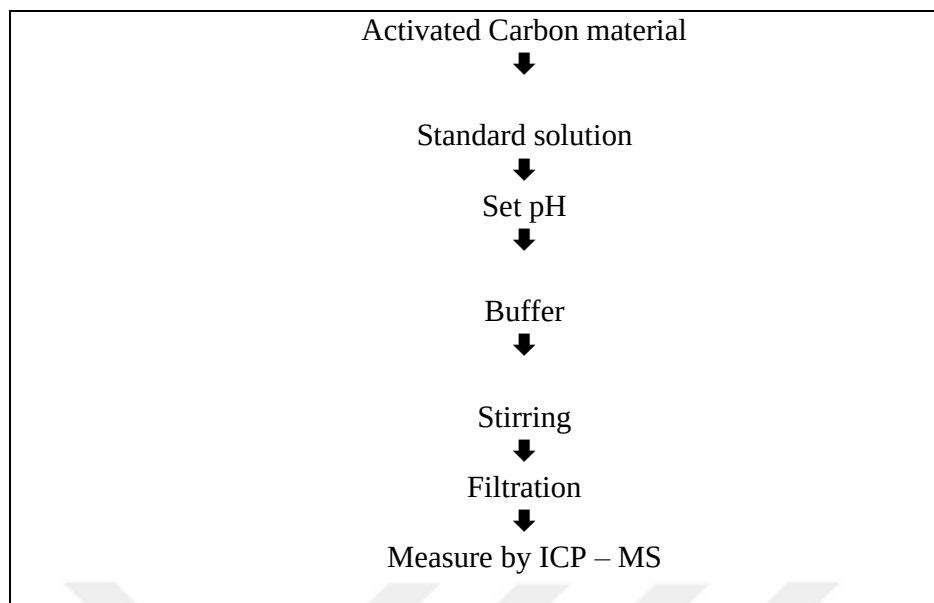


Figure 3.8. Scheme of preconcentration steps

4. RESULTS AND DISCUSSION

4.1. Characterization with FTIR Spectroscopy

FTIR (Fourier transform infrared spectroscopy) spectra were taken from Olive seed samples of the characterization of activated carbon synthesized in the raw, post-modification, and final step. For this purpose, after mixing the sample in a mortar with KBr = 1/100, a disk was formed under 10 tons of pressure, the spectra of the prepared discs were obtained by FTIR spectroscopy in the range of 400-4000 cm^{-1} .

The spectra of the FTIR spectrophotometer are taken for the following samples:

- 1- Raw Olive seed after grinding and sieving before chemical modification.
- 2-Before pyrolysis, after chemical modification using H_2SO_4 at different concentrations and stirring time.

4.2. The Synthesis of Activated Carbon.

FTIR is used for the determination of chemical and physical properties of the obtained AC or modification of Olive seed; FTIR was used to analyze the functional group.

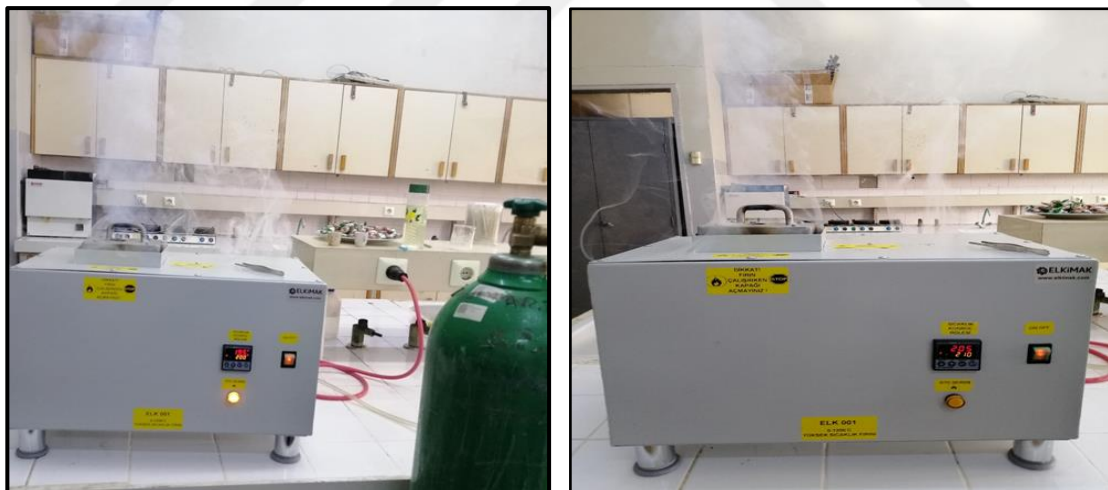


Figure 4.1. Increase evaporation of gases at 205°C by Furnace

4.3. Pyrolysis Step

Pyrolysis parameters will be studied and optimized at different times and different temperatures. pyrolysis procedure in inert N_2 gas (550 and 650 °C) is carried out; pyrolysis step is done by furnace device which opened and putting crucible to inside it and closed then increasing the temperature slowly step by step we see 100 °C gas started to evaporate at 150 °C the evaporating

of gas increases this is between 10 minutes at 175 °C and more gas evaporation increase, as in **Hata! Başyuru kaynağı bulunamadı..** At 200- 300 °C increases, at 300 °C we see gas already decreased at 370-500 °C no gas was seen at 550 °C very low gas were seen after 40 minutes at 650 °C gas is removed; gas that evaporate at 400 °C is very toxic to human.

4.4. Preconcentration

In applications for preconcentration and removal of Pb solutions with known concentrations of ppb made; In this step, the optimum conditions were determined by working with different pH and different stirring times. At this step 150ml of D.W + standard Pb solution + 0.05 gr activated carbon +15ml buffer solution.

4.5. Preparation of Related Solutions

For quantitative analysis, stock and dilute solutions were prepared at certain concentrations to obtain working curves. Stock metal solutions of 1000 ppm metal nitrate salts containing 100 mg of metal were dissolved in dilute nitric acid and made up to 100 ml.

Model solution: Solutions containing 30ppb of Pb.

18% HCl solution: Take 10 mL of 36% concentrated acid with $d=1.19$ g/mL and add it to 20 mL. diluted.

0.1 M CH_3COONa : After 2.05 g solid CH_3COONa was taken and dissolved in water, it was diluted to 250 ml with distilled water.

0.1 M CH_3COOH : Y $d=1.05$ g/mL, 0.6 mL of 100% concentrated acid was taken and diluted to 100 ml.

4.6. Preconcentration Step

The use of biowastes, including olive seed, inactivated carbon synthesis, has been published in previous studies. However, for this purpose, optimization of H_2SO_4 concentration, time, and temperature in the synthesis step has not been investigated, in this study, the thesis subject is unique and it is predicted that the data to be obtained will contribute to science and technology since the optimum conditions will be determined by studying the H_2SO_4 concentration in the range of 10% to 40% given the stirring time in the range of 4-16 hours and the temperature in the range of 550-650 °C .

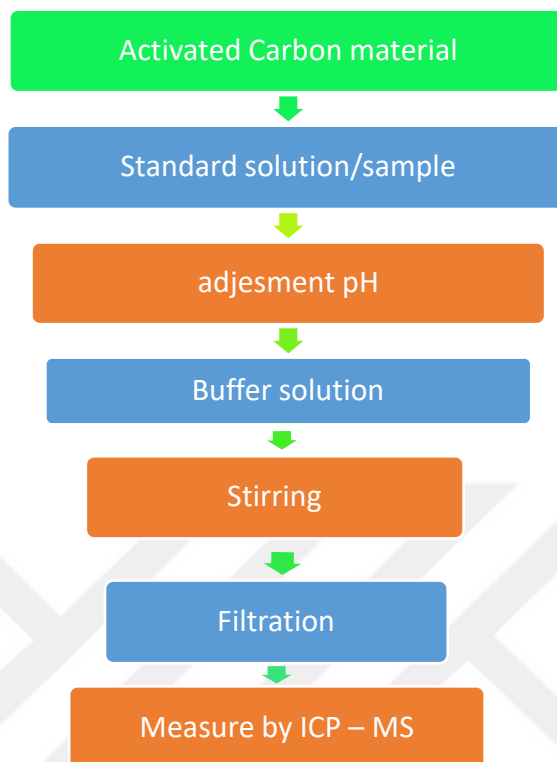


Figure 4.2. Scheme of pre-concentration steps

4.7. Determination of Metals with ICP-MS

The ICP-MS method was preferred because it provides multi-element analysis. At this stage, the calibration graphs drawn using a series of standard solutions (Pb solutions) in the range of 0-1000 ppb are given in Figure 4.3, Figure 4.4, Figure 4.5, Figure 4.6. After the pre-concentration step for the sample, the concentrations of the metals in the filtrate were measured with the ICP-MS device using these calibration charts.

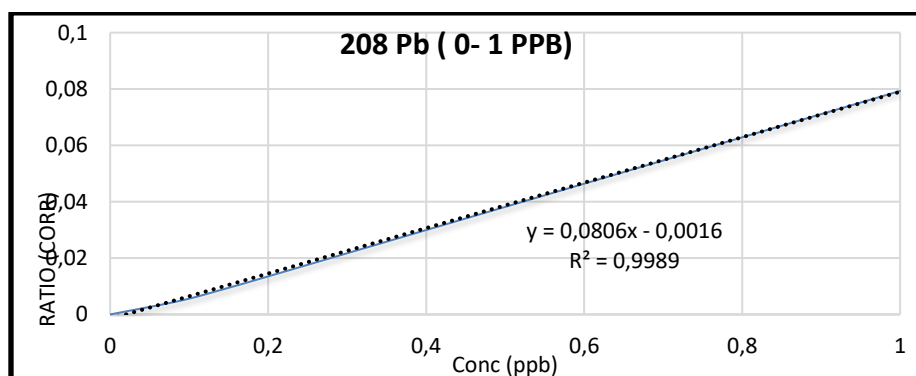


Figure 4.3. ICP - MS calibration graph for Pb in the range of 0 – 1.0 ppb

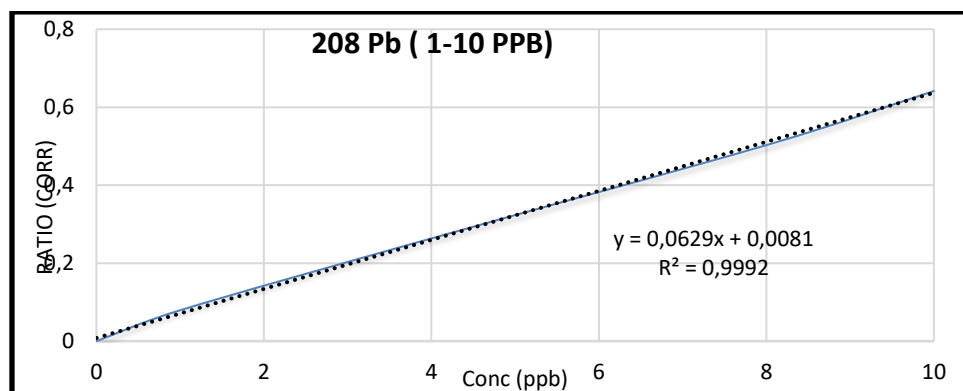


Figure 4.4. ICP - MS calibration graph for Pb in the range of 1 - 100 ppb

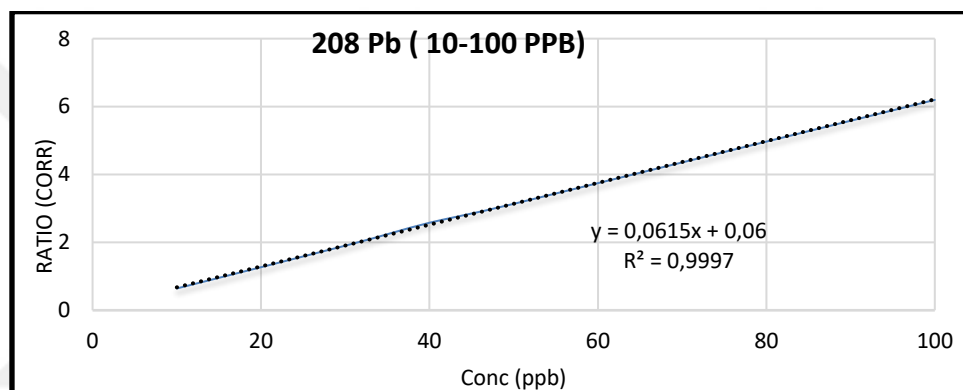


Figure 4.5. ICP - MS calibration graph for Pb in the range of 10 - 1000 ppb

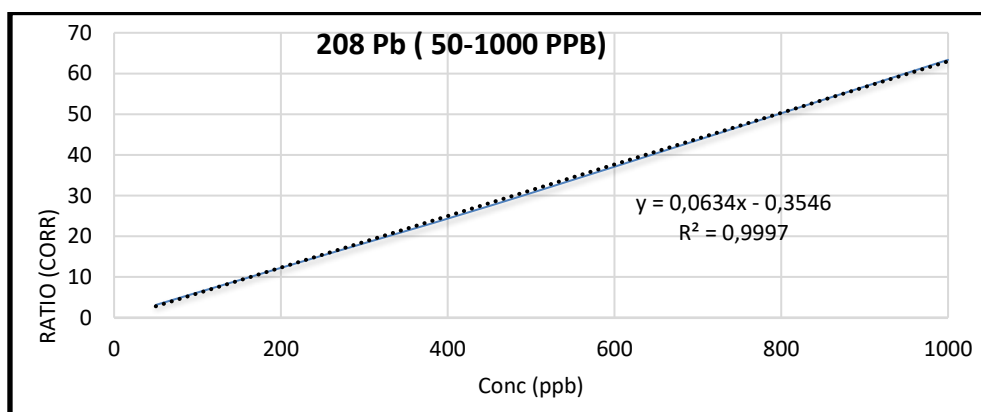


Figure 4.6. ICP - MS calibration graph for Pb in the range of 50 - 1000 ppb

According to the above calibration charts, LOD - LOQ values for Pb were calculated as 0.02 - 0.06.

4.8. Studies on Finding Optimum Values

The optimum results are described in detail as follows:

4.8.1. Determining the Optimum pH Range

To determine the optimum pH range, 0.05 g of the adsorbent, which was evaluated as the optimum AC, was added to the 150 mL model solutions. The pH of the solutions (in the range of 3-6) was adjusted with 0.1 M NaOH and 0.1 M HCl. After adding the buffer solution, the preconcentration steps in Figure 4.2 were applied and the clear solutions were analyzed by ICP MS. pH-% yield graphs containing optimum values are given in the Findings section.

4.8.2. Determining stirring Time

To determine the optimum stirring time, 0.05 g of the adsorbent, which was evaluated as optimum AC, was added to the 150 mL model solutions. After adding 15 mL of buffer solution to the solutions adjusted to optimum pH (5.0 for Pb), the preconcentration steps in Figure 4.2 were applied between 15-60 minutes. The solutions obtained after preconcentration were analyzed by ICP-MS. stirring time was plotted against concentration values proportional to the signal read from ICP-MS. The results found are given in the findings section.

4.8.3. Effect of Initial Volume on Leading

50 - 100, 150, and 300 ml, together with other parameters found suitable (optimal pH and stirring time) to find the optimum initial volume amount. The model metal solutions were subjected to preconcentration steps by working with the first volume solutions. At the end of the process, when the metal concentrations of the filtrates were determined by ICP-MS, the efficiency was found to be sufficient for all the volumes studied, while the initial volume was 150 mL in optimization studies, while 300 mL samples were preconcentrated in application studies to natural water samples.

4.9. Findings

Conductivity measurements of the obtained AC's were made. The data are in Table 4.1 Conductivity values for activated carbon were obtained using various conditions of Olive seed.

The conductivity of our sample was measured by the GW Lnstek LCR-811OG instrument and our results were shown in Table 4.1. The instrument consisted of two electrodes that were immersed in the sample and the frequency is stabled at 10 MHz. The active carbon was measured according to the sulfuric acid concentration (H_2SO_4), time for stirring, and pyrolysis temperature.

Three different H₂SO₄ conc. (10, 25, 40%) were used for the preparation of activated carbon. Generally, the time of stirring sample was found at 4, 8, and 16, whereas the pyrolysis temperatures were about 550 and 650. When the stirring time was equivalent to 4 and 8 for both temperatures for all H₂SO₄ the was not found the favorable connectivity, while by increasing the stirring and higher temperature (650 °C) the conductivity was increased. The bast conductivity was equal to 7×10^{-5} which are found at 16h for stirring time, 650 °C for temperature, and the conc. for H₂SO₄ is 25%. All results were compared with commercial activated carbon.

Table 4.1. Conductivity values found for ACs obtained from the Olive seed

H ₂ SO ₄ Conc. %	Stirring Time, h	Pyrolysis Temp. °C	Conductivity Siemens
10	4	550	1x10 ⁻⁶
25			3.0x10 ⁻⁶
40			2.0x10 ⁻⁶
10	8		2x10 ⁻⁶
25			4.0x10 ⁻⁶
40			3.0x10 ⁻⁶
10	16		4x10 ⁻⁶
25			7x10 ⁻⁶
40			5x10 ⁻⁶
10	4	650	4x10 ⁻⁵
25			6x10 ⁻⁵
40			5x10 ⁻⁵
10	8		5x10 ⁻⁵
25			7x10⁻⁵
40			5x10 ⁻⁵
10	16		6x10 ⁻⁵
25			7x10⁻⁵
40			6x10 ⁻⁵

4.9.1. Characterization of Synthesized Adsorbents by FTIR

The FTIR spectra were represented for raw material. activated carbons produced from biowastes modified with sulfuric acid and synthesized after pyrolysis and commercial activated carbon are given in Figure 4.7 , Figure 4.8, Figure 4.9, Figure 4.10, Figure 4.11, Figure 4.12, and Figure 4.13.

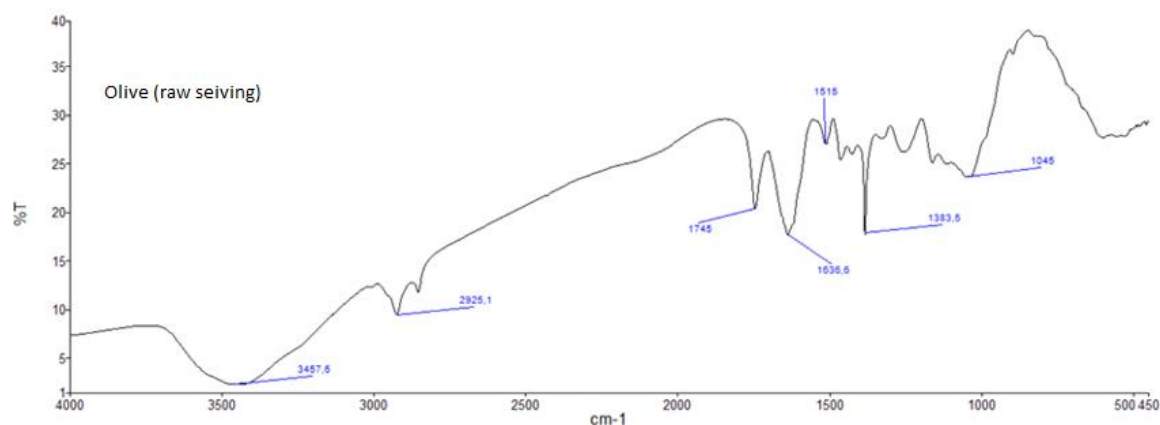


Figure 4.7. FT-IR spectrum of raw Olive seed after grinding and sieving

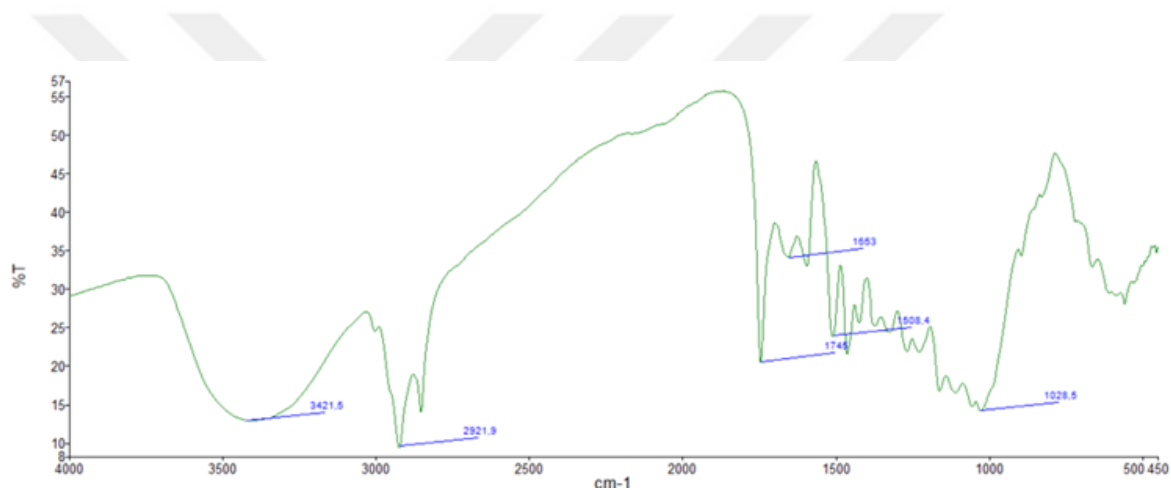


Figure 4.8. FT-IR spectrum of Olive seed after modification and before pyrolysis

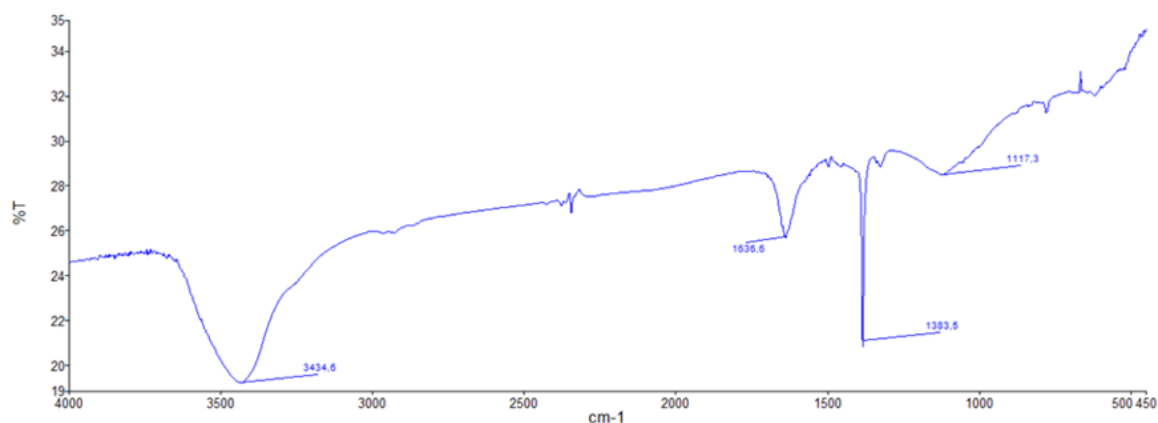


Figure 4.9. FT-IR spectrum of Olive seed after modification and before pyrolysis 650°C

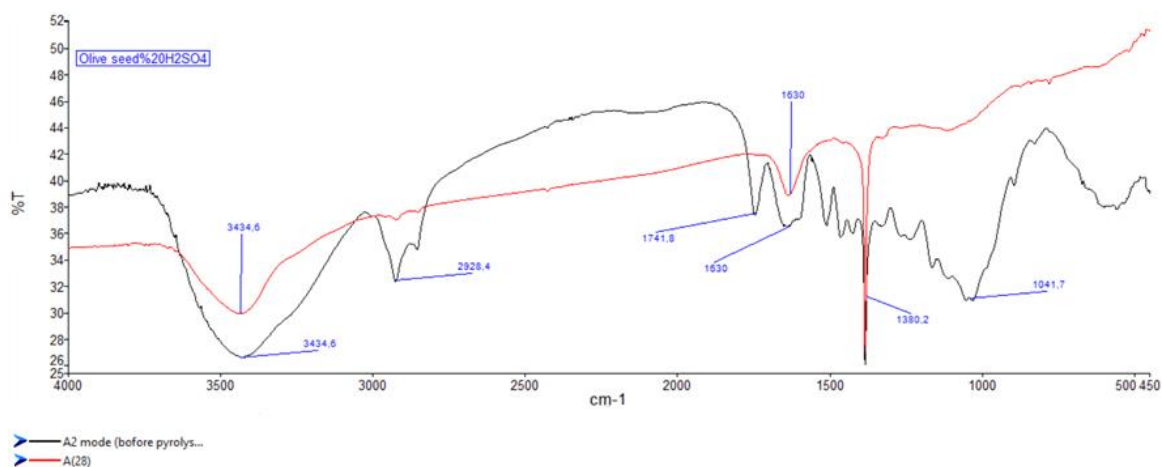


Figure 4.10. FT-IR spectrum of Olive seed modification (and 20% H_2SO_4 before pyrolysis at 650 °C)

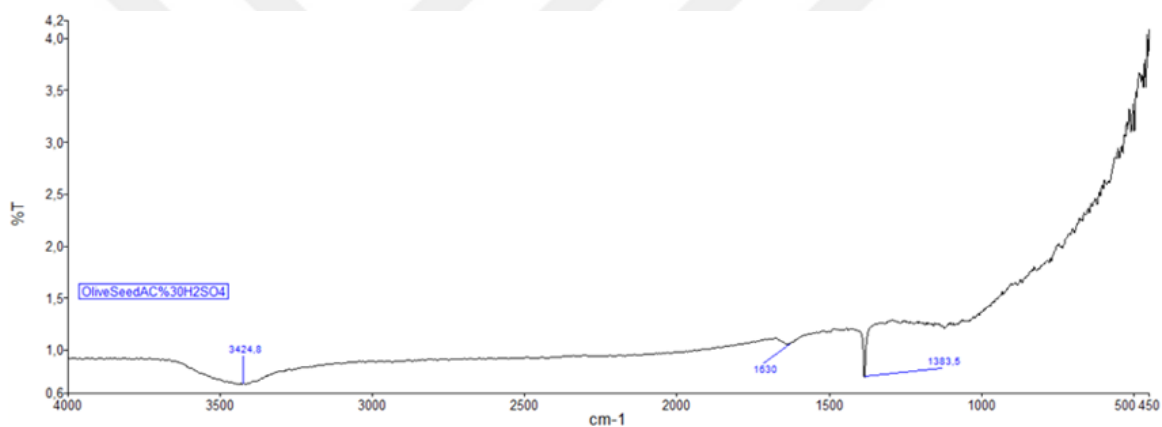


Figure 4.11. FT-IR spectrum of olive seed after modification (30% H_2SO_4 before pyrolysis at 650 °C)

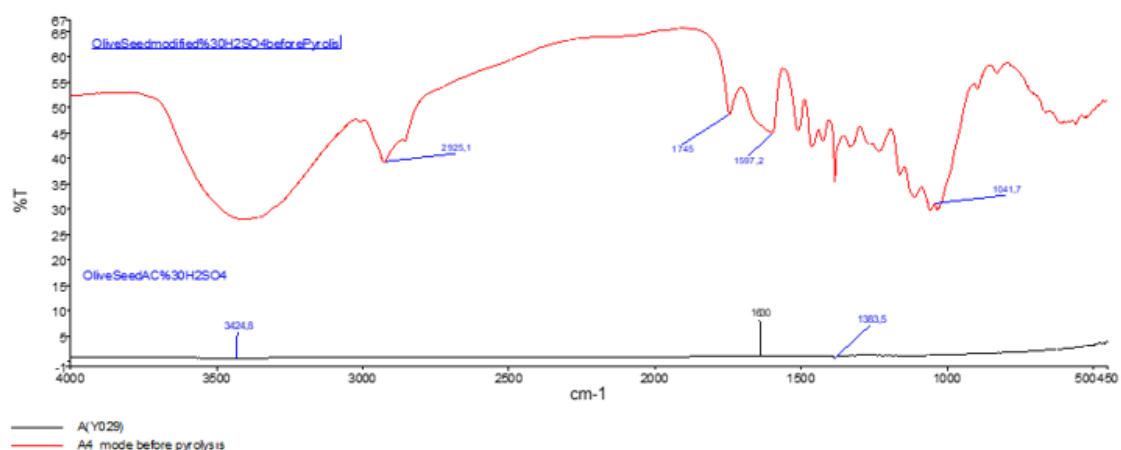


Figure 4.12. FT-IR spectrum of olive seed modification (30% H_2SO_4 before pyrolysis at 650 °C)

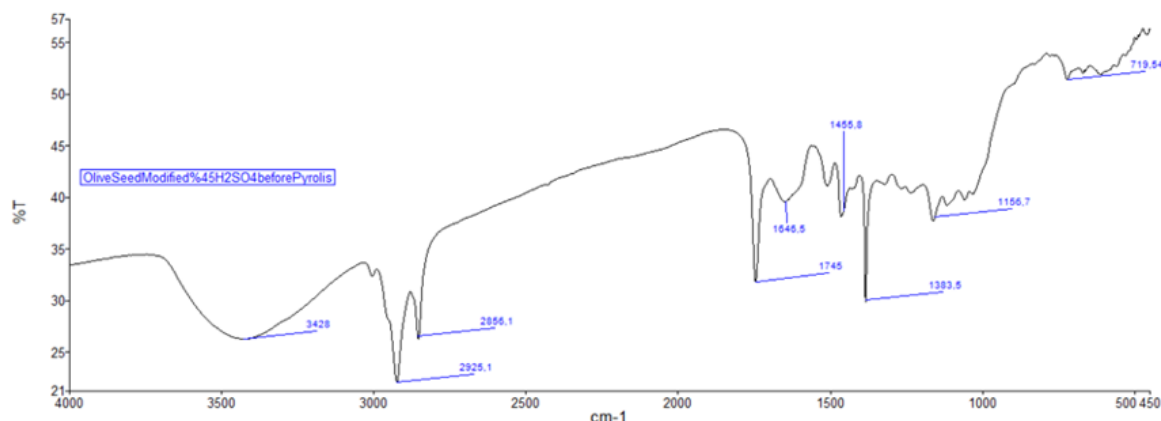


Figure 4.13. FT-IR spectrum of olive seed modification (45% H₂SO₄ before pyrolysis at 650 °C)

The FTIR spectra for raw olive seed were present in Figure 4.7. The peaks were observed 1045, 1383.6, 1515, 1636.6, 1745 cm⁻¹. The peaks of 2925.1 and 3457.6 are assigned. The FTIR spectra in Figure 4.8 after modification and before pyrolysis the C = O peak stretching and sharp at around 1745cm⁻¹, and Figure 4.10 for commercial activated carbon It is similar to the spectrum in FTIR spectra of AC obtained from Olive seed modified with H₂SO₄. strong band OH- peak in the range of 3000 - 3600 cm⁻¹, aliphatic C - H in the range of 2900 - 3000 cm⁻¹ The peak of the stretching, vibrations are C = O (ketone, aldehyde, lactone, etc.) around 1600 cm⁻¹ carboxyl groups) stretching vibration and C=C aromatic stretching vibration, around 1400 cm⁻¹ In addition to the C - N stretching vibration, the aromatic C=C stretching as a result of the formation of activated carbon vibration is observed. These peaks come from the peptide bonds of the proteins in the structure of biowaste.

Its severity decreases after activation on raw Olive seed in 1383.6cm⁻¹, on the other hand, C - O - C etheric stretching vibrations originating from the cellulosic structure are seen. Still, after activation, the intensity of the C - C stretching vibrations increased and shifting is compatible with the formation of activated carbon. The FTIR spectrum of commercial activated carbon is given in Figure 4.9. With this spectrum, When the activated carbons are compared in terms of their FTIR spectra, these activated carbons are almost OH- vibration at approximately 3400 cm⁻¹ in all, aliphatic C - H stretching vibration at 2850 cm⁻¹, There is C = O vibration at 1650 cm⁻¹ and C - O vibration at 1100 cm⁻¹.

In figure 4.7. the shows different peaks which are 1045, 1383.6, 1515, 1636.6, 1745, 2925.1, 3457 cm⁻¹, respectively. 1045 cm⁻¹ is a very low peak indicate to the C-O and C-H the sharp band appears in the 1382 cm⁻¹. 1515cm⁻¹ The low peak indicated the N-H bend. The carboxylic function groups appeared in this spectrum around 1636.6. 1745 cm⁻¹ which is a medium sharp peak indicate of presence (ketone, aldehyde, ester). 2925.1cm⁻¹ which is a weak bend indicated to the C-H stretching. 3457cm⁻¹ the broad peak presence OH.

In Figure 4.8. shows different peaks which are 1028.5, 1508.4, 1653, 1745, 2921.9, 3421.5 cm^{-1} , respectively. 1028.5 cm^{-1} is a very low peak indicating to the C-H bending and C-C the low band appears in the 1508.4 cm^{-1} . 1653 cm^{-1} The low peak indicated the C=O stretching bend. In figure 4.9 C-O is a very low peak appearing in the 1117.3 cm^{-1} . In figure 4.10 some peaks have been removed compared to the previous figure due to the ratio of concentrated sulfuric acid. The carboxylic function groups appeared in this spectrum around 1630. In figure 4.11 we have only three peaks (1383.5, 1630, 3424.8) we are already described it.

Figure 4.12 compared olive seeds modification 30% H_2SO_4 before pyrolysis and Olive seeds AC 30% H_2SO_4 . 1041 cm^{-1} is a very low peak indicated to the C-O. C-C the low band appears in the 1507.2 cm^{-1} . the olive seed AC has only three peaks compared to olive seeds modification, and each one peaks very low. in Figure 4.13 the peak is 719.54 cm^{-1} in the region fingerprint. 1455.8 cm^{-1} medium vibration bending indicated to the (-C-H). The 2856.1 cm^{-1} low peak indicated the C-H stretching bend.

4.9.2. Characterization of the obtained activated carbons by SEM

In this study, SEM images of the adsorbent of activated carbon synthesized by pyrolysis after modification with sulfuric acid are given in Figure 4.14 a,b,c.

Figure 4.14a before elements adsorption at 2500 X zoom. Figure 4.14 b-Before elements adsorption at 5000 X zoom. Figure 4.14c- before elements adsorption at 10000 X zoom. Figure 4.14d- Before elements adsorption at 20000X zoom. Figure 4.14e- Before elements adsorption at 40000X zoom. Figure f- Before elements adsorption at 60000X zoom.

SEM images of the structure of the adsorbent modified with H_2SO_4 using olive seeds are shown in.

When the adsorbent structure is examined, it is seen that it has an anisotropic particle size. The non-homogeneous structure of the particle sizes created different voids on the particle surface. When these voids are detailed with 10000, 20000, and 60000 magnifications, it is seen that the material has macro voids that can show adsorption. Again, it can be said that a strong adsorbent is obtained when interpreted with the adsorption results.

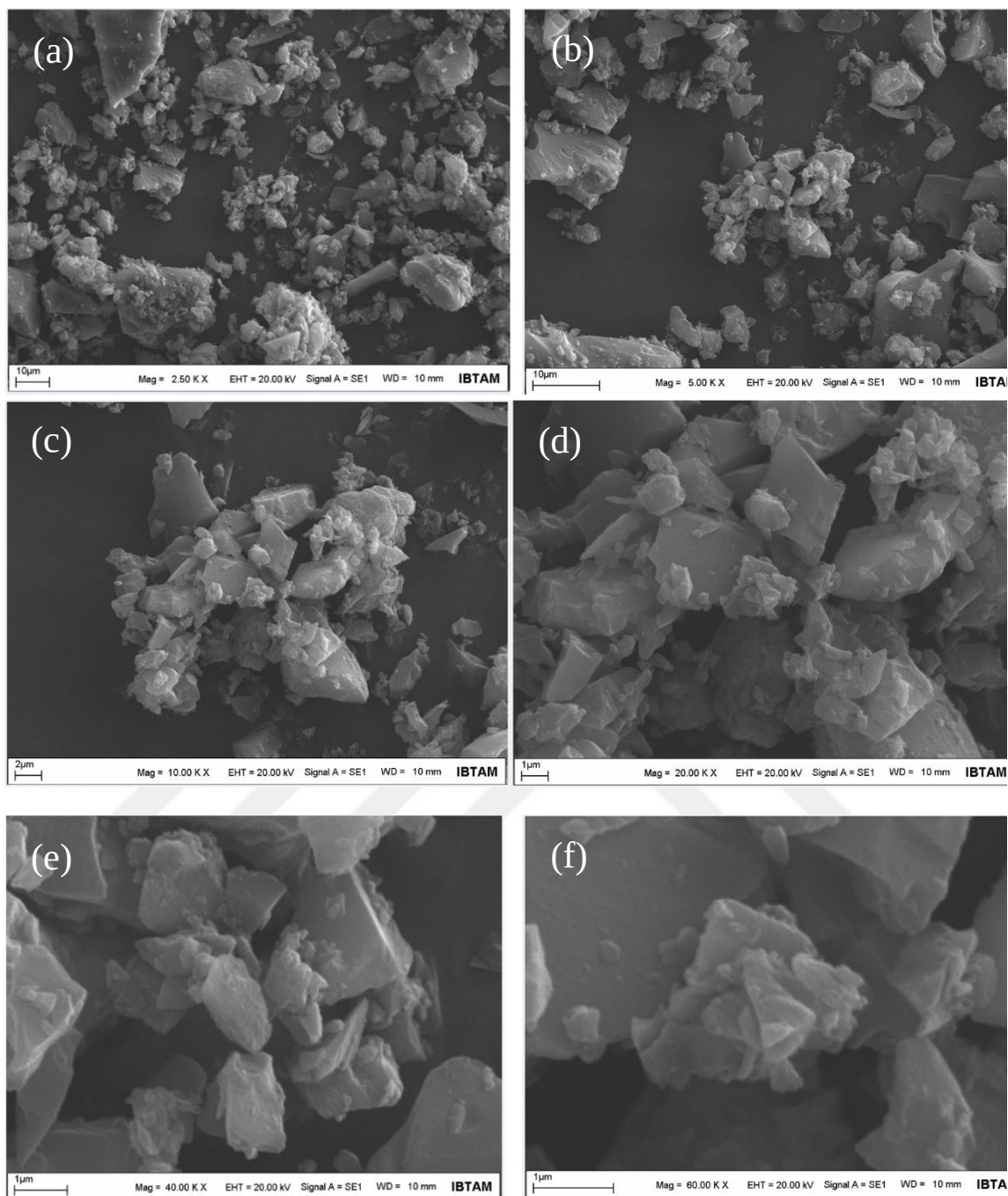


Figure 4.14. AC-SEM images modified with 25% H_2SO_4 for 16 hours

4.9.3. Characterization of the synthesized adsorbent with BET

To assess the porosity of carbonaceous adsorbents, such as surface area, pore size, and pore volume, nitrogen adsorption is one of the most used methods. Adsorption–desorption isotherm data from the BET method Figure 4.15 reveals that the optimized AC corresponds to type I isotherm characteristic of activated carbons as defined by the International Union of Pure and Applied Chemistry (IUPAC). For microporous substances with narrow pores and tiny exterior surfaces, type

I isotherms show that uptake is limited by micropore volume rather than just the effective surface area. The surface area is found to be 180 m²/cm.

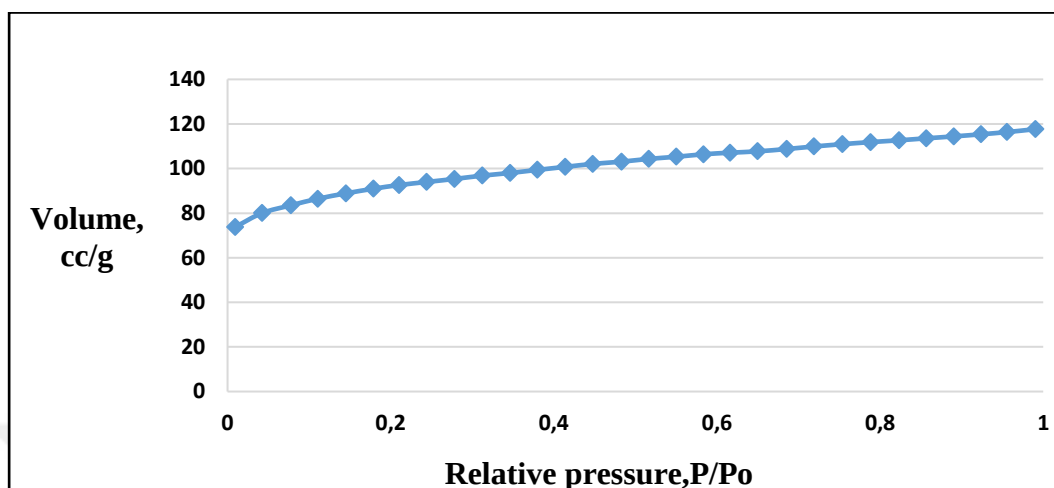


Figure 4.15. The adsorption isotherm (N₂) of the activated carbon from Olive seed

4.9.4. PH effect on Preconcentration

The process steps in Figure 4.2 were applied separately to the activated carbon samples obtained under optimum conditions by adding model metal solutions at different pH Figure 4.16. The studies of the element with high yield value (Pb) are detailed.

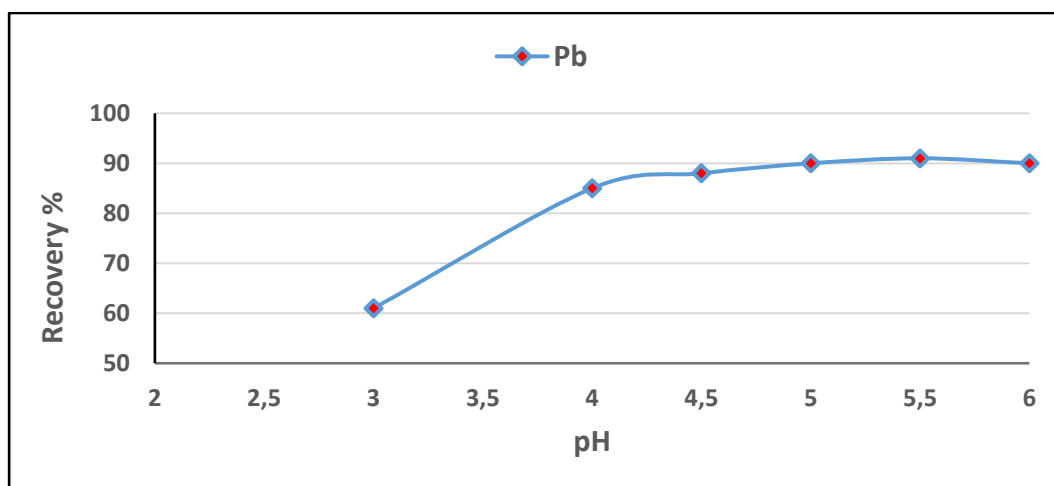


Figure 4.16. pH- yield vibration for Pb

4.9.5. Effect of stirring time on Pre-concentration process

From the graphs related to optimum pH values, it was decided to carry out further studies only for Pb. As seen in Figure 4.17, it is understood that the stirring time of 30 minutes is sufficient

at constant values of pH=3 for Pb, different stirring times between 15-60 minutes applied with the steps in preconcentration step.

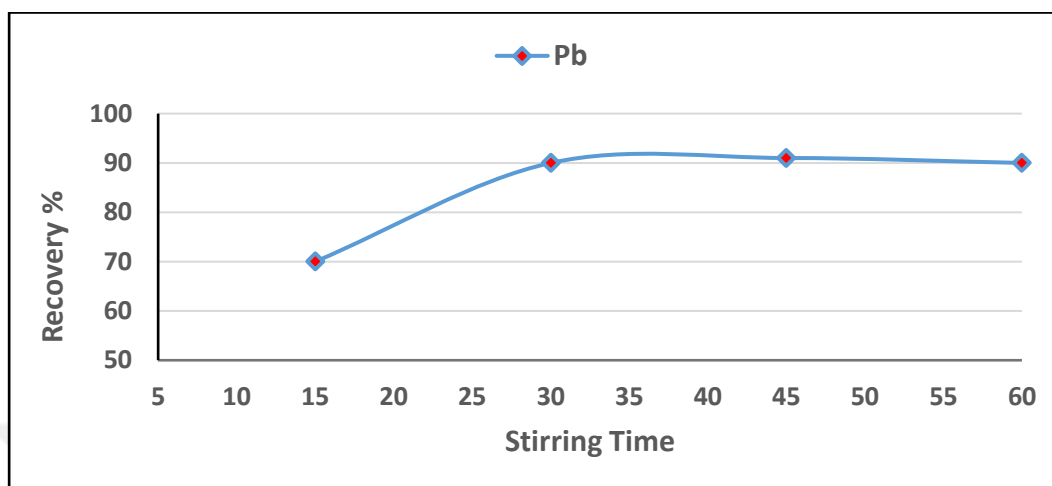


Figure 4.17. Stirring time – yield vibration for Pb

4.9.6. Application of the Optimized Method to Natural Samples

Figure 3.1. for water samples obtained from different regions under optimized conditions for Pb, the scheme shown in has been applied. For this purpose, 300 mL of water samples were studied. Figure 4.3, Figure 4.4 ,Figure 4.5 , Figure 4.6 Element concentrations in the samples using the calibration charts given in the range calculated. The results found are given in Table 4.2. From the results found, the limit of Pb concentrations allowed by the World Health Organization was observed below the levels.

Table 4.2. Table The obtained results for Lead (Pb) concentration in natural water by using the developed method.

Sample	Pb, ppb
Tape water	2.1 ± 0.3
Keban Dam Lake (Firat river)	1.3 ± 0.2
Hazar Lake	1.5 ± 0.2

Due to the increase in urbanization, as a result of the widespread use of industrial products, ppb the presence of toxic trace metals concentrations at the same level is mandatory due to health risks is seen. Sensitivity of AAS and AES methods available in many laboratories' ppb Insufficient to detect many toxic metals at high levels. Therefore, preconcentration methods use remains up-to-date. This study, it is aimed to use Olive seeds, which are eco-friendly as well as being economical.

It is a solid-phase extraction-based method containing no ligands in the preconcentration step. The precursor method was developed.

For this purpose, Olive seeds are mixed with sulfuric acid in different concentrations. was modified with and at different stirring times. Active in nitrogen gas environment at 550 and 650°C modified biomass converted to carbon by conductivity, FTIR, SEM, and BET methods. characterized by its use. Again, in the preconcentration step, the ppb level of toxic metal Factors similar to pH and stirring time were investigated for the determination of ions.

The characterization of the synthesized activated carbons was elucidated by FTIR and the changes in the bonds. interpreted and carbon formations confirmed. Raw Olive seed and chemically modified Especially the peaks at 1745 cm^{-1} of the intermediate product FTIR spectra are in the FTIR spectra of AC, has disappeared. Voids in structures and regions suitable for metal adsorption using SEM viewed. It was found that the adsorbent obtained from the BET plot was in type I structure. Obtained In SEM images, even at the lowest magnification, there are gaps in the structure, and increasing at magnification, the images of these cavities become more evident. From the results found, it was found that Pb was adsorbed at pH 5.

found below. Therefore, more detailed studies were performed for Pb. For the other optimized parameter, stirring time, 60 min for Pb. It was observed that the time was sufficient. In the studies carried out to find the optimum initial volume, the 300 ml volume was studied in terms of efficiency. Since it is the same as the other volumes, 150 mL in optimization studies, Pb determination studies, a volume of 300 ml was used. ICP-MS was used as the analysis technique. ICP-MS includes preconcentration of 300 mL of solution (or natural water) to a final volume of 5 ml Using the method, the LOD, and LOQ values of the method are 0.02 and 0.06 ppb for Pb, respectively.

This technique developed in this way, the dam collected around Elazig, it was applied to the determination of Pb in natural water such as lake and river. From the results found, the studied lead concentrations in waters are in the range of 1.3 - 2.1 ppb for Pb. observed. Considering these data, the World Health Organization (WHO) and the Ministry of Health found them to be below the permissible limit concentrations. In conclusion, the results observed in the studied samples are consistent with the literature. Supply from biowaste Pb in $\mu\text{g/kg}$ or it was found that $\mu\text{g/L}$ concentrations precipitated to ppm level with 90% efficiency. The developed method is in addition to being environmentally friendly and economical, is also beneficial in terms of evaluation of natural wastes considered as an advantageous method.

5. CONCLUSIONS

In this thesis; the Olive seed is used for the removal of Pb toxic elements from drinking water by converting Olive seed to AC by modifying with Sulfuric acid of different concentrations and activating with acid; characterized with FTIR, SEM, and BET techniques. Then preconcentration steps for the adsorption of these toxic elements on AC with different pH, stirring time for the determination of optimum pH, and stirring time to determine the ppb levels of toxic elements such as Pb which is the aim of this study.

In the end, it was found that the Olive seed is abundant biomass for adsorbent of this element on it; and the data measured with ICP-MS and found optimum pH was pH=5 for Pb optimum stirring time was 30min and LOD-LOQ (0.02-0.06) ppb respectively; the method applied for the determination and removing toxic elements was a model aqueous solution.

Related with the other elements including Cr, Ni and U using the same adsorbent, low yields were obtained and thus no further studies have been conducted for those elements.

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