



**PREPARATION OF ACTIVATED CARBON FROM
AGRICULTURAL WASTES AND REMOVAL OF
DIMETHOATE FROM WATER USING THIS
ACTIVATED CARBON**

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MASTER THESIS
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July 2021**

I certify that in my opinion the thesis submitted by Ahmad Mohamed Ramdan ABUDAIA titled “PREPARATION OF ACTIVATED CARBON FROM AGRICULTURAL WASTES AND REMOVAL OF DIMETHOATE FROM WATER USING THIS ACTIVATED CARBON” is fully adequate in scope and in quality as a thesis for the degree of Master of Science.

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Ahmad Mohamed Ramdan ABUDAIA

ABSTRACT

M. Sc. Thesis

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Water pollution, a worldwide problem, is caused by the increase in chemicals used by industrial enterprises and the rapid progress in the agricultural sector. Pesticides used to combat harmful organisms in agricultural areas have an important share in water pollution. The aim of this study was obtain activated carbon from agricultural waste, corncob and rice husk and to remove dimethoate from water by using these activated carbon obtained from agricultural wastes. Thus, agricultural wastes will be transformed into valuable products. Corncob and rice husk are suitable materials for obtaining activated carbon due to their structure. The raw material to be activated carbon was washed with distilled water to clean the corncob and rice husk and dried by oven at 105 ° C for 24 hours. Then, carbonization process was carried out by waiting for 1.5 hours at 450 degrees in the furnace where nitrogen gas is passed through. The material obtained was crushed and kept in KOH solution. The resulting

mixture was heated at 780 degrees for 1 hour to activate. The physical properties of the obtained activated carbon was determined using Scanning Electron Microscopy (SEM). The mass percentage was determined using EDAX spectra. Dimethoate was removed from the dimethoate solution prepared with deionized water in different concentrations using the obtained activated carbon. The Batch adsorption were investigated using dimethoate solution of 10 to 100 $\mu\text{g/L}$ concentrations. The obtained data from experiments showed that activated carbon obtained from corncob and rice husk can be used as an activated carbon to remove the dimethoate from water.

Keywords : Dimethoate, Corncob, Rice Husk, Activated Carbon, Sorption, Characterization.

Science Code : 90314

ÖZET

Yüksek Lisans Tezi

TARIMSAL ATIKLARDAN AKTİF KARBON ELDE EDİLMESİ VE BU AKTİF KARBONLA SULARDAN DİMETHOATE’NİN GİDERİLMESİ

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Dünya çapında bir sorun olan su kirliliği, sanayi işletmelerinin kullandığı kimyasalların artması ve tarım sektöründeki hızlı ilerlemeden kaynaklanmaktadır. Tarım alanlarında zararlı organizmalarla mücadelede kullanılan pestisitler, su kirliliğinde önemli bir paya sahiptir. Bu çalışmanın amacı, tarımsal atıklardan, mısır koçanı ve pirinç kabuğundan aktif karbon elde etmek ve tarımsal atıklardan elde edilen bu aktif karbonları kullanarak dimethoatı sudan uzaklaştırmaktır. Böylece tarımsal atıklar değerli ürünlere dönüşecektir. Mısır koçanı ve pirinç kabuğu, yapıları gereği aktif karbon elde etmek için uygun malzemelerdir. Aktif karbon olacak hammadde mısır koçanı ve pirinç kabuğunun temizlenmesi için distile su ile yıkandı ve 105 °C'de 24 saat etüvde kurutuldu. Daha sonra nitrojen gazının geçtiği fırında 450 derecede 1.5 saat beklenerek karbonizasyon işlemi gerçekleştirilmiştir. Elde edilen malzeme ezildi ve KOH çözeltisi içinde tutuldu. Ortaya çıkan karışım, aktive etmek için 1 saat 780 derecede ısıtıldı. Elde edilen aktif karbonun fiziksel özellikleri, Taramalı Elektron Mikroskobu (SEM) kullanılarak belirlendi.

Kütle yüzdesi, EDAX spektrumları kullanılarak belirlendi. Elde edilen aktif karbon kullanılarak farklı konsantrasyonlarda deiyonize su ile hazırlanan dimethoate çözeltilisinden dimethoate uzaklaştırıldı. Batch adsorpsiyonu, 10 ila 100 µg/L konsantrasyonlarda dimethoate çözeltilisi kullanılarak araştırıldı. Deneylelerden elde edilen veriler, mısır koçanı ve pirinç kabuğundan elde edilen aktif karbonun, dimetoatı sudan uzaklaştırmak için aktif karbon olarak kullanılabilceğini göstermiştir.

Anahtar Kelimeler: Dimethoate, Mısır Koçanı, Pirinç Kabuğu, Aktif Karbon, Sorpsiyon, Karakterizasyon.

Bilim Kodu : 90314

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PART 1

INTRODUCTION

1.1. OVERVIEW

Recently, the major studies focused on persistence methods and pesticide transmission in isolated operations including water or soil/sediment. However, little work has been implemented on pesticide existence in natural water-sediment operations. Understanding the pesticide activity in sedimentary phases and water must allow pesticide persistence in the environment to be forecasted. There is a need to conduct more research on the current irregular use of pesticides and the fate of pesticides in water-sediment to promote risk management, health and policy. Protection of plants has been widely and extensively used of pesticide in agriculture. Pesticides are commonly used not only in agriculture but also in homes and industry in order to avoid disease caused by insect-borne and/or fungal pests.

The use of any chemicals constitutes dangerous not only on human health but on non-target animals and the entire world. It is found that the continuous use of pesticides adds harmful contaminants to the soil, surface waters and groundwater and sediments

[1-5].

Pesticides can move to untargeted regions by different transportation means including water, wind and soil particles. Soil particles that sorb pesticides can move to the water marine sediment system easily and quickly. Many processing processors are likely to happen in water-sediment systems including microbial degradation, volatilization, photolysis, animal or plant absorption, soil/sediment sorption/desorption and hydrolysis [6-7].

These processes are affected by the environmental features of pesticides and the physicochemical properties of pesticides [6]. The concentration of pesticide in various environmental sections have been forecasted by the use of pesticide fate simulation of new pesticide and currently used pesticide. The predicated model differs from the measured results [8].

Generally, field data are necessary in the model prediction in order to verify the results and ensure that they are accurately similar to the ground status. Input data uncertainty and model parameter uncertainty represent a type of variance. For instance, the pesticide fate in the environmental system is a dynamic process that differs from one pesticide to another and field to field which makes half-lives on a pesticide basis are inadequate to determine all the environmental conditions [9]. Bromilow et al. (2006) proved that laboratory experiments in the natural water system may accurately reproduce the pesticide fate such as pendimethalin, chlorotoruron, chlorpyrifos and isoproturon [6]. The findings of many studies do not clarify why some pesticides are successful while others are not. This refers that there is a need to further studies and researches to extrapolate the experimental results of complex field systems. Other benefits including timelines, repeatability and costs may emerge unless using the data which have been collected by the laboratory without needing to field data.

1.2. WATER, WATER RESOURCES AND WATER TREATMENT

Water is the most important element to the survival of all species and climate. The drinking water in the world is less than the total amount of freshwater. However, there is an uneven distribution of water around the world [10]. Therefore, this mismanagement has led to many problems, wars and conflicts in many parts of the world. Millions of people around the world lack access to and use clean waters [11]. Many people are unable to access clean water facilities and get rid of and treat wastewater and therefore many children will die. The risk of children's death will decrease and the medium of their age increases only when enough and clean waters are collected. Water lack is an expected issue. Moreover, the water scarcity lack has been calculated and amounted to be about EUR 485 million per year. Alternatively,

the use and supply of water are closely associated with living circumstances. The consumption of waters varies in different countries where the United States consumes 9,718 m³/inhab per year, Mozambique consumes 8,870 m³/inhab per year and Spain consumes 2384 m³/inhab per year.

Spain is a hot country with few environmental problems because of renewable resources and uncontrolled precipitation of rain. The average per capita (m³/inhab year) water withdrawal in the United States and Mozambique is 1583, 46.05, and 694 respectively. This refers that Spain will extract a high amount of water because of the country's condition despite that it is calm in Mozambique and the United States. The population growth, increasing irrigation and industry create demand differences and water supply. This may cause conflicts, water shortages, increasing concern of people and additional contaminating [10]. In this case, new measurements must be taken in order to enhance the health of people, the environment and livestock.

1.3. EMERGING AND ORGANIC MICROPOLLUTANTS

During the last decades, the environmental effects of the organic compounds have been increased and the emerging pollutants have been taken into account. Food additives personal care products, pesticides, organic compounds and medicines are separated into various groups. Most of these compounds are rapidly introduced to the marine environment because they are soluble in water and are poisonous to most marine organisms. These organisms may work as bio accumulators which help them to enter the chain of human foods. The growth, reproduction, genetics and development of these molecules are affected by the long periods of interaction with many organisms [12].

1.4. ORIGINS AND FATE OF ORGANIC MICROPOLLUTANTS

The fears faced by the emerging contaminants in the environment need a high knowledge of their origins, final destination, sources and transformation in order to find ways to accomplish measure to decrease their effect on the environment. Figure 1.1 shows the complex pathways, origins and special sources of new pollutants

consumption in addition to their primary and final sources and contaminants travel in many directions. This can be noticed in many directions but the entire contaminants have the same goal which is water treatment in a WWTP.

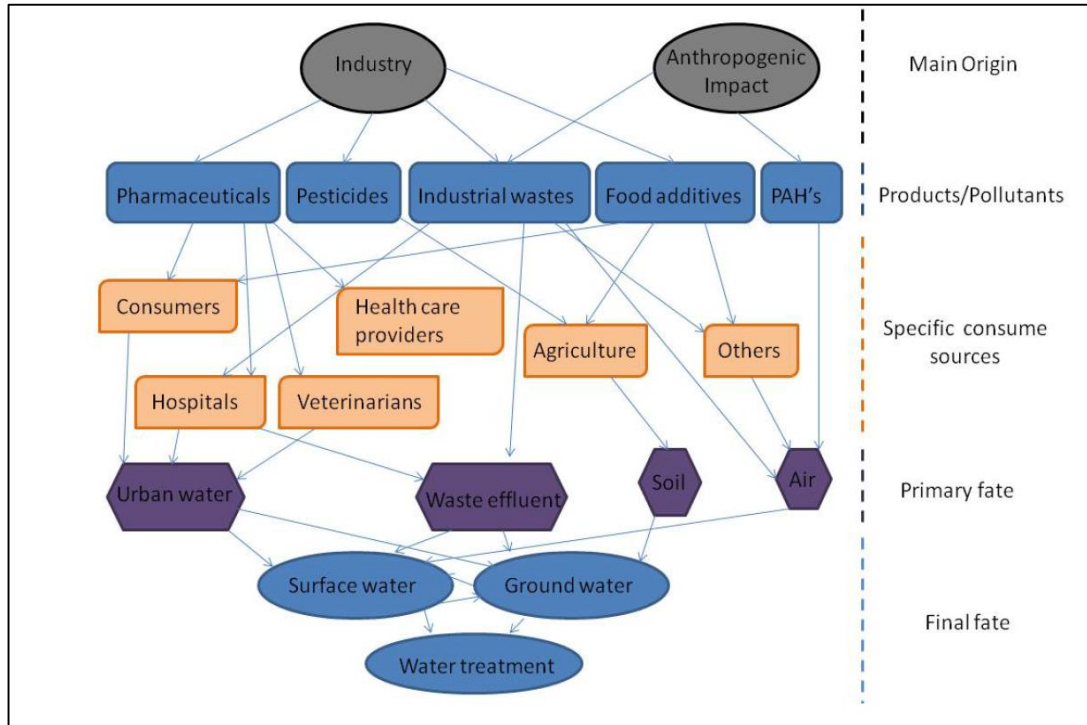


Figure 1.1. Emerging pollutants pathway [13].

The main source for all of these pollutants is industrial activities. Similar compounds are developed in many ways such as cosmetics and pharmaceutical industries, agricultural food industries or they may be released to the media in the form of gaseous or liquid effluents not correctly treated. Before that, for each party, a specific source of consumption is high different. In terms of medicine and pharmaceuticals (veterinarians and humans), humans and animals are taken, metabolized in their bodies and recoiled to the urban wastewaters plant by the sweating, excretion and urine. In health care environments (orphanages, hospitals, doctors and dentists), the same fate and direction are obstacles by the compounds where the patient will get many types of quantities of drugs and discard them (urine and excretion). There are high amounts of them are discarded in sewage, garbage and chemist. The contaminants of hospital take many paths but all of which end in the hospital effluent. Some of the hospitals consist of water treatment facilities but not all of

them. Drugs, pharmaceuticals and pesticides which discard in the garbage will collect on the river surface or land because of rain or dissolution [14].

The micropollutants are caused by other sources such as walls, cruise ships and underground laboratories (such as drugstores manufacturers and other materials). As clarified in Figure 1.1, the wastewater treatment plant (WWTP) is the final destination for all emerging contaminants. During the treatment process, various compounds in the WWTP are retained on the sludge, biodegraded or precipitated. Nevertheless, other chemical contaminants may be found in the rivers or effluents of treatment plants. Aquatic types which join the chain of food will bioaccumulate and constitute a threat to the health of humans.

1.5. ROUTES OF EXPOSURE TO PESTICIDE

As shown in Figure 1.2, pesticides may inject or released across the dust, fine mist, dermis and injection-induced inhalation. Pesticides can be found in polluted air, fruit and beverages where they can be placed on the skin of humans, bees and plants (Figure 1.3) [15].

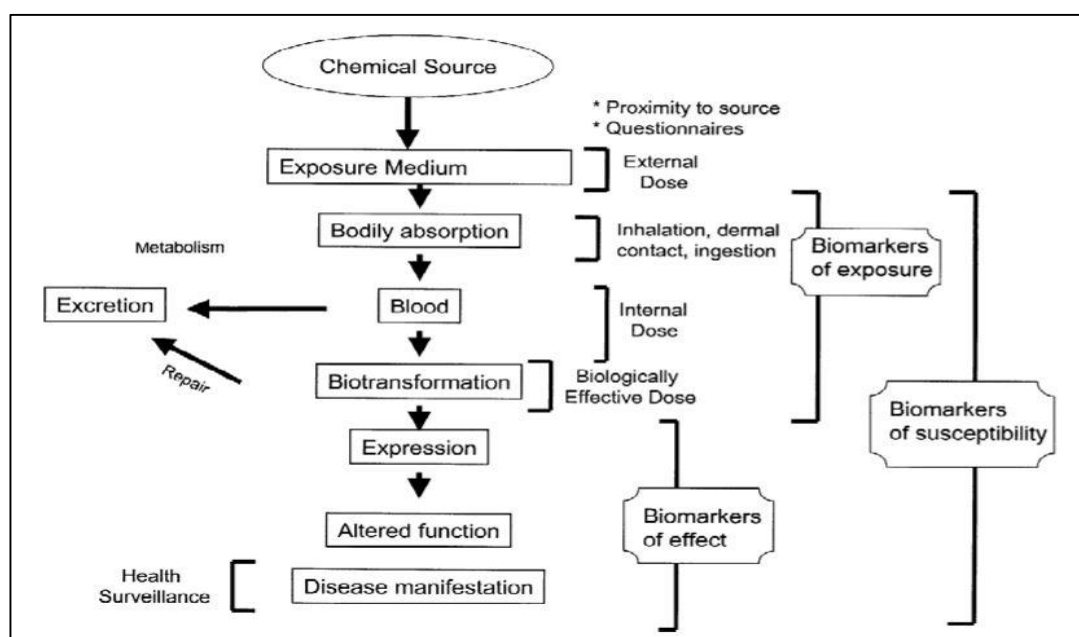


Figure 1.2. Pesticide pathway of exposure and health effects.

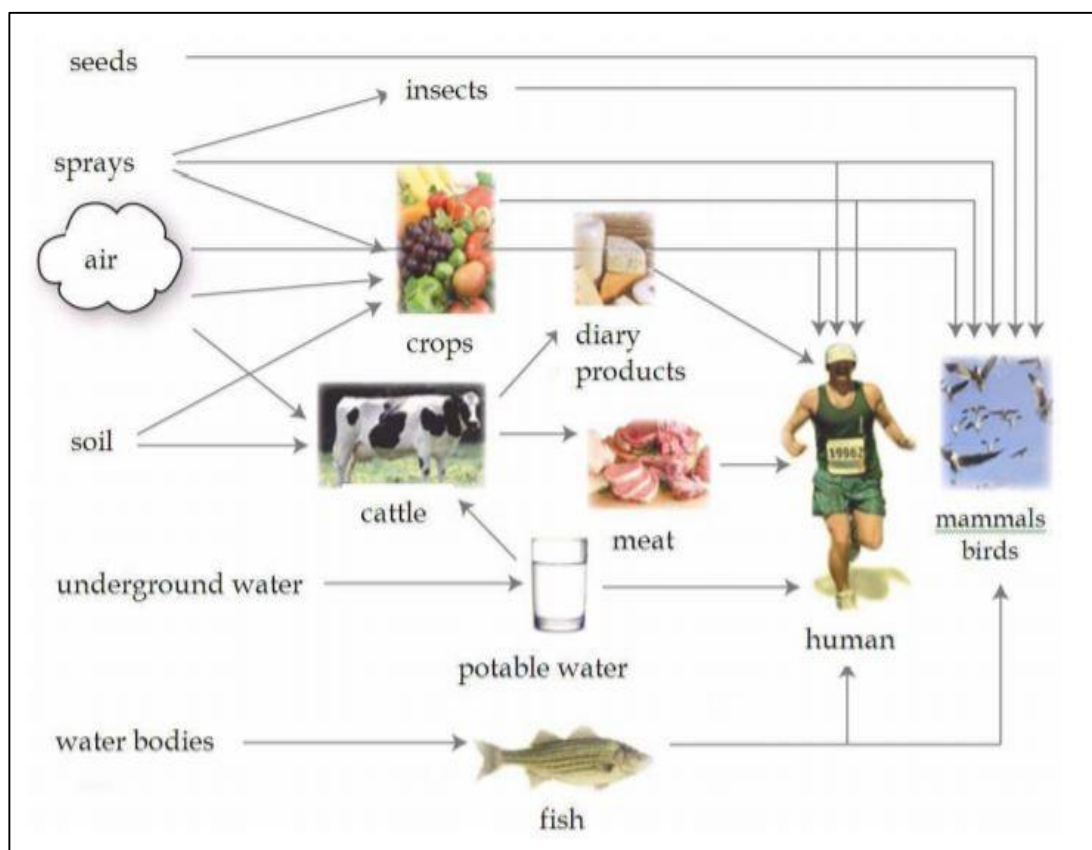


Figure 1.3. Routes of exposure to OPs [15].

1.6. AIM OF THE STUDY

The main goal of this study can be summarized as follows:

1. Look to the use of corncob adsorption to remove the pesticides from water.
2. Decide the best sorption quality by various adsorbents.
3. To look at the following:
 - i. The impact of adsorbate concentration and sorbent contact time.
 - ii. The impact of pH on pesticide adsorption.
 - iii. The impact of temperature on pesticide adsorption.
 - iv. Adsorption equilibrium time of chosen pesticides into potassium hydroxide corncob.
 - v. Adsorbent dosage impact.
 - vi. Determining the kinetics and adsorption temperature.

PART 2

LITERATURE REVIEW

Organophosphorus Pesticides (OP) are widely used by agriculturalists [16]. Dimethoate is considered an important OP that is used for field and fruit crops because of the low persistence of agricultural production and biodegradation [17]. The chemical composition of dimethoate is shown in Figure 2.1. However, the high use of dimethoate may cause the accumulation of excess waste through the food chain in the environment and human body [18-19]. So, the efficient removal of Ops is important to control the compounds of the environment and food particularly potable water resources. One of the key methods to remove pesticides from waters is the adsorption of many types of materials [20]. The literature includes many studies about the absorption of Ops mineral surface [21-22] and carbon dependent materials in addition to graphene materials [23-25]. Currently, nanoparticles and activated carbon are used in environmental remediation such as water purification by removing OPs as a result of the advantages provided by the nanomaterial chemistry if compared with conventional systems [16,26].

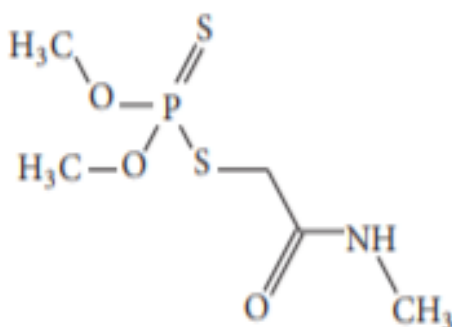


Figure 2.1. Dimethoate.

2.1. DIFFERENT METHODS OF TREATMENT

The following methods of treatment are used in wastewaters and drinking waters by decreasing dynamically the pesticide concentration before human ingestion or discharge.

2.1.1. Chlorination

This method is widely used to purify the water to deactivate the unwanted microorganisms and decreasing the concentration of pesticide by chemical oxidation. The derivatives of chlorine or pure chlorine are applied to the water resources in different concentrations [27]. Free chlorine is found in the form of pure chlorine (Cl_2) dissolved in water, hypochlorous acid ($HOCl$), or the hypochlorite ion (OCl^-) that is formed when hypochlorous acid separates because of pH. [28].



2.1.1.1. Feasibility and Economics

The chlorination process is considered one of the most cost-effective treatment options. Therefore, this process is usually used in treatment plants of wastewaters and drinking waters. Nevertheless, to satisfy the suitable limits, the concentration of residual chlorine should be reduced before discharging to the public water supply systems. The high amounts of chlorine may be harmful because various compounds of chlorine have proven their carcinogenic [29,27].

2.1.1.2. UV-photolysis

Another important method to reduce the pesticide levels in water and wastewaters to acceptable levels is the use of UV treatment. UV light is a form of electromagnetic radiation and its wavelength is ranging between 100-400 nanometers. UV exists in four groups (200 to 100 nm) as UV-A (400 and 315 nm), UV-B (315 to 280 nm), UC-C (280 to 200 nm) and vacuum UV. The low-pressure mercury lamp (LP-UV) which is used in water treatment produces UV at a wavelength of 253.7 nanometers while the medium-pressure mercury lamp (MP-UV) produces UV and visible light ranging between 200-800 nanometers. The output of power for LP-UV is up to 0.4 kW whereas the output of power for MP-UV lamps is up to 30 kW. UV treatment is considered an Advanced Oxidation Process (AOP) which causes contaminants and organic photodegradation in water. Photolysis is the degradation of contaminants into simpler compounds because of exposure to UV. Generally, photolysis arises at a similarly low rate with UV only, hydrogen peroxide is generally added to offer active radicals of hydroxide which bind to contaminants and oxidize compounds in parallel and concurrent reactions. Photocatalysis is a term that is used to describe the addition of semiconductor catalysts to fasten the formation of active radicals of hydroxyl which target the substrate of pesticide. UV treatment provides many benefits such as the ability of full oxidation of organics in just a few hours [30].

2.1.1.2.1. Feasibility and Economics

Due to the high success of UV treatment, it is still used in water treatment plants over the last few decades. UV treatment is a common and widely used microbial method to deactivate pathogens and can also be used to decrease organic concentrations including pesticides. UV is considered a good selection of large-scale treatment facilities because of the increasing limits of stringent chlorine and related concentration reduction cost of chlorine treatment in addition to the possible dangers which chlorine gas store faces. Nevertheless, it consists high initial cost of investment with many resources.

2.1.1.3. Fenton Oxidation

Fenton method is another oxidation method used to degrade and treat pesticides as a part of the oxidative mechanism. In low pHs, this method is made up of iron salt and hydrogen peroxide (H_2O_2) [31]. Formation of strongly reductive hydroxyl, the iron salts work as a catalyst and increase the strength of the H_2O_2 . The radicals can oxidize other species which can be illustrated as follows [32]:



This pesticide treatment method includes many advantages such as simplicity, low cost, ease of use and a wide range of temperatures that can be used with this treatment method [32]. Nevertheless, the use of this treatment method causes the production of unwanted and harmful materials.

2.1.1.4. Ozonation

Ozonation is a common treatment method used widely in the eighteenth century. Currently, this treatment method is broadly used in United States, Europe and Asian countries. This method is a strong oxidation technique that includes forcing a form of oxygen across a contaminated sample of liquid [32,33]. Ozonation can oxidize various contaminants across the oxidation reaction. The agents which leave the solutions as gas besides the oxygen gas and excess ozone are denoted as byproducts. Nevertheless, some ozone is left in the solution after the ozonation process. The half-life of ozone in the water is about thirty minutes. Many methods are used to extract the ozone left in the solution. These methods include water agitation by a quick stir bar and place the solution in the sonication bath. In addition, the agitation may be used in water treatment plants on a much larger scale. Nevertheless, agitation can be implemented by the use of the turbulent flow of water instead of using a physical object to blend.

2.1.1.4.1. Feasibility and Economics

For many years, there are many types of research and studies have been implemented about the economic feasibility of using ozone in water treatment plants. Research performed by Spartan Environmental Technologies shows that ozonation in large-scale treatment plants needs liquid oxygen which is very expensive.

2.1.1.5. Reverse Osmosis

The reverse osmosis method is a water purification method that is used to purify the drinking water by the use of a semipermeable membrane. This method uses the applied pressure to resolve the osmotic pressure. The reverse osmosis method can remove the ions and molecules from the solutions such as pesticides and it is widely used in drinking and industrial waters treatment [34]. Consequently, the pure solvent can pass through the membrane whereas the solute is trapped on the pressurized side of it. The small components of solution pass through the pores (holes) of the membrane but the ions and larger molecules including solvent do not.

2.1.1.6. Feasibility and Economics

The household reverse osmosis units use a high amount of energy because of the low backpressure. Therefore, the system only covers 5-15% of the entering waters. The residual waters are disposed of as wastewaters. Since wastewaters include the rejected pollutants, this method is not practicable for household use. So, the transportation of these wastewaters to different environmental fields may cause damages. Moreover, reverse osmosis can extract beneficial minerals and harmful pollutants from the water due to its fine membrane structure. This process is considered a costly process and fouling of membrane may cause a big problem.

2.1.1.7. Adsorption

The absorption process is a mass transfer process where the material is transferred from the liquid phase to the solid surface and includes chemical or physical

interaction. The efficiency of this process is affected by the solid and liquid equilibrium in addition to mass transfer ratios. The absorption process can be separated into the following three phases:

1. Transfer the adsorbed molecules by the film which covers the absorbent;
2. Adsorption on the surface of particles;
3. Adsorption within the adsorbent particles.

The adsorption technique is divided into two classifications depending on the attraction mechanism between the adsorbate and adsorbent. Physical adsorption which is also called Van der Waal's adsorption and chemisorption is two types of adsorption.

2.1.1.7.1. Adsorption by Physical Means

The physical adsorption involves the interaction of Van der Waal forces. This phenomenon can be reversed easily. This type of adsorption involves heat adsorption ranging between 20–40 kJmol⁻¹. This adsorption process is multilayer and followed by a decrease in the adsorption system's free energy and entropy which make the mechanism reversible and exothermic.

2.1.1.7.2. Chemisorption is the Process of Absorbing Chemicals

A lot of activation energy is needed in the first step of the chemisorption process. The chemisorption does not look like the physical adsorption where it is permanent and needs monolayer adsorption. Recently, many low-cost adsorbent materials including modified biopolymers, the natural materials derived from the agricultural wastes, byproducts industrial and biomass have been developed and used to remove the pesticides from the contaminated wastewaters. The high percentage of adsorbents include complex porous structures and these pores with different forms and sizes. The complete porosity is usually divided into three classes: micropores (diameter, $d < 2$ nm), mesoporous ($2 < d < 50$ nm), and macropores (diameter, $d > 50$ nm). The adsorption in micropores is generally a process of filling the pores where the volume of a pore

is the most important factor whereas in mesoporous where the walls are in the form of a high number of adsorbent molecules or atoms, the boundaries of interphase have distinctive physical sense. So, the mono and multilayer adsorption in mesoporous surfaces happened sequentially and their final filling happens through the process of capillary adsorbent condensation. The mesoporous is defined by various basic parameters including the distribution of pore size, pore volume and particular surface area. The adsorption process on the surface of the macropores is matching to that on the flat surface. Nevertheless, the macropores do not subject to capillary adsorbate condensation like that existed with mesoporous. The adsorption on the precise surface areas in macropores resources is typically overlooked because their resources are very limited.

2.1.1.7.3. Feasibility and Economics

The adsorption treatment method is optimal to be used in household treatment plants due to its ease to use and being readily available. Recently, it is proven that the adsorption treatment method is the most appealing method among all of the other treatments because it removes the pesticides from waters effectively in addition to the economic, technical and ecological advantages provided by this method [35]. In general, activated carbons are efficient adsorbents where they can efficiently remove the pesticides included in wastewaters even at low concentrations depending on their adsorption effectivity. Although the activated carbons and the manufacture of activated carbon fibers are expensive, there was interest to use low-cost raw materials as an adsorbent for pollutants including pesticides.

2.2. ACTIVATED CARBON

Marsh and Rodriguez (2006) mentioned that activated carbon is any carbonaceous material with high porosity degree and large inter-particulate surface area which available for chemical reactions or adsorption[36,37]. The majority of carbon materials are made up of element carbon. It is possible to bond the carbon element with itself or other various elements due to its atomic structure [38]. Therefore, every

single activated carbon enjoys by distinct features which are determined by the existence of material, pores structure or chemical origin.

2.3. TEXTURAL AND CHEMICAL PROPERTIES

2.3.1. Pore Texture

The porous is the basic structure of carbon. This structure is a result of the cross-linked macromolecular types and amorphous porosity distribution and some of them have pseudo graphitic character (as shown in Figure 2.2) (a mix of graphite such as crystallites and non-organized phase composed of composite aromatic-aliphatic practices).



Figure 2.2. Activated structure of carbon [39].

The most distinctive physical properties of activated carbon are maybe its porous structure and this structure consists of various sizes of pores. According to IUPAC, this structure is divided into three main groups and one subgroup as shown in Table 2.1.

Micro pores are characterized by the wide surface area wherein various activated carbon, may account for up to 90% of the total surface area and these pores take the

form of the slit [37]. According to Bansal and Goyal (2005), mesoporous represents about 5% of the total surface area [37]. Currently, mesoporous activated carbon represents more than 25% of the total surface area.

Table 2.1. Different pore diameters according IUPAC.

Main group	Sub group
Micropores $\text{Ø} < 2 \text{ nm}$	Ultramicropores $< 0.7 \text{ nm}$ Supermicropores $0.7\text{-}2 \text{ nm}$
Mesopores $\text{Ø} 2\text{-}50 \text{ nm}$	
Macropores $\text{Ø} > 50 \text{ nm}$	

Mesoporous are very significant to the final application of activated carbon because of adsorption ability or transfer to micropore. The macropores are very important because they allow access to the internal workings of the mesoporous and macropores [40]. There are two more structure features of pores which are pore surface area and volume. Pore volume indicates the volume of space occupied by many pores and may range from 0.1 to more than $2 \text{ cm}^3 \text{ g}^{-1}$. The micropores evaluate the surface area of activated carbons and may range between $500\text{-}2000 \text{ m}^2 \text{ g}^{-1}$. Despite that most of the activated carbons characterize by the low surface area of mesoporous, many of them may have well-developed mesoporosity ($200 \text{ m}^2 \text{ g}^{-1}$ or even more) [38]. Nevertheless, some super-activated carbons may have unreasonable high values which may reach $4000 \text{ m}^2 \text{ g}^{-1}$.

2.3.2. Chemical Composition and Surface Chemistry

Carbon is made of poly-condensed aromatic species and it is considered the main ingredient of activated carbons. However, many other elements may be presented such as Sulphur, hydrogen, oxygen and nitrogen. Many activated carbons may include varying amounts of mineral matter (ash content) based on used raw material quality. The existence of all of these elements works to make the surface of activated carbons more functional. The most presenting elements are those derived from oxygen including phenolic, quinines, lactones and carbonyl [41,42]. However, there are nitrogen functions including imine, nitrile, nitroso, pyridine, amine, lactam, nitro

and pyrrole [43,44]. The polarity of carbon surface is increased by these groups and helps different interactions depending on the functional groups which make each activated carbon unique [45,46].

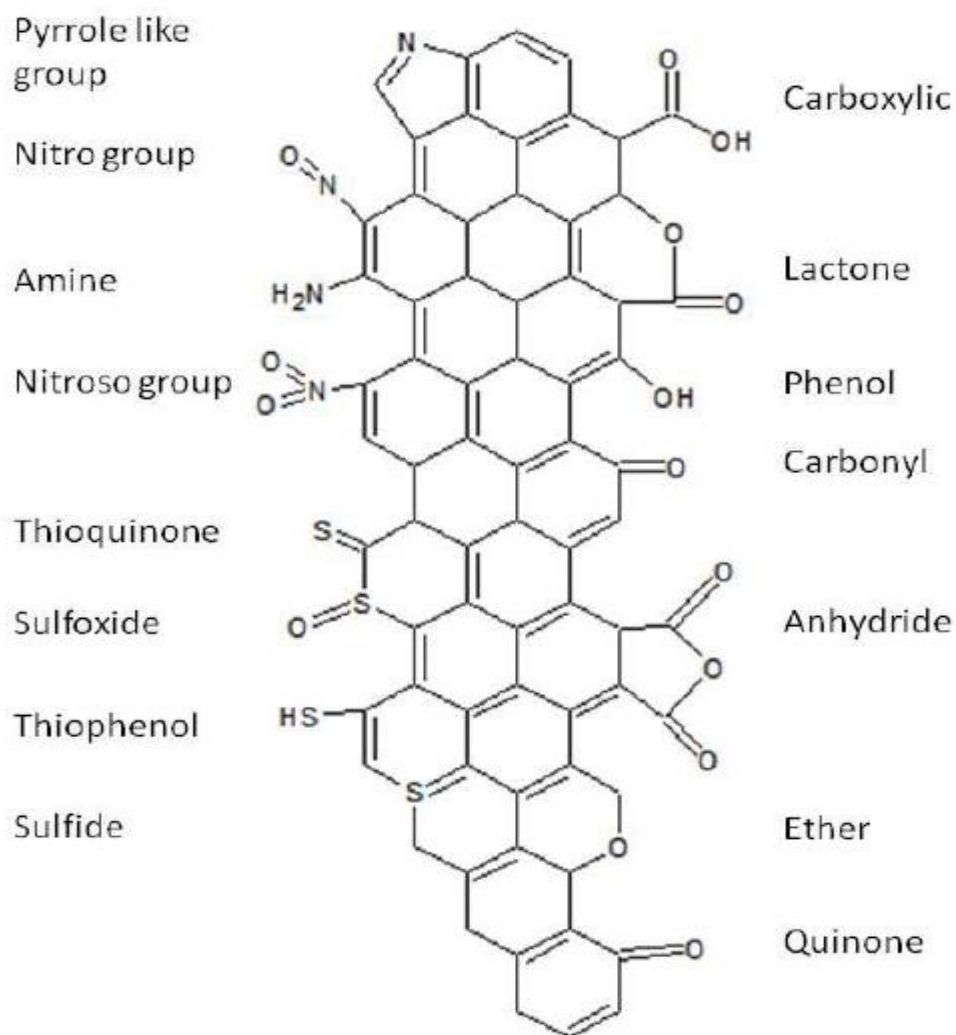


Figure 2.3. Different functional groups on surface activated carbons.

2.3.3. pH, Charge and Hydrophobicity

Another element to take into account is that the activated carbon is an amphoteric substance. This means that the existence of many functional groups on the surface makes the adsorbent acid or simple based on its source. Moreover, mineral matters (including ash in the case of activated carbon) may influence the adsorbent total basicity [44]. When the activated carbon is dissolved in an aqueous solution, it

generates a surface charge which helps the dissociation of surface groups [47]. The features of carbon surface and solution media determine the surface charge. If the pH media is larger than the pH of the activated carbon, the acidic functions may dissociate and leave a surface with a negative charge on the activated carbon (the basic medium).

As shown in Figure 2.4, the activated carbon surface is positively charged in an acidic medium (pH medium < pH activated carbon) [38]. Therefore, the electrostatic force and charge of molecules and activated carbon may influence solute adsorption. Cations are desired if the carbon surface is negatively charged whereas the ions will be absorbed on a positively charged surface.

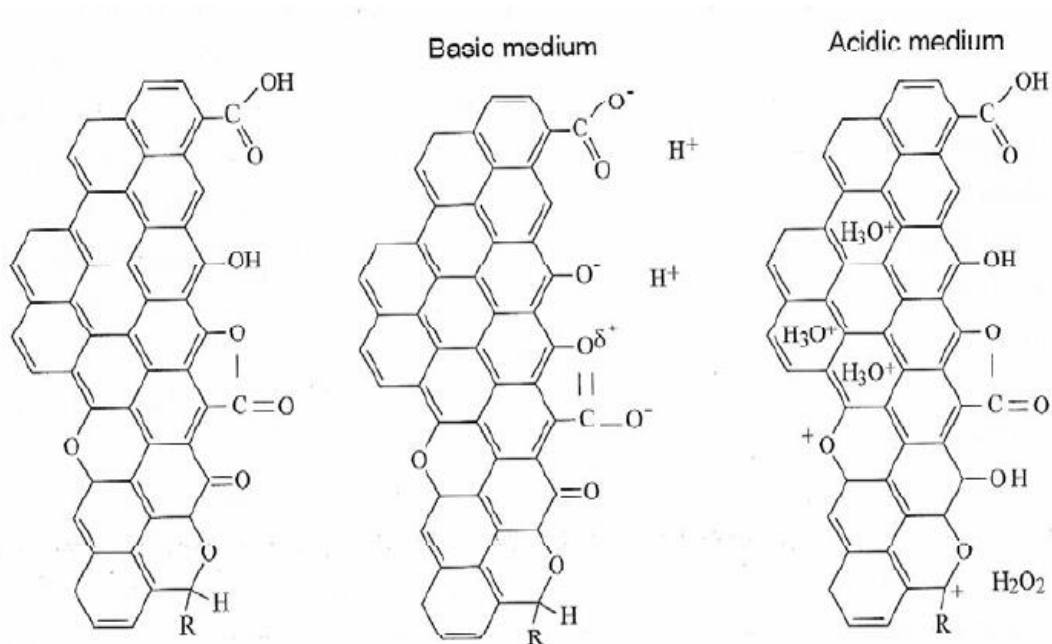


Figure 2.4. Representation of the basic and acidic behavior of the oxygen-containing surface groups [38].

Generally, the activated carbons are hydrophobic materials. The existence of neutral, acidic and basic functional groups may bind to molecules of water through hydrogen bond formation. It causes an increase in hydrophilicity because of the connection of oxygen and water atoms with the surface of carbon [48,49]. Isotherms of water adsorption may help to clarify this fact, nitrogen and oxygen groups may work as nucleation centers in different phases of cluster formation and pores filling [50]. Pore

and clusters filling with water improve the hydrophilicity of carbon and decrease the number of available adsorption locations of the solute and block the entrances of the micropore [51].

2.4. PRODUCTION OF ACTIVATED CARBON

2.4.1. Raw Materials

The most common raw materials used to manufacture the activated carbon is coal in different maturation phases. Nevertheless, since the demand for activated carbon is grown continuously due to the generation of many traditional biomass wastes, the market of activated carbon precursors have been extended to consist of shells (hazelnut, almond, walnut and coconut), wood and fruit stone (pit) including cherry, olive and peach [52]. Moreover, the last economic crisis imposed on industry to search for less expensive other options to produce activated carbons from different new wastes. The sludge from sewage has been used to generate these wastes [53,54], tires [55,56], leather industry [57,58], Agar-Agar industries [59,58], oil industry [60]. Figure 2.5 clarifies different percentages of key raw materials which are used in the manufacturing of activated carbon.

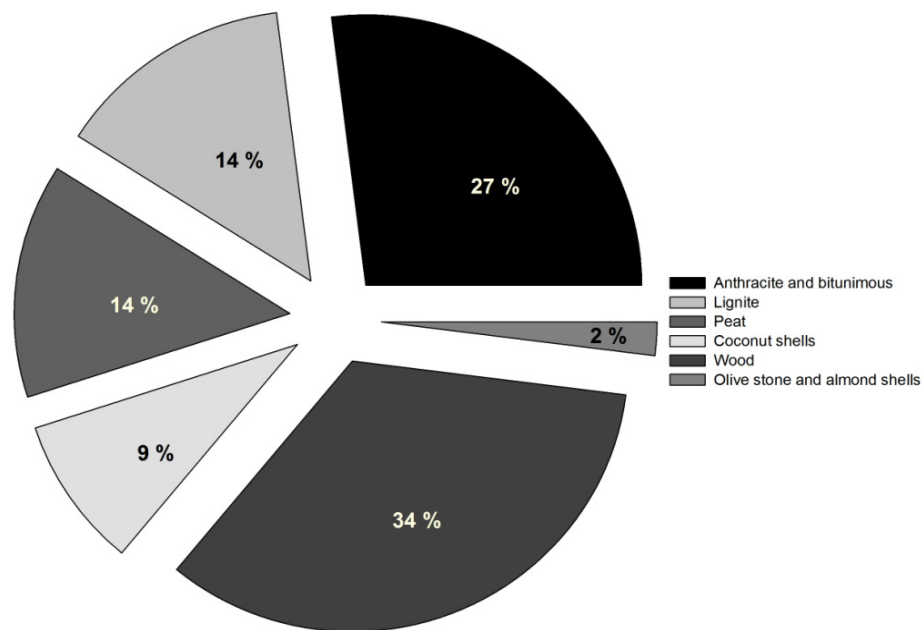


Figure 2.5. Most used raw materials to the production of activated carbon.

There are many criteria which determine the selection of raw materials including ability to create good activated carbon in terms of hardness, density and adsorption power; availability and cost. There is only a few of inorganic material and the activation is easy.

2.4.2. Preparation of Activated Carbon

The two main processing processes of activated carbon are chemical activation and physical activation which is also named thermal activation. The main difference between the two activation processes is the number of steps in the process and the type of activation factor. Figure 2.6 shows the general diagram to create the activated carbons.

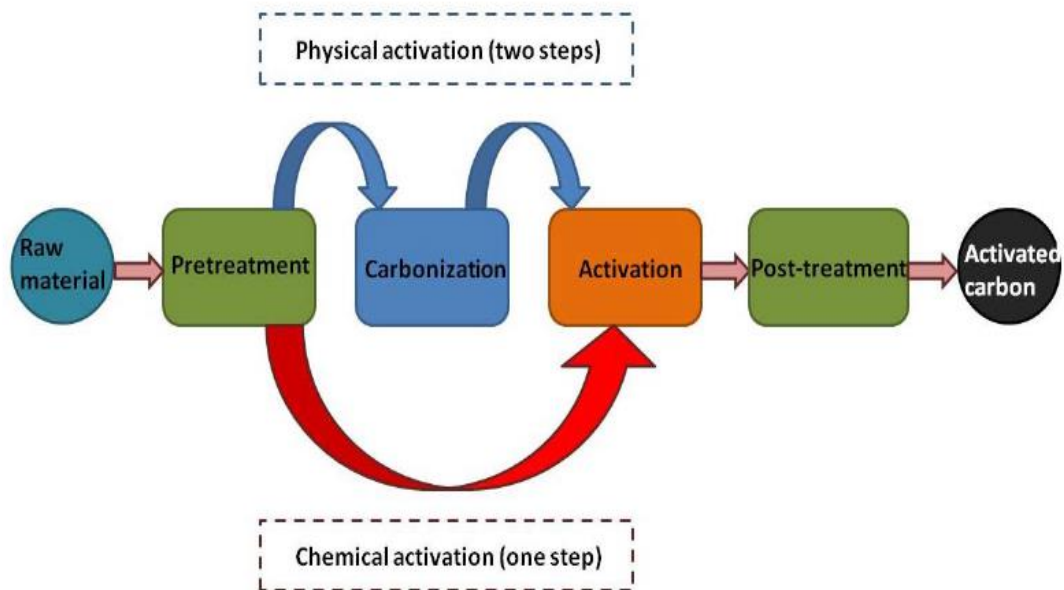


Figure 2.6. General diagram of activated carbon process.

2.4.2.1. Pre-Treatment

To accomplish the particle size of powder or granular carbon, the raw material is usually pulverized, crushed and sieved. There may be a necessity to decreasing the mineral matter content of the sample or peroxidation treatment to stabilize the coal.

2.4.2.2. Pyrolysis

Pyrolysis can be described as the thermal decomposition of a specific substance in absence of oxygen or in the existence of another reactive which includes oxygen including water, carbon dioxide and air. This method causes the volatilization of organic substance on the material that includes heating in an inert atmosphere in a furnace. Many products can be derived from this process where the volatiles can be extracted as a gas fraction and carbon solid which is known as "char". Generally, the fraction of gas is composed of CH₄, CO, H₂, C₂H₂ and CO₂. After the suitable pre-treatment, these gases can be used as fuel or combustible in other operations. As well as, they can be used to produce syngas and generate electricity [61]. A fraction of the gas can also be condensed in a liquid fraction. Moreover, this liquid can be used as fuel in many machines including turbines, boilers and generators [62,63]. Also, the raw material of the manufacture can be used in many chemical compounds such as flammable extracts, insecticides and fungicides [64]. The solid fraction which is known as char is a carbonaceous material where the decomposition process causes an increase in carbon content and growth in the micropore structure. Therefore, it is possible to use this substance as activated carbon. Moreover, this substance is used in combustion and/or gasification processes as a combustible substance.

2.4.2.3. Process and Reactions in the Pyrolysis

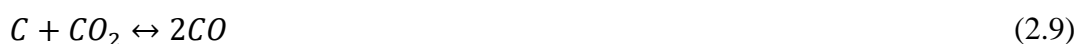
The thermal composition of carbonaceous substances involves different mass and heat transfer and chemical reactions. The two main steps in the global pyrolysis process are primary and secondary pyrolysis. The primary pyrolysis at a temperature lower than 400 °C causes the thermal decomposition of carbonaceous material. This process involves the formation of different reactions with basic, multicomponent and intermediate products simultaneously which result in gas, liquid and char products. The secondary pyrolysis at a temperature greater than 400 °C causes decomposition reactions in carbonaceous substances. Examples of these reactions are polymerization, partial oxidation, condensation and cracking phase that are classified as homogenous and heterogeneous. It is thought that pyrolysis starts at 250 degrees Fahrenheit and ends at about 500 degrees Fahrenheit.

During the pyrolysis process, the pyrolytic decomposition removes the existence of hydrogen and oxygen from the materials in the form of gas. The aromatic rings are formed by rearranging the free carbon and these are the building blocks of basic structure. Moreover, intermediate decomposition products including tar are formed and deposited in the interstitial spaces [61].

2.4.2.4. Physical activation

The thermal or physical activation is an operation of two steps where the first one is carbonization or pyrolysis and the second one is activation. The remaining char from the pyrolysis is partially gasified with oxidizing factor (gas) in direct fir furnaces through the psychical or thermal activation. Steam is the most common factor but oxygen, carbon dioxide or a combination of all of the three factors are usually used [65]. Carbon atoms interact with the gas in order to extract some of the mass from the internal surface which results in microporous material with a large particular surface area. This process is allowed by heating to a high temperature ranging between (800-1000 °C).

The formation of chemisorbed oxygen is resulted during the activation process by the general reactions of (2.6), molecular oxygen (2,7)(2.8) and carbon dioxide (2.9), as well as develop porosity and generate gaseous reaction products.



Marsh and Rodriguez (2006) detected that the chemisorbed oxygen which is also known as surface oxygen complexes may form species of complexes on the surface of materials (descriptive equation (2.10), with no stoichiometry)[36].



The complexes of surface oxygen work as both a reaction ratio retarder during the activation stage and reaction intermediate. Also, during the activation of steam, hydrogen may be chemisorbed on the surface of carbon (2.11).



The carbon reaction ratio may be inhibited (slow down) because of the formation of many hydrogen and oxygen complexes. This influence is not negative at all due to its help in controlling the gasification and followed growth of porosity by avoiding the reaction between oxygen and carbon.

2.4.2.5. Chemical Activation

Marsh and Rodriguez (2006) define an approach that includes mixing a chemical compound (named a chemical agent) with a mesh and subject it to chemical treatment (400-700 °C) [39,37,66]. The activation and carbonization are usually implemented in the same place in operation with one step. The tar formation and volatile matter are decreased by the chemical agent while the content of carbon is increased. The most common chemical agents include alkaline hydroxides (including NaOH and KOH), acids (H₂SO₄ and H₃PO₄) and Chlorides (including ZnCl₂) and many carbonates [67-69].

The largest amount of these chemical agents are dehydrating compounds which influence the decomposition of the activation process. The activated agents which have been used in this study include KOH, NaOH and K₂CO₃, and the reactions which arise during the activation stage are shown in Table 2.2. The main result of the use of hydroxides in chemical activation is the formation of hydrogen and carbonates, potassium and sodium.

Table 2.2. Reactions produced in the chemical activation with KOH.

$6 \text{ KOH} + 2 \text{ C} \rightarrow 2 \text{ K} + 3 \text{ H}_2 + 2 \text{ K}_2\text{CO}_3$ (5)	Main reaction with KOH in activation process
$2 \text{ KOH} \rightarrow \text{K}_2\text{O} + \text{H}_2\text{O}$ (360°C) (6)	
$\text{C} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}$ (7)	
$\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$ (8)	
$\text{K}_2\text{O} + \text{CO}_2 \rightarrow \text{K}_2\text{CO}_3$ (9)	Reaction (9) is a competitive reaction with (5) which carbonates are formed
$\text{K}_2\text{O} + \text{H}_2 \rightarrow 2 \text{ K} + \text{H}_2\text{O}$ (10)	
$\text{K}_2\text{O} + \text{C} \rightarrow 2 \text{ K} + \text{CO}$ (11)	
$\text{K}_2\text{CO}_3 + 2 \text{ C} \rightarrow 2 \text{ K} + 3 \text{ CO}$ (12)	

As well as, the carbonates may produce CO_2 that needs physical activation in the process and on the carbonaceous content. This physical activation may occur because of the decomposition of K_2CO_3 at around 900 degrees Celsius.

2.4.2.6. Post Treatment

Although the porosity has been constructed on materials obtained after the activation process, they are not ready to use as adsorbents. They need into a washing process in order to eliminate undesired substances including ashes which fill the pores in addition to any probable agents caused by the increase of triggering reagent (mostly in chemical activation). The activated carbon is washed by water to get simple activated carbon or with water and HCL to get acid-activated carbons based on the final application [57]. Other operations including pulverization and extrusion can be used based on the final application of activated carbon.

2.4.3. Types and Shapes of Activated Carbons

The types of activated carbon are classified based on the size of particles into Granular Activated Carbon (GAC) and Pulverized Activated Carbon (PAC). The size of PAC is ranging between 1-100 m while the size of GAC is ranging between 1-5 mm. The most common sizes of PAC are ranging between 15 and 25 m. GAC

adsorbent can also be categorized into two types broken or unshaped GAC and formed GAC of specific shape (disks, bead and cylinder). The broken GAC can be made by sieving, milling and categorizing various sizes of pulverized carbon whereas the formed GAC can be made by extrusion or pelletizing of pulverized carbon which is mixed with another binder. Activated carbon exists in many forms and shapes such as template derived carbons, monolithic structures, carbon films, felts, carbon fabrics and Carbon fibers, and carbon nanotubes.

2.4.4. Liquid and Gas Applications

Activated carbon has many applications of gases and liquids between other things and the most critical application of them can be summarized as follows:

1. Storing of methane, carbon dioxide and hydrogen [57, 70- 73].
2. Gold recovery [74].
3. Recover sweet of odors in order to enhance the consistency of product [75].
4. Manufacturing of inhalators and masks.
5. System of drinking water and wastewater treatment plant [7677]
6. Remove the emerging pollutant from hospital wastewaters [78].
7. Discoloration of justice, carbohydrates, honey, liquors and vinegars [79].
8. Medical use adsorbents [80-81].
9. Get rid of mercury[58].

2.5. ADSORPTION IN AQUEOUS PHASE

Adsorption is the process where the activated carbon removes the contaminants which emerge in the aqueous phase. Adsorption is the preservation of ion, molecule or electron (all of them denoted as adsorbates) on the solid material surface (considered an adsorbent). This method depends on the mass transfer phenomenon which arises because of many interactions between the adsorbent's surface and molecules. The molecules from the liquid or gas phases will be physically bound to the board of activated carbon. The adsorption operation is separated into three phases as follows:

1. Macrotransport: it is the process of transfer the organic molecules through the activated carbon macropore system.
2. Microtransport: it is the process of transferring the molecules mainly over the high-diameter mesopores and micropores.
3. The sorption indicates the physical binding of the organic molecules in mesopores and micropores.

Before designing the dynamic reactor, there was a necessity for dynamic studies and batch studies (kinetics and equilibrium adsorption) in order to understand the adsorption process and activated carbon behavior.

2.5.1. Batch studies and equilibrium adsorption

The mass transfer from liquid to the solid phase is produced in the system where the adsorbate is in contact with the mass of the adsorbent. The equilibrium is accomplished by the system when no more molecules are adsorbed and the adsorbent is exhausted. The water temperature and concentration of solute determine the equilibrium. There are many models that have been suggested in order to interpret the mechanism of adsorption and the most significant methods are Froehlich and Langmuir. These models show the practical isotherms that describe the relationship between the adsorbed quantities at a solute concentration (C_e) and equilibrium (q_e).

2.5.1.1. Langmuir Model

$$q_e = \frac{q_m k_L c_e}{1 + k_L c_e} \quad (2.12)$$

Where K_L represents the equilibrium constant of Langmuir ($L \text{ mg}^{-1}$ or $L \text{ mmol}^{-1}$), q_e represents the adsorbed quantity at the equilibrium (mg g^{-1} or mmol g^{-1}), q_m represents the highest adsorption quantity (mg g^{-1} or mmol g^{-1}) and C_e represents the concentration of equilibrium (mg L^{-1} or mmol L^{-1}). The assumption of this model can be described as follows [82]:

The types of adsorbed have not any interaction between them, each adsorbate-adsorbent connection is characterized by the same structure and arises by the same method. The entire location of the solid (adsorbent) characterize by the same behavior of adsorption (surface is homogeneous) and no interaction occurs between the types of adsorbed. The adsorbent preserves only one molecule in each pore or location. This means that the adsorbed layer is a monolayer.

2.5.1.2. Freundlich Model

$$q_e = K_f C_e^{1/n} \quad (2.13)$$

Where K_f represents the constant of Freundlich adsorption ($(\text{mg g}^{-1}) (\text{L mg}^{-1})^{1/n}$) and n is the constant associated with the intensity of adsorption. Both of the constants are based on the temperature and solute adsorbent interaction. If the relation $1/n < 1$ the adsorption is favorable, whereas if $1/n > 1$ the adsorption is not favorable. This model depends on the experimental data and supposes that the adsorption locations are heterogeneous. It is used only with low and intermediate solute concentration and has not physical senses where it is free of full adsorption capacity [83].

2.5.2. Fixed Bed Adsorption

The adsorption in water treatment is usually implemented in fixed bed adsorbers with granular activated carbon. The water is enforced within the filter either by pressure or gravity. The dynamic phase of the fixed bed is separated into three sections: the area in which the molecule will be adsorbed, the mass transfer area in which the molecule has been absorbed but the adsorption equilibrium has not been accessed yet and the exhausted area (saturated area) where it is reached to the full adsorption of carbon and no more molecules will be adsorbed. Figure 2.7 shows the saturation area progress in the filter. In order to obtain continuous inlet flow, the depleted area is pushed through the filter and towards the end of the bed until the effluent concentration surpasses that of the fluent and no more removal is required [84]. When the activated carbon is totally depleted, the filter will be drained and then

refilled with new activated carbon. The exhausted activated carbon can be regenerated by using the thermal process.

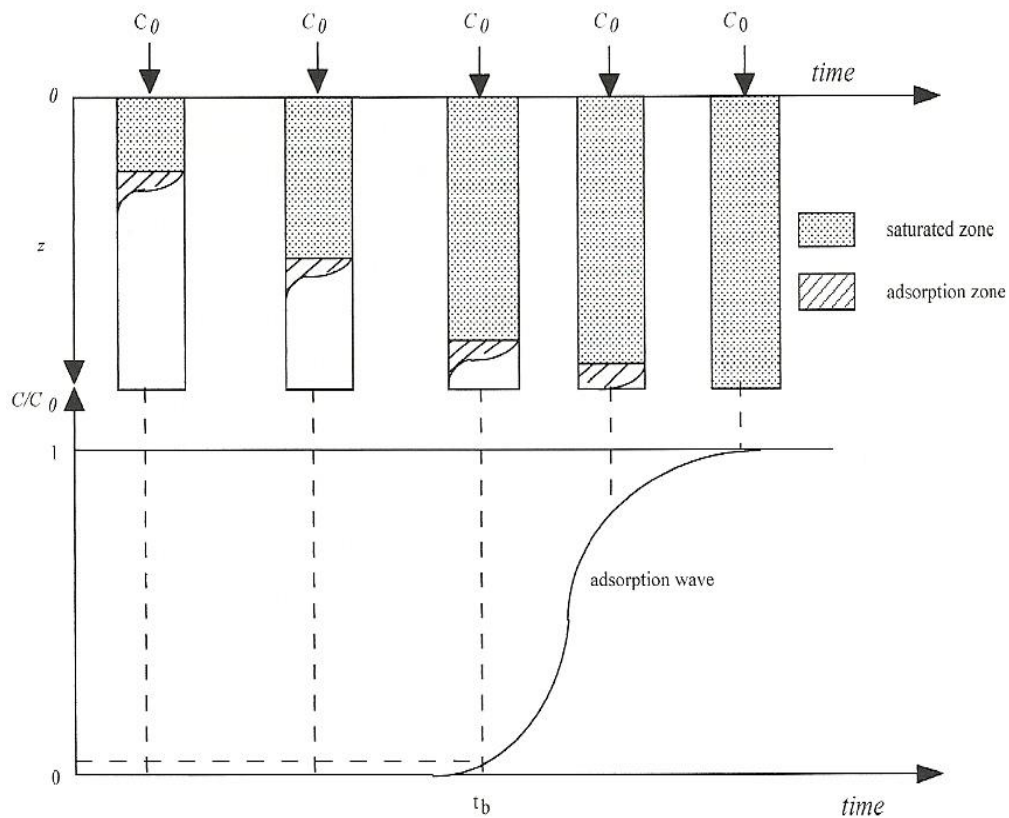


Figure 2.7. Fixed bed adsorber – adsorption zone progression [84].

2.5.3. Adsorption Interactions

Activated carbons are used in many areas during the water treatment process (drinking and waste). The activated carbon features (such as the chemistry of surface and distribution of pore size) are very necessary to the process because they organize many characteristics of the equilibrium adsorption. Instead, water features are very important because they influence the adsorption of activated carbon including the existence of Natural Organic Matter (NOM), hardness, pH, temperature and the adsorbate form to name a few. There are three forms of interactions that control the adsorption of adsorbate by activated carbon in the water adsorption process as follows [85]:

1. Adsorbate-activated carbon.
2. Adsorbate-water.

3. Activated carbon water.

2.5.3.1. Adsorbate-Activated Carbon Interactions

The small molecules with molecular surface areas amounted of 1-3 nm² are used to be organic contaminants (as emergent compounds) [86]. Since the molecules may enter the micropores of the activated carbon, the physical adsorption between the adsorbent and adsorbate can be determined by the surface area and distribution of pore size (activated carbon, AC). The adsorption is influenced by many elements including the chemical surface composition of activated carbon, the functional molecules groups and solution chemistry. In activated carbon, the oxygen is considered the most abundant atom in the functional groups which provides the surface with many adsorption options of organic pollutants. - π - π dispersal interactions among the aromatic adsorbate ring and the basal activated carbon plane [87], electrostatic attraction-repulsion interactions, bonding of hydrogen between surface functional groups and aromatic molecules [50], electron acceptor-donor complex-forming method. Moreover, the existence of Natural Organic Matter (NOM) in the ground and surface water has the ability to make the interaction between water and organic compounds. NOM can be described as complex molecules with aromatic functions which may detect the adsorption of the organic compound [88]. As well as, in the pH water treatment spectrum, molecules of NOM influence the net negative charge. Therefore, electrostatic power (attraction and repulsion) play a significant role in NOM and the adsorption of an organic molecule [89, 90].

2.5.3.2. Adsorbate –Water Interactions

The chemical and physical properties of adsorbate affect the interaction between molecules and water. The resistance of organic compounds causes escaping power from the solution of water to the interface surface. In other words, because the activated carbon is partially hydrophobic, it seems that the organic compound can be brought to the surface. The name of this phenomenon is Solvent-motivated adsorption [91]. The rules of Lundelius and Traube states that when the solubility of a

compound decrease, its adsorption will decrease similarly [85]. The interaction of molecules with water is highly affected by their polarity. The different electronegativity between the atoms is the result of irregular distribution of electron density which results in polarity. The adsorption must be decreased because increasing the polarity enhances the organic molecule's aqueous solubility.

2.5.3.3. Activated carbon – water interactions

The existence of nitrogen, oxygen and other functional groups change the polarity of activated carbon. Water molecules interact with these groups which increase the adsorbent's hydrophilicity, form clusters and blocking many pores.

2.6. AN OVERVIEW OF CORNCOB

Naturally, cellulose is a renewable and abundant biopolymer and its structure is crystalline which consists of crystalline and amorphous areas [92]. Cellulose consists of many properties including strong mechanical properties, biocompatibility, biodegradability and non-toxicity [93]. Consequently, attention has been focused on cellulose in many fields such as pharmaceuticals, cosmetics and foods [94,95]. Microcrystalline cellulose (MCC) is considered an important good in the family of original cellulose which is generally made by treating the cellulose with high amount of mineral acids to degrade the largest quantity of amorphous areas and decrease the cellulose fiber to micron phase [96].

MCC is an important natural source that is derived from many types of sources such as cotton, agricultural residues, algae, wood, bacteria, grass and other natural materials. Recently, there are various agricultural residuals were used to prepare MCC including sago seed shells, oil palm fibers, pomelo peel, banana plant waste, tea waste, rice straw and rosella fiber [97, 94,98, 96, 99-101]. Much attention has been paid to the MCC isolated from the agricultural residuals. Corn exists in all parts of our world and its production is increased year by year wherein 2018-2019, its global production amounts about 10.990 108 tons [100].



Figure 2.8. Corncob.

It is assumed that the rate of corn grain to corncob is about 100:18 [102] and therefore the amount of corncob which is produced annually is approximately 19.782×10^7 tons (Figure 2.8). The corncob has been used previously in many areas such as the production of biochar, animal feed, char and polisher [103][104]. Despite this, high amounts of corncob are discarded as agricultural wastes after harvesting the grains. Many studies have been implemented on the high value of corncob due to its carbohydrate-rich chemical composition. Researchers mentioned that corncob is used to obtain aminophenol's [105], bio-based rigid polyurethane foam [106], bio adsorbent [107], hollow spherical carbon [108], phenolic compounds [109] and p-hydroxycinnamic esters [109]. Moreover, they stated that hemicellulose isolated from corncob is used to produce propionic acid, furfural, ethanol, xylitol and succinic acid [110-113]. Some attention has been made to the use of corncob cellulose. Jantip et al. (2011) made MCC from corncob by the use of 5 g/l hydrogen dioxide, 2 N sulfuric acid and 15 percent wt sodium hydroxide [114]. Suvachitanont and Ratanapan (2011) isolated the corncob MCC by the use of 25 percent sodium chlorite, ten percent (w/w) hydrochloric acid and 10 percent (w/w) sodium hydroxide. Azubuiké et al. (2012) isolated the MCC from corncob by the use of 3.2 percent sodium hypochlorite, 17.5 percent sodium hydroxide and 2 N hydrochloric acids [115]. Purwanti et al. (2015) and Kampeerappun (2015) confirmed that the high concentration of sulfuric acid (50-62 percent (v/v)) hydrolyzed corncob cellulose can be used to produce nanocrystalline cellulose [116,117].

PART 3

METHODOLOGY

This chapter highlights step by step of different methods used in carrying out the preparation of corncob activated carbon and rice husk activated carbon with potassium hydroxide and adsorption of dimethoate pesticide.

3.1. MATERIALS

Dimethoate; 99.5% was supplied from Reference Chemistry Company, in Turkey while hydrochloric acid; 37% (analytical grade), liquid chromatography gradient grade of methanol and acetonitrile were supplied from ISOLAB Chemical Company, in Turkey. Corncob were obtained from producers of corn (zeamais) in Karabük, in Turkey as a raw source of material for the preparation of corncob KOH activated carbon. Rice husk was obtained from producer of rice from Edirne, in Turkey.

3.2. METHOD

10 mg dimethoate was dissolved in 10 mL methanol to achieve a stock solution of 1 mg/mL concentration of dimethoate and a different working standard was prepared by diluting with distilled water.

3.3. PROXIMATE ANALYSIS

In proximate analysis of this study, moisture content analysis was done by oven drying method (ASTM D2867—09) and volatile content while the inorganic deposit after pyrolysis of the sample is fixed carbon and ash (ASTM—D2866-94) as biomass material.

Hence, as indicated by Demirbas, (2009) proximate analysis is majorly the analysis used in characterizing the activated carbon depending on its application.

3.4. PREPARATION OF ACTIVATED CARBON

Preparation of activated carbon processes was carried according to the method by [118]. In order to remove contaminants from corncob, distilled water was used in washing the corncob before oven dried at 110 °C for 24 h placed in a ceramic oven. Later, the corncob was heated at a rate of 5 °C/min from room temperature to 450 °C and at the same time N₂ was poured into the oven at a rate of 3 dm³/min for 1.5 h. In this oxygen-deficient conditions, corncobs were thermally decomposed to porous carbonaceous materials and hydrocarbon compound. This is the carbonization step. After this step chars were removed, crushed and sieved to uniform size ranging from 1.0-1.5 mm.

The carbonized corncob was soaked in impregnation KOH proportion ratio (KOH: corncob) of 1:1 in a stainless steel beaker for 12 h and the impregnated samples were then dried in an oven at 105 °C for overnight. In initiating its activation, the prepared samples were then heated at 780 °C for 1 h under the flow of N₂ 3 dm³/min. The prepared activated carbon was cooled to a temperature of 25 °C and washed with deionized water. These sample soaked for 1 h in 0.1 M hydrochloric acid (HCl) in order to eliminate the residual ash content. Finally, they were rinsed with hot distilled water until pH reached to 6-7 and dried by 105 °C drying overnight and labelled KOHCC activated carbon. Using same procedure, we obtained activated carbon from Rice husk and labelled KOHRH.

3.5. CHARACTERIZATION OF ACTIVATED CARBON

The spectrum of the corncob activated carbon was determined using FTIR (IRPrestige—21, Shimadzu, Japan) between the spectra of 4000 and 400 cm⁻¹. X-ray diffraction (XRD) measurements were performed on Ultima IV, Rigaku, Japan at wavelength ($\lambda = 0.15406$ nm) with graphite monochromatized CuK α and the 1.0°s⁻¹ scanning rate with a 0.02° scanning step applied in recording the pattern at 10–80°

range of Cu radiation with Ni filter which was given at 40 kV and 20 mA. The sample holder is custom-made with shallow well used for sample mounting. The sample was pulverized with SPEX sample Prep mixer/mill 8000M, USA. Scanning electron microscope (SEM) micrographs of CC-900 and CCAC-900, were obtained using JOEL JSM—6610LV, Japan, while compositional analysis was carried out by electron dispersive X-ray spectroscopy (EDAX). Specific surface area and pore dimension analysis with the multipoint surface area were determined via Quantachrome instrument Nova 4000, USA by nitrogen adsorption in order to determine different parameters associated with pore distribution size, area and volume methods like Brunauer—Emmett—Teller (BET) for specific surface area (S_{BET}).

3.6. POINT OF ZERO CHARGE

The point of zero charge, known as pH_{pzc} , is the pH at which the net charge of the surface is zero. The nature and amount of functional groups at the surface of the activated carbon determine the value of pH_{pzc} . Therefore, in this study, 0.2 g CC-900 and CCAC-900 activated carbon was weighed into 10 mL of 0.1 M NaNO_3 solution in a sealed bottle and shaken for 24 h for 2-12 starting pH of the arrangement and then at balance pH, the suspensions were filtered and measured with a microelectrode, depending on a method portrayed by Carrott et al., (2001).

3.7. ADSORPTION EXPERIMENTS

Serial dilutions of the stock solution of dimethoate were prepared for different concentrations with distilled water. In the kinetic and equilibrium studies, pH and temperature were determined by pH and temperature effect experiments. Batch desorption studies were performed by agitating 250 mL of 20—100 mg L^{-1} initial concentrations of dimethoate with optimal dosage of CC-900 and CCAC-900 in 500 mL Erlenmeyer flasks. The mixture was shaken for 90 min at 150 r/min and the samples were withdrawn at appropriate time intervals (5, 10, 25, 30, 45, 75 and 90 min and 24 h), the mixture in vial was filtered through a 0.45 μm film channel joined to a syringe. The concentration of dimethoate was analyzed utilizing high-

performance liquid chromatography LCMS Agilliant fitted with UV/VIS SPD—20A detector. Separation was achieved using Inertsil ODS—4, C18 reverse phase analytical column (4.6 mm i.d., 250 mm long, 5 μm particle size; GL Sciences, Japan). Binary gradient chromatography was performed using an optimization mixtures ratio of acetonitrile to water as mobile phase with a flow rate of 1.0 mL min^{-1} . The UV detector was used and wavelength of 210 nm at a determined retention time. The amount of dimethoate sorbed at time t , q_t (mg g^{-1}) and at equilibrium, q_e (mg g^{-1}) and the removal efficiency of adsorption (%) onto CCAC-900 were calculated by using Eqs. (3.1), (3.2) and (3.3).

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (3.1)$$

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (3.2)$$

$$\text{Removal efficiency (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (3.3)$$

Where C_0 , C_t and C_e (mg/L) are the concentrations aqueous solution of dimethoate at initial, time t and equilibrium respectively. V (L) is the volume of the aqueous solution in the adsorption experiment and W (g) is the CCAC-900 mass which was used.

3.7.1. Effect of Sorbent Dosage

To investigate the effect of sorbent dosage, the sorption of dimethoate onto KOHCC and KOHRH were carried out considering four different sorbent dosages (0.05, 0.1, 0.15 and 0.2 g) for the starting concentration of 10 mg L^{-1} at optimum temperature and pH while keeping other conditions constant.

PART 4

RESULTS AND DISCUSSION

4.1. PHYSICAL PROPERTIES OF ACTIVATED CARBONS

Pore size and pore structure of activated carbon from corncob and rice husk were determined using Scanning Electron Microscopy (SEM). Typical SEM photographs of activated carbon with the KOH/char values of 1 for KOHCC are shown in Figure 4.1- 4.4.

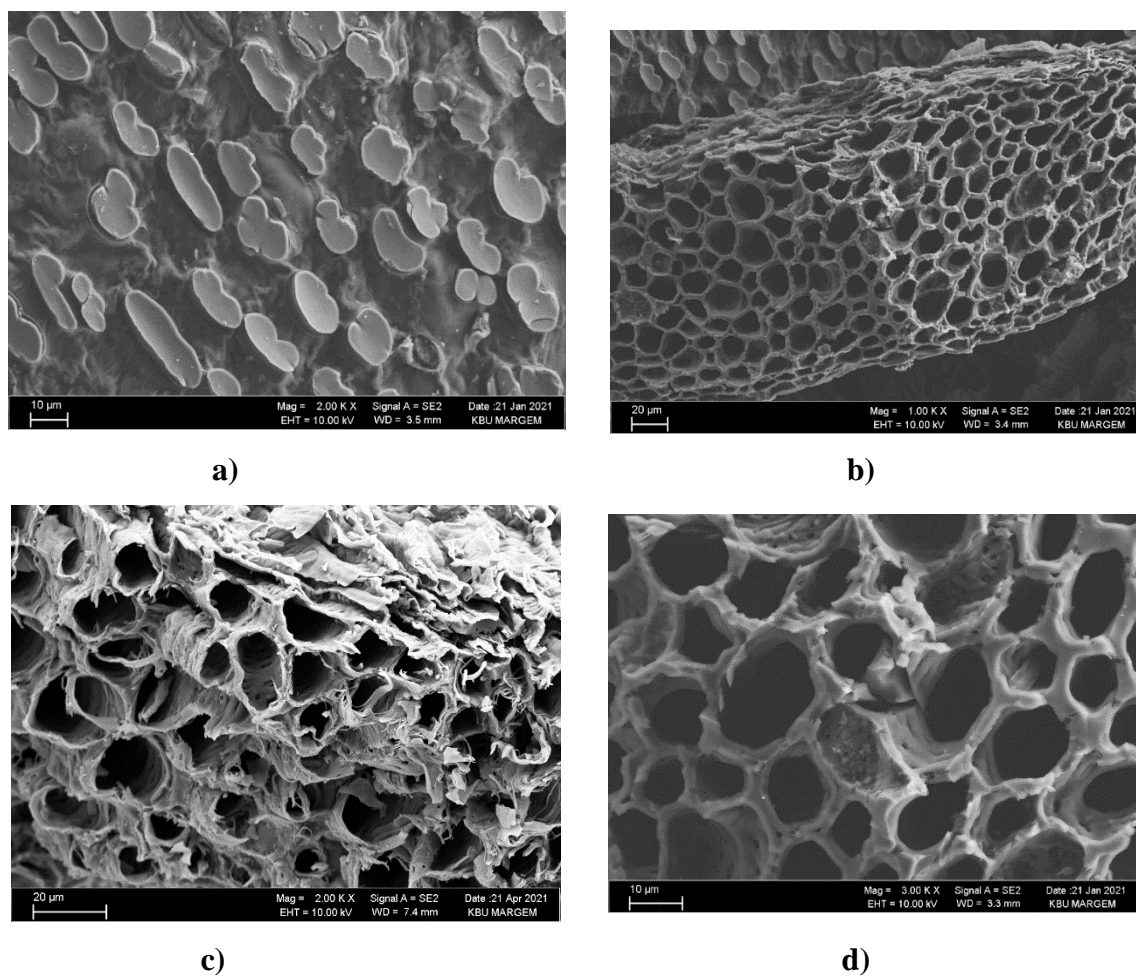


Figure 4.1. SEM images of activated carbon from Corncob.

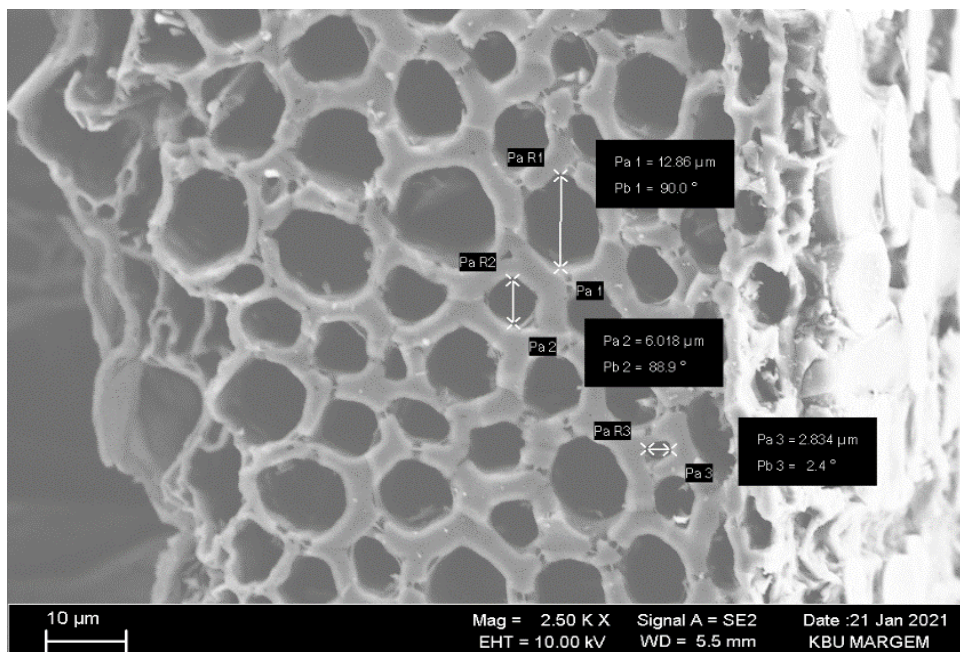
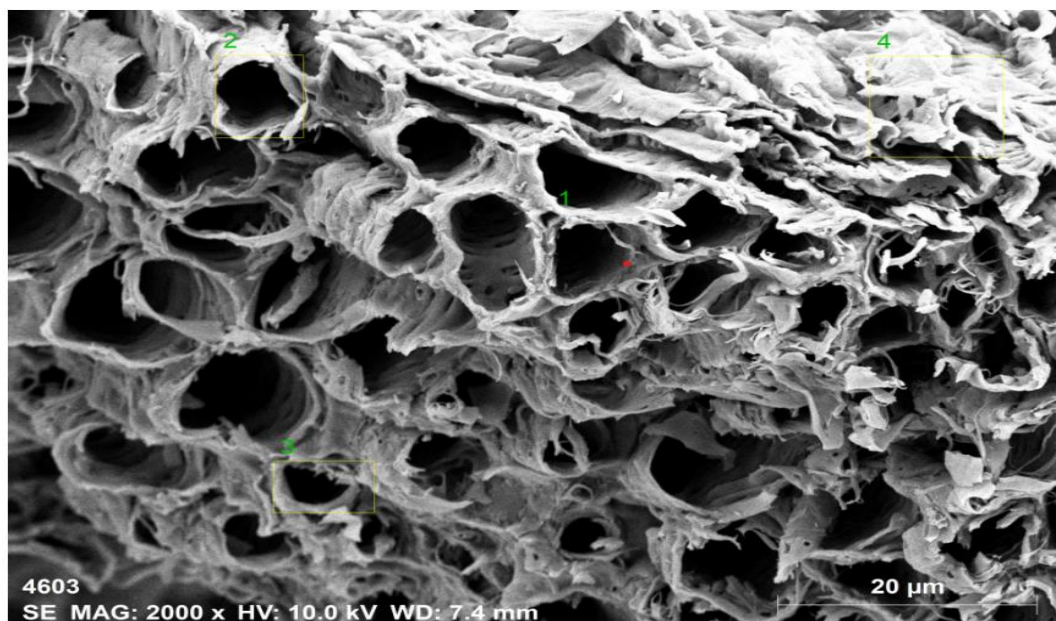


Figure 4.2. Pore size of activated carbon from Corncob.



Mass percent (%)												
Spectrum	C	N	O	Si	P	S	Cl	K	Ca	Fe	Cu	Se
1	78.13	0.00	7.41	0.00	13.15	0.19	0.81	0.00	0.31	0.00	0.00	0.00
2	83.57	0.00	2.85	0.25	11.45	0.00	0.38	0.37	0.07	1.06	0.00	0.00
3	54.02	0.00	0.07	0.32	38.08	0.00	5.02	2.22	0.00	0.00	0.00	0.26
4	77.90	0.00	10.08	0.01	9.57	0.00	0.38	0.18	0.07	1.82	0.00	0.00
Mean value:	73.41	0.00	5.10	0.14	18.06	0.05	1.65	0.69	0.11	0.72	0.00	0.07
Sigma:	13.18	0.00	4.49	0.16	13.43	0.10	2.26	1.03	0.14	0.89	0.00	0.13
Sigma mean:	6.59	0.00	2.24	0.08	6.71	0.05	1.13	0.52	0.07	0.44	0.00	0.07

Figure 4.3. EDAX spectra of corn cob (KOHCC) after activation.

EDAX spectra indicates prominent peaks for corncob (Fig.4.3) as C, P, O, Cl and Fe with average percent of 73.41 %, 18.06%, 5.10 %, 1.65 %, 4.08% and 0.72, respectively.

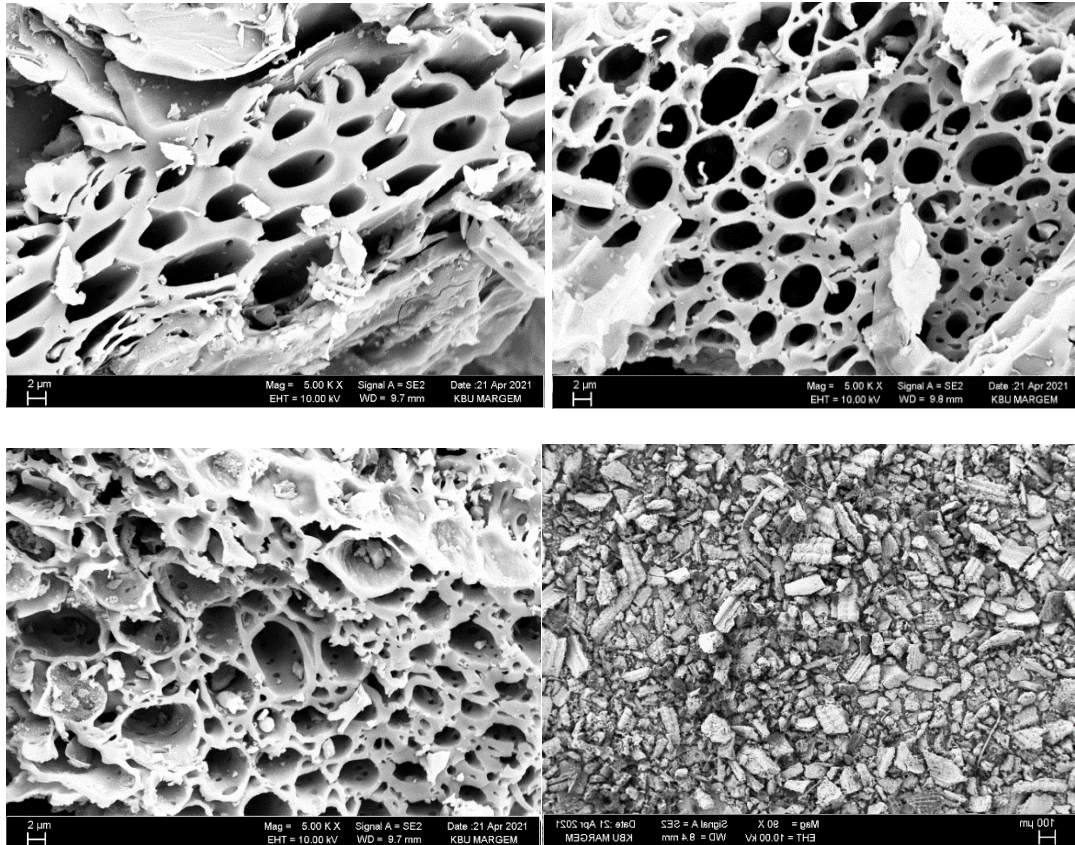


Figure 4 4. SEM images of activated carbon from rice husk.

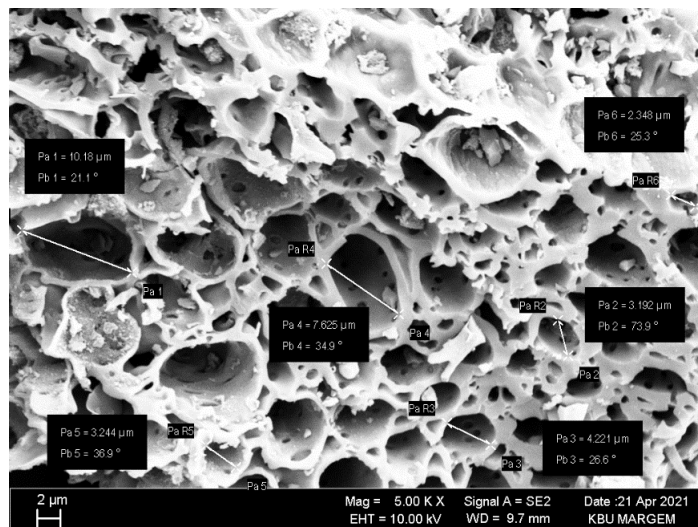
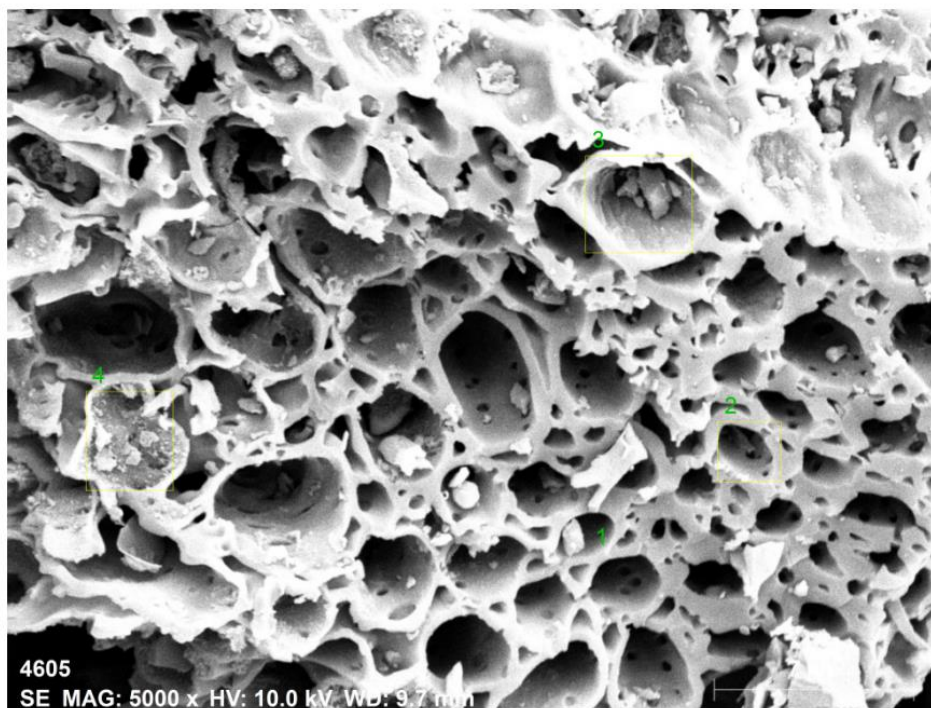


Figure 4.5. Pore size of activated carbon from rice husk.

The scanning electron microscopy (SEM) image for KOHCC shows an irregular pore structure in different size and there significant amount of cavities.



Mass percent (%)

Spectrum	C	N	O	Si	P	S	Cl	K	Ca	Fe	Cu	Se
1	61.94	0.00	5.09	3.89	25.14	0.00	1.62	0.43	0.00	1.89	0.00	0.00
2	69.64	0.00	1.14	0.69	18.70	0.16	0.42	0.00	0.09	9.17	0.00	0.00
3	79.79	0.00	2.38	1.41	15.14	0.00	0.63	0.12	0.26	0.00	0.11	0.16
4	55.77	0.00	13.54	10.72	13.87	0.20	0.13	0.10	0.34	5.25	0.00	0.09
Mean value:	66.78	0.00	5.53	4.18	18.21	0.09	0.70	0.16	0.17	4.08	0.03	0.06
Sigma:	10.36	0.00	5.58	4.57	5.05	0.10	0.64	0.19	0.16	4.03	0.05	0.08
Sigma mean:	5.18	0.00	2.79	2.28	2.53	0.05	0.32	0.09	0.08	2.01	0.03	0.04

Figure 4.6. EDAX spectra of rice husk (KOHHRH) after activation.

EDAX spectra indicates prominents peaks for rice husk (Fig.4.6) as C, P, O, Si and Fe with average percent of 66.78%, 18.21%, 5.53 %, 4.18% and 4.08%, respectively.

4.2. ADSORPTION EXPERIMENTS

Dimethoate was dissolved in methanol and 10 ppb and 100 ppb solutions were prepared. 0.1 mg activated carbon were added to this solutions. Removal of dimethoate from waters was calculated according to the following formula:

$$\text{Removal efficiency (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (4.1)$$

Where C_0 and C_t (mg/L) are the concentrations aqueous solution of dimethoate at initial, time t and equilibrium respectively.

Table 4.1. Removal of dimethoate from water using activated carbon obtained from corncob and rice husk.

	Contact time (minute)	% Removal with Rice husk (KOHRH)	% Removal with Corncob (KOHCC)	% Removal with commercial activated carbon (AC) (control)
10ppb (10.000) dimethoate solution	5	92	87,57	93,88
	10	89,6	83,86	99,76
	25	78	83,88	97,50
	45	93	93,33	99,94
	75	98	82,56	-
100ppb (100.000) dimethoate solution	5	91,8	87,2	-
	10	89,3	89,6	99,68
	25	94	86,3	99,97
	45	94,7	87	99,87
	75	98,8	86,1	99,83 (90 min)

According to the removal study results, in this study, the data obtained regarding the removal of dimethoate from waters by activated carbon (KOHRH) from rice husk showed that the highest removal (98% and 98%) was obtained for the 75-minute contact time in both 10 ppb and 100 ppb initial concentration of dimethoate.

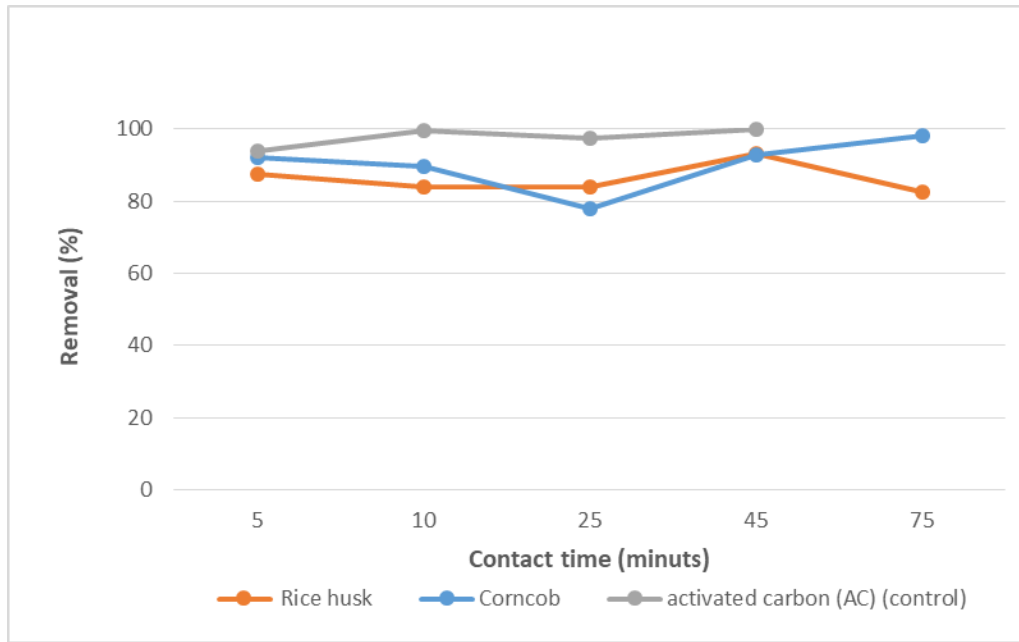


Figure 4.7. Effect of contact time on removal using 10ppb initial concentration of dimethoate using activated carbon.

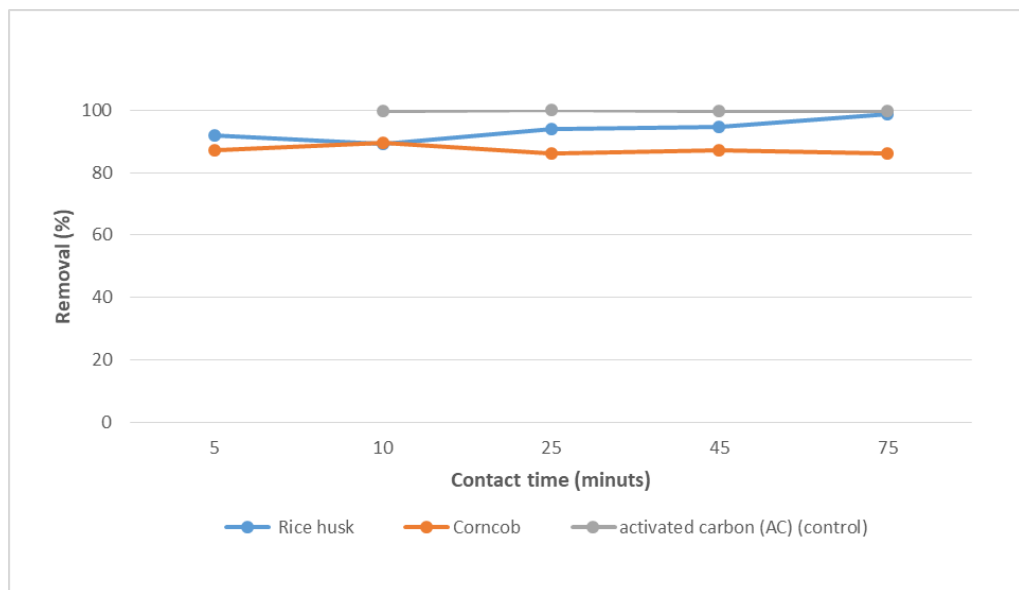


Figure 4.8. Effect of contact time on removal using 100ppb initial concentration of dimethoate using activated carbon.

In the study conducted with KOHCC obtained from corncob, the highest efficiency was obtained in the 45-minute contact time in the 10 ppb starting solution and in the 10-minute contact time in the 100 ppb starting solution. Activated carbon used as a control in the trials, on the other hand, achieved the highest removal rate in the initial

solution of 10ppb in 45-minutes contact time, and in the starting solution of 100ppb in 25 minutes.

The efficiency of dye removal was increased when the contact time increased and lower initial dye concentration [117]. Ndifreke and Pasaoglulari Aydinlik studied the effect of contact time on sorption of dimethoate onto KOHTPS using 0.2 g, 10 mg/L for sorbent dose and sorbate concentration respectively at 40°C and the experimental results indicates that equilibrium time was achieved at 90 min for all concentrations [118].

This study focused on obtaining activated carbon from agricultural waste (corn cob and rice husk) and removal of dimethoate pesticide from water using eco-friendly agricultural waste based activated carbon. The adsorption has been examined with the variations in parameters of initial dimethoate concentration and contact time.

PART 5

SUMMARY

In this study, the KOHRH and KOHCC were obtained using thermal and chemical method. The sorption of dimethoate from aqueous solution using KOH modified rice husk activated carbon (KOHRH) and KOH modified corncob (KOHCC) activated carbon were investigated. The materials used to obtain activated carbon in this study are easily available and inexpensive materials. As a removal efficiency, a high yield was obtained. Therefore, it can be used for wide application areas. Agricultural wastes may offer an inexpensive and renewable additional source of activated carbon. One of the important features of activated carbons used in removal of pesticides from waters is their capacity to adsorb various pollutants.

As a result, low cost agricultural waste adsorbents such as corncob and rice husk can be used as an alternatives to commercial activated carbon for the removal of dimethoate contaminated waters.

REFERENCES

1. Riise, G., Lundekvam, H., Wu, Q. L., Haugen, L. E., & Mulder, J., "Loss of pesticides from agricultural fields in SE Norway—runoff through surface and drainage water", *Environmental Geochemistry AND Health*, 26(2): 269-276 (2004).
2. Kruawal, K., Sacher, F., Werner, A., Müller, J., & Knepper, T. P., "Chemical water quality in Thailand and its impacts on the drinking water production in Thailand", *Science of the Total Environment*, 340(3): 57-70 (2005).
3. Abd Naser, H. S., "Organochlorine pesticide residues in the major rivers of Southern Thailand", *Environment Asia*, Thailand, 30-34 (2008).
4. Jaipieam, S., Visuthismajarn, P., Sutheravut, P., Siriwong, W., Thoumsang, S., Borjan, M., & Robson, M., "Organophosphate pesticide residues in drinking water from artesian wells and health risk assessment of agricultural communities", *Human and Ecological Risk Assessment*, 15(6): 1304-1316 (2009).
5. Poolpak, T., Pokethitiyook, P., Kruatrachue, M., Arjarasirikoon, U., & Thanwaniwat, N., "Residue analysis of organochlorine pesticides in the Mae Klong river of Central Thailand", *Journal of Hazardous Materials*, 156(3): 230-239 (2008).
6. Katagi, T., "Behavior of pesticides in water—sediment systems", *Reviews of Environmental Contamination and Toxicology*, 18(7): 133-251 (2006).
7. VanLoon, G. W., & Duffy, S. J., "Environmental chemistry: a global perspective", *Oxford University Press*, 45-52 (2017).
8. Beulke, S., Dubus, I. G., Brown, C. D. & Gottesbüren, B., "Simulation of pesticide persistence in the field on the basis of laboratory data—a review", *Journal of Environmental Quality*, 29(5): 1371-1379 (2000).
9. Internet: "Developed by the Agriculture & Environment Research Unit (AERU)", <http://www.herts.ac.uk/aeru/footprint/>(2009).
10. Internet: "Food and Agriculture Organization of the United Nations (FAO)", <http://www.fao.org/nr/water/aquastat/main/index.stm/> (2015).
11. Internet: "World Health Organization (WHO)", <http://www.who.int/en/> (2015).

12. Schreurs, R. H., Legler, J., Artola-Garicano, E., Sinnige, T. L., Lanser, P. H., Seinen, W., & Van der Burg, B., "In vitro and in vivo antiestrogenic effects of polycyclic musks in zebrafish", *Environmental Science & Technology*, 38(4): 997-1002 (2004).
13. Heberer, T., "Occurrence, fate and removal of pharmaceutical residues in the aquatic environment: a review of recent research data", *Toxicology Letters*, 131(2): 5-17 (2002).
14. Petrovic, M., & Barceló, D., "Analysis, fate and removal of pharmaceuticals in the water cycle", *Wilson & Wilson's Comprehensive Analytical Chemistry*, New York, USA, 56-71 (2007).
15. Internet: "World Health Organization (WHO)", <http://www.who.int/en/> (2001).
16. Bootharaju, M. S., & Pradeep, T., "Understanding the degradation pathway of the pesticide, chlorpyrifos by noble metal nanoparticles", *Langmuir*, 28(5): 2671-2679 (2012).
17. Lv, Y., Lin, Z., Feng, W., Zhou, X., & Tan, T., "Selective recognition and large enrichment of dimethoate from tea leaves by molecularly imprinted polymers", *Biochemical Engineering Journal*, 36(3): 221-229 (2007).
18. Van Dyk, J. S., & Pletschke, B., "Review on the use of enzymes for the detection of organochlorine, organophosphate and carbamate pesticides in the environment", *Chemosphere*, 82(3): 291-307 (2011).
19. Du, J. J., Gao, R. X., Yu, H., Li, X. J., & Mu, H., "Selective extraction of dimethoate from cucumber samples by use of molecularly imprinted microspheres", *Journal of Pharmaceutical Analysis*, 5(3): 200-206 (2015).
20. Simeonidis, K., Mourdikoudis, S., Kaprara, E., Mitrakas, M., & Polavarapu, L., "Inorganic engineered nanoparticles in drinking water treatment: a critical review", *Environmental Science: Water Research & Technology*, 2(1): 43-70 (2016).
21. Clausen, L., Fabricius, I., & Madsen, L., "Adsorption of pesticides onto quartz, calcite, kaolinite and α -alumina", *Journal of Environmental Quality*, 30(3): 846-857 (2001).
22. Mirković, M. M., Pašti, T. L., Došen, A. M., Čebela, M. Ž., Rosić, A. A., Matović, B. Z., & Babić, B. M., "Adsorption of malathion on mesoporous monetite obtained by mechanochemical treatment of brushite", *Rsc Advances*, 6(15): 12219-12225 (2016).
23. Ayranci, E., & Hoda, N., "Adsorption kinetics and isotherms of pesticides onto activated carbon-cloth", *Chemosphere*, 60(11): 1600-1607 (2005).

24. Wang, P., Yin, Y., Guo, Y., & Wang, C., "Preponderant adsorption for chlorpyrifos over atrazine by wheat straw-derived biochar: experimental and theoretical studies", *RSC Advances*, 6(13): 10615-10624 (2016).
25. Lazarević-Pašti, T. D., Pašti, I. A., Jokić, B., Babić, B. M., & Vasić, V. M., "Heteroatom-doped mesoporous carbons as efficient adsorbents for removal of dimethoate and omethoate from water", *RSC Advances*, 6(67): 62128-62139 (2016).
26. Pradeep, T., & Bootharaju, M. S., "Detection and extraction of pesticides from drinking water using nanotechnologies", *William Andrew Publishing*, Germany, 241-270 (2014).
27. Droste, R. L., "Theory and practice of water and wastewater treatment", *John Wiley & Sons*. New York, USA, 87-102 (1997).
28. White, G. C., "White's handbook of chlorination and alternative disinfectants", *Wiley*, USA, 45-56 (2010).
29. Cancer, I. A., "Overall evaluations of carcinogenicity: an updating of IARC Monographs volumes", *1 to 42. IARC Lyon*, France, 12-19 (1987).
30. Muszkat, L., Feigelson, L., Bir, L., & Muszka, K. A., "Reaction patterns in photooxidative degradation of two herbicides", *Chemosphere*, 36(7): 1485-1492 (1998).
31. Sun, Y., & Pignatello, J. J., "Chemical treatment of pesticide wastes. Evaluation of iron (III) chelates for catalytic hydrogen peroxide oxidation of 2, 4-D at circumneutral pH", *Journal of Agricultural and Food Chemistry*, 40(2): 322-327 (1992).
32. Ozdemir, C., Sahinkaya, S., & Onucyildiz, M., "Treatment of pesticide wastewater by physicochemical and Fenton processes", *Asian Journal of Chemistry*, 20(5): 3795 (2008).
33. Maldonado, M. I., Malato, S., Pérez-Estrada, L. A., Gernjak, W., Oller, I., Doménech, X., & Peral, J., "Partial degradation of five pesticides and an industrial pollutant by ozonation in a pilot-plant scale reactor", *Journal of Hazardous Materials*, 138(2): 363-369 (2006).
34. Chian, E. S., Bruce, W. N., & Fang, H. H., "Removal of pesticides by reverse osmosis", *Environmental Science & Technology*, 9(1): 52-59 (1975).
35. Gupta, V. K., & Ali, I., "Removal of DDD and DDE from wastewater using bagasse fly ash, a sugar industry waste", *Water Research*, 35(1): 33-40 (2001).
36. Bansal, R. C., & Goyal, M., "Activated carbon adsorption", *CRC Press*, Florida, USA, 67-78 (2005).

37. Menéndez-Díaz, J. A. and Martín-Gullón, I. "Types of carbon adsorbents and their production," *In Interface Science and Technology*, 7(2):1–47 (2006).
38. Bansal, S. H. F. & Donet J. B., "Active carbon", *Springer*, New York, 23-30 (1988).
39. Sing, K. S., "Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984)", *Pure and Applied Chemistry*, 57(4): 603-619 (1985).
40. Fuente, E., Menendez, J. A., Suarez, D., & Montes-Morán, M. A., "Basic surface oxides on carbon materials: a global view", *Langmuir*, 19(8): 3505-3511 (2003).
41. Montes-Morán, M. A., Suárez, D., Menéndez, J. A., & Fuente, E., "On the nature of basic sites on carbon surfaces: an overview", *Carbon*, 42(7): 1219-1225 (2004).
42. Bandosz, T. J., & Ania, C. O., "Surface chemistry of activated carbons and its characterization", *In Interface Science and Technology*, 7(2): 159-229 (2006).
43. Montes Morán, M. Á., Suárez Rodríguez, D., & Menéndez Díaz, J. Á., "The basicity of carbons", *Novel Carbon Adsorbents*, Germany, 12-19 (2012).
44. Figueiredo, J. L., Pereira, M. F. R., Freitas, M. M. A., & Orfao, J. J. M., "Modification of the surface chemistry of activated carbons", *Carbon*, 37(9): 1379-1389 (1999).
45. Rodriguez-Reinoso, F., & Molina-Sabio, M., "Textural and chemical characterization of microporous carbons", *Advances in Colloid and Interface Science*, 7(6): 271-294 (1998).
46. Moreno-Castilla, C., "Adsorption of organic molecules from aqueous solutions on carbon materials," *Carbon N. Y.*, 42(1): 83–94 (2004).
47. Vartenytyan, R. S., Voloshchuk, A. M., Dubinin, M. M., & Babkin, O. E., "Adsorption of water vapor and microporous structures of carbonaceous adsorbents Communication 10. The effect of preliminary preparation conditions and the modification of activated charcoals on their adsorption properties", *Bulletin of the Academy of Sciences of the USSR, Division of chemical science*, 35(9): 1763-1768 (1986).
48. Alcañiz-Monge, J., Linares-Solano, A., & Rand, B., "Mechanism of adsorption of water in carbon micropores as revealed by a study of activated carbon fibers", *The Journal of Physical Chemistry B*, 106(12): 3209-3216 (2002).
49. Tóth, A., & László, K., "Water adsorption by carbons. Hydrophobicity and hydrophilicity", *In Novel Carbon Adsorbents*, Germany, 147-171 (2012).

50. Franz, M., Arafat, H. A., & Pinto, N. G., "Effect of chemical surface heterogeneity on the adsorption mechanism of dissolved aromatics on activated carbon", *Carbon*, 38(13): 1807-1819 (2000).
51. Pollard, S. J. T., Fowler, G. D., Sollars, C. J., & Perry, R., "Low-cost adsorbents for waste and wastewater treatment: a review", *Science of the Total Environment*, 116(2): 31-52 (1992).
52. Smith, K. M., Fowler, G. D., Pullket, S., & Graham, N. D., "Sewage sludge-based adsorbents: a review of their production, properties and use in water treatment applications", *Water Research*, 43(10): 2569-2594 (2009).
53. Lladó, J., Lao-Luque, C., Ruiz, B., Fuente, E., Solé-Sardans, M., & Dorado, A. D., "Role of activated carbon properties in atrazine and paracetamol adsorption equilibrium and kinetics", *Process Safety and Environmental Protection*, 9(5): 51-59 (2015).
54. Gupta, V. K., Gupta, B., Rastogi, A., Agarwal, S., & Nayak, A., "A comparative investigation on adsorption performances of mesoporous activated carbon prepared from waste rubber tire and activated carbon for a hazardous azo dye—Acid Blue 113", *Journal of Hazardous Materials*, 186(1): 891-901 (2011).
55. Acevedo, B., Rocha, R. P., Pereira, M. F., Figueiredo, J. L., & Barriocanal, C., "Adsorption of dyes by ACs prepared from waste tyre reinforcing fibre. Effect of texture, surface chemistry and pH", *Journal of Colloid and Interface Science*, 45(9): 189-198 (2015).
56. Gil, R. R., Ruiz, B., Lozano, M. S., & Fuente, E., "Influence of the pyrolysis step and the tanning process on KOH-activated carbons from biocollagenic wastes. Prospects as adsorbent for CO₂ capture", *Journal of Analytical and Applied Pyrolysis*, 1(10): 194-204 (2014).
57. Lopez-Anton, M. A., Ferrera-Lorenzo, N., Fuente, E., Díaz-Somoano, M., Suarez-Ruiz, I., Martínez-Tarazona, M. R., & Ruiz, B., "Impact of oxy-fuel combustion gases on mercury retention in activated carbons from a macroalgae waste: Effect of water", *Chemosphere*, 1(25): 191-197 (2015).
58. Ferrera-Lorenzo, N., Fuente, E., Bermúdez, J. M., Suárez-Ruiz, I. & Ruiz, B., "Conventional and microwave pyrolysis of a macroalgae waste from the Agar–Agar industry. *Bioresource Technology*, 15(1): 199-206 (2014).
59. Gee, I. L., Sollars, C. J., Fowler, G., Ouki, S. K., & Perry, R., "Use of a liquid chemical waste to produce a clay–carbon adsorbent", *Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental AND Clean Technology*, 72(4): 329-338 (1998).
60. Rodríguez Gil, R., "Aprovechamiento integral de residuos sólidos de curtición", *Implicaciones Medioambientales*, Spain, 78-92 (2014).

61. Murugan, S., Ramaswamy, M. C., & Nagarajan, G., "A comparative study on the performance, emission and combustion studies of a DI diesel engine using distilled tyre pyrolysis oil–diesel blends", *Fuel*, 87(11): 2111-2121 (2008).
62. Gökalp, I., & Lebas, E., "Alternative fuels for industrial gas turbines (AFTUR)", *Applied Thermal Engineering*, 24(12): 1655-1663 (2004).
63. Keskin, A., Gürü, M., & Altıparmak, D., "Biodiesel production from tall oil with synthesized Mn and Ni based additives: effects of the additives on fuel consumption and emissions", *Fuel*, 86(8): 1139-1143 (2007).
64. Serrano-Talavera, B., Muñoz-Guillena, M. J., Linares-Solano, A., & Salinas-Martinez de Lecea, C., "Activated carbons from Spanish coals. 3. Preoxidation effect on anthracite activation", *Energy & Fuels*, 11(4): 785-791 (1997).
65. Llán-Gómez, M. J., Garcia-Garcia, A., Salinas-Martinez de Lecea, C., & Linares-Solano, A., "Activated carbons from Spanish coals. 2. Chemical activation", *Energy & Fuels*, 10(5): 1108-1114 (1996).
66. Lillo-Ródenas, M. A., Ros, A., Fuente, E., Montes-Morán, M. A., Martín, M. J., & Linares-Solano, A., "Further insights into the activation process of sewage sludge-based precursors by alkaline hydroxides", *Chemical Engineering Journal*, 142(2): 168-174 (2008).
67. Lozano-Castello, D., Lillo-Ródenas, M. A., Cazorla-Amorós, D., & Linares-Solano, A., "Preparation of activated carbons from Spanish anthracite: I. Activation by KOH", *Carbon*, 39(5): 741-749 (2001).
68. Lillo-Ródenas, M. A., Cazorla-Amorós, D. & Linares-Solano, A., "Understanding chemical reactions between carbons and NaOH and KOH: an insight into the chemical activation mechanism", *Carbon*, 41(2): 267-275 (2003).
69. Choi, Y. K., & Park, S. J., "Preparation and characterization of sucrose-based microporous carbons for increasing hydrogen storage", *Journal of Industrial and Engineering Chemistry*, 2(8): 32-36. (2015).
70. Sangchoom, W., & Mokaya, R., "Valorization of lignin waste: carbons from hydrothermal carbonization of renewable lignin as superior sorbents for CO₂ and hydrogen storage", *ACS Sustainable Chemistry & Engineering*, 3(7): 1658-1667 (2015).
71. Bimbo, N., Physick, A. J., Noguera-Díaz, A., Pugsley, A., Holyfield, L. T., Ting, V. P., & Mays, T. J., "High volumetric and energy densities of methane stored in nanoporous materials at ambient temperatures and moderate pressures", *Chemical Engineering Journal*, 27(2): 38-47 (2015).

72. Ferrera Lorenzo, N., "Aprovechamiento integral del residuo de macoralga procedente de la obtención industrial de Agar-Agar", *Aplicación En El Campo De La Energía Y El Medioambiente. University of Oviedo*, Spain, 67-81 (2015).
73. Oraby, E. A., & Eksteen, J. J., "The leaching of gold, silver and their alloys in alkaline glycine–peroxide solutions and their adsorption on carbon", *Hydrometallurgy*, 15(2): 199-203 (2015).
74. Zuim, D. R., Carpiné, D., Distler, G. A. R., de Paula Scheer, A., Igarashi-Mafra, L., & Mafra, M. R., "Adsorption of two coffee aromas from synthetic aqueous solution onto granular activated carbon derived from coconut husks", *Journal Of Food Engineering*, 104(2): 284-292 (2011).
75. Afif, M. T., & Pratiwi, I. A. P., "Analisis perbandingan baterai lithium-ion, lithium-polymer, lead acid dan nickel-metal hydride pada penggunaan mobil listrik-review", *Rekayasa Mesin*, 6(2): 95-99 (2015).
76. Luo, Y., Guo, W., Ngo, H. H., Nghiem, L. D., Hai, F. I., Zhang, J. & Wang, X. C., "A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment", *Science of the Total Environment*, 47(3): 619-641 (2014).
77. Kovalova, L., Siegrist, H., Von Gunten, U., Eugster, J., Hagenbuch, M., Wittmer, A., & McArdell, C. S., "Elimination of micropollutants during post-treatment of hospital wastewater with powdered activated carbon, ozone and UV", *Environmental Science & Technology*, 47(14): 7899-7908 (2013).
78. Caqueret, V., Cagnon, B., Bostyn, S., & Fauduet, H., "Removal of dark coloured and polyphenolic compounds of sugar beet vinasse by adsorption onto activated carbons: application to a crosscurrent adsorption process", *The Canadian Journal of Chemical Engineering*, 90(2): 403-411 (2012).
79. Chyka, P. A., Seger, D., Krenzelok, E. P., and Vale, J. A., "American academy of clinical toxicology; European association of poisons centres and clinical toxicologists. Position paper: single-dose activated charcoal", *Clin Toxicol*, 43 (2): 61–87 (2005).
80. Chyka, P. A., & Seger, D., "Position statement: single-dose activated charcoal. American Academy of Clinical Toxicology; European Association of Poisons Centres and Clinical Toxicologists", *Journal of Toxicology. Clinical Toxicology*, 35(7): 721-741 (1997).
81. Choy, K. K., Porter, J. F., & McKay, G., "Langmuir isotherm models applied to the multicomponent sorption of acid dyes from effluent onto activated carbon", *Journal of Chemical & Engineering Data*, 45(4): 575-584 (2000).

82. Pikaar, I., Koelmans, A. A., & van Noort, P. C., "Sorption of organic compounds to activated carbons. Evaluation of isotherm models", *Chemosphere*, 65(11): 2343-2351 (2006).
83. Cloirec, P., & Faur, C., "Adsorption of organic compounds onto activated carbon—applications in water and air treatments", *In Interface Science and Technology*, 7(5): 375-419 (2006).
84. Karanfil, T., "Activated carbon adsorption in drinking water treatment", *In Interface Science and Technology*, 7(2): 345-373 (2006).
85. Okouchi, S., Saegusa, H., & Nojima, O., "Prediction of environmental parameters by adsorbability index: water solubilities of hydrophobic organic pollutants", *Environment International*, 18(3): 249-261 (1992).
86. Keiluweit, M., & Kleber, M., "Molecular-level interactions in soils and sediments: the role of aromatic π -systems", *Environmental Science & Technology*, 43(10): 3421-3429 (2009).
87. De Ridder, D. J., Verliefde, A. R. D., Heijman, S. G. J., Verberk, J. Q. J. C., Rietveld, L. C., Van Der Aa, L. T. J., ... & Van Dijk, J. C., "Influence of natural organic matter on equilibrium adsorption of neutral and charged pharmaceuticals onto activated carbon", *Water Science and Technology*, 63(3): 416-423 (2011).
88. Bjelopavlic, M., Newcombe, G., & Hayes, R., "Adsorption of NOM onto activated carbon: effect of surface charge, ionic strength, and pore volume distribution", *Journal of Colloid and Interface Science*, 210(2): 271-280 (1999).
89. Newcombe, G., & Drikas, M., "Adsorption of NOM onto activated carbon: electrostatic and non-electrostatic effects", *Carbon*, 35(9): 1239-1250 (1997).
90. Weber, W. J., & DiGiano, F. A., "Process dynamics in environmental systems", *John Wiley & Sons, Inc.*, New York, USA, 45-58 (1996).
91. Zeni, M., Favero, D., Pacheco, K., & Grisa, A., "Preparation of microcellulose (Mcc) and nanocellulose (Ncc) from eucalyptus kraft ssp pulp", *Polym. Sci*, 1(1): 7 (2016).
92. Kuang, Y., Chen, C., Pastel, G., Li, Y., Song, J., Mi, R. & Hu, L., "Conductive cellulose nanofiber enabled thick electrode for compact and flexible energy storage devices", *Advanced Energy Materials*, 8(33): 1802398 (2018).
93. Fan, G. Z., Wang, Y. X., Song, G. S., Yan, J. T., & Li, J. F., "Preparation of microcrystalline cellulose from rice straw under microwave irradiation", *Journal of Applied Polymer Science*, 134(22): 344-456 (2017).

94. Sun, B., Zhang, M., & Ni, Y., "Use of sulfated cellulose nanocrystals towards stability enhancement of gelatin-encapsulated tea polyphenols", *Cellulose*, 25(9): 5157-5173 (2018).
95. Kian, L. K., Jawaid, M., Ariffin, H., & Alothman, O. Y., "Isolation and characterization of microcrystalline cellulose from roselle fibers", *International Journal of Biological Macromolecules*, 10(3): 931-940 (2017).
96. Naduparambath, S., & Purushothaman, E., "Sago seed shell: determination of the composition and isolation of microcrystalline cellulose (MCC)", *Cellulose*, 23(3): 1803-1812 (2016).
97. Zhao, T., Chen, Z., Lin, X., Ren, Z., Li, B., & Zhang, Y., "Preparation and characterization of microcrystalline cellulose (MCC) from tea waste", *Carbohydrate Polymers*, 18(4): 164-170 (2018).
98. Ibrahim, M. M., El-Zawawy, W. K., Jüttke, Y., Koschella, A., & Heinze, T., "Cellulose and microcrystalline cellulose from rice straw and banana plant waste: preparation and characterization", *Cellulose*, 20(5): 2403-2416 (2013).
99. Liu, Y., Liu, A., Ibrahim, S. A., Yang, H., & Huang, W., "Isolation and characterization of microcrystalline cellulose from pomelo peel", *International Journal of Biological Macromolecules*, 1(11): 717-72 (2018).
100. Xiang, L. Y., Mohammed, M. A. P., & Baharuddin, A. S., "Characterisation of microcrystalline cellulose from oil palm fibres for food applications", *Carbohydrate Polymers*, 14(8): 11-20 (2016).
101. Cao, Q., Xie, K. C., Bao, W. R., & Shen, S. G., "Pyrolytic behavior of waste corn cob", *Bioresource Technology*, 94(1): 83-89 (2004).
102. Branca, C., & Di Blasi, C., "Oxidation reactivity of chars generated from the acid-catalyzed pyrolysis of corncobs", *Fuel Processing Technology*, 12(3): 47-56 (2014).
103. Kenter, J. O., O'Brien, L., Hockley, N., Ravenscroft, N., Fazey, I., Irvine, K. N., & Jobstvogt, N., "The final published version is available direct from the publisher website at", *Ecosystem Services*, 2(1): 194-207 (2016).
104. Jiang, Z., He, T., Li, J., & Hu, C., "Selective conversion of lignin in corncob residue to monophenols with high yield and selectivity", *Green Chemistry*, 16(9): 4257-4265 (2014).
105. Xue, B. L., Huang, P. L., Sun, Y. C., Li, X. P., & Sun, R. C., "Hydrolytic depolymerization of corncob lignin in the view of a bio-based rigid polyurethane foam synthesis", *RSC Advances*, 7(10): 6123-6130 (2017).

106. Duan, C., Meng, X., Liu, C., Lu, W., Liu, J., Dai, L., & Ni, Y., "Carbohydrates-rich corncobs supported metal-organic frameworks as versatile biosorbents for dye removal and microbial inactivation", *Carbohydrate Polymers*, 22(2): 115042 (2019).
107. Pan, Z. Z., Dong, L., Lv, W., Zheng, D., Li, Z., Luo, C., & Kang, F., "A Hollow Spherical Carbon Derived from the Spray Drying of Corncob Lignin for High-Rate-Performance Supercapacitors", *Chemistry–An Asian Journal*, 12(5): 503-506 (2017).
108. Zhang, W., Fina, A., Ferraro, G., & Yang, R., "FTIR and GCMS analysis of epoxy resin decomposition products feeding the flame during UL 94 standard flammability test. Application to the understanding of the blowing-out effect in epoxy/polyhedral silsesquioxane formulations", *Journal of Analytical and Applied Pyrolysis*, 13(5): 271-280 (2018).
109. Yu, J., Li, Z., Ye, Q., Yang, Y., & Chen, S., "Development of succinic acid production from corncob hydrolysate by *Actinobacillus succinogene*", *Journal of Industrial Microbiology and Biotechnology*, 37(10): 1033-1040 (2010).
110. Xu, W., Zhang, S., Lu, J., & Cai, Q., "Furfural production from corncobs using thiourea as additive", *Environmental Progress & Sustainable Energy*, 36(3): 690-695 (2017).
111. Sharma, A., Nain, V., Tiwari, R., Singh, S., & Nain, L., "Optimization of fermentation condition for co-production of ethanol and 2, 3-butanediol (2, 3-BD) from hemicelulosic hydrolysates by *Klebsiella oxytoca* XF7", *Chemical Engineering Communications*, 205(3): 402-410 (2018).
112. Ribeiro, L. S., Delgado, J. J., de Melo Órfão, J. J., & Pereira, M. F. R., "A one-pot method for the enhanced production of xylitol directly from hemicellulose (corncob xylan)", *RSC Advances*, 6(97): 95320-95327 (2016).
113. Jantip, S., & Suwanruji, P., "Preparation and properties of microcrystalline cellulose from corn residues. *In Advanced Materials Research, Trans Tech Publications Ltd*, 33(2): 1781-1784 (2011).
114. Ghehsareh, A. M., "Effect of date palm wastes and rice hull mixed with soil on growth and yield of cucumber in greenhouse culture", *International Journal of Recycling of Organic Waste in Agriculture*, 2(1): 1-5 (2013).
115. Purwanti, E., Wulandari, W. T., Rochliadi, A., Bundjali, B., & Arcana, I. M., "Preparation of nanocrystalline cellulose from corncob used as reinforcement in separator for lithium ion battery", *In Proceedings of the Joint International Conference on Electric Vehicular Technology and Industrial, Mechanical, Electrical and Chemical Engineering*, Surakarta, Indonesia, 365-369 (2015).

116. Kampeerappun, P., "Extraction and characterization of cellulose nanocrystals produced by acid hydrolysis from corn husk", *Journal of Metals, Materials and Minerals*, 25(1): 132-144 (2015).
117. Demirbas, A., "Agricultural based activated carbons for the removal of dyes from aqueous solutions: a review," *J. Hazard. Mater.*, 167(3): 1–9 (2009).

RESUME

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