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Presented by: Youbi Oussama

Contribute to the preparation of conditions for improving activated carbon from agriculture wastes by removing water pollution

Discussed on:

Before the committee consisting of gentlemen

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Dedications

"I don't know what your destiny will be, but one thing I know: the only ones among you who will be really happy are those who have sought and found how to serve."

Albert Sweitzer

For those who answer the call from near and from far, for those who answer the call for help with no expectation of personal gain, to my beloved parents: I am so proud and so delightful to dedicated this dissertation to you. To my dear Mother: words cannot describe my gratitude and my love to you. To my father: This modest work is dedicated to you as well; you've waited so long for this moment, thank you for all love and support. To my brother who supports me in my worst times. To all my friends who helped me to reach this point.

Thanks and gratitude

First of all, we thank God Almighty for the blessings bestowed upon us and grant us the strength to complete this memorandum.

I express our deepest gratitude and thanks to the distinguished professor Dr. Zerrouki Hayat who spared no effort to guide us through all stages of this memorandum.

I also extend our thanks to the discussion committee that accepted the discussion of our memorandum, and we especially mention the chairman of the discussion committee Dr. Belfar Mohammed Lakhdar.

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List of tables

List of figures

Contents

Summary:

The conditions of activation agent, time, temperature, pH and adsorbent amount of agriculture wastes adsorbents to adsorb Methylene blue dye and Zinc(Zn^{2+}), Nickel(Ni^{2+}), Copper (Cu^{2+}), Cadmium (Cd^{2+}), Lead (Pb^{2+}) and Chromium (Cr^{6+}) heavy metals are discussed. The activated carbon prepared from Factory-rejected tea fund to be as an efficient removal of methylene blue from waste water. Persian mesquite grain, pomegranate peel, banana peel and Date press cake activated carbons are appropriate to adsorbPb^{2+}, Zn^{2+}, $Ni^{2+}$and Cr^{6+} anions, respectively with high efficiency. Beside, the high ability to adsorb Cu^{2+} and Cd^{2+} anions from contaminated water found it in coir pith activated carbon, with more tendencies toward copper ions.

Keywords: Agricultural wastes, Activated carbon, Waste water, Heavy metals, Water treatment and Adsorption.

ملخص:

في هذا العمل، تم التطرق الى مختلف ظروف -عامل التنشيط، مدة التنشيط، درجة الحرارة، درجة الحموضة وكمية المادة المازة –تنشيط الكربون النشط و المُحضر من النفايات الزراعية لإمتزاز صبغة المثيلين الزرقاء و المعادن الثقيلة المتمثلة في ايونات الزنك (Zn^{2+})، النيكل (Ni^{2+})، النحاس (Cu^{2+})، الكادميوم (Cd^{2+})، الرصاص (Pb^{2+}) والكروم (Cr^{6+}). وُجد ان الكربون النشط المُحضر من الشاي له قدرة عالية على إمتزاز صبغة المثيلين الزرقاء من المياه الملوثة به. في حين ان الكربون النشط المُحضر من كل من حبوب نبات المسكيت الفارسي، قشور الرمان، قشور الموز و كعكة التمر أظهروا فعالية عالية على إمتزاز كل من أيونات Pb^{2+}، Zn^{2+}، Ni^{2+} و Cr^{6+}، بينما أيونات Cu^{2+} و Cd^{2+} فإنها تُمتز بشكل فعال من طرف الكربون النشط المُحضر من لُب جوز الهند، مع فعالية اكثر اتجاه ايونات النحاس (Cu^{2+}).

الكلمات المفتاحية: المخلفات الزراعية، الكربون النشط، المياه الملوثة، المعادن الثقيلة، معالجة المياه و الإمتزاز.

General introduction

Life on earth was established and has been sustained due to one very essential resource, water. Water plays a considerable role in every aspect of our lives-from being the integral part of our bodies to having colossal importance in many operations. Water is the most important natural and vital source for the survival of life on the earth. Almost 71% of the earth's total surface is covered with water. It is a well-known fact that fresh water is an important necessity for our health. Fresh water is a resource that has many uses, including drinking, irrigation recreation, transportation, hydroelectric power and domestic, industrial, commercial uses, and habitat for economically important animals. Water is said to be pure when it is colorless, free from turbidity and abnormal taste and smell. Water is said to be polluted when it contains micro-organisms of human or animal origin, poisonous chemical substances, industrial or domestic sewage, organic and inorganic substances. Water pollution is the contamination of natural water bodies (like lakes, rivers, oceans, and groundwater) by chemical, physical, radioactive or pathogenic microbial substances that change in the quality of water that has a harmful effect on any living thing that drinks or uses or lives (in) it. The most common source of drinking water for the rural people is groundwater. Groundwater gets polluted as a result of human activities including extensive use of pesticides, herbicides, fertilizers, leaking fuel, chemical tanks, industrial chemical spills, drainage of house hold chemicals and badly managed landfills etc. About 1.2 billion people in the world do not have safe, potable and affordable water for their domestic use. Diseases: cholera, diarrhea, dysentery, hepatitis A, etc. are directly linked to the unhygienic and contaminated potable water. It is estimated that each year more than 842,000 people die from diarrhea globally. The various conventional technics used for waste water treatment and water purification include coagulation, sedimentation, filtration, aeration and also disinfectant processes are present since ancient times, but they are very costly and not economical. Aluminum salts are most common coagulation agents used in water purification all over the world, but they have serious draw backs such as Alzheimer’s disease associated with high aluminum residuals in treated water [1]. Advanced new green technical methods are being introduced to overcome the conventional methods of wastewater treatment. Among all new green methods, adsorption technique using natural adsorbents have been attracting wide interest of researchers because they have the advantages of safe for human health, environmental friendly, generally toxic free and produce no secondary pollution. These adsorbents utilized are natural sources and renewable, such as plants; wood or agriculture wastes; fruit and vegetables. The raw materials are often available locally and hence, a low-cost alternative to other methods. Plant-based adsorbents and their composites can absorb organic compounds and heavy metals by H-bonding, ion exchange, complication, n-π interactions etc. The adsorption mechanism depends on the properties of adsorbent and adsorbate like nature of surface, functional sites on the surface, interaction behavior of adsorbing molecule/ions [2].

The aim in this study is to present and discus the conditions of activation agent, time, temperature, pH, adsorbent amount and equilibrium time of plant-based adsorbents for sequestration of various dyes and heavy metals from water effluents to obtain appropriate and better stipulations and requirements to adsorb and extract contaminants. The adsorption of Methylene blue dye and Zinc(Zn^{2+}), Nickel(Ni^{2+}), Copper(Cu^{2+}), Mercury(Hg^{2+}), Lead(Pb^{2+}) and Chromium(Cr^{6+}) heavy metals are discussed in this study.

First chapter :

Water pollution

I.1 Introduction:

Pollution is the quantitative and qualitative change – Negative or positive, Accidental or intentional - that occurs to one or more of the components or elements of the environmental, and would harm the life of the organism and weaken the ability of ecosystems to continue its production. Water is colorless, transparent, odorless, tasteless liquid at room temperature. Is a substance contains hydrogen, oxygen and existing in gaseous, liquid and solid states. Has ability to dissolve many other substances. That forms the seas, lakes, rivers, and rain and is the basis of the fluids of living organisms. It is sufficient to say that water represents no less than 75% of the composition of the human body and about 90% of the composition of plants **[3].** Water pollution is defined as the presence of foreign substances or impurities (organic, inorganic, biological or radiological) in water, thus degrading its quality and rendering it toxic to humans or the environment. According to Water pollution act (1974) contamination of water or such alteration of the physical, chemical or biological properties of water or such discharge of any sewage or trade effluent or of any other liquid, gaseous or solid substance into water (whether directly or indirectly) as may, or is likely to, create a nuisance or render such water harmful or injurious to public health or safety, or to domestic, commercial, industrial, agricultural or other legitimate uses, or to the life and health of animals or plants or of aquatic organisms. Water is polluted by both natural (volcanic eruptions, earthquakes, tsunamis, underground rocks and soils etc.) as well as man-made activities (sewage, industrial effluents, fertilizers etc.). They are known to alter water and contaminate it **[4].**

I.2 Physicochemical parameters of water:

Humans need water in many daily activities like drinking, washing, bathing, cooking, domestic, agricultural or industrial purpose, etc, because due to use of contaminated water, human population suffers from varied of water diseases. The availability of good quality water is an indispensable feature for preventing diseases and improving quality of life. Thus, the quality of water should be checked at regular time interval before it is used. The water quality usually described according to its physical, chemical and biological characteristics. The physicochemical parameters used to quantify the quality of drinking water presented in *Figure 1*, which are used for testing of water quality to identify the pollution sources **[1].**

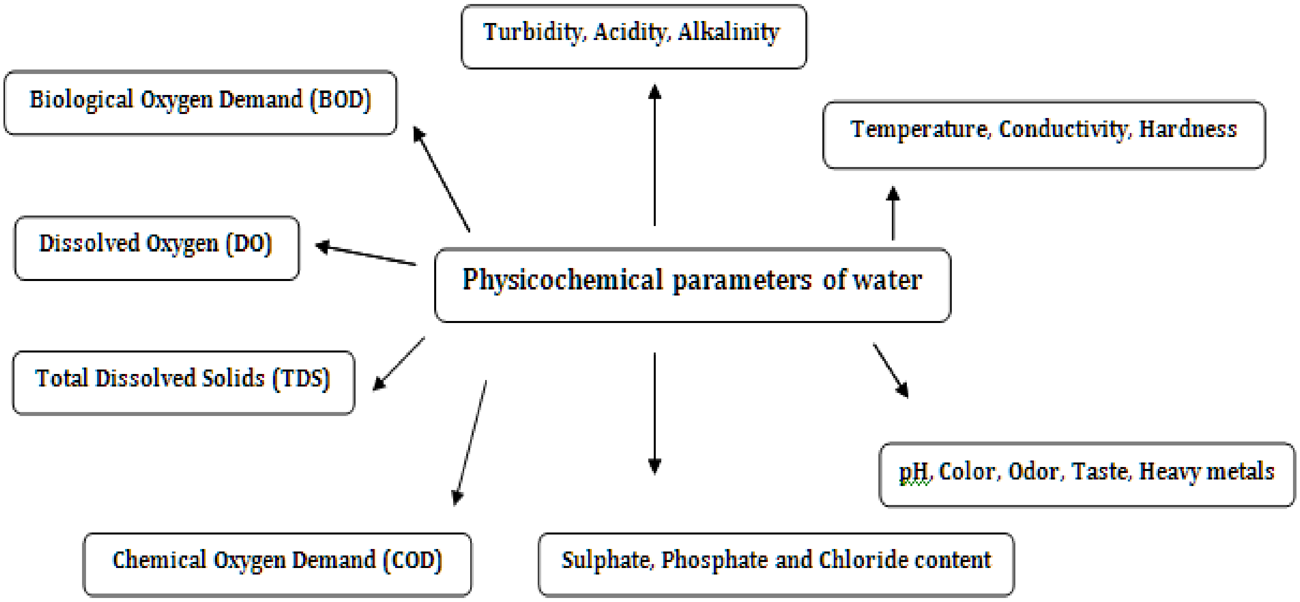


Figure I-1. **Physicochemical parameters used for testing water quality.**

I.3 Types of water pollution:

- Surface water: Surface water is called to huge oceans, lakes, and rivers etc; they contaminated, usually, by chemicals, nutrients, and heavy metals, also sometimes spoiled by oil spills **[4].**
- Ground water: Water stored underground in aquifers is known as groundwater. Groundwater gets polluted when contaminants (pesticides, fertilizers) or waste leached from landfills and septic systems. It is virtually impossible to remove contaminants from groundwater. Groundwater can also spread contamination into streams, lakes, and oceans **[4].**

I.4 Types of pollution:

Physical pollution: This type of pollutants change the color, taste, and smell results from suspending organic and inorganic materials in water **[3].**

Chemical pollution: This type of pollution results from the presence of excessive amounts of dissolved salts, acids, nitrates, phosphates, chlorides, fluorides, heavy metals, organic materials, dyes, fertilizers and pesticides **[3].**

Bio-pollution: The sources of these pollutants are human and animal excreta. They are transferred to the water when it mixes with sewage, that cause biological contamination includes vital pollutants such as pathogenic bacteria, viruses, and parasites [3]. Radioactive pollution: Radioactive materials are the main source of this type of pollution, which are the result of nuclear activity and the attempt to dispose of nuclear waste [3].

I.5 Causes of water pollution:

Growing populations and expanding industries are pulling on water resources while adding nutrients and pollutants to water sources, when water is polluted, it becomes unsafe for human consumption because the water contains dangerous or toxic substances and disease-causing bacteria and organisms, Figure I-2 shows most water pollution causes [1].

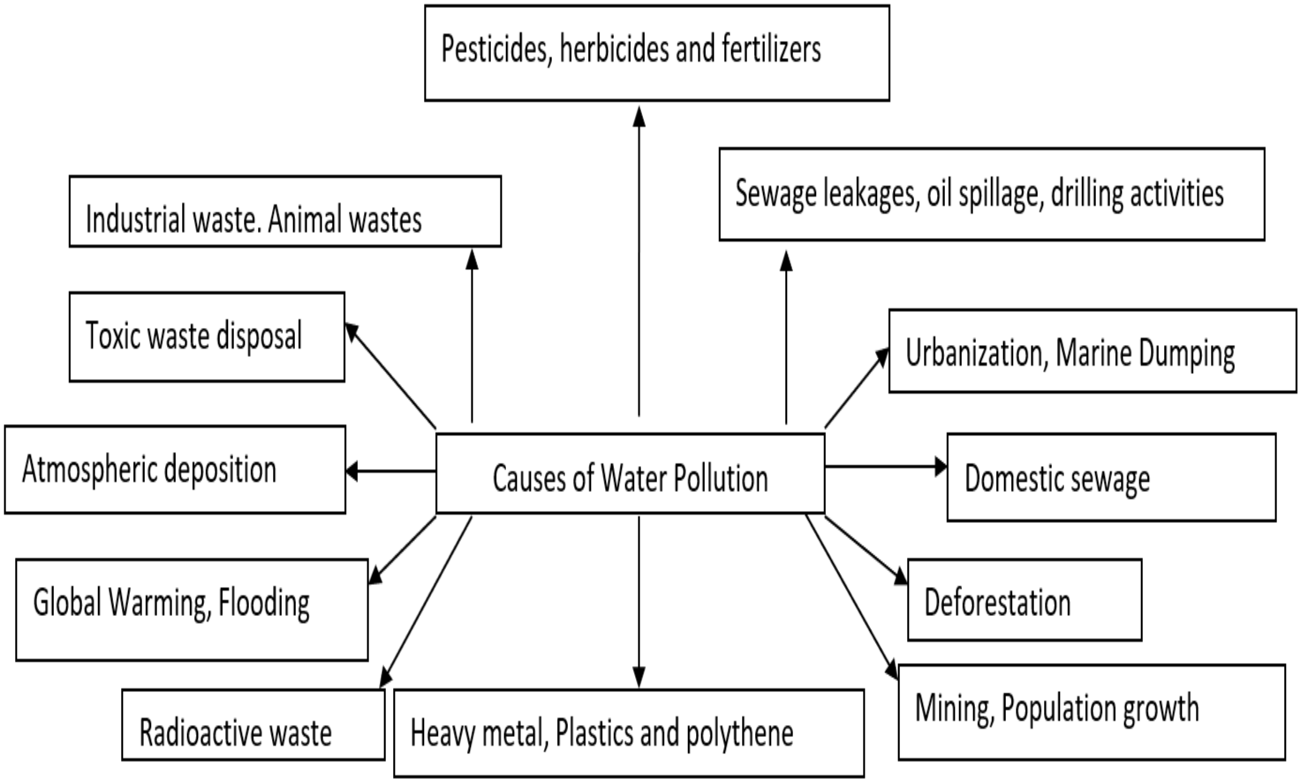


Figure I-2. **Deferent contaminates cause water pollutions.**

I.5.A Heavy metals:

Heavy metals are metals that have densities greater than 5 g/cm^3 such as nickel, cadmium, copper and zinc. Heavy metals it can cause negative health effects to humans or animals like cancer, nausea, vomiting, mental retardation, liver, and kidney failure, Tab I-1, especially nickel and zinc infection, which they are persistent, already, in nature and tend to accumulate in soils and plants by transferring to living organisms through the food chain. Moreover, heavy metal pollution, it is considered as one of the most serious environmental problems, most likely, becouse of industries, such as metal plating, mining operations, surface finishing industry, radiator manufacturing, alloy, and batteries industries usually release heavy metals in water **[5].**

Table 1. **Heavy metals and its toxicity effect on living organisms** [6].

Heavy metal	Sources	Tolerance limit	Effects on the living organisms
Chromium (Cr)	Metal finishing, mining, electroplating, tannery and leather industries.	0.05 ppm	Its carcinogenic nature leads to cancer, kidney and liver damage. It reduces the growth of plants, grain weight and weight of vegetables.
Lead (Pb)	Lead acid battery, paints, electronics, metallurgical, ceramics and pesticide industries.	0.05 ppm	It causes harmful effects on human brain and nervous systems. It damages the circulatory system and kidney function. It leads to high blood pressure.
Mercury (Hg)	Electronics, electrical manufacturing and coal combustion industries.	0.001 ppm	It causes harmful effects on the human nervous system, digestive system, kidney function and circulatory function.
Copper (Cu)	Mining, electroplating, smelting and refining industries.	0.01 ppm	It affects the human blood coagulation. It cause to melena, hypertension, Wilson diseases, gastrointestinal distress and insomnia.
Arsenic (As)	Pesticide/insecticide, smelting operations, thermal power plants and metallurgical industries.	25 ppb	It leads to skin cancer, visceral cancer, kidney failure, bladder damage, abdominal pain and visceral cancer. Also it decreases red and white blood cell production in the human body.
Cadmium (Cd)	Metal plating, pigments, paints, plastic production, fertilizer and pesticide industries.	0.01 ppm	It is carcinogenic which leads to itai-itai disease, kidney damage and renal disorder.
Iron (Fe)	Metallurgical, steel manufacturing, pharmacy production, heavy machinery, food and medicine industries.	1.0 ppm	The overload of iron content causes mutation in the gene. It also causes stomach problems, nausea and vomiting.
Zinc (Zn)	Hydrometallurgical, electroplating, cosmetics, pharmaceuticals, plastics, inks, textiles, batteries, soaps and electrical equipment industries.	0.5 ppm	It leads to hypertension, lethargy, neurotic effects and edema of lungs. Excess of zinc in drinking water affects the internal organs in living organisms.
Nickel (Ni)	Smelting operations, thermal power plants, alloys and battery industries	2 µg/L	It causes lung embolism, asthma and liver and kidney damage with chronic bronchitis.

μg: Micrograms, ppm: part per million.

I.5.B Dyes:

Dyes are molecules that contain chromophore and auxochrome. The chromophore group causes the dye to have its own color since it has a double bond that oscillates to adsorb light, they commonly used in foods, clothes, and also medicines. Many different types of dyes have been produced such as acidic, basic, disperse, azo, anthraquinone based and metal complex dyes; [5], Fig I-3. Cationic dyes are basic dyes while anionic dyes are direct, acid and reactive dyes [7].

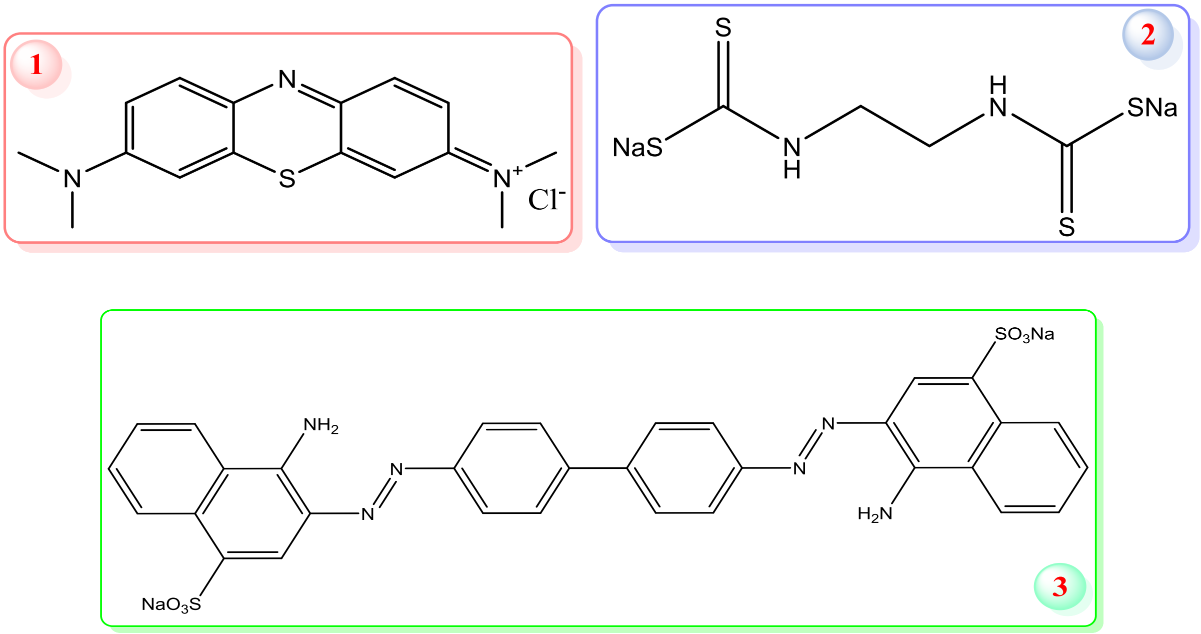


Figure I-3. **Molecular structure of most used dyes: Basic, Methylene blue and Nabam (1, 2), in order. Acidic. Congo red (3).**

A.a Classification of dyes:

Dyes are the coloring agents with annual production of about 7 × 105 t and usually employed in various industries like papers, plastics, processing of food, cosmetics, textiles, pharmaceutical etc. Dyes have been classified on the basis of method of application, nature of chromophore, origin and solubility in water [2], as shown in Fig I-4.

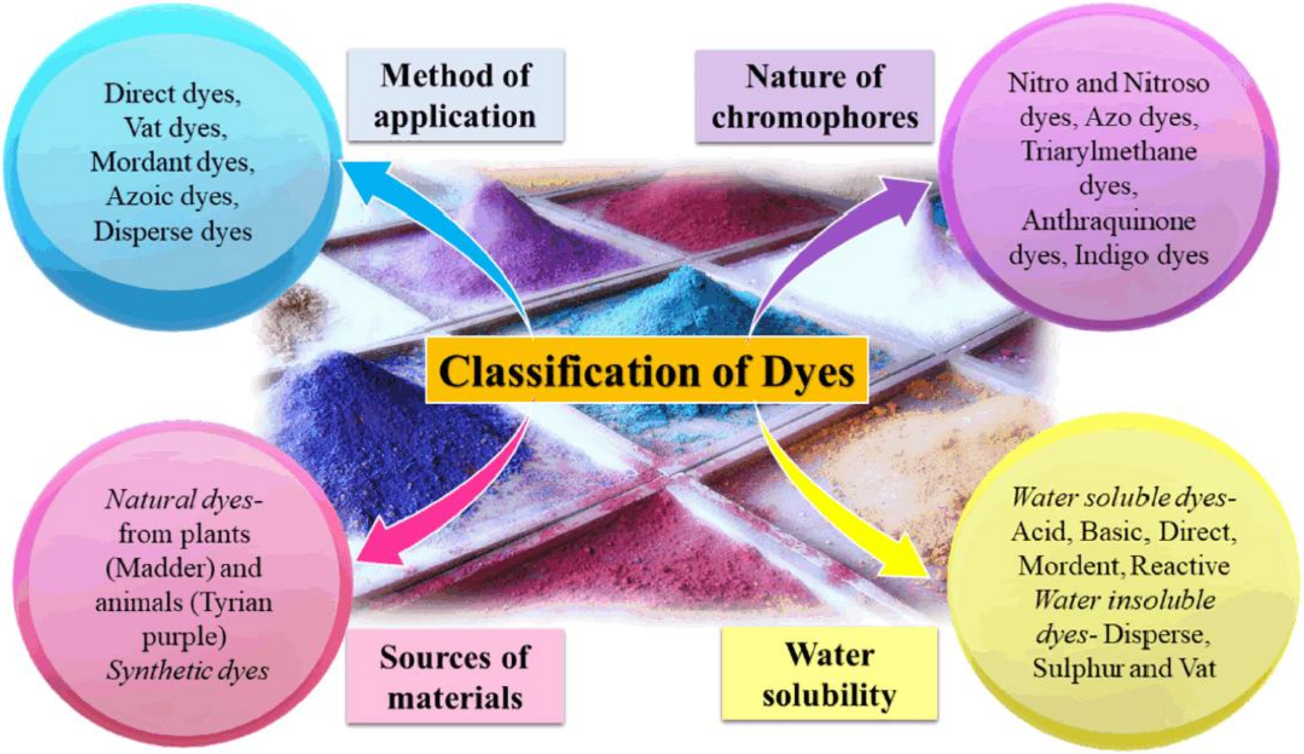


Figure I-4. **Classification of dyes based on nature and**

A.b Toxic effects of dyes and heavy metals:

Due to toxicity of dyes and heavy metals and non-biodegradable characteristics, they have health effects for examples they are cancer, allergic respiratory problem, and skin and mucous membrane irritation, besides, dyes also have environmental pollution which decrease photosynthetic activity in water by affects on the symbiotic process and prevents light penetration [5]. 2000 report approximately 70–80% of total illnesses in developing countries are caused by different water contaminants, predominantly affecting women and children, according to World Health Organization (WHO) and United Nations International Children’s Emergency Fund (UNICEF). According to an estimate by United Nations, three in ten people have deficit ingress to clean drinking water. Contaminated drinking water cause many diarrheal deaths per year. Only 3% of ground water is present in pure form and can be used for drinking and domestic purpose. The amount of various new type contaminants ever increasing in hydrological environments and the availability of pure water is shrinking continuously that's why by 2025 half of the world population will be living in drinking water- deficient areas, so to avoid these difficulties and toxic effects, the water remediation becomes more challenging [2]. Figure I-5 shows various toxic effects caused by dyes and heavy metals.

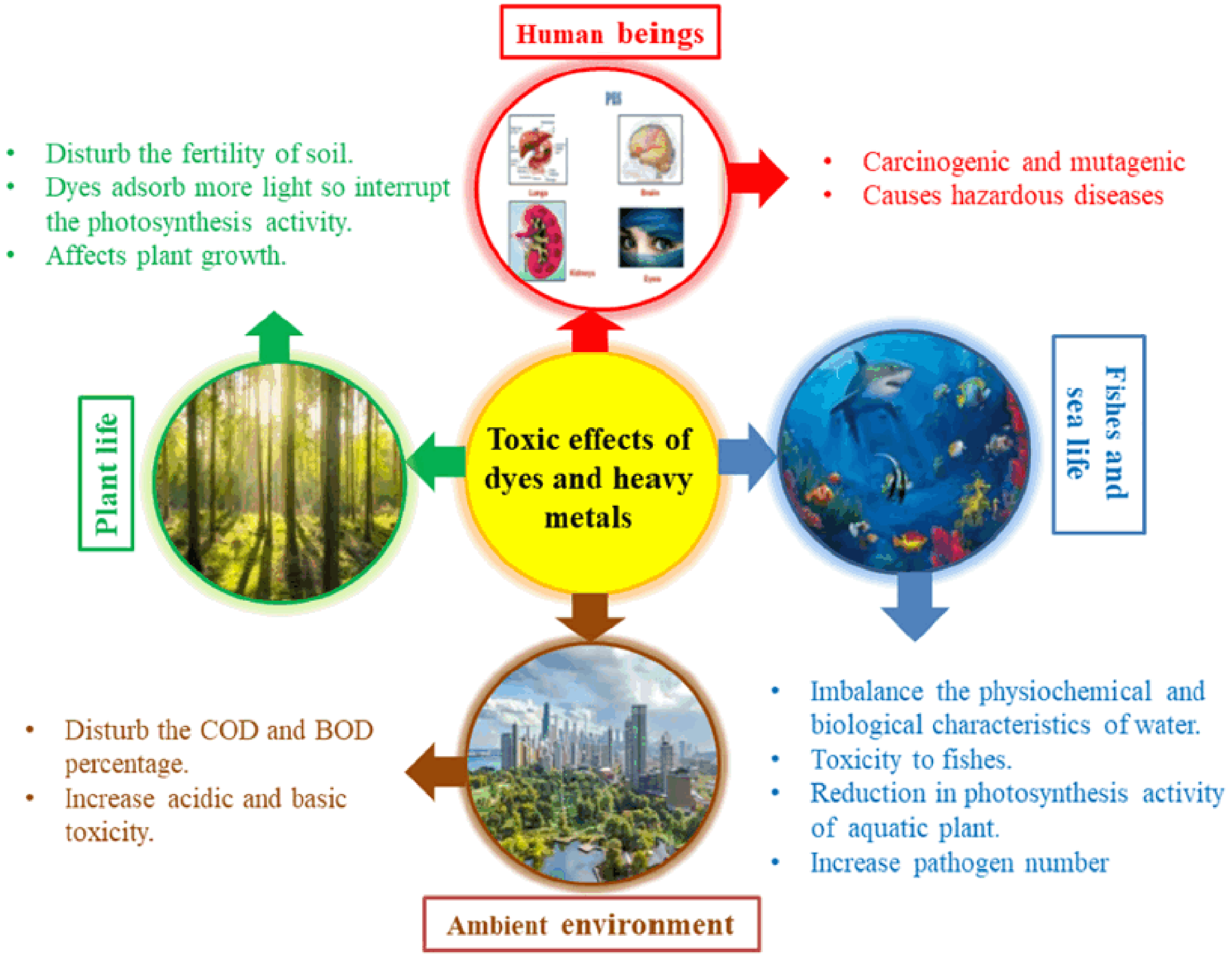


Figure I-5. **Toxicity effects of dyes and heavy metals on deferent living organism.**

I.5.C PAHs compounds:

Polycyclic aromatic hydrocarbons (PAHs) are a group of compounds, which are composed of two or more fused aromatic rings. PAHs have different functional groups in the benzene rings or lateral chains which causes it to have different chemical properties. PAHs are usually emitted as a mixture and the relative molecular concentration ratios are usually treated as the characteristics of the emission source. Besides that, PAHs can also enter the environment through incomplete combustion processes such as the processing of coal and crude oil during refining, coal gasification, and coking. The prevalence of this compound is released into various water bodies which will cause serious health and environmental problems. PAHs are known for their genotoxic, mutagenic, and carcinogenic effects on humans. Other than that, due to its persistent nature, toxicity and bioaccumulation this compound also affects the environment especially soil. Thus, it is important to protect the environment by removing this compound from it, [5] The largest used polycyclic aromatic hydrocarbons (PAHs) are: Phenanthrene, Naphthalene ... etc, Fig I-6.

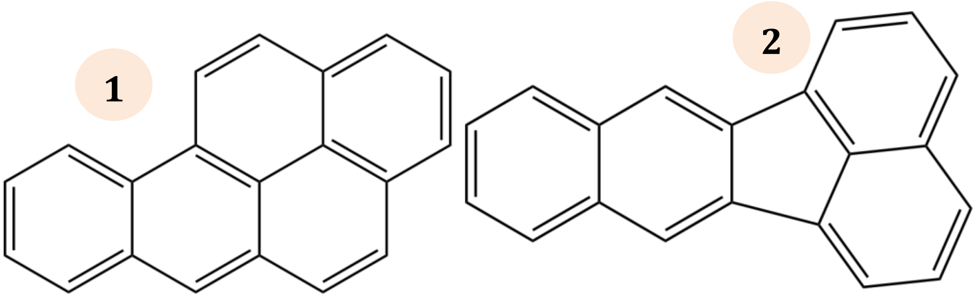


Figure I-6. **Molecular structure of polycyclic aromatic hydrocarbons (PAHs): 1). Benzo[a]pyrene and 2). Benzo[k]fluoranthene.**

I.5.D Pesticides:

Pesticides are chemically prepared from different types of substances such as such as fungicides, rodenticides, weed killers, insecticides, and antimicrobials. This organic material is used to kill targeted pests. Pesticides can be divided into classes which are organophosphates, organochlorines, carbamates, chlorophenol, and synthetic pyrethroids pesticides. Organophosphorus pesticides (OPs) are the most used pesticides in agriculture because it is more biodegradable and has shorter persistence compared to organochlorines pesticides. It protects the crops by inhibiting acetyl cholinesterase enzyme activity in insects. There are few major groups of pesticides that are carcinogenic to living organisms which are organophosphates, organochlorines, carbamates, and pyrethroids. Besides health problems, pesticides affect the ecosystems as well due to their persistent nature, [5].

There are benched of them, according to the types of pests they kill:

- Insecticides-insects.
- Herbicides-plants.
- Rodenticides-rate and mice.
- Bactericides-bacteria.
- Fungicides-fungi.
- Larvicides-Larvae.

Include: 2,4-dichlorophenoxyacetic acid, carbofuran …. etc, Fig I-7.

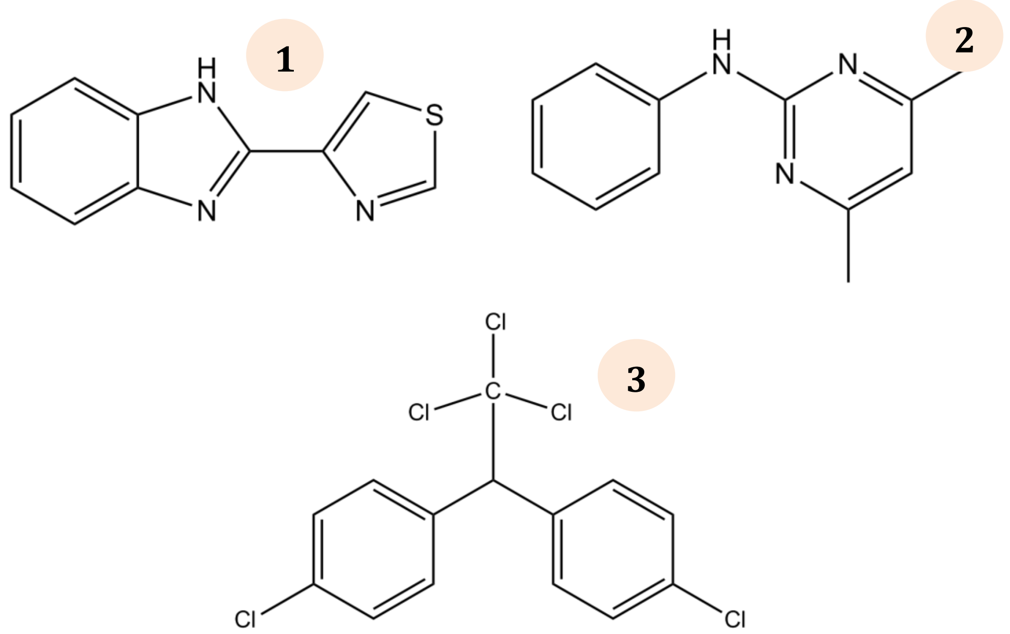


Figure I-7. **Molecular structure of pesticides: 1). Thiabendazole, 2). Pyrimethanil, and 3). 4,4'-(2,2,2-trichloroethane-1,1-diyl)bis(chlorobenzene) or DDT.**

I.6 Sources of Water Pollution:

→ Industrial sources: Most pollutants are exported from factories such as tanning factories, lead, mercury, copper and nickel, paints, cement, glass, detergents, dairy sterilization plants, slaughterhouses, sugar refineries, hydrocarbon pollution resulting from oil pollution, factory water and their wastes contain 60% of the total pollutants [3].

→ Waste water: Disposing of waste water is a major problem. It comes from our sinks, showers, and toilets (sewage) and from commercial, industrial, and agricultural activities (metals, solvents, and toxic sludge). Over 30 billion tons of urban sewage discharged into lakes, rivers and oceans each year [4].

→ Oil Pollution: Marine water is especially affected by this form of pollution. Oil spill occurs due to the release of a liquid petroleum hydrocarbon into the aquatic environment. They are caused by breakage of oil tankers, oil pipe leakage, and human transport or recreational activities cleaning of tanks, refineries, drilling rigs and storage facilities [4].

→ Solid Waste: Dumping of solid wastes include glass, plastic, aluminum, Styrofoam etc. Every day, humans are generating millions of tons of solid waste. Most of those wastes (approximately 70%) are plastics. About 80% of the water pollution is caused due to domestic sewage like throwing garbage [4].

→ Acid rain: Pure rainwater is acidic due to the dissolution of carbon dioxide in its drops. It is not considered rain as an acidic, since its pH estimated to be about 5.6. Acid rains are a result of the formation of sulfuric and nitric acids and the interaction of sulfur and nitrogen oxides in raindrops. The main reason for occurrence of acid rain is attributed to human activity, such as the various combustion processes of fuels. Also, the occurrence of acid rain is attributed to some natural phenomena such as volcanoes. Not all rainwater is necessarily acidic. There are also base rains whose pH may reach more than 8.4. This type of rain does not pose a risk in comparison with acid rain [3].

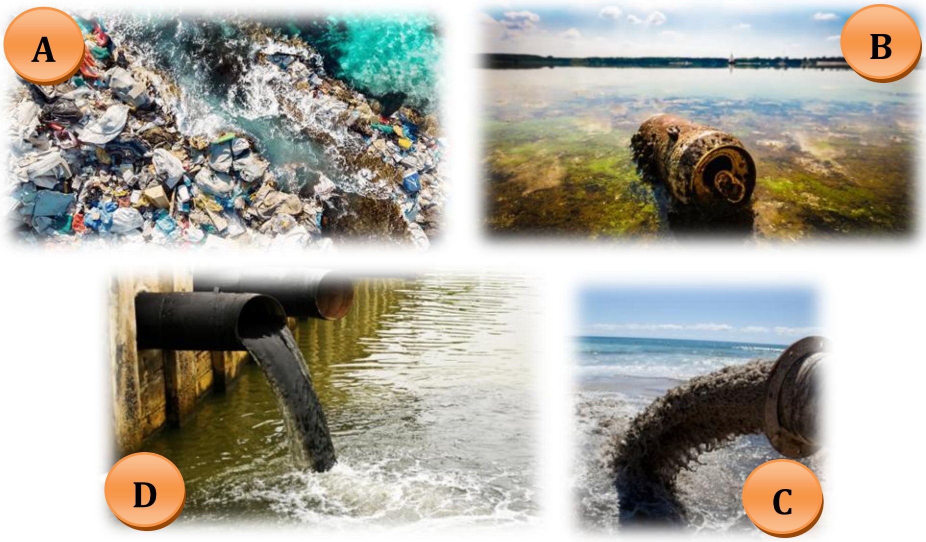
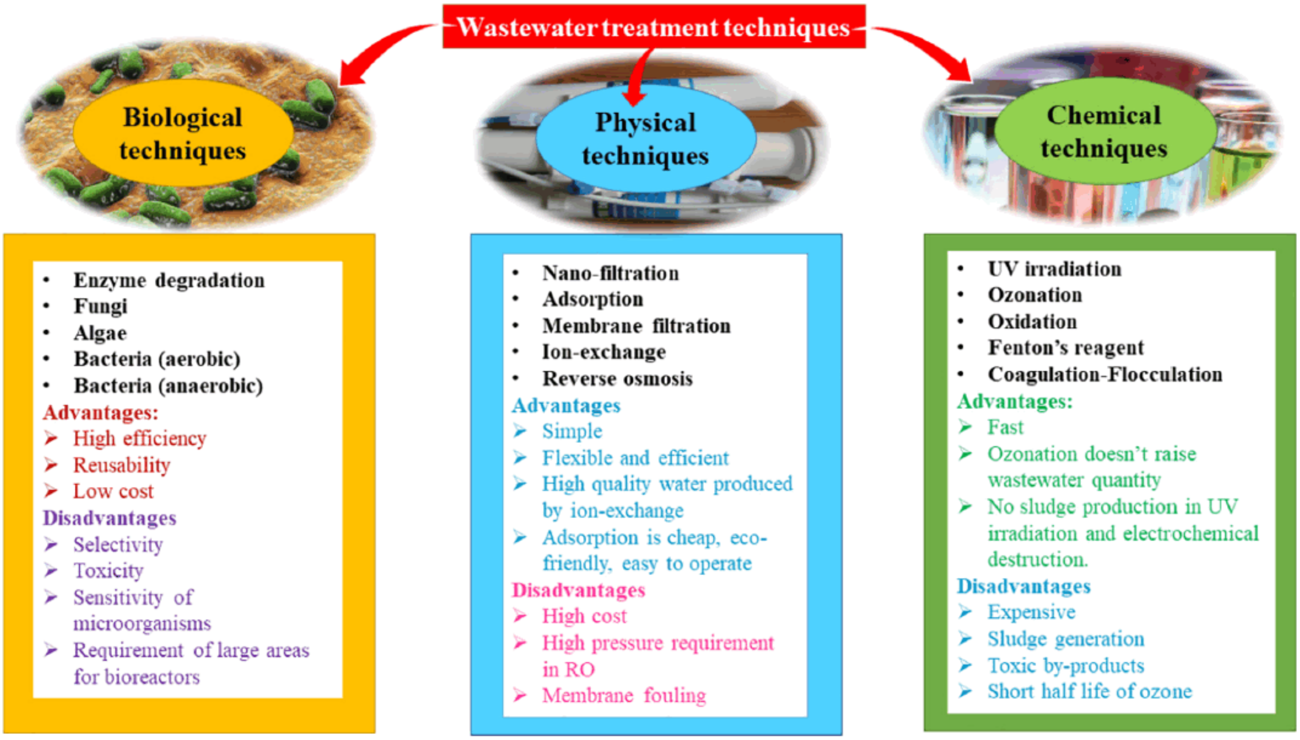


Figure I-8: (Fig A, B, C and D **Represents water pollution granaries.**

I.7 Methods for wastewater treatment:

The removal of dyes and heavy metals from wastewaters is considered an environmental challenge and an effective removal process is their adsorption onto agricultural wastes [7]. There are several techniques for wastewater treatment which can be classified as (i) Physical (ii) Chemical (iii) Biological as presented in Fig I-9. Numerous microorganisms (fungi, algae, bacteria etc.) and enzymes have been studied by researchers for biodegradation and bioaccumulation of various contaminants [2]. Among all the remediation methods, adsorption is highly selective, more efficient, low cost and easy and simple method to operate [7], toughness towards harmful contaminants, low energy consumption. It can remove a number of contaminants like organic, inorganic and biological substances including soluble and non-soluble compounds from wastewater without producing toxic by-products [2].



- Enzyme degradation
- Fungi
- Algae
- Bacteria (aerobic)
- Bacteria (anaerobic)

Advantages:
- High efficiency
- Reusability
- Low cost

Disadvantages
- Selectivity
- Toxicity
- Sensitivity of microorganisms
- Requirement of large areas for bioreactors

- Nano-filtration
- Adsorption
- Membrane filtration
- Ion-exchange
- Reverse osmosis

Advantages
- Simple
- Flexible and efficient
- High quality water produced by ion-exchange
- Adsorption is cheap, eco-friendly, easy to operate

Disadvantages
- High cost
- High pressure requirement in RO
- Membrane fouling

- UV irradiation
- Ozonation
- Oxidation
- Fenton's reagent
- Coagulation-Flocculation

Advantages:
- Fast
- Ozonation doesn't raise wastewater quantity
- No sludge production in UV irradiation and electrochemical destruction.

Disadvantages
- Expensive
- Sludge generation
- Toxic by-products
- Short half life of ozone

Figure I-9. **Deferent technologies that used to remove contaminate form wastewater.**

I.8 Classification of adsorbent types:

Adsorption is occurs when a gas or liquid solute accumulates on a surface of a solid or a liquid (adsorbent) forming a molecular or atomic layer (adsorbate).

Several materials have been studied as potential adsorbents to fulfill the industrial demands for a cheap and efficient low cost biomaterial. These adsorbents are classified into two types: conventional and non-conventional, as shown in Figure I-10. Conventional adsorbents have been used on limited scale, including alumina, zeolite, activated carbon, silica gel and bauxite [8].

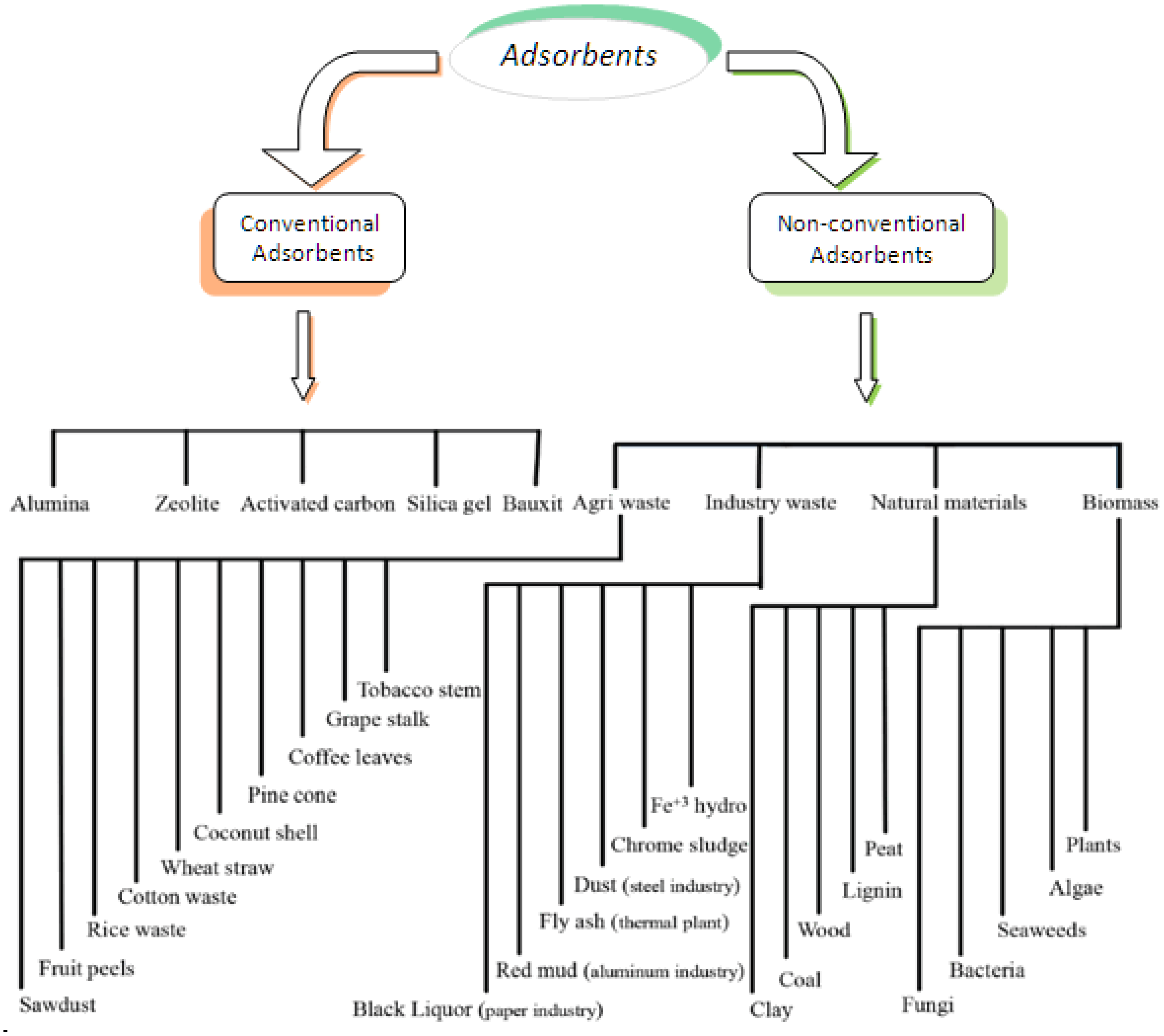


Figure I-10. **The conventional types and non-conventional types of adsorbents.**

I.9 Adsorption Mechanism:

Several non-conventional and cost-effective biomass derived adsorbents have been studied in relation to the treatment of wastewater. The adsorption process is an efficient, affordable, and widely utilized color and heavy metal elimination, bio adsorbents made from bacteria or fungi are promising ecologically acceptable adsorbents. Biomass is commonly used as a low-cost activated carbon in wastewater remediation for the removal of impurities. Charcoal-derived activated carbon was revealed to be the most superior adsorbent with an efficiency of 99.8%, it has drawbacks such as high capital costs, high energy consumption, and sorption–desorption cycles. Most commonly, thermal activation involves the annealing of carbon adsorbent at high temperatures with nitrogen gas (N_2) flowing through it. Functional groupings such as the aromatic ring,$—\mathrm{C=O}$, $—\mathrm{C—O—C}-$, $—\mathrm{OH}$, $—\mathrm{NH_2}$, $—\mathrm{C=S}$, $—\mathrm{C=N}$, and $—\mathrm{S=O}$ on the carbon surface also play important roles in improving the adsorption capacity in terms of MB's disconnection from water. MB is a positively charged chemical. It has a six-carbon aromatic ring, sulfur, and nitrogen in its chemical structure. Figure I-11 shows that the electron dispersion forces between the carbon surface functional groups and MB molecules induce, via electrostatic contact, hydrogen bridge generation, electron donor–acceptor relationships, and $\pi—\pi$ forces after MB's adsorption on carbon [9].

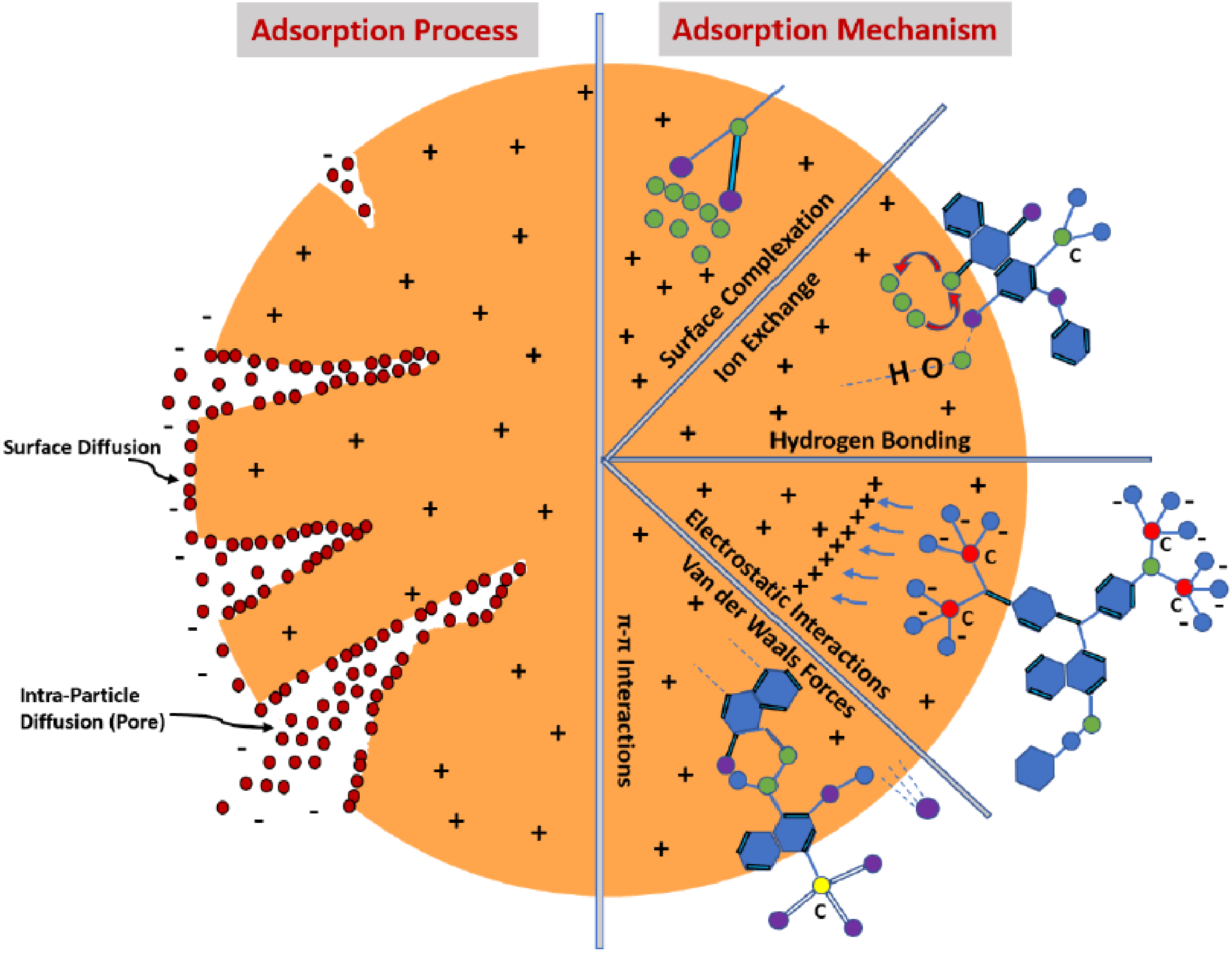


Figure I-11.**Mechanism of adsorption process to eliminate dye (MB).**

I.10 Advantages and disadvantages of wastewater treatment techniques:

Although of various developed methods for the remediation of contaminated water, but it does not perfect, Tab I-2 represent the advantages and disadvantages of techniques that used in water treatment.

Table 2. **Advantages and disadvantages of various used techniques to remove contaminants from wastewater** [6].

Heavy metal removal methods	Advantages	Disadvantages
Electrochemical Treatment	Highly selective, no sludge production and nonhazardous	High cost of electricity
Oxidation	Rapid removal capacity for toxic metal removal.	Formation of secondary by-products and costly.
Precipitation	Relatively simple, non-metal selective and inexpensive.	Secondary pollution formation, large production of sludge, poor settling time and slow metal precipitation.
Coagulation / flocculation	Economical and simple technology	High sludge production and formation of large particles.
Ion exchange	Metal selective, fast rate and high regeneration efficiency.	High maintenance cost.
Membrane process	Easy operation, efficient loading capacities and gets high-quality effluents.	High cost, low flow rate and possesses the limited screen size.
Adsorption	High efficiency, non-toxic, environmentally compatible and easily operated.	Removal capacity depends upon the nature of adsorbents and highly pH-dependent.
Ozonation	Reaction by-products are less harmful, short reaction time and gets high quality of water.	Equipment malfunction, some ozone produce by-products, higher initial cost and regeneration is not possible.
Aerobic process	Fewer operational problems, less daily maintenance and lower BOD produced.	Higher energy requirements and high sludge productions.
Filtration	Low cost and easy to operate.	Not suitable for the removal of all heavy metals, very low flow rate and non-selective.

I.11 Effects of Water Pollution:

Water-related diseases can be classified according to the following- [3]:

- Waterborne diseases: Cholera, typhoid, dysentery bacillus, and infectious hepatitis etc. are caused by drinking water containing infectious viruses or bacteria, which often come from human or animal waste.
- Water-washed diseases: Diseases that occur due to water use for hygiene, like scabies, skin rot and ulcers, leprosy, lice, trachoma, and others.
- Water-based diseases: Water-based diseases like schistosomiasis, filariasis, and nematode worm.
- Water-related: Insects transmit the disease germs, such as mosquitoes and black fly, associated with water, which are yellow fever, dengue fever, filariasis, malaria and others.

I.12 Control Measures [4]:

- Educating people and Media involvement.
- Recycling and Reuse of water can improve the availability of fresh water. Reclaimed polluted water can be used in making fertilizers as it is rich in phosphorous, potassium and nitrogen. Also, it can be used for the irrigation and factories purposes.
- Preventing soil erosion: planting more trees to stop soil erosion, prevent water from getting polluted.
- Cleaning of water ways and the beaches.
- Adopting organic farming it will control runoff of harmful chemicals into water bodies.
- Industries should dispose their wastes properly, also required to modify their methods of manufacturing or develop techniques to prevent water pollution.
- Compliance with all the laws regarding water pollution could reduce water pollution effectively.
- Sewage treatment plans could convert pollutants into non-toxic substances and reduce water pollution.

Second chapter:

Agriculture wastes

II.1 **Introduction:**

Agricultural wastes (AW) can be defined as the residues from the growing and first processing of raw agricultural products such as fruits, vegetables, meat, poultry, dairy products and crops. AW can be in the form of solid, liquid or slurries depending on the nature and type of agricultural activities. Agricultural waste otherwise called agro-waste is comprised of animal waste (manure, animal carcasses), food processing waste (only 20% of maize is canned and 80% is waste), crop waste (corn stalks, sugarcane bagasse, drops and culls from fruits and vegetables, pruning) and hazardous and toxic agricultural waste (pesticides, insecticides and herbicides, etc). Agricultural industry residues and wastes constitute a significant proportion of worldwide agricultural productivity. Although the quantity of wastes produced by the agricultural sector is significantly low compared to wastes generated by other industries, the pollution potential of agricultural wastes is high on a long-term basis. The opportunity and feasibility for recycling these wastes comes from two directions: the care for environment reflected by new sets of rules and regulation and the potential to add value to these wastes by adding positive elements. Moreover, they can be used as precursors in many other sectors such as membranes, biosorbents or activated carbons for the removal of dyes, organic molecules, heavy metals and fertilizer **[10]**.

Different types of agricultural wastes, i.e. coconut shell, hyacinth roots, rice husk, banana stalk, olive stones, almond shells and peach stones and more are ideal raw materials for different industrial applications due to their low cost, non-toxic content and their abundance. The final products derived from agricultural wastes have shown equal or even better properties compared to conventional products concerning separation, adsorption and fertility **[7].**

II.2 **Types of agriculture wastes:**

The agriculture waste introduced by United Nations as: The various operations agricultural produce agriculture waste. It includes manure and other wastes from farms, poultry houses and slaughter houses; harvest waste; fertilizer run- off from fields; pesticides that enter into water, air or soils; and salt and silt drained from fields **[11],** as presented in Fig Ⅱ-1.

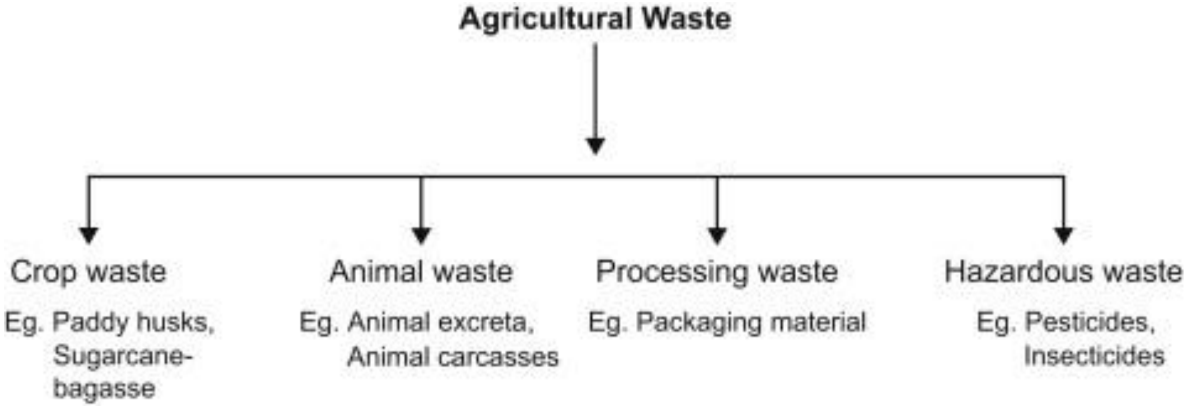


Figure Ⅱ-12. **Types of agricultural waste.**

II.2.A Animal production solid wastes:

Animal production solid wastes are solid wastes generated from the production of livestock such wastes include bedding/litter, animal carcasses, damaged feeders, and water-trough, etc **[12]**.

II.2.B Food and meat processing solid wastes:

The processing of crop or animal products for such as abattoir or slaughterhouses produces such wastes. Food and meat processing agricultural solid wastes include hoofs, bones, feathers, banana peels, etc **[12]**, Fig Ⅱ-2.

Figure Ⅱ-2: Fig A and B represent **Food agricultural solid waste.**

II.2.C Crop production solid wastes:

These wastes, typically, are produced from agricultural activities involving crop production such as crop residues, husks, etc **[12]**.

II.2.D Industrial agricultural solid wastes:

Agricultural produce and livestock are used for other uses that result in agricultural solid wastes, such activities as paper production using agricultural products as raw materials also generate some quantities of agricultural solid wastes **[12]**.

II.2.E Chemical wastes:

These kinds of agricultural solid wastes generated from the use of pesticides, insecticides and herbicides on the farm or store, such as pesticide containers or bottles. Agricultural activities still depend on the use of pesticides, insecticides, and herbicides, being handled by many uneducated and untrained farmers in developing countries, resulting in abuse by these uneducated farmers **[12]**.

II.3 **Agricultural products and geographical area:**

The fact that the quantity and composition of agricultural waste, as presented in Table Ⅱ-1, are dictated by the geographical and cultural aspects of a country or a region, as shown in Table Ⅱ-2, and also the extent of land used for agriculture **[11].**

Table Ⅱ-1. **Most agricultural waste composition.**

	Source	Composition
1	Rice	Husk, Bran
2	Wheat	Husk, Bran
3	Oat	Straw
4	Maize	Stover, Husk, Skins trimming, Cobs
5	Millet	Stover
6	Pineapple	Outer peel, crown, bud ends, fruit trimming
7	Sugarcane	Sugarcane tops, bagasse, molasses

An FAO report of 2011 showed that annual food losses accounted for 40–50% for root crops and fruit and vegetables, 30% for cereals and fish, and 20% for meat and dairy products, **[13]**, presented in Tab Ⅱ-2.

Table Ⅱ-2. **Total Agricultural land and Total Waste generation.**

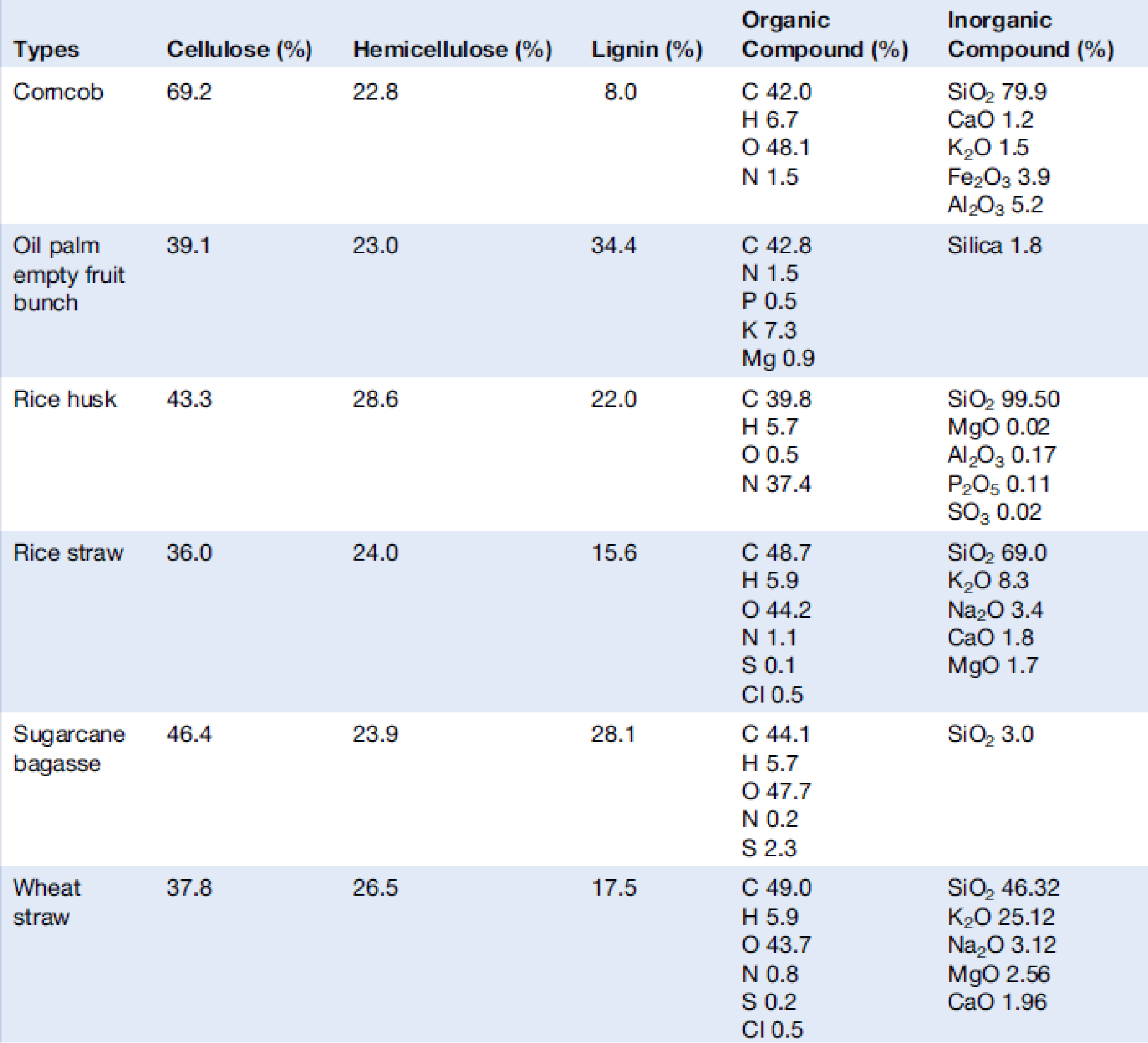
Geographical country	Roots and Tubers	Fruits and Vegetables	Cereals	Fish and Seafood	Meat	Dairy Products
Europe	52%	46%	34%	31%	22%	12%
North America and Oceania	60%	52%	35%	49%	23%	20%
Industrialized Asia	48%	36%	34%	36%	21%	11%
Sub-Saharan Africa	45%	52%	19%	33%	27%	25%
North Africa, West and Central Asia	33%	56%	30%	30%	23%	20%
South and Southeast Asia	41%	52%	20%	35%	19%	22%
Latin America	39%	56%	26%	29%	21%	22%

The crops are considered to be the world's most produced and consumed agricultural products, Tab Ⅱ-3; accordingly, the associated solid wastes are available in plentiful amount **[14]**.

Table Ⅱ-3. **Estimation production of most crops agricultural product.**

Types	Production (Million Tons)	Country of Origin
Corncob	81	USA
	49	China
	20	Brazil
	13	EU
	9	Argentina
Oil palm empty fruit bunch	37	Indonesia
	19	Malaysia
	2	Thailand
	1	Colombia
	0.9	Nigeria
Rice husk	39	China
	30	India
	10	Indonesia
	9	Bangladesh
	8	Vietnam
Rice straw	149	China
	114	India
	39	Indonesia
	36	Bangladesh
	30	Vietnam
Sugarcane bagasse	94	Brazil
	93	India
	55	EU
	38	Thailand
	29	China
Wheat straw	128	EU
	110	China
	40	USA
	25	Canada
	22	Pakistan

Sugarcane, corn, rice, and wheat are the top four of the world's largest produced crops by quantity. Together, rice, corn, and wheat supply more than 42% of all calories consumed by the whole human population, whereas palm oil produced from the oil palm tree is one of the most consumed and produced oils in the world. Cultivation and manufacturing processes, which use these crops as raw material, generate solid wastes such as rice straw, rice husk, corncob, wheat straw, and oil palm empty fruit bunch (OPEFB). It is not only the amount of these solid wastes that creates significant concern but also their characteristic as a lignocelluloses, which poses a challenge in treating or utilizing them. Figure Ⅱ-3 shows chemical composition of most agricultural product of crops **[14].**



Types	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Organic Compound (%)	Inorganic Compound (%)
Corncob	69.2	22.8	8.0	C 42.0 H 6.7 O 48.1 N 1.5	SiO_2 79.9 CaO 1.2 K_2O 1.5 Fe_2O_3 3.9 Al_2O_3 5.2
Oil palm empty fruit bunch	39.1	23.0	34.4	C 42.8 N 1.5 P 0.5 K 7.3 Mg 0.9	Silica 1.8
Rice husk	43.3	28.6	22.0	C 39.8 H 5.7 O 0.5 N 37.4	SiO_2 99.50 MgO 0.02 Al_2O_3 0.17 P_2O_5 0.11 SO_3 0.02
Rice straw	36.0	24.0	15.6	C 48.7 H 5.9 O 44.2 N 1.1 S 0.1 Cl 0.5	SiO_2 69.0 K_2O 8.3 Na_2O 3.4 CaO 1.8 MgO 1.7
Sugarcane bagasse	46.4	23.9	28.1	C 44.1 H 5.7 O 47.7 N 0.2 S 2.3	SiO_2 3.0
Wheat straw	37.8	26.5	17.5	C 49.0 H 5.9 O 43.7 N 0.8 S 0.2 Cl 0.5	SiO_2 46.32 K_2O 25.12 Na_2O 3.12 MgO 2.56 CaO 1.96

Figure Ⅱ-3. **Chemical composition of agricultural produced from crops.**

II.4 Agriculture and irrigation:

Irrigation agriculture is projected as a major global strategy to meet agricultural production targets, especially in developing economies. As early as in 1996, the FAO had projected that an estimated 90% of agricultural land will be under irrigation by 2000. As presented in Fig Ⅱ-4, irrigation is a top priority component of water managers in developing countries **[14].**

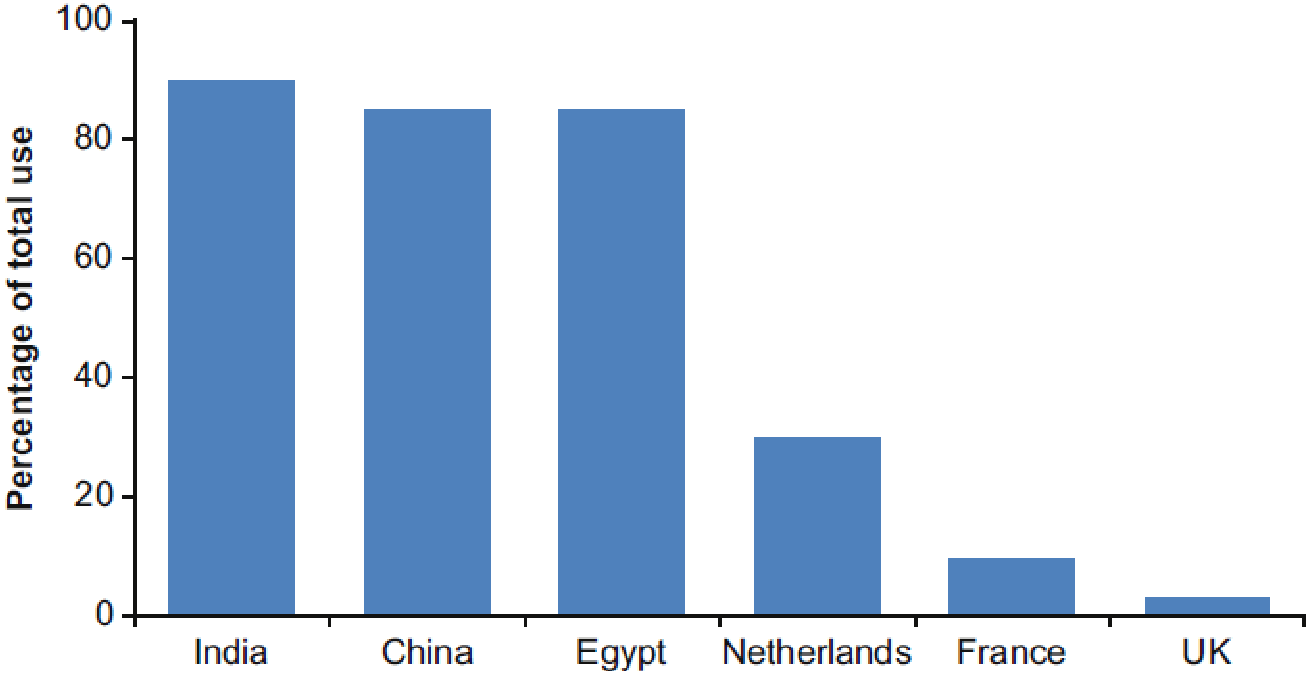


Figure Ⅱ-4. **Total water used to irrigation in some countries.**

II.5 Agricultural and water pollution:

Agriculture is a major source of pollution of water and land resources. It is an acknowledged fact that agriculture is the largest user of freshwater resources, using a global average of 70% of all surface water supplies. As a result, agriculture is a major cause of degradation of surface and groundwater resources. Erosion and post precipitation run-off of chemicals used in fertilizer and pesticide formulations are the major processes responsible for degrading the quality of receiving water bodies. Agriculture-driven water quality problems are complex in nature and require multidisciplinary input and approach for proper understanding of the same **[11],** as presented in Fig Ⅱ-5.

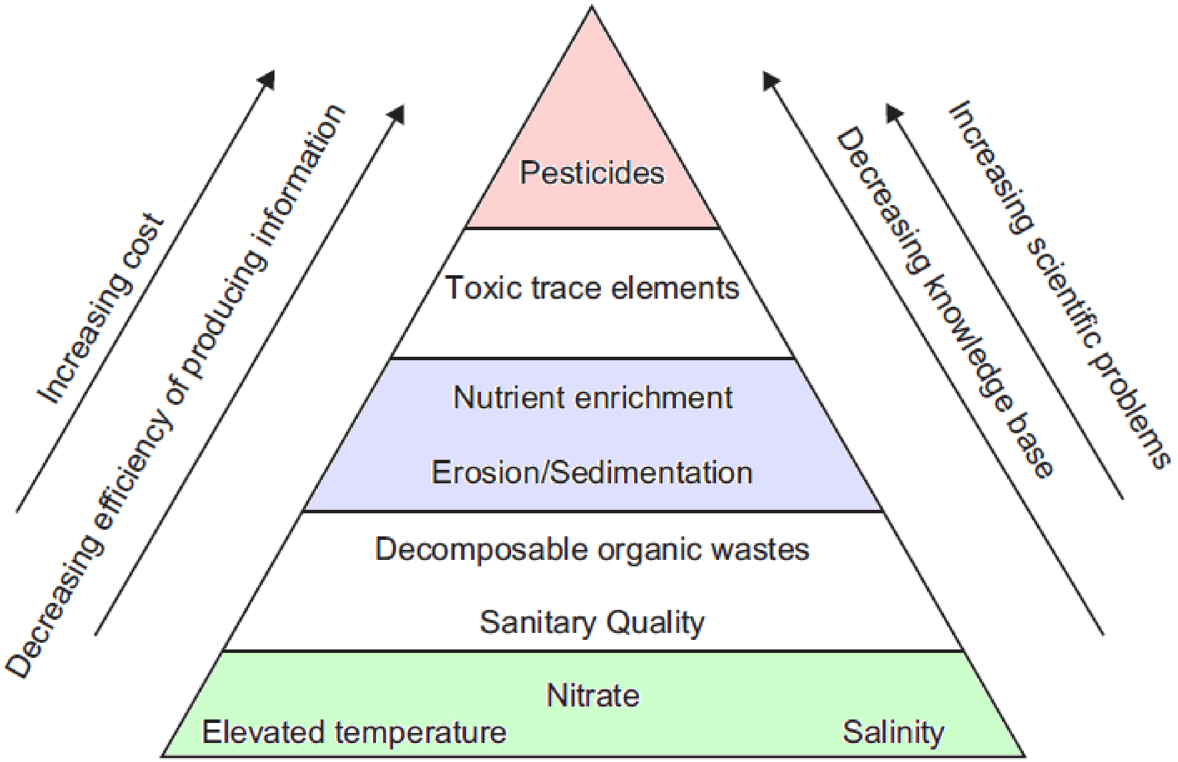


Figure Ⅱ-5. **Hierarchical complexities of agricultural related to water quality problems.**

It found that long-term exposure to agricultural waste water has caused a gradual deterioration in the water quality of Poyang Lake, the largest fresh-water lake in China, with increases in TSS, CODCr, BOD5, TN and TP. A second study estimated the total waste N released to surface water in China at 11.4 kg N in 2008, a figure amounting to 40% of the total fertilizer N application to China's cropland raised concerns about manure used as agricultural fertilizer, which can introduce natural and synthetic hormones to both agricultural fields and aquatic ecosystems. In a study in the Midwestern United States, hormone concentrations in subsurface tile drains were found to increase during effluent irrigation and storm events. Problems also appeared to persist over winter, with pollutant-releases to drainage ditches after snowmelt increasing hormone concentrations in the water (87ng/L for total estrogens and 52ng/L for natural androgens) **[15].**

Third chapter:

Activated carbon

III.1 **Introduction:**

Activated carbon (AC) is a member of a carbons family ranging from carbon blacks to nuclear graphites, from carbon fibers and composites to electrode graphites, and many more. All come from organic parent sources but with different carbonization and manufacturing processes [16]. Activated carbon (AC) popularly, known as activated charcoal or activated coal, and is a common term for carbon materials, which comprises charcoal. The fine structure possessed by AC increased the surface area (>1000 m^2/g) of pores that result in the possession of powerful adsorptive properties. Carbon is available in three main forms; these are; powder, granular and pellet. Nonetheless, the most frequently used are granular and powdered AC [17].

Synthesis of activated carbon from biomass can reduce environmental pollution and the cost of disposal [18]. Although activated carbons from biomasses are used in many industrial applications, the biggest challenge in producing activated carbon is the cost of production, uncertain methods, and also regeneration process [19].

Activated carbon does not just happen; it has to be synthesized. The porosities of a carbon, as initially prepared by carbonization, are not sufficiently developed for most applications and some amelioration is a prerequisite step. This is done in several ways involving creation of further porosity, widening of existing porosity, modifications to the surfaces of porosities and also modifying the carbonization process itself [16].

In the adsorption process, adsorbent primarily depends on the surface chemistry and pore structure of the material. Method of activation and nature of precursor tremendously affect the surface functional groups and porous structure. The surface functional groups provide vital information involving removal of cationic and anionic adsorbate [20]. For example, when activated carbon is treated with acid, the activated carbon will have negatively charged acid groups and able to absorb cationic adsorbate and vice versa [21].

The four major commercial adsorbents are the following: zeolite molecular sieves (ZMS), activated alumina, silica gel, and activated carbon. The surfaces of activated alumina and most molecular-sieve zeolites are hydrophilic, and will preferentially adsorb water over organic molecules. Silicalite, which is a hydrophobic zeolite, is the main exception. The surface of silica gel is somewhere in between these limits and has affinity for both water and organics. Activated carbon, on the other hand, preferentially adsorbs organic and non-polar or weakly polar compounds over water **[22],** which is the main subject of our study.

III.2 Methods to Manufacturing activated carbon:

The activation process is added to improve the porous structure of the carbonaceous materials, i.e., increase the volume of the pores and the specific surface. There are two main types: chemical activation and physical activation, shown in Fig III-1, addition to pyrolysis step. The main difference between the two is the reactivity of the compounds used as activating agents. The activation process is important when hydrothermal carbon adsorbents are prepared because their capacity is often related to their specific surface and their porous structure. This aspect is more important in adsorption than in other applications of HTCs. HTCs are chars with high oxygen content, a large number of functional groups, and low porous development. They have been used to remove numerous contaminants of all types, they are produced by heating an organic material in the presence of water in a closed vessel at temperatures above 100 °C **[23].**

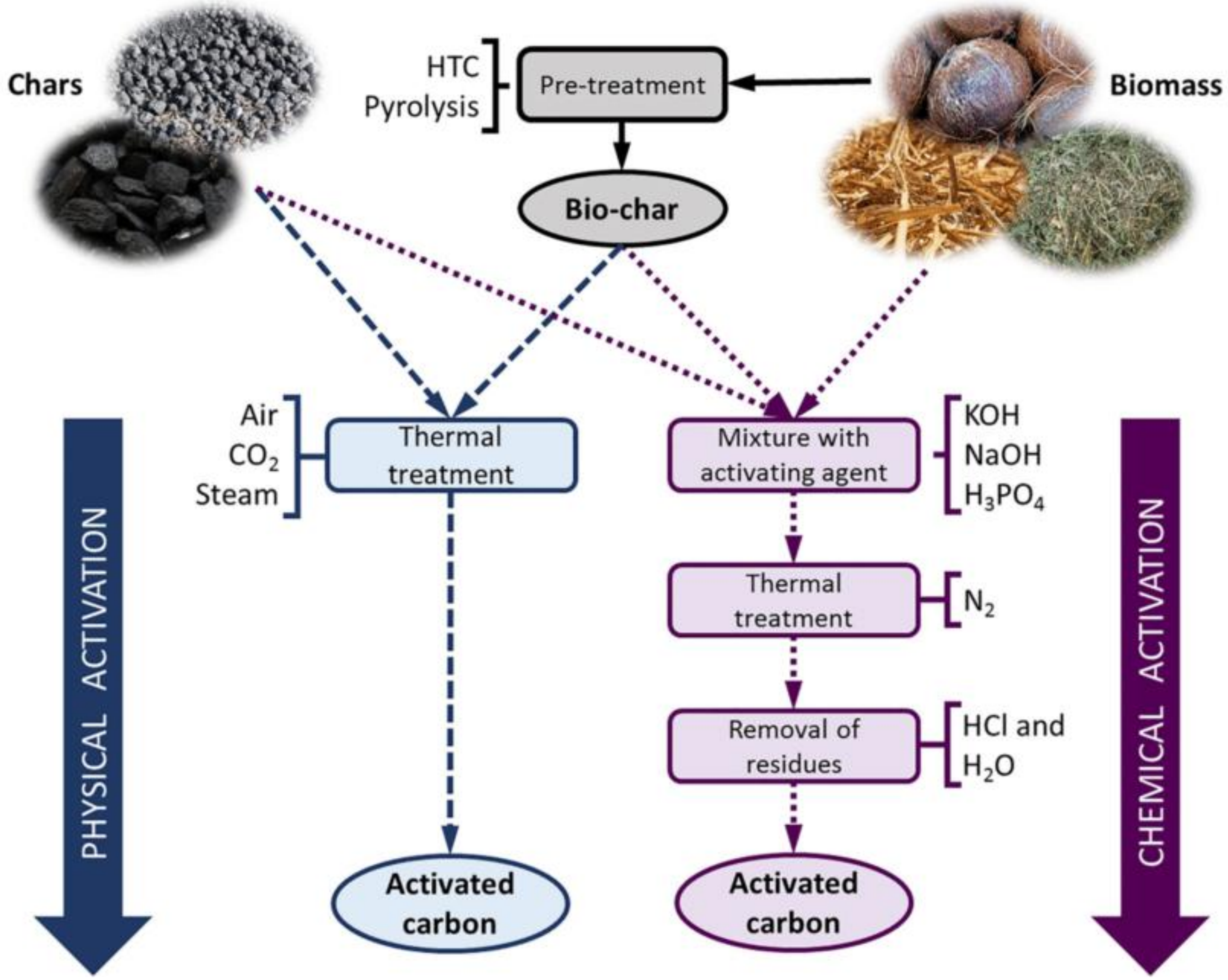


Figure III-1. **Schematic production of activated carbons from biomass and char by different processes.**

III.2.A Pyrolysis process:

Pyrolysis is a simultaneous process that changes both the chemical composition and physical phase of materials (Thermo-chemical conversion of organic biomass) at extremely high temperature in the absence of halogen (mainly oxygen) and is irreversible. Pyrolysis process, Fig III-2, is mostly observed when materials are exposed to higher temperatures. Some features of pyrolysis such as temperature has the most significant effect and then followed by retention time, heating rate and nitrogen flow rate. Normally, when the reaction temperature increased, causes reduction in both AC and char production, while at the same time increasing the pyrolysis temperature leads to a drop off of solid yield and an increase in both gases and liquid percentages yield. On the other hand, raising the temperature leads to raised ash and AC percentage, whereas the volatile matter gets reduced. Therefore, AC with greater quality is obtained at a higher temperature. Moreover, increasing the temperature that eventually decreases char yield could also be because of major decomposition of biomass at elevated temperatures or in the course of secondary decomposition of char residues. At the same time, higher temperatures at which secondary decomposition occurs could lead to getting some gaseous products that are non-condensable and ultimately increasing gas yield **[17]**.

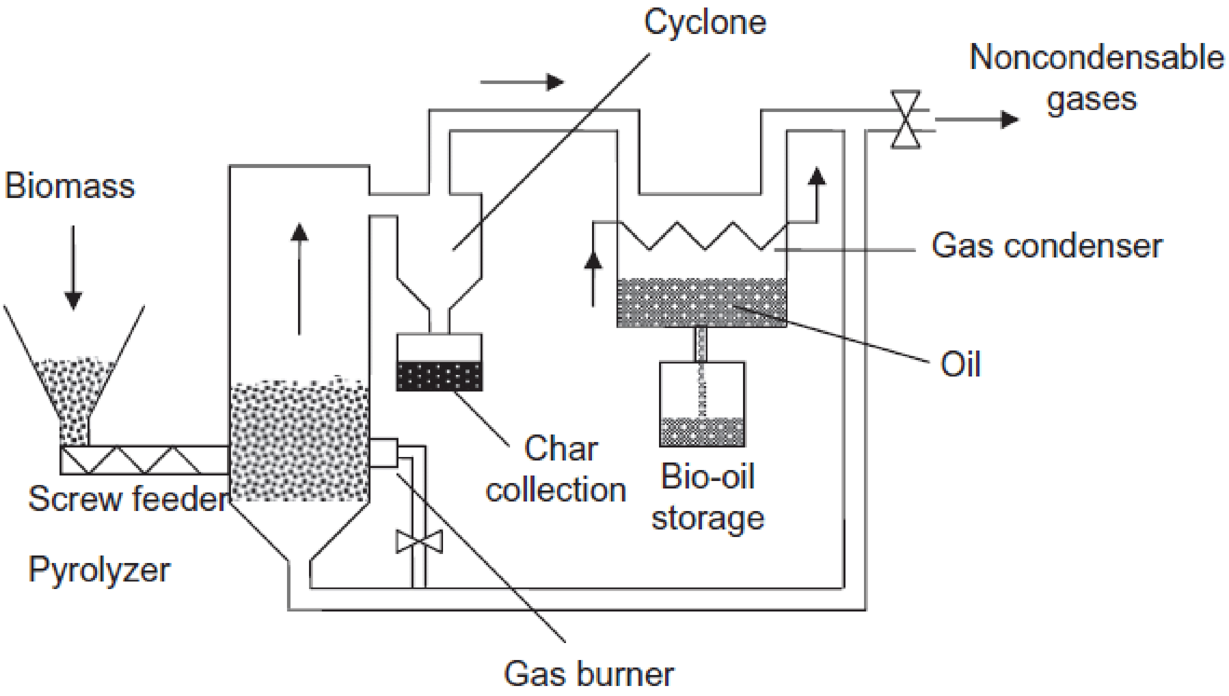


Figure III-2. **Schematic representation of pyrolysis activation process of AC.**

III.2.B Thermal or Physical activation process:

Physical activation is a two-step process. Carbonization of carbonaceous materials comes first, then activation process. Carbonization processes: A temperature range of 400°C and 850°C for between 6 and 8 hours for between 6 and 8 hours. Activation processes: The activation of the resulting char at high temperatures in the presence ofCO_2, steam, air or three mixtures serving as oxidizing gases. The CO_2 is usually used as activation gas being easy to handle, clean and possesses a slow reaction rate at a temperature between 600°C and 900°C, which facilitates control of the activation process **[17]**. The reaction is known as the Water-Gas presented by Eq 1:

$$C + H_2O \rightarrow CO + H_2 \qquad (1)$$

The AC produced using physical activation method, presented in Fig III-3, is somehow deficient in some qualities, which makes them unsuitable to be use as filters or as adsorbents. It worth mentioning that physical activation can be performed using various agricultural biomass residues such as mango pits, rice husk, rice hull, sawdust, sunflower shells, corncobs, olive pits, pine cone, wood waste, corn-hulls, cotton residues, oak, tobacco stems, corn stover, coconut coir pith, almond shells and peanut hulls **[17]**. Activation by carbon dioxide and steam produce carbons with different porosities. In simple terms, thermal activation is a process of selective gasification (removal) of individual carbon atoms. Not all carbon atoms are of equal reactivity **[16]**. However, in the process of the physical activation of activated carbon, the long activation time and low adsorption capacity of prepared activated carbon and its high energy consumption are the main disadvantages **[24]**.

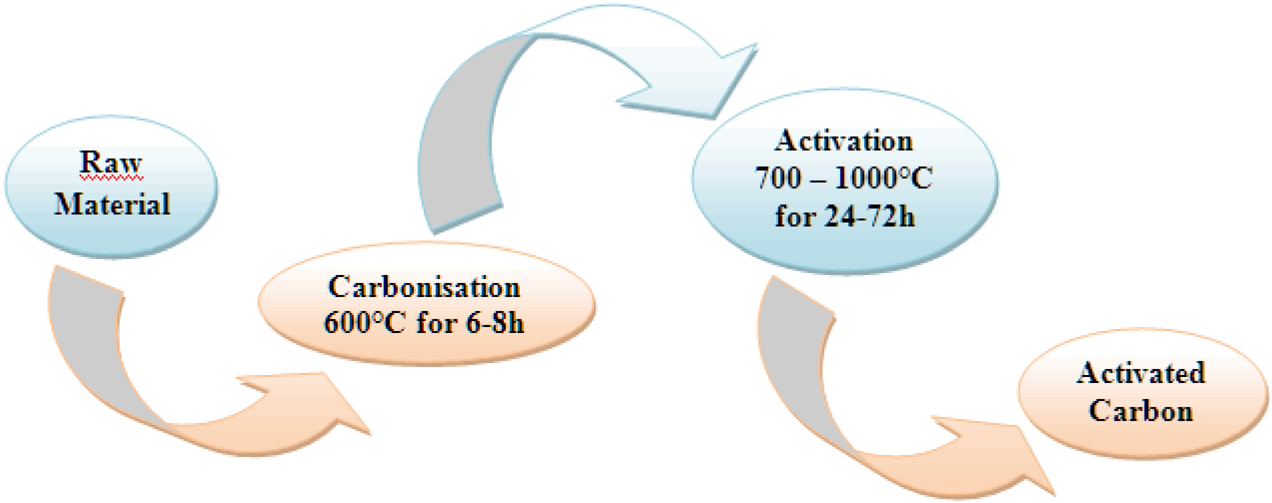


Figure III-3. **Schematic representation of physical activation pretreatment of AC.**

III.2.C Chemical activation process:

Chemical activation, known as wet oxidation, is usually used for raw materials containing cellulose, such as wood, sawdust or fruit pits. These materials are also called biomass resources. In chemical activation for the preparation of activated carbon, organic precursors are activated in the presence of chemicals at high temperatures. For chemical activation, as Fig III-4 shows, the raw material, in the first stage, is saturated with oxidizing and highly dehydrated chemicals. After impregnation, the suspension is dried and the remaining mixture is heated for a given time. Depending on the activating material and the properties of the final product, activation can take place at temperatures ranging from 400 to 900 °C, at which cellulose is degraded. Eventually, activated carbon is obtained from the repeated washing of the resulting mixture **[25].**

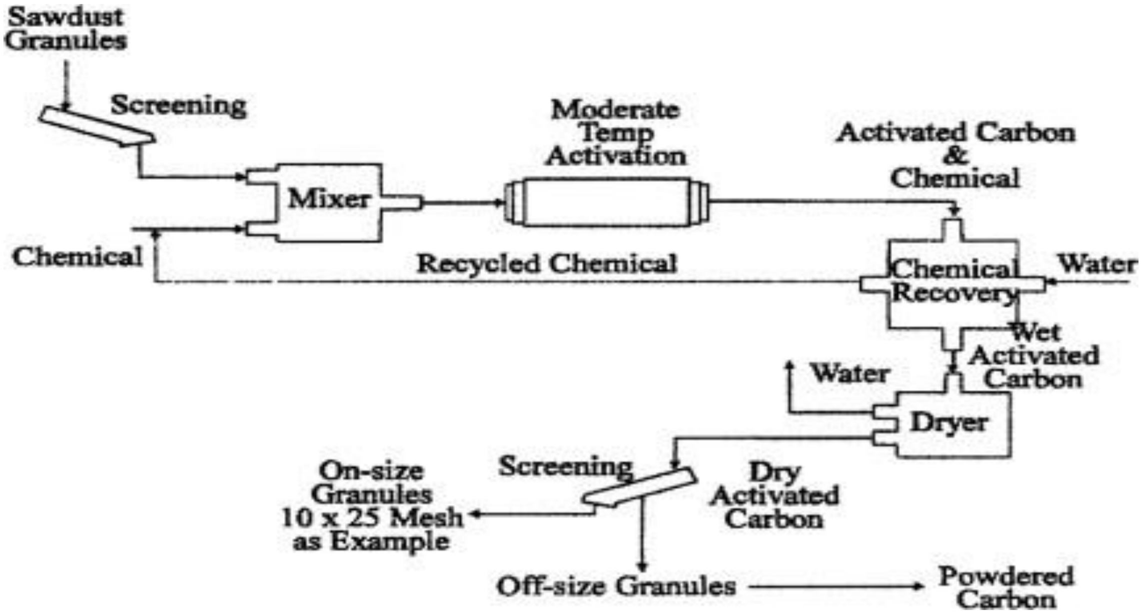


Figure III-13. **Schematic diagram of chemical activation pretreatment of AC.**

Different types of chemicals have different reactions with precursors and thus affect the adsorption behavior. The main chemicals which have been used as potential activators are potassium hydroxide (KOH), sodium hydroxide ($NaOH$), calcium chloride ($CaCl_2$) and potassium carbonate (K_2CO_3), acidic groups such as phosphoric acid (H_3PO_4) and sulphuric acid (H_2SO_4), intermediate metal salts such as ($ZnCl_2$) and other activating agents. The proposed reactions during activation by NaOH are presented in Eqs 2–4 [25], as follows:

$$6\mathrm{NaOH} + 2\mathrm{C} \rightarrow 2\mathrm{Na} + 2Na_2CO_3 + 3H_2 \tag{2}$$

$$Na_2CO_3 \rightarrow Na_2O + CO_2 \tag{3}$$

$$2\mathrm{Na} + CO_2 \rightarrow Na_2O + \mathrm{CO} \tag{4}$$

The main may reactions that occur between the activating agent of potassium carbonate and activated carbon under gasification conditions (during the activation process) are presented in Eqs 5–7 [25], as follows:

$$K_2CO_3 + 2\mathrm{C} \rightarrow 2\mathrm{K} + 3\mathrm{CO} \tag{5}$$

$$K_2CO_3 \rightarrow K_2O + CO_2 \tag{6}$$

$$K_2O + 2\mathrm{C} \rightarrow 2\mathrm{K} + \mathrm{CO} \tag{7}$$

The possible reactions that may occur during the activation process with potassium hydroxide are presented in Eqs 8–11 [25], as follows:

$$2\text{KOH} \rightarrow K_2O + H_2O \quad (8)$$

$$\text{C} + H_2O \rightarrow H_2 + \text{CO} \quad (9)$$

$$\text{CO} + H_2O \rightarrow H_2 + CO_2 \quad (10)$$

$$K_2O + CO_2 \rightarrow K_2CO_3 \quad (11)$$

In the chemical activation method, the parameters of the chemical agent effect, impregnation ratio and method, temperature, final temperature of carbonization, carbonization time, activation space (under atmospheric conditions) and activation method have been investigated. Compared to physical activation, this type of activation is more economical because it requires a lower activation temperature, shorter processing time and higher carbon efficiency **[26].** Also, the activated carbon prepared through chemical activation has a more porous structure than that of physical activation **[27]**. Performing activation and carbonization simultaneously during the chemical activation process at lower temperature results in having better porous structures of AC, even though, concern about environmental protection may limit the use of chemical agents for activation **[17].** All activation reactions are heterogeneous use is made of either carbon dioxide or steam or mixtures of these two gases **[16].**

III.2.D Steam pyrolysis process:

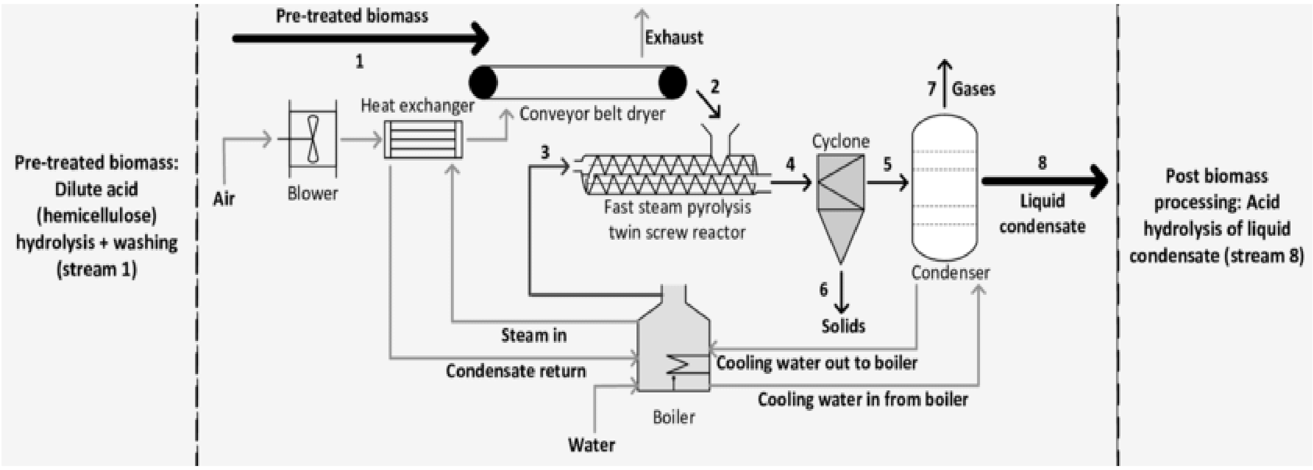


Figure III-14. **Schematic representation of steam pyrolysis activation process of**

Steam pyrolysis has been widely studied and successfully applied on various types of agricultural waste biomass such as rice husk, jujube seed, sawdust, tropical wood waste, palm shells, durian peel, corn cobs, coconut shells, tobacco stems, hazelnut shell, banana peels, mangos teen shells, etc. In this process, Fig III-5, the raw agricultural waste materials are either heated at a temperature range of 500–700°C under a flow of pure steam or heated at a higher temperature range of 700–800°C under a flowing steam. However, the AC produced by steam pyrolysis was generally reported to be less effective, with an exception of those produced from cherry stones, apricot and almond shell **[17].**

III.3 Activated carbon from different waste materials:

The sources of AC-based waste materials can be divided into two categories: natural and man-made wastes. The natural wastes are created by the usage of natural materials such as agriculture products, vegetables, fruits, woods and seeds. The man-made wastes created by human activities include industrial, municipal, plastic and e-wastes. These waste materials can be utilized for the synthesis of AC which can be applied in various wastewater treatments especially the removal of heavy metal **[6].**

III.3.A From Agricultural Wastes:

Agricultural waste is unsalable or unwanted materials produced entirely from the results of various agricultural operations which directly related to the growing of crops.

III.3.B From Biological Wastes:

The biological waste materials that exist in nature may produce the effects upon biological organisms. The important biological waste materials include buffing dust, bovine skin obtained from leather industries, etc., which may cause itself a serious problem until it gets disposed or reused. Hence, the preparation of AC from these biological waste materials has been taken into account in which it is applied in the environmental remediation.

III.3.C From Fruit Wastes:

Fruit wastes occur when sorting and selecting are done during the fruit production processes. The development of fruits may produce two types of waste as the solid waste of peel/skin, seeds, stones, etc. and the liquid waste of juice and its wash waters. The various solid fruit wastes like orange peels, banana peels, grape seeds, pomegranate peels, palm shells, meddler seeds, etc. are utilized for the preparation of AC for pollutant removal from water.

III.3.D From Vegetable Wastes:

These waste materials mainly comprised of the various vegetable matters. A lot of vegetable wastes such as soybean hulls, pumpkin stem waste, etc. have been utilized for the preparation of AC towards toxic metal removal from water, where they are burnt in the air to attain the function of the rapid removal of soil and water pollution in the environment.

III.3.E From Plastic Wastes:

The numerous plastic waste materials such as polyethylene terephthalate bottles, rubber tires, polystyrene tires, etc. are refers to a wide range of synthetic organic amorphous solid materials which derived from natural gas and oil. Plastic waste, namely, polyethylene terephthalate (PET), has been utilized for the synthesis of AC by chemical activation with potassium hydroxide (KOH) and physical activation with steam under limited heating levels and atmospheric condition.

III.3.F From Electronic Wastes (e-Wastes):

In electronic industries, e-waste materials have become the most important problems raised by the public in the past few years. The sources of e-wastes are mobile phones, discarded computers, entertainment device electronics, office electronic equipment, refrigerators and television sets which are destined for resale, reuse, recycling, salvage or disposal, etc. A low-cost AC material derived from many e-wastes such as printed circuit boards and disposal of printed track boards has been utilized for heavy metal removal from water.

III.4 Basic forms of activated carbon:

Activated carbons are divided to three basic forms: Granular Activated Carbon (GAC), Powdered Activated Carbons (PAC) and Extruded Activated Carbon (EAC), [28].

1. **Granular activated carbon (GAC):**

   Granular activated carbons, particle sizes range of 0.2 mm to 5 mm and can be used in both gas and liquid phase applications. GACs are popular because they offer clean handling and tend to last longer than PACs. Additionally, they offer improved strength (hardness) and can be regenerated and reused Fig III-6.

2. **Powdered activated carbon (PAC):**

   → Powdered activated carbons, generally contain the particle size range of 5 to 150 Å, with available of some outlying sizes.

- → PAC's are essentially used in liquid-phase adsorption applications and offer reduced processing costs and flexibility in operation, Fig III-6.

3. **Extruded Activated Carbon (EAC):**
   - → Extruded activated carbons are a cylindrical pellet product ranging in size from 1 mm to 5 mm.
   - → Typically used in gas phase reactions; EACs are a heavy-duty activated carbon as a result of the extrusion process, Fig III-6.

Figure III-15. **Presentation of Extruded, Granular and Powdered activated carbon respectively.**

III.5 Additional Types of activated carbon:

Subsidiary varieties of activated carbon include **[28]:**

- Bead Activated Carbon (BAC): Highly spherical activated carbon with petroleum pitch as its raw material. Have various features: small particle, high fill capability, high flow-ability, high purity, low dust, high strength, high wear resistance, narrow particle size distribution. Used as solvent recovery, gas treatment of filters, water treatment etc, Fig III-7.

Figure III-16. **Bead Activated Carbon (BAC) activated carbon.**

- Impregnated Carbon: Impregnation of activated carbon gives the activated carbon additional properties to be applicable for Mercury removal from natural gas, purification of waste odors, removal of chemicals, desulphurization of biogas; fume purification in laboratory; home water treatment in bacteriostatic water filters.
- Polymer Coated Carbon: The porous carbon coated with a biocompatible polymer to give a smooth and permeable coat without blocking the pores, which resulting carbon is useful for hemoperfusion.
- Activated Carbon Cloths (ACC): used in many odor control situations including industrial, medical, and domestic applications, Fig III-8.

Figure III-17. **Activated Carbon Cloths activated carbon.**

- Activated Carbon Fibers (ACF): is a promising microporous material with a fiber shape and well-defined porous structure, manufactured from synthetic carbon fiber (CF) with providing an additional activation process. Major application: Water filters (removal of chlorine, organic matter, etc.), surface treatment liquid cleaning, gas phase applications (deodorization/VOC adsorption), Fig III-9.

Figure III-18. **Activated Carbon Fibers (ACF) activated**

III.6 Affecting factors on AC productions:

a) **Raw materials:**

Most organic substances with high carbon content are potential raw materials for AC production. To produce a porous carbon structure in general, selection of raw material depends on seven important criteria:

→ High carbon content
→ Low inorganic content (i.e. low ash)
→ Potential extent of activation
→ Low degradation upon storage
→ High density and sufficient volatile content
→ Stability of supply in the countries
→ Inexpensive materials.

Lignocelluloses materials were generally accepted as precursor for AC production and constitute about 45% of the total raw materials used **[17].**

b) **Temperature:**

The activation temperature plays a vital role in affecting the characteristic of the AC produced. As for commercial purposes AC, it is normally carried out in a mixture of steam and CO2 at a temperature above 800°C. The activation temperature is between 200 to 1100°C. However, a temperature range of 400 to 500°C was reported by previous researchers to be considered regardless of time taken and the impregnation ratio for a variety of raw materials. Therefore, increasing activation temperature always results in the reduction of AC yield during production, which at the same time results in increasing the volume of volatile substances released. Generally, it is inappropriate to prepare AC at a temperature above 800°C. The Brunauer, Emmett and Teller (BET) surface area (Adsorption on the upper layer commences immediately after the first layer has completed) is suggested to be another important feature showing the influence of production temperature on the AC characteristics. As the BET surface area increases, the activation temperature also increases. This might be due to the advancement of new pores due to the release of volatile matter and the broadening of presence ones as the activation temperature goes high **[17].**

c) **Activation time:**

The activation time also has a greater influence on both the carbonization process and properties of AC in addition to the activation temperature. Few decades earlier, it was established that the activation times widely used were range from 1 to 3 hours. Previous studies have reported that as the activation time increased gradually, the BET surface area also increased while the AC percentage yields decrease, and observed that as excessive activation time occurs, it causes the reduction in product yield. These might be attributed to the volatilization of organic substances from raw agricultural waste residues **[17].**

d) **The size and shape of porosity:**

Activated carbon has been widely used in adsorption due to its high surface area, high pore volume, [29].

Table III-1. **Different types of pores sizes of typical activated carbon.**

Types of pore	Diameter of pore (nm)	Pore Volume (cm^3/g)	Surface area (m^2/g)
Micro-pores	< 0.2	0. 10	600 - 1900
Meso-pores	0.2 - 5	0. 02	20 - 70
Macro-pores	> 5	0.20 - 0.80	0.5 - 2

Activated carbon is porosity (space) enclosed by carbon atoms, and it has a complex porous structure with disordered (amorphous) arrangements of carbon atoms. The size of the pore, shown in Fig III-10, determines how adsorption takes place in a pore be it narrow and wide microporosity is less then 2.0nm, mesoporosity 2.0-50 nm and microporosity is more then50nm, [16], presented in Tab III-1.

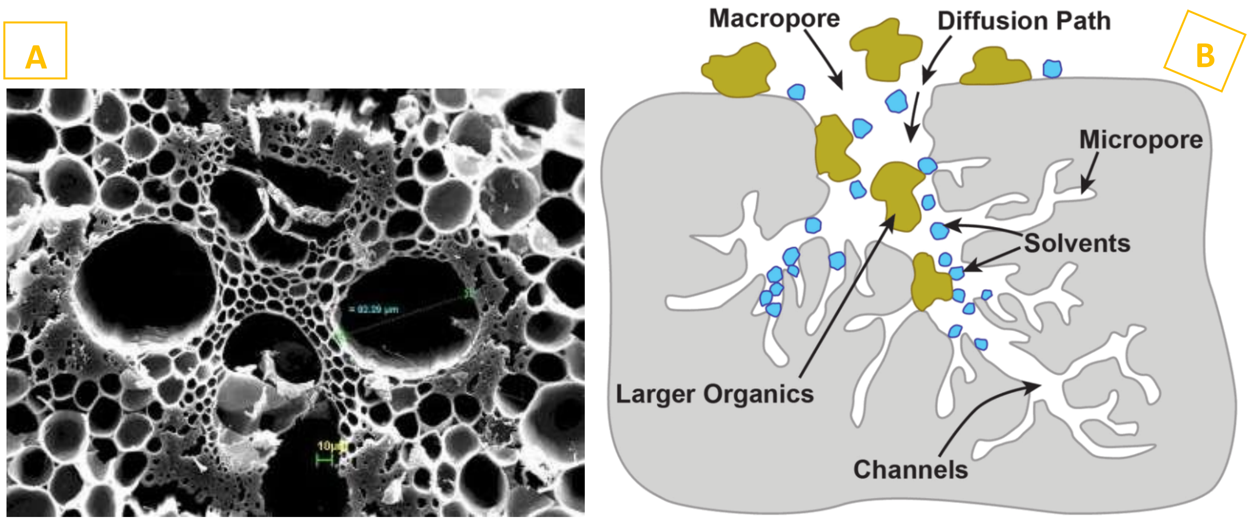


Figure III-19. **Microporous structure (A) and Schematic diagram (B) of activated carbon.**

III.7 Description of adsorption steps:

Molecules from gas or liquid phase will be attached in to the surface from activated carbon. In this case the adsorption process takes place in three steps:

1. Macro transport: The movement of organic material through the macro-pore system of the active carbon (macro-pore >50nm).
2. Micro transport: The movement of organic material through the meso-pore and micro-pore system of the active carbon (micro-pore <2nm; meso-pore 2-50nm).
3. Sorption: The physical attachment of organic material on the surface of active carbon in the meso-pores and micro-pores of the active carbon, **[30].**

Fourth chapter:

Adsorption

IV.1 **Introduction:**

As a separation process, adsorption is widely applied in our manufacturing economy and in our daily life. Adsorption operations exploit certain solids' ability to preferentially concentrate specific substances from solutions (gaseous or liquid) onto their surfaces. Thus, by contacting fluids with such solids, the desired objective of purification or separation may be achieved. In practice, adsorption performance is also strongly influenced by the mass transfer of the species between the solution and the adsorbent surfaces and the adsorption reaction rate, **[31].** Adsorption is a process whereby a substance (adsorbate or sorbates) is accumulated on the surface of a solid (adsorbent, or sorbent). The adsorbate can be in a gas or liquid phase. The driving force for adsorption is unsaturated forces at the solid surface which can form bonds with the adsorbate, **[22].** The transference of the adsorbate from the liquid phase to the solid phase continues until the equilibrium to be reached between the amount of adsorbate linked in the adsorbent and the amount of adsorbate remaining in the solution. The affinity degree between the adsorbent and adsorbate determines this distribution in liquid and solid phases. In general, the adsorption can be classified according to the type of interaction that occurs between the adsorbent and adsorbate. If there is an electron transfer between the adsorbent and adsorbate, then, it is a chemical adsorption or chemisorption. In this case, the adsorption involves electron transfer, who reveals the fact of ionic or covalent bonds could be made. Otherwise, if no electron exchange is observed, a physical adsorption or physisorption occur and the interactions between the adsorbent and adsorbate could be electrostatic, hydrogen bonds, van der Waals, or dipole–dipole. It should be noted that this classification between physical and chemical adsorption is a general behavior, but is not a dogma. Each case should be examined separately, **[32].** The strength of this interaction dictates the relative ease or difficulty in removing (desorbing) the adsorbate for adsorbent regeneration and adsorbate recovery, **[22].**

IV.2 **Definition of adsorption terms:**

Adsorption: the process where a substance is accumulated on an interface between phases. Adsorbent: the phase that collects the substance to be removed at its surface. Adsorbate: the solute that is to be adsorbed (removed from the gas or liquid stream). Isotherm: A relation between the equilibrium amount of a substance adsorbed per weight of sorbent and its concentration in the liquid or gas stream at constant temperature, **[22].**

IV.3 **Adsorption principles**

IV.3.A Physical adsorption:

Physical adsorption occurs due to van der Waals (dispersion) or electrostatic forces. The attraction depends on the polar nature of the fluid component being adsorbed as well as that of the adsorbent. Van der Waals forces are directly related to the polarizability. An estimate of the relative strength of interaction is based on the sorbates size and polarizability. Electrostatic forces include polarization forces, field–dipole interactions and field gradient–quadruple interactions. These forces arise when the surface is polar. In the case of a polar solvent like water with non-polar organic impurities, the organic molecules will prefer to stick to a non-polar adsorbent such as activated carbon rather than remain in the polar solvent. Physical adsorption is reversible. Physical sorption is sensitive to temperature, relatively non-specific regarding sorbates, relatively fast kinetically, and has a low heat of adsorption energy ranging from 5 to 40 kJ/mol. Multiple sorbates layers can form on the sorbent surface, **[22].**

IV.3.B Chemical adsorption:

If there is an electron transfer between the adsorbent and adsorbate, then, it is a chemical adsorption or chemisorption. In this case, the adsorption involves electron transfer, and it is of high energy, ranging from 40 to 800 kJ/mol and, consequently, desorption is difficult, and thus the process is irreversible and only a monolayer is observed. In chemisorption, the interactions are strong, can be occurred mainly by ionic or covalent bonds, **[32].** Chemisorption is typically more specific, kinetically slower and has a larger heat of adsorption, **[22],** presented in Tab Ⅳ-1.

Table Ⅳ-1. **Comparison between physisorption and chemisorption.**

Properties	Physisorption	Chemisorption
Type of bonding forces	Van Der Wals	Similar to chemical bond
Adsorption heat	Low	High
Chemical change of adsorptive	None	Formation of a surface compound
Reversibility	Reversible	Irreversible
Activation energy	Very low	High
Formation of multi-layer	Yes	No

IV.4 **Sorption kinetic models**

In the adsorption process, kinetics plays an important role as it provides vital information about the reaction pathway and the rate-controlling mechanism of reactions. The pseudo-first order, pseudo-second order, and intraparticle diffusion models are used in this study to examine the adsorption rates of crystal violet and Methylene blue onto Millettia thonningii seed pods activated carbon, **[33].**

IV.4.A The pseudo-first-order kinetic model:

The pseudo-first-order kinetic model (Lagergren 1898) expresses the mechanism of removal as adsorption preceded by diffusion through a boundary, **[33].** The nonlinear form of the model is given as in Eq 12:

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{12}$$

Where q_e and q_t are the amount of dye adsorbed (mg/g) at equilibrium and at time $(t, \min)$, respectively, and k_1 $(\min^{-1})$ is the pseudo-first-order rate constant. The pseudo-first-order equation assumes the adsorption of one adsorbate molecule onto one active site on the adsorbent surface.

IV.4.B The pseudo-second-order kinetic model:

The pseudo-second-order kinetic model, first proposed by Blanchard et al. (1984), is based on the assumption that adsorption follows a second rate kinetic mechanism. The model describes the sorption process as being controlled by chemisorption involving sharing or exchange of electrons between the solute and the sorbent. It assumes the adsorption of one adsorbate molecule onto two active sites on the sorbent surface, **[33].** It can be represented in the following form, Eq 13:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{13}$$

Where q_e and q_t are the amounts of dye adsorbed $\left(\frac{mg}{g}\right)$ at equilibrium and at time t (min), respectively, and k_2 $\left(\frac{g}{mg}.\min\right)$ is the pseudo-second-order rate constant.

IV.4.C The intraparticle diffusion model:

The intra-particle diffusion model, based on the theory proposed by Weber and Morris (1963), is used to interpret experimental kinetics data, **[33]**, from a mechanistic viewpoint and is expressed as follows, Eq 14:

$$q_t = k_{id}\sqrt{t} + C \tag{14}$$

Where q_t is the amount of dye adsorbed per unit weight of sorbent, $C\left(\frac{mg}{g}\right)$ is a constant which gives information about the boundary layer and k_{id} $\left(mg/\left(g.min^{1/2}\right)\right)$ is the intraparticle diffusion rate constant and t is the contact time. When the value of $C = 0$, intraparticle diffusion is the sole rate-limiting step. However, $C \neq$ zero indicates the presence of some degree of boundary layer control and depicts that intraparticle diffusion is not the only rate- limiting step.

IV.5 Adsorption isotherm models expressions:

IV.5.A Monolayer Adsorption:

A.a Langmuir equation:

Several adsorption isotherms were used to evaluate the adsorption process and gain mechanistic assumption of adsorbed molecules onto adsorbent surfaces form an adsorbate layer constituting a distinct phase, such as nonlinear expression of the Langmuir, Eq 15, adsorption isotherms.

$$q_e = \frac{Q_{max}\, K_L\, C_e}{1+K_L\, C_e} \tag{15}$$

Where q_e is the amount of solute adsorbed at equilibrium per unit mass of adsorbent (mg/g), Q_{max} is the amount of solute needed to cover the surface of the adsorbent with a monolayer of adsorbed molecules (mg/g), C_e is the adsorbate concentration (mg/L) in solution at equilibrium (unadsorbed solute) and K_L is the Langmuir equilibrium adsorption constant of adsorbent- adsorbate couple (L/mg) related to energy of adsorption which quantitatively reflects the affinity between the adsorbent and adsorbate, **[33].**

A.b The Freundlich isotherm:

The Freundlich isotherm model is based on the assumption that the adsorption occurs on a heterogeneous surface. It is applicable to monolayer adsorption (chemisorption) and multilayer (Van der Waals adsorption) adsorption. The nonlinear expression of the Freundlich equation is given as Eq 16:

$$q_e = K_F C^{\frac{1}{n}} \tag{16}$$

Where K_F is the Freundlich constants associated with adsorption capacity and $\frac{1}{n}$ is the heterogeneity factor. A large value of the adsorption capacity K_F, indicates a higher adsorption capacity. Favorable adsorption is inferred when the magnitude of $\frac{1}{n_F}$ ranges between 0 and 1, becoming more heterogeneous as its value tends to zero. The Freundlich equation is characterized by an adsorption isotherm lacking a plateau, indicating multilayer adsorption, **[33].**

The physical simplicity of the isotherm is based on four assumptions, **[32]**:

- Adsorption cannot occur beyond monolayer coverage.
- Each site can hold only one adsorbate molecule.
- All sites are energetically equivalent and the surface is uniform.
- The ability of a molecule to adsorb in a given site is independent of the occupation of neighboring.

IV.5.B Multilayer Adsorption

B.a The BET Isotherm:

When the initial adsorbed layer becomes a surface for further adsorption, instead of the isotherm stabilized in a saturated monolayer, the formation of multi-layers can be expected. The most widely used isotherm for the multilayer adsorption was derived by Brunauer et al. (1938) and is called the BET isotherm, Eq 17. In liquid systems, the BET isotherm, **[32],** equation is:

$$q_e = \frac{q_{BET} k_1 C_e}{(1-k_2 C_e)(1-k_2 C_e + k_1 C_e)} \tag{17}$$

Where q_{BET} is the monolayer adsorption capacity (m^2/g), k_1 and k_2 are the BET constants (L/mg), the adsorbed phase equilibrium concentration refers to C_e and q_e is the adsorption capacity at equilibrium.

B.b The Redlich-Peterson isotherm:

The Redlich-Peterson isotherm, a three-parameter isotherm was proposed by Redlich and Peterson (1959). The mechanism of adsorption can be described as a hybrid one that does not follow ideal monolayer adsorption. The model incorporates features of both the Freundlich and Langmuir models and can be applied in describing sorption equilibrium over a wide range of adsorbate concentrations. The nonlinear form of this empirical model is given in Eq 18 as follows:

$$q_e = \frac{K_{RP} C_e}{1 + a_{RP}\, C_e^{g}} \tag{18}$$

Where C_e is the adsorbate concentration (mg/L) in solution at equilibrium, K_{RP} (L/g) and a_{RP} $(mg/L)^{-g}$ are the Redlich–Peterson constants and g is an exponent whose value must lie between 0 and 1. Equation 18 becomes a linear isotherm when $g = 0$, reduces to the Langmuir isotherm when $g = 1$, and transforms into the Freundlich isotherm when K_{RP} and a_{RP} are $\gg 1$ and $g \leq 1$. Hence, if the g value falls outside the range of 0–1, the data are not sufficiently explained by the Redlich-Peterson equation. The ratio of $\frac{K_{RP}}{a_{RP}}$ indicates the adsorption capacity, **[33].**

IV.6 **Gas adsorption equilibrium:**

Accurate adsorption equilibrium data are essential to the analysis and design of adsorptive separation processes. For gas adsorption, a number of measurement methods; volumetric/manometric, gravimetric, and their combination, have been developed that have enabled the determination of the amount of equilibrium adsorbate uptake as a function of gas phase conditions. The equilibrium behavior may be classified into five types as shown in Fig Ⅳ-1.

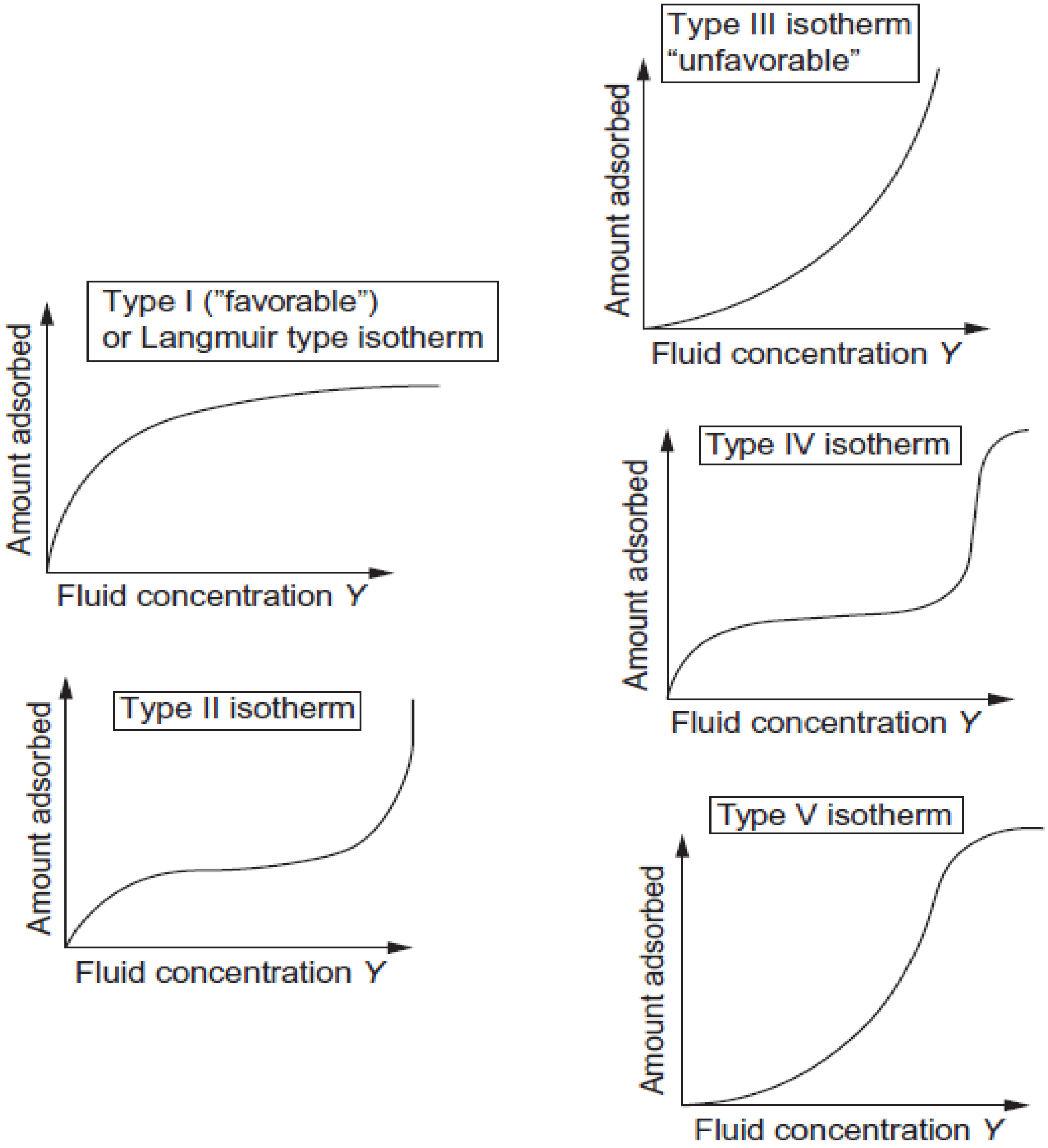


Figure Ⅳ-20. **The five isotherm classifications.**

The type 1 isotherm represents unimolecular adsorption, and applies to microporous adsorbents with small pores. Adsorbents displaying type 2 or 3 behavior are characterized by a wide range of pore sizes, such that adsorption may extend from the monolayer to the multilayer, and ultimately to capillary condensation. An isotherm of type 4 suggests that adsorption causes the formation of two adsorbate surface layers. A type 5 behavior is found in the unfavorable adsorption of water vapor with activated carbon, **[31].**

IV.7 **The applications of adsorption:**

The fundamental practical applications of adsorption and related areas are following:

- Separation and purification of liquid and gas mixtures, bulk chemicals, isomers and air.
- Drying gases and liquids before loading them into industrial systems.
- Removal of impurities from liquid and gas media.
- Recovery of chemicals from industrial and vent gases.
- Water purification.

Water purification is some of the most widespread uses of activated carbons for liquid-phase adsorption are those in water treatment. Recent years have seen remarkable increase in the level of synthetic organic chemicals (SOC). In public water supplies hundreds of SOCs such as pesticides, herbicides, detergents, polycyclic aromatic hydrocarbons, nitrosamines, phenol compounds, trihalomethanes and other pollutants have been identified in drinking water supplies**[34].**

V Discussions previous articles:

V.1 **Absorption of dyes using agriculture wastes:**

Dye is a molecule that contains chromophore and auxochrome. The chromophore group causes the dye to have its own color since it has a double bond that oscillates to adsorb light. Many different types of dyes have been produced such as acidic, basic, disperse, azo, anthraquinone based and metal complex dyes. Dyes can have health effects due to their toxicity and non-biodegradable characteristics. Examples of health problems are cancer, allergic respiratory problem, and skin and mucous membrane irritation. Besides health effects, dyes also cause environmental pollution as it affects the symbiotic process in water as it prevents light penetration and causes the photosynthetic activity to decrease, [5]. This study spotlights on Methylene blue dye, Fig Ⅴ-1, as most dye used, which is found in water with much amounts than usual, that because of cationic –basic- type where become easy to dissolve.

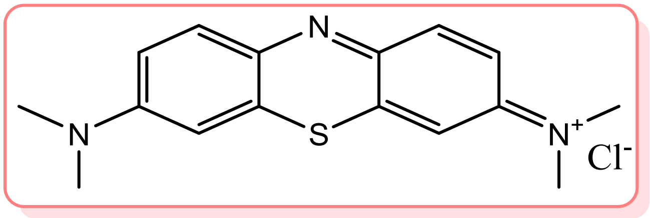


Figure Ⅴ-21. **Molecular structure of basic dye: Methylene blue (MB).**

V.1.A Activated by NaOH agent:

The activation mechanism with NaOH is according to the following Eq 19, [35]:

$$6NaOH + 2C \rightarrow 2Na_2CO_3 + 2Na + 3H_2 \tag{19}$$

Which Na_2CO_3 degraded into CO_2 and H_2O.

The nitrogen (N_2) adsorption-desorption isotherms at 77 K it used to evaluate the surface area and pore characteristics of prepared activated carbons. The isotherms show the characteristics of type I and type II of the Brunauer, Deming, Deming and Teller (BDDT) classification. The conventional Brunauer-Emmett-Teller (BET) equation was applied to determine the BET surface area (S_{BET}) (m2/g) of each carbon. The isotherms exhibit a steep initial part and a well developed knee bend at $P/P_0 = 0.1 - 0.2$. The narrow closed hysteresis loop exhibited by the investigated sorbent may be taken as evidence of capillary condensation in the microspores. The total pore volume $\mathrm{V_T}$ (ml/g) of each carbon was also calculated from the volume of nitrogen adsorbed near saturation. The mean pore radius (nm), **[36]**, was calculated from Eq 20:

$$\mathrm{r} = \frac{2\mathrm{V_T} \times 10^3}{\mathrm{S_{BET}}} \tag{20}$$

Where $\mathrm{V_T}$ is total pore volume, and $\mathrm{S_{BET}}$ is the BET surface area.

According to IUPAC, the isotherms that show reversibility are classified as type I, which also are known as Langmuir. This type of isotherm indicates that the adsorbate and adsorbent have a high affinity, and that the material in question consists mostly of micro-pores, **[35].**

Table Ⅴ-1. **Comparison of the functional properties and textural characteristics of activated carbon prepared from various agricultural wastes activated by NaOH.**

	pH	S_{BET}	APD	Reference
Coconut shell	4.7	2825	22.7	[35]
Rice husk	7.3	1958	12.5	[36]
Factory-rejected tea	7.4	369	23.0	[37]
Rattan (Lacosperma secundiflorum)	5.0	1135	35.5	[38]

S_{BET}: The BET surface area (m^2/g), APD: average pore diameter (Å).

The highest BET surface area ($2825\mathrm{m}^2/\mathrm{g}$) was exhibit it by **[35]** for activated carbon prepared from Coconut shell and **[37]** found lower surface area of $369\mathrm{m}^2/\mathrm{g}$ of prepared activated carbon from Factory-rejected tea while **[36]** and **[38]**present 1958, $1135\mathrm{m}^2/\mathrm{g}$ for Rice husk, Rattan (Lacosperma secundiflorum) activated carbons, in order, Tab Ⅴ-1. **[37]** show mean pore radius of 23.02 (Å) for activated carbon prepared from Factory-rejected tea and pore radius of 22.7 (Å) for activated carbon prepared from Coconut shell, **[35]**, while the highest mean pore radius (35.5 Å) for activated carbon prepared from Rattan, **[38]**, revealed the meso-porous structure of prepared AC according to the IUPAC classification, otherwise **[36]** exhibit lower mean pore radius 12.5 (Å) for Rice husk activated carbon which is less than 1.8 nm (18 Å) radius, that suggests the existence of both meso-pores and micro-pores in the structure of AC. The effect of pH for MB adsorption by various agriculture activated carbons examined is demonstrated in

Tab Ⅴ-1. The pH_{pzc} is the pH where the adsorbent net surface charge corresponds to zero, and it offers the possible mechanism about the electrostatic interaction between adsorbent and adsorbate, **[38].** pH_{pzc} of 4.7 and 7.3, 7.4 and 5.0 for Rattan, Factory-rejected tea, Rice husk and Coconut shell, respectively. This may be taken as evidence that acid functional groups slightly predominate on the surface of Rattan AC and Coconut shell AC. whereas the base functional groups very slightly predominate on the surface of Factory-rejected tea and Rice husk ACs. MB adsorption on AC is driven my electrostatic force, when an activated carbon is placed in aqueous solution, the acidic surface groups, present on the carbon surface, and undergo ionization producing H^+ ions that are directed towards the liquid phase leaving the carbon surface with negatively charged sites. The larger the number of acidic groups on the carbon surface, the greater the negative charge on the carbon surface will be. This enhances the electrostatic attractive interactions between the negatively charged carbon surface and the positively charged Methylene blue cations, increasing the adsorption, **[39].** The type of interactions between the cationic dye and AC surfaces are electrostatic in both cases. The increase in electrostatic interactions between the cationic dye and AC surface in first case due to de-protonation of surface active sites which decrease -by time- that occurs as a increasing pH and decrease in the surface charge density of the adsorbent. The application of adsorption isotherms is very useful to describe the interaction between the adsorbate and the adsorbent of any system. The parameters obtained from the different models provide important information on the sorption mechanisms and the surface properties and affinities of the adsorbents. There are several equations for analyzing experimental adsorption equilibrium data, **[35].** Freundlich and Langmuir isotherm models are the most accepted surface adsorption model for single solute systems were applied to portray the relationship between equilibrium concentration and adsorbed amount of MB dye by various agriculture activated carbons. The Freundlich isotherm describes the adsorption process on heterogeneous surfaces.

Table Ⅴ-2. **The Langmuir isotherm parameter for adsorption of MB of deferent agriculture wastes activated by NaOH.**

	T_a	Q_{max}	R^2	K_L	Reference
Coconut shell	25	916	0.881	1.800	[35]
Rice husk	45	571	0.994	0.162	[36]
Factory-rejected tea	30	487	0.948	0.023	[37]
Rattan (Lacosperma secundiflorum)	30	359	0.920	0.450	[38]

T_a: adsorption temperature (°C), Q_{max}: the adsorption capacities (mg/g), R^2: correlation coefficient, K_L: equilibrium adsorption constant of Langmuir ($g/(g.min)$).

By contrast, the Langmuir isotherm describes sorption on the homogeneous surface with monolayer adsorption systems, [37]. The linear form of the Langmuir isotherm equation can be represented as the following, Eq 21:

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_{max}} + \frac{C_e}{Q_{max}} \tag{21}$$

Plots of C_e/q_eversus C_e for the adsorption of methylene blue onto AC give a straight line of slope = $(1/Q_{max})$ and an intercept = $(1/K_L)$.

For our comparison study, Langmuir isotherm is the most appropriate model that describes the adsorption data.

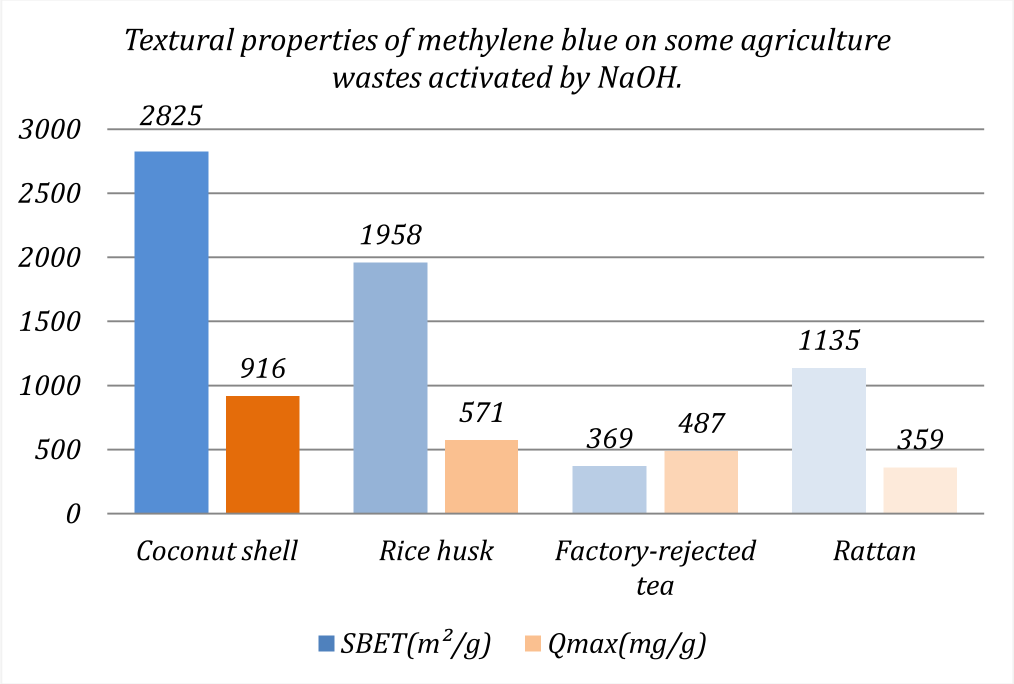


Figure Ⅴ-22. **Textural properties of Methylene blue on some agriculture wastes activated by NaOH.**

The MB concentration was determined by comparing absorbance of the supernatant solutions before and after adsorption were determined using a UV–Vis spectrophotometer at its maximum wavelength (λ) of 664 nm. The amount of MB adsorbed onto AC, **[36],** Q_{max} (mg/g) was calculated by Eq 22:

$$Q_{max} = \frac{(C_0 - C_e)\,V}{W} \tag{22}$$

Where C_0 and C_e (mg/l) are the initial and equilibrium liquid concentrations of MB, respectively, V (l) is the volume of the solution, and W (g) is the mass of dry adsorbent used. The maximum adsorption capacities (Q_{max}) of activated carbons are 916, 571, 487 and 359mg/g, for Coconut shell, Rice husk, Factory-rejected tea, and, Rattan ACs, respectively, Tab Ⅴ-2 and Fig Ⅴ-2.

Coconut shell AC show high adsorption capacity at 25°C, whereas Rice husk AC has been studded at deferent temperatures (25, 35 and 45°C) and records deferent adsorption capacity (359, 359 and 359mg/g, in order), we can note increasing in adsorption capacity with increases temperature, but the adsorption capacity of Coconut shell AC at 25°C is almost triple than Rice husk AC at the same temperature, which is directly related to high surface area (S_{BET}).

Moreover, the Langmuir equilibrium adsorption constant (K_L) of Coconut shell AC is higher (1.8) than other ACs, indicate that the interactions between adsorbent and adsorbate are strong, also, the Langmuir's monolayer of adsorbed methylene blue molecules (MB) is confirmed. The correlation coefficient (R^2) values are greater than 0.8 indicate that the isotherms of all the adsorbents can be well fitted using Langmuir model with more advantage to Rice husk AC. The Kinetic study is a time dependent factor to determine the equilibrium time for specific adsorbents, which will help to industrial design process for waste water treatment, **[37].** The most appropriate model that describes the adsorption kinetic data is pseudo- second-order (PSO), Tab Ⅴ-3. The amount of MB adsorbed at equilibrium time (q_t, mg/l), **[36],** was calculated by Eq 23:

$$q_t = \frac{(C_0 - C_t)\,V}{W} \tag{23}$$

Where C_t is the liquid-phase concentration of MB at anytime (mg/l).

Removal efficiency calculated (E_r) using Eq 24:

$$E_r = 100 - \left(\frac{(Q_{Max} - q_e)}{Q_{Max}}\right) \times 100 = 100 - \left(1 - \left(\frac{q_e}{Q_{Max}}\right)\right) \times 100 \tag{24}$$

Where q_e and Q_{Max} are the amounts of dye adsorbed at equilibrium and maximum adsorption capacity.

Table Ⅴ-3. Pseudo- second-order (PSO) parameter for MB adsorption of deferent activated carbons activated by NaOH activation agent.

	Q_{max}	CI	Et	K_2	R^2	Reference
Coconut shell	901	1000	25	9.20E-04	0.9959	[35]
Rice husk	474	500	48	8.21E-06	0.998	[36]
Factory-rejected tea	348	500	30	1.30E-04	0.968	[37]
Rattan (Lacosperma secundiflorum)	305	350	30	6.00E-04	0.98	[38]

CI: initial concentration of MB dye (mg/l), Et: equilibrium time (Hours).

The correlation coefficients (R^2) for all ACs were greater than 0.96 in different concentrations, being that the highest values were observed for the pseudo-second kinetic model.

The adsorption equilibrium (q_e) is achieved after approximately 25, 48, 30 and 30 h with a maximum capacity of 900.96, 473.93, 348.32 and 305 mg/g for 1000, 500, 500 and 350 mg/l initial dye concentration for Coconut shell, Rice husk, Factory-rejected tea, and, Rattan ACs, respectively. The high q_e value of Coconut shell is presence of a high mass of solute the forces, thus the diffusion from the adsorbate towards the adsorbent become larger, as a sequence, it reveals high rate constant $\left(K_2 = 9.2 \times 10^{-5}(g/(g.min))\right)$, as such as removal efficient (98%), shown in Fig 10.

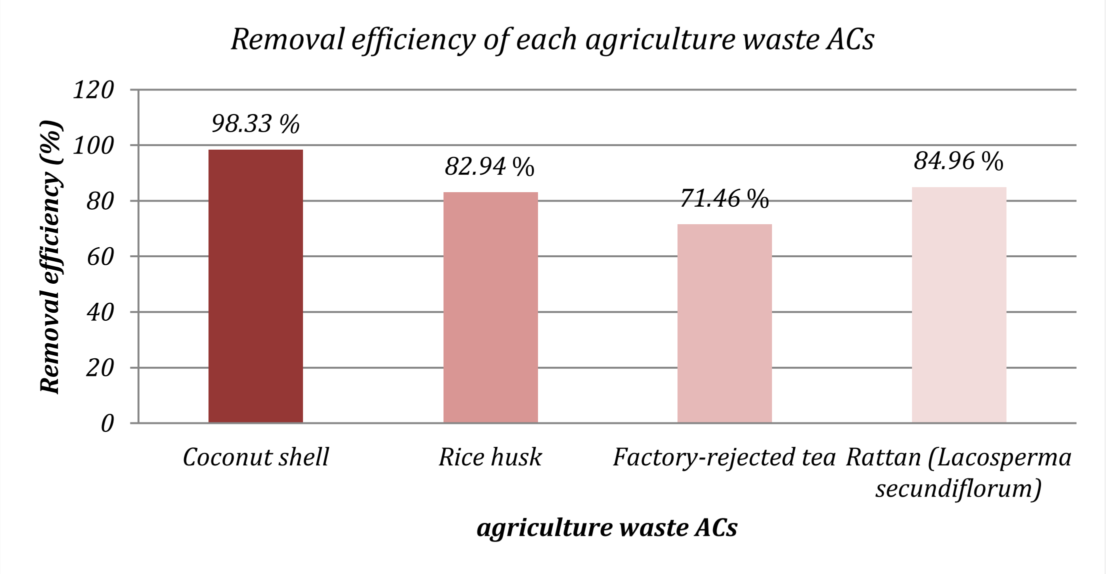


Figure Ⅴ-3. **MB removal efficiency of each agriculture waste ACs activated by NaOH.**

Conclusion-1:

From the comparison study of ACs who made form some agriculture wastes (Coconut shell, Rice husk, Factory-rejected tea, and, Rattan-Lacosperma secundiflorum), by chemical precursor using NaOH as an activator agent, conclude that the better conditions that used to produce more efficient activated carbon are 800°C for 1houre for activation temperature and immerged time (activation process), to develop the porosity of the material, and 350 mg/l as initial concentration for 30h at 30°C (Batch equilibrium), without considering type of material. The adsorption of MB becomes more favorable at high adsorption temperatures at neutral pH. In addition, the increase of NaOH to char promoted a development of meso-pore and consequently a decrease in the micro-pore percentages which is more responsible for adsorption of MB molecular.

Activated by KOH agent:

Table Ⅴ-4. Physical parameters for MB adsorption of deferent activated carbons treated by KOH activation agent.

	t	Ta	S_{BET}	APD	Q_{max}	Reference
Cane pith	1	780	2207	24	685	[40]
Rice straw	1	800	1554	/	395	[41]
Bamboo	2	850	1896	23	455	[42]
Date press cake	1.5	750	2633	19	547	[43]
Chickpea peel	2	800	917	/	448	[44]
Oil palm empty fruit bunch	0.25	360W	808	21	345	[45]
Oil palm shell	2	850	596	/	244	[46]
Orange peel	1	800	1371	/	318	[47]
Coconut husk	0.1	600W	1356	23	418	[48]

Ta: activation temperature (°C), t: time of activation (Hours), W: Watt is the energy transferred to heat by micro-wave, in this case.

Comparisons of prepared AC from different agriculture waste such as Cane pith, Rice straw, Bamboo, Date press cake and chickpea peel, Tab Ⅴ-4, using KOH as an activation agent at different temperature(780, 800, 800, 850, 750 and 800) for different activation time (1, 1, 2, 1.5 and 1 hours), respectively. The AC prepared from Cane pith has maximum adsorption capacity 685 mg/g with high BET surface area of 2207m^2/g, so is the diameter of porous 24 Å.

Conclusion-2:

Chickpea peel, Oil palm empty fruit bunch, Oil palm shell and cane pith have efficient adsorption toward methylene blue molecular and important capacity of adsorption.

V.1.B Activated by H_3PO_4 agent:

Table Ⅴ-5. Physical parameters for MB adsorption of deferent activated carbons treated by H_3PO_4 activation agent.

	t	Ta	S_{BET}	APD	Q_{max}	Reference
Date palm pits	1.2	450	952	29	455	[49]
Vetiver roots	1	600	1272	28	394	[50]
Coffee grounds	1	450	925	20	367	[51]
Peach stones	2	500	1393	10	362	[52]
Cotton cake	1.5	450	584	20	250	[53]
Bamboo	1	600	1335	19	183	[54]
Rice straw	2	450	522	/	109	[55]

Comparisons of prepared AC from different agriculture waste such as date palm pits, vetiver roots, coffee grounds, peach stones, cotton cake, bamboo and rice straw, Tab Ⅴ-5, using H_3PO_4 as an activation agent at different temperature(450, 600, 450, 500, 450, 600 and 450) for different activation time (1.2, 1, 1, 2, 1.5, 1 and 2 hours), respectively. The AC prepared from date palm pits shows maximum adsorption capacity 455 mg/g while total surface area of $1393 m^2/g$ recorded to peach stones AC, whereas the structural parameters calculated from nitrogen adsorption isotherms indicate that the high average pore diameter of 29 Å, returns to activated carbon made from date palm pits.

Conclusion-3:

High tendency of activated carbon to adsorb methylene blue that made from date palm pits, cotton cake and coffee grounds.

V.1.C Activated by $\mathbf{ZnCl_2}$ agent:

Table Ⅴ-6. Physical parameters for MB adsorption of deferent activated carbons treated by $ZnCl_2$ activation agent.

	t	Ta	S_{BET}	APD	Q_{max}	Reference
Tea seed shells	1	500	135	20	325	[56]
Date stone	1.2	500	1045	10	382	[57]
Waste apricot	1	500	106	30	137	[58]
Waste potato residue	1	600	1357	29	540	[59]
Coconut coir dust	2	800	1884	20–40	140	[60]
Pineapple waste	1	500	915	24	288	[61]
Orange peel	1	800	144	/	282	[47]
watermelon rind	1	700	1156	32	231	[62]

Comparisons of prepared AC from different agriculture waste such as Tea seed shells, Date stone, Waste apricot and Waste potato residue, Tab Ⅴ-6, using $ZnCl_2$ as an activation agent at different temperature(500, 500, 500 and 600) for different activation time (1, 1.2, 1, 1 and 1 hours), respectively. The AC prepared from Date palm pits AC records maximum adsorption capacity 540 mg/g while Coconut coir dust AC show high total surface area to 1357m^2/g, with meso-porous structure according to large average pore diameter range.

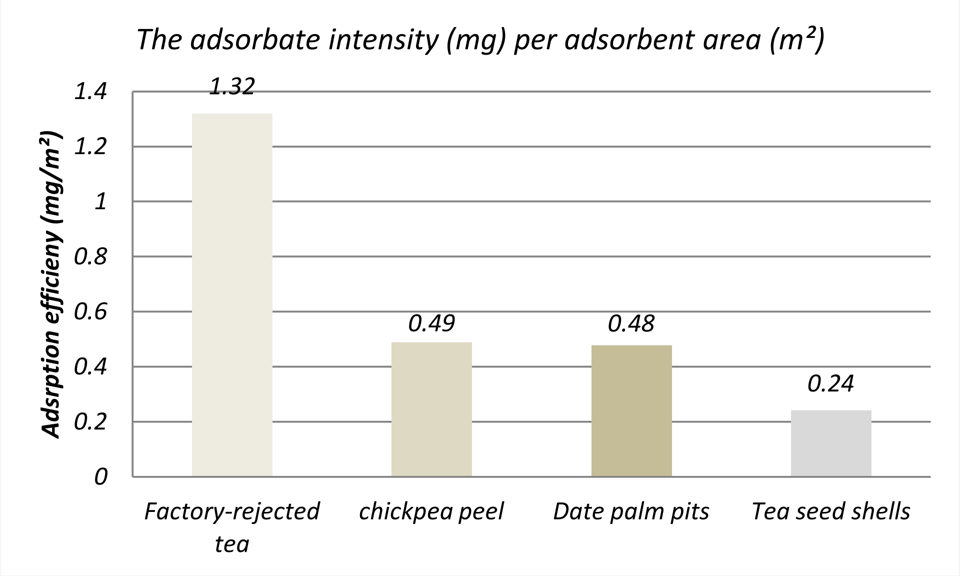


Figure V-4. **The density of MB molecular that removed by agriculture waste ACs activated using $NaOH$, KOH, H_3PO_4 and $ZnCl_2$.**

Conclusion-4:

The activated carbons that prepared from tea seed shells, orange peel, waste apricot, waste potato residue, date stone and pineapple waste are reveals high efficient adsorption of methylene blue with significant capacity.

V.2 Conclusion:

Factory-rejected tea, chickpea peel, date palm pits and tea seed shells are produce high efficient activated carbon, when activated by $NaOH$, KOH, H_3PO_4 and $ZnCl_2$ in the ratio of 1:3, 1:3, 1:3 and 1:1 (AC: Activated agent, w:w) under 800, 800, 450and 500℃ for 1, 2, 1.2 and 1 hour, respectively. Also, solution pH equal to 7.3, 7, not adjustment and 7.5 under 25, 25, 30 and 25℃ with activated carbon amount of 1, 2.5, 0.5 and 0.025 g/l as adsorption conditions.

V.3 Absorption of Heavy Metals using agriculture wastes:

Heavy metals are metals that have densities greater than 5 g.cm^{-3} such as arsenic, cadmium, chromium, mercury, lead, copper, zinc and nickel. Heavy metal pollution is one of the most serious environmental problems. Industries such as metal plating, mining operations, surface finishing industry, radiator manufacturing, alloy, and batteries industries usually release heavy metals in wastewater. Other than that, nickel and zinc are persistent in nature and tend to accumulate in soils and plants which can be transferred to living organisms through the food chain. When humans or animals consume any of these heavy metals it can cause negative health effects like cancer, nausea, vomiting, mental retardation, liver, and kidney failure. Therefore, it is necessary to removal of heavy metals from the environment, [5]. The most dangerous heavy metals anions that cause serious environmental problems are: Zinc(Zn^{2+}), Nickel(Ni^{2+}), Copper(Cu^{2+}), Mercury(Hg^{2+}), Lead(Pb^{2+}) and Chromium(Cr^{6+}). Recently agriculture wastes are used for prepare activated carbon to remove heavy metals anions from waste water such as Fruit/Vegetable waste based adsorbents and Rice husk ash, Wheat straw, Wheat bran and more. Pb^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+} and Cr^{6+} are the main heavy metals that being studied their adsorption process by various agriculture wastes which they are treated with different activation agent.

V.3.A Adsorption of lead anions ($\mathbf{Pb^{2+}}$):

Lead acid battery, paints, electronics, metallurgical, ceramics and pesticide industries are most significant uses of lead, whereas it has large and dangerous effects especially when contact the water and increase it is amount more than 0.05 part per million, which harmfully effects on human brain and nervous systems, [6]. Various procedures used to remove lead anions from waste water, include agriculture wastes, as presented in Tab Ⅴ-7.

Table Ⅴ-7. Textural proprieties of various agriculture wastes using different activating agents for lead anions (Pb^{2+}) adsorption.

Agriculture waste AC	t	Ta	Aa	S_{BET}	Q_{max}	Reference
Pine cone	1	500	H_3PO_4	1094	27.53	[63]
Persian mesquite grain	2	600	H_3PO_4	1243	273	[64]
Guava	1	600	H_2SO_4	471.3	11	[65]
Lemon peel	1	500	H_3PO_4	1158	90.91	[66]
Date pits	1	500	H_3PO_4	502.2	220	[67]
Olive Stone	2.5	380	H_3PO_4	1194	147.53	[68]
Oil palm shell (wet)	1	500	H_2SO_4	/	74.63	[69]
Oil palm shell (semi-dried)	1	500	H_2SO_4	/	63.69	[69]
Coconut shell	1	500	H_3PO_4	/	73.53	[69]
Maize stalks	1	700	KOH	1414	347	[70]
Coffee residue	1	600	H_3PO_4	1003	89.28	[71]
Coffee residue	1	600	$ZnCl_2$	889	63.29	[71]
Chickpea husk	/	850	KOH	2082	135.8	[72]
Banana peel	0.5	500	KOH	63.5	34.5	[73]
Watermelon shell	1.12	500	H_3PO_4	710	40.98	[74]
Walnut shell	1.12	500	H_3PO_4	789	32.36	[74]

Ta: *activation temperature (°C),* ***t:*** *time of activation (Hours),* ***Aa:*** *activation agent,* S_{BET}*: the BET area (m^2/g),* Q_{max}*: adsorption capacity (mg/g).*

Pine cone, Persian mesquite grain, Lemon peel, Date pits, Olive Stone, Coconut shell, Coffee residue, watermelon shell and Walnut shell ACs are all activated by H_3PO_4 under temperatures between 500-600°C for 1-2.5 hours, Tab Ⅴ-7. Persian mesquite grain, Olive Stone, Lemon peel, Pine cone and Coffee residue ACs are shows high BET area of 1243, 1194, 1158, 1094 and 1003 m^2/g, respectively. Whereas high adsorption capacities of 273, 220, 147.53 and 90.91 mg/g are recorded to Persian mesquite grain, date pits, olive stone and Lemon peel ACs. The conditions of 500, 700 and 850°C for 0.5, 1 hour were used to produce activated carbon for banana peel, maize stalks and chickpea husk wastes with KOHas activation agent, Tab Ⅴ-7. Chickpea husk and maize stalks are exhibits highest BET surface area of 2082 m^2/g and highest adsorption capacity of 347 mg/g, in order.

Table Ⅴ-8. Adsorption conditions of lead anions (Pb^{2+}) by various agriculture wastes activated using deferent activating agents.

Agriculture waste AC	pH	Et	Ie	Ia	Td	Reference
Pine cone	> 6.7	180	0.002	100	25	[63]
Persian mesquite grain	6	40	3.33	40	/	[64]
Guava	5	/	1	50	30	[65]
Lemon peel	7	25(5)	5	50	25	[66]
Date pits	5.2	720	4	100	25	[67]
Olive Stone	5	200(25)	6	414	30	[68]
Oil palm shell (wet)	5	3 days	2	48.7	/	[69]
Oil palm shell (semi-dried)	5	3 days	2	48.7	/	[69]
Coconut shell	5	3 days	2	71.6	/	[69]
Maize stalks	/	1 day	0.5	70	25	[70]
Coffee residue	5.8	102(15)	1	90	25	[71]
Chickpea husk	8	90	2	400	40	[71]
Banana peel	6.1	/	0.9	74.4	/	[72]

***Et:** equilibrium time (>90% of ions removed, Minutes), **Ie:** the amount of adsorbent (g/l), **Ia:** the amount of adsorbate (mg/l), **Td:** adsorption temperature (°C).*

0.5, 3.3, 4, 6 and 5 g/l of maize stalks, Persian mesquite grain, date pits, olive stone and Lemon peel ACs, in order, are record high adsorption capacity, they subjected to adsorb lead anions with concentration of 70, 40, 100, 414 and 50 g/l, respectively, Tab Ⅴ-8, the equilibrium time of lemon peel activated carbon is 25 Min, with ~95% of the total Pb^{2+} ions was removed within 5 Min, while equilibrium time of Persian mesquite grain and maize stalks activated carbons are 40 min and 1 day.

Conclusion-1:

The activated carbon that activated by H_3PO_4, KOH and H_2SO_4 under 500, 600 and 850°C for 1 hour were produced from agriculture waste presented in pine cone, chickpea husk and Guava have high tendency to adsorb lead anions within short time.

V.3.B Adsorption of zinc anions ($\mathbf{Zn^{2+}}$):

The zinc metal is used in cosmetics, pharmaceuticals, plastics, inks, textiles, batteries, soaps and electrical equipment industries whereas irrational use of metal could cause many environment issues if pass it tolerance limit of 0.5ppm in aquatic area, which lead to effects on the living organism and it could cause hypertension, lethargy, neurotic effects and edema of lungs, [6]. Thus the activated carbon were fabricated from carbonaceous sources by different processes, it was used as low cost adsorbents. Table Ⅴ-9 represents various carbonaceous sources using different activating agents for zinc anions adsorption.

Table Ⅴ-9. Textural proprieties of various agriculture wastes using different activating agents for zinc anions (Zn^{2+}) adsorption.

Agriculture waste AC	t	Ta	Aa	S_{BET}	Q_{max}	Reference
Watermelon shell	1.12	500	H_3PO_4	710	11.31	[74]
Walnut shell	1.12	500	H_3PO_4	789	6.079	[74]
Rice husk	2	600	H_2SO_4	886.72	11.14	[75]
Olive Stone	0.5	700	KOH	877	176	[76]
Coir pith	2	75	KOH	/	37.08	[77]
Orange peel	2	75	$ZnCl_2$	/	35.66	[77]
Pomegranate peel	2	75	$ZnCl_2$	/	37.23	[77]
Pineapple peel	3	105	$ZnCl_2$	/	37.64	[77]
Orange peel	3	105	H_2SO_4	/	37.17	[77]
Pomegranate peel	3	105	H_2SO_4	/	36.99	[77]

Olive Stone activated carbon shows high surface area (886.72m^2/g) with average pore diameter of 49.2 Å, Tab Ⅴ-9, indicated that the AC was in the meso-porous region, after the activation process, the volatile matter content decreased significantly, whereas the fixed carbon content increased in olive stone AC. This resulted from the pyrolytic effect, by which most of the organic substances are degraded and discharged as gas and liquid tars leaving a material with high carbon purity, [75], and S_{BET} area of coir pith AC is 877 m^2/g, while high adsorption capacity recorded to coir pith AC of 176 mg/g, continued by 37.64, 37.23 and 37.17 mg/g for orange peel, pineapple peel ACs were activated using $ZnCl_2$ and pomegranate peel AC activated by H_2SO_4, Tab Ⅴ-9. Watermelon shell AC that activated under 500°C for 1.12 hours, exhibit significant BET surface area of 710 m^2/g, but in other hand, the adsorption capacity is very low of 11.31 mg/g even high average pore diameter of 40 Å.

Table Ⅴ-10. **Adsorption conditions of zinc anions (Zn^{2+}) by various agriculture wastes activated using deferent activating agents.**

Agriculture waste AC	Aa	pH	Et	Ie	Ia	Td	Reference
Watermelon shell	H_3PO_4	4.5	2 weeks	10	50	25	[74]
Walnut shell	H_3PO_4	4.5	2 weeks	10	10	25	[74]
Rice husk	H_2SO_4	6	~120	1	50	25	[75]
Olive Stone	KOH	5	180	3	20	30	[76]
Coir pith	KOH	6	180	0.8	50	25	[77]
Orange peel	$ZnCl_2$	/	120	0.25	40	22	[77]
Pomegranate peel	$ZnCl_2$	/	240	0.25	40	22	[77]
Pineapple peel	$ZnCl_2$	/	240	0.25	40	22	[77]
Orange peel	H_2SO_4	/	240	0.25	40	22	[77]
Pomegranate peel	H_2SO_4	/	120	0.25	40	22	[77]
Pineapple peel	H_2SO_4	/	240	0.25	40	22	[74]

Orange peel (activated by $ZnCl_2$) and pomegranate peel AC (activated by H_2SO_4) have shortest time of equilibrium (2 hours) at same activated carbon amount (0.25 g/l) and Zn^{2+} ions concentration (40 mg/l), while equilibrium time of activated carbon from coir pith (activated by KOH) and rice husk (activated by H_2SO_4) retched after 3 and 2 hours at activated carbon amount of 0.8 and 1 g/l in 50 mg/l Zn^{2+} ions concentration, Tab Ⅴ-10.

Conclusion-2:

Orange peel (activated by $ZnCl_2$ under 105°C for 3hours), pomegranate peel AC (activated by H_2SO_4 under 105°C for 3hours) and coir pith (activated by KOH under 700°C for 0.5hours) are effective agriculture wastes to remove zinc anions from water waste.

V.3.C Adsorption of copper anions ($\mathbf{Cu^{2+}}$):

Mining, electroplating, smelting and refining industries these are some fields that use copper. Copper polluted water refer to water that contains more than 0.001ppm, whose cause serious damage to human body which affects the human blood coagulation. It leads to Wilson diseases, gastrointestinal distress and insomnia human blood coagulation, [6]. Table Ⅴ-11 shows some agriculture wastes that used to adsorb copper anions from aquatics area.

Table Ⅴ-11. Textural proprieties of various agriculture wastes using different activating agents for copper anions (Cu^{2+}) adsorption.

Agriculture waste AC	t	Ta	Aa	S_{BET}	Q_{max}	Reference
Olive Stone	2.5	410	H_3PO_4	1194	14.16	[68]
Potato peel	4	550	$ZnCl_2$	1078	74	[78, 79]
Coir pith	0.5	700	KOH	877	264	[76]
Chickpea husk	/	850	KOH	2082	56.2	[72, 73]
Banana peel	0.5	500	KOH	63.5	14.3	[73]
Hazelnut husks	4	700	$ZnCl_2$	1092	6.645	[78]
Olive Stone	2.5	380	$ZnCl_2$	1194	17.665	[68]

The activation conditions of 410 and 380°C for 2.5 hours produce significant surface area of 1194 m^2/g with pore diameter of 40 Å that is recorded for olive stone AC activated by $H_3PO_4$and $ZnCl_2$, whereas Chickpea husk AC activated by KOH records high surface area 2082 m^2/g where activated under 380°C for 2.5 hours. Coir pith AC shows high capacity of adsorption 264mg/g, while record low surface area 877 m^2/g, Tab Ⅴ-11.

Table Ⅴ-12. **Adsorption conditions of copper anions(Cu^{2+}) by various agriculture wastes activated using deferent activating agents.**

Agriculture waste AC	Aa	pH	Et	Ie	Ia	Td	Reference
Olive Stone	H_3PO_4	5	600	6	32-320	30	[68]
Potato peel	$ZnCl_2$	7	8 days	5	100	25	[78, 79]
Coir pith	KOH	6	180	0.4	50	25	[76]
Chickpea husk	KOH	8	90	3	400	40	[72, 73]
banana peel	KOH	6.5	/	2.4	85	/	[73]
hazelnut husks	$ZnCl_2$	6.7	60	12	30	18	[78]
Olive Stone	H_3PO_4	5	600	6	128	30	[68]

Coir pith, Chickpea husk and hazelnut husks ACs with dose of 0.4, 3 and 12 g/l are used to adsorb 50, 400 and 30 mg/l of copper, in order, Tab Ⅴ-12.

Conclusion-3:

The organic wastes whose exhibit significant tendencies to adsorb Cu^{2+} ions are AC prepared from coir pith and chickpea husk and activated by KOHin 700°C for 0.5 hours and in 850°C.

V.3.D Adsorption of cadmium anions ($\mathbf{Cd^{2+}}$):

Carcinogenic which leads to itai-itai disease, kidney damage and renal disorder are most consequences of cadmium infection. Contaminated water is considerate as most carrier of infection especially when the amounts of cadmium anions on water are breaches the tolerance limit of 0.01ppm. Adsorption phenomenon was used to eliminate cadmium anions from waste water by activated carbon prepared from different agriculture wastes, [6], Tab Ⅴ-13.

Table Ⅴ-13. Textural proprieties of various agriculture wastes using different activating agents for cadmium anions (Cd^{2+}) adsorption.

Agriculture waste AC	t	Ta	Aa	S_{BET}	Q_{max}	Reference
Coffee residue	1	600	H_3PO_4	1003	46.95	[71]
Coffee residue	1	600	$ZnCl_2$	889	37.04	[71]
Olive Stone	2	650	$ZnCl_2$	790	1.88	[80]
Olive Stone	2	600	KOH	887	7.80	[75]
Coir pith	0.5	700	KOH	877	192	[76]
Olive Stone	2.5	380	H_3PO_4	1194	57.10	[68]

Activated Olive Stone waste using $ZnCl_2$, KOHand H_3PO_4under temperatures of 650, 600 and 380°C for 2, 2, 2.5 hours shows deferent results. Olive Stone that activated under high temperature exhibit low surface area (790m^2/g), so is adsorption capacity (1.88mg/g), while Olive Stone that activated under low temperature and for long time reveals high surface area 1194m^2/g and high adsorption capacity (57.10mg/g), Tab Ⅴ-13. H_3PO_4 were used to activate Coffee residue shows high surface area 1003m^2/g and adsorption capacity (46.95mg/g) even the average pore diameter is low (24.6 Å) compare to that activate by $ZnCl_2$, which records low surface area and low adsorption capacity (889m^2/g, 37.04mg/g) even high pore diameter (34.4 Å), Tab Ⅴ-13. Nevertheless, the highest BET surface area recorded to coir pith AC which found to be 192m^2/g.

Table Ⅴ-14. Adsorption conditions of cadmium anions (Cd^{2+}) by various agriculture wastes activated using deferent activating agents.

agriculture waste	Aa	pH	Et	Ie	Ia	Td	Reference
Coffee residue	H_3PO_4	5.8	120(50)	1	90	25	[71]
Coffee residue	$ZnCl_2$	5.8	120(50)	1	90	25	[71]
Olive Stone	$ZnCl_2$	> 6	90(60)	20	45	30	[80]
Olive Stone	KOH	5	180	3	20	30	[75]
Coir pith	KOH	6	180	0.6	50	25	[76]
Olive Stone	H_3PO_4	5	200	6	560	30	[68]

Coffee residue AC dose of 1g/l is used to adsorb 90 mg/l of cadmium anions at 25°C in pH of 5.8 for deferent activator, which record 2 hours as equilibrium time with fast rate of adsorption within 50 Minutes, Tab Ⅴ-14. Olive Stone AC that activate by $ZnCl_2$ exhibit equilibrium time within 90 Minutes and 1 hour as fast rate of adsorption which 20g/l of activated carbon is used to adsorb 45 mg/l of cadmium anions at 30°C in pH greater than 6. 3 hours is required time to arrive the equilibrium time that is what Coir pith AC shows with dose of 0.6g/l and 50 mg/l as a concentration of cadmium anions.

Conclusion-4:

The carbons that prepared from Coffee residue, Olive Stone and Coir pith are activated using H_3PO_4, $ZnCl_2$ and KOH, respectfully, under activation conditions of 600, 650 and 700°C for 1, 2, 0.5 hours, shows significant trend toward adsorption of cadmium anions.

V.3.E Adsorption of nickel anions ($\mathbf{Ni^{2+}}$):

The nickel has various uses -special in industry fields- as alloys and batteries, whereas irrational use of metal could cause many environment issues if pass it tolerance limit of 2µg/l in aquatic area, which lead to effects on the living organism as lung embolism, asthma and liver and kidney damage with chronic bronchitis, [6]. Thus the activated carbon were fabricated from carbonaceous sources by different Technics, it was used as low cost adsorbents. Tab Ⅴ-15 represents various carbonaceous sources using different activating agents for nickel anions adsorption.

Table Ⅴ-15. Textural proprieties of various agriculture wastes using different activating agents for nickel anions (Ni^{2+}) adsorption.

Agriculture waste AC	t	Ta	Aa	S_{BET}	Q_{max}	Reference
Olive Stone	2.5	410	H_3PO_4	1194.0	12.91	[81]
Oil palm shell (wet)	1	500	H_2SO_4	/	10.83	[69]
Oil palm shell (semi-dried)	1	500	H_2SO_4	/	19.61	[69]
Coconut shell	1	500	H_3PO_4	/	12.18	[69]
Lignin of papermaking black liquor	1	750	KOH	2943.0	14.02	[82]
Olive Stone	2	600	KOH	886.72	8.42	[75]
banana peel	0.5	500	KOH	63.50	27.40	[73]

The efficient of activated carbon depends on many conditions as activating agent which effect on efficient adsorption. From Tab Ⅴ-15, H_3PO_4 used to activate olive stone and coconut shell ACs under different activation conditions (410°C for 2.5 and 500°C for 1h), that effect on textural properties (12.91 and 12.18 mg/g), respectfully. Lignin of papermaking black liquor, olive stone and banana peel ACs are activated under 750°C for 1 h, 600°C for 2 h and 500°C for 1 Min using KOH as an activator agent. Banana peel AC reveals higher adsorption capacity of 27.4 mg/g with lowest BET area of 63.5 m^2/g, while the highest area of 63.5 m^2/g recorded to Lignin of papermaking black liquor AC.

Table Ⅴ-16. Adsorption conditions of nickel anions (Ni^{2+}) by various agriculture wastes activated using deferent activating agents.

Agriculture waste AC	Aa	pH	Et	Ie	Ia	Td	Reference
Olive Stone	H_3PO_4	5	6	6	30-300	30	[81]
Oil palm shell (wet)	H_2SO_4	5	2	2	6.06	/	[69]
Oil palm shell (semi-dried)	H_2SO_4	5	2	2	6.06	/	[69]
Coconut shell	H_3PO_4	5	2	2	6.06	/	[69]
Lignin of papermaking black liquor	KOH	6.4	0.5	1	10	30	[82]
Olive Stone	KOH	5	3	3	20	30	[75]
banana peel	KOH	6.4	/	1.8	90.3	/	[73]

Olive stone AC and coconut shell AC are applied on solutions with pH of 5, 6 g/l of olive stone AC is studied for solution contain onions concentration of 40 mg/l under 30°C, while the amount of coconut shell AC (2 g/l) is used for solution contain of 6.06 mg/l concentration of nickel anions. Coconut shell AC rich the equilibrium within 2 hours, while olive stone AC rich it in 6 hours, this may refer to high dose of anions, which require more time to equilibrium. Oil palm shell (wet) and Oil palm shell (semi-dried) ACs activated by H_2SO_4 under same activation conditions (500°C for 1h) the textural properties are 10.83 and 19.61 mg/g, respectfully, Tab Ⅴ-16, even the same activation and adsorption conditions. Indicate that activated Oil palm shell (semi-dried) AC by H_2SO_4 is more favorable to evaluate textural properties and adsorption efficiency. Small amount of banana peel AC (1.8 g/l) is used to adsorb 90.3 mg/l of adsorbate, which shows more adsorption capacity than 3 g/l of olive stone AC that used to adsorb just 20 mg/l of adsorbate, indicating to high tendency of banana peel AC to adsorb nickel anions.

Conclusion-5:

Banana peel AC, oil palm shell (semi-dried) AC and coconut shell AC activated by KOH, H_2SO_4 and H_3PO_4 under activation conditions of 500°C for 1, 1, 0.5 hours, respectively, are most effective when used amount (1-2 g/l) to purifies water whose contaminate with 6-90 mg/l of nickel.

V.3.F Adsorption of chromium anions ($\mathbf{Cr^{6+}}$):

0.05ppm considerate as a tolerance limit of chromium concentration on water, more doses of it could lead to cancer, kidney and liver damage [6].

Table Ⅴ-17. Textural proprieties of various agriculture wastes using different activating agents for chromium anions (Cr^{6+})adsorption.

Agriculture waste AC	t	Ta	Aa	S_{BET}	Q_{max}	Reference
Oil palm shell (semi-dried)	1	500	H_2SO_4	/	46.3	[69]
Wood	2	700	KOH	1255	180.3	[83]
Date press cake	1.5	650	NaOH	2026	282.8	[84]
Orange Peel	0.5	700	$ZnCl_2$	1228.2	133.33	[85]
Chickpea husk	/	850	KOH	2082	59.6	[72]

Activation agent of KOHused to activate wood show AC significant value of BET area of 180.3m^2/g and Orange Peel AC, activate by $ZnCl_2$ records 180.3m^2/g as surface area, while Date press cake revealed high value of 282.8m^2/g so is the adsorption capacity 2026 mg/g, Tab Ⅴ-17, the microscopic shape of Date press cake AC is an agglomeration of sub-micrometric particles, where the average pore diameter determined to be 18.39 Å.

Table Ⅴ-18. **Adsorption conditions of chromium anions (Cr^{6+}) by various agriculture wastes activated using deferent activating agents.**

Agriculture waste AC	Aa	pH	Et	Ie	Ia	Td	Reference
Oil palm shell (semi-dried)	H_2SO_4	5	3 days	2	6.06	/	[69]
Wood	KOH	3	150	0.6	60	40	[83]
Date press cake	NaOH	2	150	1	300	25	[84]
Orange Peel	$ZnCl_2$	1	100	3	300	25	[85]
Chickpea husk	KOH	8	90	3	400	40	[72]

The amount (0.6g/l) of wood AC adsorb 60 mg/l of solution concentration, which retches the equilibrium within 150 Min, as date press cake but at 1g/l of AC amount and 300 mg/l of solution concentration, Tab Ⅴ-18.

Conclusion-6:

The activated carbons of wood, date press cake and orange peel activated under activation conditions of 700, 650 and 700°C for 2, 1.5, 0.5 hours, have high trend to adsorption chromium anions from wastewater.

Ⅴ.4 General conclusion:

The activated carbon prepared from Persian mesquite grain, pomegranate peel, banana peel and Date press cake that activated by H_3PO_4, H_2SO_4, KOH and $ZnCl_2$ are appropriate to adsorb Pb^{2+}, Zn^{2+} , $Ni^{2+}$and Cr^{6+} anions, respectively. While using KOH as activation agent, to activate Coir pith waste, is produce activated carbon has ability to adsorb Cu^{2+} and Cd^{2+} anions with more advantage to copper ions. Tab Ⅴ-19, detailed the activation and adsorption conditions of each activated carbon.

The activated carbon fabricated from Factory-rejected tea that activated by $NaOH$ the ratio of char to $NaOH$ 1:3 (w:w), under 800°C for 1 hour with adsorption conditions of pH equal to 7.3, 25°C, and amount of 1 g/l is great choice to use as adsorbent agent to remove methylene blue from contaminated water, unless the activated carbon from tea seed shells by $ZnCl_2$ in the ratio of char and Activated agent to, 1:1 (w:w) under 500°C for 1 hour, and in adsorption conditions of pH equal to 7.5 under 25°C with activated carbon amount of 0.025 g/l is a best choice as economically option, Tab Ⅴ-20.

Table Ⅴ-19. **The best activation and adsorption conditions to activate agriculture wastes to adsorb heavy metals from wastewater.**

Agriculture waste	Activation conditions				Adsorption conditions				Reference
	Activation agent	t(h)	T(°C)	Ratio	pH	adsorbent (g/l)	Temper (°C)	Heavy metal	
Persian mesquite grain	**H_3PO_4**	2	600	11	6	3.33	30	Pb^{2+}	[64]
pomegranate peel	**H_2SO_4**	3	105	13	/	0.25	22	Zn^{2+}	[77]
Coir pith	**KOH**	0.5	700	11	6	0.4	25	Cu^{2+}	[76]
Coir pith	**KOH**	0.5	700	11	6	0.6	25	Cd^{2+}	[76]
banana peel	**KOH**	0.5	500	11	6.4	1.8	/	Ni^{2+}	[73]
Date press cake	**$ZnCl_2$**	1.5	650	12	2	1	25	Cr^{6+}	[84]

Table Ⅴ-17. **Appropriate conditions to activate agriculture wastes for remove Methylene blue dye from wastewater.**

Agriculture waste activated carbons	Activation conditions				Adsorption conditions			Reference
	Activation agent	t(h)	T(°C)	Ratio	pH	Adsorbent (g/l)	Temper (°C)	
Factory-rejected tea	**NaOH**	1	800	1:3	7.3	1	25	[37]
Chickpea peel	**KOH**	2	800	1:3	7	2.5	25	[44]
Date palm pits	**H_3PO_4**	1.2	450	1:3	not adjusted	0.5	30	[49]
Tea seed shells	**$ZnCl_2$**	1	500	1:1	7.5	0.025	25	[56]

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