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Removal of Benzene and Toluene from Industrial Wastewater in Fluidized bed by Adsorption

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بسم الله الرحمن الرحيم

(اقْرَأْ بِاسْمِ رَبِّكَ الَّذِي خَلَقَ * خَلَقَ الْإِنْسَانَ مِنْ عَلَقٍ * اقْرَأْ
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[العلق: 1 – 5]

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To the Imam of my time, the goal of my aspirations, and the embodiment of my hopes, to the revered figure, my master, and the owner of the era and age.

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To the light of my eyes, the guiding star of my path, and the essence of my life, my mother, then my mother, and my mother, whose prayers have always accompanied me.

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And finally, to all those who taught me a skill and a letter."

ABSTRACT

Benzene and toluene (BT compounds) are hydrocarbons frequently found in water due to various human activities and accidental events like oil spills. They can cause health issues, including nervous system irritation, liver lesions, and cancer. This study aimed to develop cost-effective adsorption techniques using adsorbents made from corn biomass to remove BT compounds from water. Activated carbon synthesized from corn biomass with zinc chloride surface modification and carbonization was tested in a continuous fluidized bed column. The adsorbents effectively removed BT compounds, with toluene being more efficiently adsorbed than benzene due to its lower water solubility. The Langmuir adsorption isotherm described the adsorption behavior best. The derived adsorbent was investigated under changed operating parameters including the flow rates (Q) (15-25 l/hr), bed heights (Z) (6-10 cm), and temperature (T) (30-40 oC) to determine their effect on BT adsorption efficiency. The major finding shows that increasing flow rate and temperature reduced BT removal while increasing bed height improved removal efficiency. However, column adsorption showed lower efficacy due to limited access of adsorbates to the surface sites on the adsorbents caused by low retention times within the column. Optimal conditions for adsorption were identified: a bed height of 10 cm, a temperature of 30°C, and a flow rate of contaminated water was 15 L/hr. According to the breakthrough curve of 0.2 mm AC particles, the maximum adsorption capacities were 0.1447 and 0.15643 (mg/g) with total removal efficacies of 46.72% and 44.894% for benzene and toluene, respectively. Overall, this study demonstrated the potential of synthesized activated carbon from corn biomass as an effective adsorbent for BT removal from contaminated water using a continuous fluidized bed column.

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Nomenclature

Symbol	Meaning	Unit
tb	Breakthrough time	min
ts	Saturation (exhausted) time	min
Cb	Breakthrough concentration	mg/ml
Cs	Saturation concentration	mg/ml
qb	Adsorption capacity at breakthrough	mg
qs	Adsorption capacity at saturation	mg
mtotal	Total amount of pollutant entering the column	mg
mout	Amount of solute that left the column unadsorbed	mg
madsorbed	Amount of solute adsorbed in the column at saturation	mg
RE (%)	Removal percentage	%
KL	Langmuir adsorption equilibrium constant	l/mg
qmax	Maximum adsorption capacity in Langmuir isotherm	mg/g
K_{AB}	kinetic constant	L /mg. min
No	concentration at saturation	mg/l
v	fluid velocity	cm/min
Z	column bed depth	cm
q0	adsorption capacity	mg/g
k_{Th}	Thomas model constant	L /min mg

CHAPTER ONE

INTRODUCTION

1.1 Introduction

Freshwater is a vital resource that is interconnected with various aspects of our world. Its availability is essential for human existence and the sustainability of the planet. Quantity and quality are crucial factors for freshwater, but despite water covering about 70% of the Earth, only 2.53% is freshwater, with less than 0.1% accessible for human consumption [1]. In recent decades, the world has witnessed serious challenges that threaten life, environmental diversity, and socio-economic development, including water scarcity [2]. The rapid pace of urbanization and industrialization, and climatic changes has severely affected the amount of potable water around the world [3]. Considering an increase in the population growth rate, there is a severe concern that 48% of the world's population (about 3.5 billion), may have insufficient access to water in the upcoming years and the availability of fresh water is predicted to decrease over time, which will negatively impacts on development across many countries [4]. Furthermore, there are various classes of contaminants found in water that contributed to worsen its quality. Thuse, consumption of untreated or partially treated wastewater contains harmful contaminants is primary reasons for the loss of human lives [1,5].

Mono-aromatic Volatile Organic Compounds (VOCs) such as Benzene and Toluene (BT) has involved in various industrial sectors due to their similarity characteristics and properties including the ability to quickly dissolve a wide range of organic compounds, the poor reactivity, the high evaporation rate, low or absence of corrosion against metals. However, discharge these compounds into the environment can cause dangerous effects on human health that make them considered by different national and international institutions priority contaminants [6]. Sources of water contamination with BT include petroleum spills or leaks, improper disposal of petroleum products, and industrial processes that use or produce petroleum products [7–9]. Groundwater and surface water can be contaminated by BT, and contamination can spread to nearby bodies of water, including lakes, rivers, and oceans [10,11]. Exposure to BT compounds can be inhaled through the air, ingested through drinking water, or absorbed through the skin [12]. BT exposure can result in a variety of health issues, including nervous system, liver, and kidney damage, as well as an increased chance of cancer [12–14].

Water contaminated with BT can be treated using a variety of methods, including activated carbon filtration, air stripping, and bioremediation [15–17]. The specific method used will depend on the type and concentration of contaminants, as well as the location and accessibility of the contaminated water [18]. Effective treatment of water contaminated with BT is important for protecting human health and the environment.

An effective method for treating water contaminated with BT is adsorption. Adsorption is a widely used and popular technique due to its high efficiency in removing organic contaminants at low-concentration level [19,20]. Additionally, adsorption is a relatively simple and cost-effective process, making it popular for both small-scale and large-scale water treatment systems [21,22]. Adsorption involves the attachment or adhesion of the contaminants onto the surface of a solid material called an adsorbent [17,23]. It is basically employing interphase transfer to removes surface active material. The adsorbent can be packed into columns or filters through which the contaminated water is passed. As the water flows through the adsorbent, the BT molecules adhere to the carbon surface, effectively removing them from the water [21,24,25].

Carbonaceous sorbents are recognized as the most effective adsorbents for adsorption process due to their profound specific surface area, pore size distribution, well-developed microporosity, the presence of surface functional groups, degree of modification, regeneration, the complex heterogeneous surface nature [15]. Activated carbon (AC) is particularly favored for BT adsorption due to its excellent adsorption capacity and versatility [26]. It is commonly available in granular, powdered, or fiber forms [15,27–29]. Commercial activated carbon is commonly used as adsorbent due to high adsorption capacity with mean of (298.62 mg/g for organic pollutants) as result of highly porous nature with average pore volume of (0.71 cm^3/g) and high surface area with mean of (844 m^2/g) [30]. However, using commercial activated carbon is costly and loss 10-15% during thermal regeneration [31,32].

In present scenario, alternative low-cost adsorbents derived from natural sources can solve many problems associated commercial adsorbents. The use of adsorbents derived from natural sources is gaining popularity due to several advantages over commercial adsorbents. Natural adsorbents are derived from renewable sources and are readily available, making them cost-effective and environmentally friendly. They can be easily produced and can replace synthetic materials, reducing the dependence on non-renewable resources [23,29,33,34]. Natural adsorbents can be obtained from various sources, such as plant-based materials, agricultural waste, and animal by-products [30]. These materials have been found to have excellent adsorption properties, and their use can be optimized by modifying their surface properties through various treatments [26,35,36].

For instance, agricultural waste-derived ACs such as stones, husk, peels, leaves, shells, have been shown to have good adsorption capacity for pollutants originating from organic and inorganic sources in wastewater including BT pollutants. These materials are generally available, abundant in carbon content, and can be simply processed into adsorbents with high surface area and porosity [30]. Similarly, natural clays, zeolites, fly ash, sawdust, miscellaneous, sludge have also been found to be effective adsorbents for BT [26,30,31]. Moreover, the use of natural adsorbents can also provide additional advantages to the environment, such as reducing disposal waste and enhancing soil fertility by serving as a nutrient-dense soil additive [31,37].

1.2 Aim of the Work

Our aim is to derive natural adsorbents from low cost and available agriculture source that effectively adsorb BT pollutants from contaminated water that responsible for environment hazardous effects. This can be done through the following objectives:

1. To synthesize activated carbon natural adsorbent derived from corn waste namely corn cobs.
2. To characterize the surface area and pore volume of synthesized adsorbent via BET analysis.
3. Design of Experiments (DOE) and optimization of operating conditions using Taguchi method to understanding the impact of each input parameter on the system output.
4. To investigate the capability of synthesized activated carbon to treat wastewater that contain BT pollutants by employing continuous flow system under variable operational conditions and evaluating its adsorptive capacity.

5. To study the effect of different conditions of temperature, bed height, flow rate and activated carbon particle size on adsorption process removal performance of contaminated water.
6. To use the obtain experimental data to identify the isotherm models fitting the study.

CHAPTER TWO

Theoretical and Literature Review

2.1 Introduction

Water contaminated with benzene and toluene (BT) is a serious environmental issue that can have detrimental effects on human health and aquatic ecosystems [38,39]. BT are highly toxic and carcinogenic chemicals that can be found in petroleum products and industrial solvents [15]. When released into water sources, BT can contaminate groundwater, surface water, and drinking water supplies [40]. Exposure to BT-contaminated water can lead to a range of health problems, including cancer, neurological disorders, and respiratory issues [13,14,41]. Furthermore, aquatic organisms can also suffer from the effects of BT contamination, leading to population declines and ecosystem imbalances [34,42]. Therefore, understanding the sources, impacts, and treatment methods of BT pollutants in wastewater is crucial to safeguard human and environmental health. This introduction will explore the effects of BT pollution in water and the various methods used to treat it.

2.2 An Overview

BT compounds, which are monocyclic aromatic hydrocarbons, are highly abundant volatile components found in gasoline. They have been designated as priority pollutants by the US Environmental Protection Agency (EPA) and are commonly detected in environmental mediums such as air, water, and soil contaminated by gasoline. Despite being classified as volatile organic compounds (VOCs), BT compounds have the capability to dissolve in water resources and exhibit persistence, particularly in groundwater plumes due to their low octanol-water partitioning coefficient (K_{ow})[43]. Furthermore, BT compounds are typically found together rather than existing individually which reflect in enhancing their toxicity through interactions [44]. Table 2.1 present physical and chemical properties of BT hydrocarbons. Benzene, being the smallest and most soluble compound among the BT compounds, tends to be more persistent in environmental media. Furthermore, benzene has a considerably lower soil-water partitioning coefficient compared to the other BT compounds. This indicates that benzene is highly mobile in soil relative to the other components such as toluene. The higher persistence and mobility of benzene are concerning due to its well-established health risks. Benzene is a known carcinogen and has been associated with cases of leukemia [45,46]. Therefore, the disposal of BT compounds into the environment, particularly when benzene is present, can aggravate the potential ill-effects and increase the risks associated with exposure to these compounds.

Table 2. 1: Physical and chemical properties of BT compounds at 25 ^{o}C [47,48].

Property	**Benzene**	**Toluene**
Chemical Formula	C_6H_6	C_7H_8
Molecular Weight (g/mol)	78.11	92.14
Boiling Point (°C)	80.1	110.6
Density (g/cm³)	0.876	0.866
Solubility in Water	1.79 g/L	0.52 g/L
Octanol-Water Partition Coeff.	2.13	2.69
Soil-water partitioning co-efficient	97	242

2.3 Occurrence and Toxicity

BT compounds can find their way into water through various sources, posing potential risks to water quality. The possible paths for BT compounds to environment is shown in figure 2.1.

Fuel spills and leaks is significant source contribute to the presence of BT compounds in water [12,43]. Accidental spills during fuel transportation, transfer, or storage can introduce these compounds into nearby water bodies such as rivers, lakes, or oceans. Additionally, leaking fuel pipelines or faulty fuel storage systems can contribute to the contamination of water resources with BT compounds. A common concern at gas stations and industrial facilities is presence underground storage tanks (USTs) [43,49,50].

Industrial activities play a significant role in the release of BT compounds into water. Processes involved in the production, use, or disposal of petroleum products, solvents, and chemicals can result in the discharge of BT compounds. Manufacturing plants, chemical refineries, petrochemical industries, and factories that use or produce paints, coatings, or degreasers are examples of industrial sources that can contribute to BT contamination in water [43,51].

Urban runoff is another source of BT compounds in water. When it rains or snow melts in urban areas, the water can pick up pollutants from roads, parking lots, and other surfaces. This runoff can carry BT compounds from vehicle exhaust, fuel spills, and other sources into water bodies [43,52]. Furthermore, improper waste disposal and the presence of landfills can lead to the contamination of water with BT compounds. Leachate from landfills can contain these compounds, which can seep into groundwater or surface water, impacting water quality.

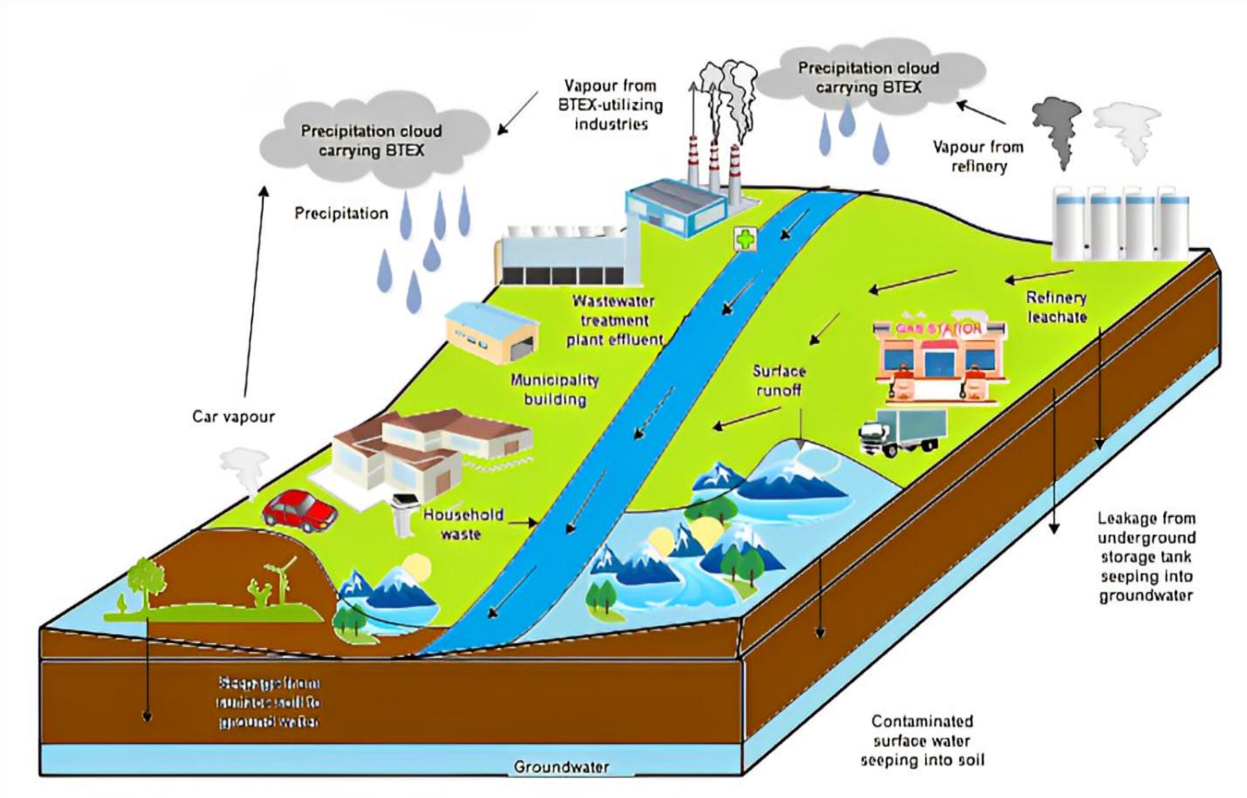

Figure 2. 1: Possible BT pathways in the environment [46]

Exposure to BT compounds can occur through inhalation, ingestion, or skin contact [53]. Regardless of how BT compounds enter the human body, several reports have emphasized common health consequences associated with their exposure. These consequences include symptoms like dizziness, liver disease, leukemia, birth defects and central nervous system (CNS) impairment [54–57]. People who work in industries that use or produce these compounds, such as petroleum refining or chemical manufacturing, are at increased risk of exposure. People living near contaminated sites or in areas with high levels of traffic pollution may also be exposed to higher levels of BT compounds [43,58]. It is important to note that the toxicity of these compounds can vary depending on the level and duration of exposure [46]. Occupational exposure to high concentrations of BT compounds, especially in industrial settings, poses greater risks compared to environmental exposure at lower concentrations [59].

Overall, the toxicity and occurrence of BT compounds make them a significant concern for human health and the environment, and measures must be taken to limit exposure and prevent contamination of air, soil, and water [60]. Table 2.2, show a common source and permissible limits of BT pollutants in drinking water according to World Health Organization Drinking Water Guidelines (WHO, 2008) and United States National Primary Drinking Water Standards (US EPA, 2003).

Table 2. 2: Source, permissible limits and health effects of various toxic BT pollutants [6,8,43].

Chemical	Common Sources	Health effects	Permissible Limits by WHO	Permissible Limits by US EPA
Benzene	Gasoline, industrial solvents, tobacco smoke, emissions from burning coal and oil	Carcinogen	10 μ g/L	5 μ g/L
Toluene	Incomplete combustion of liquid fuels, paint thinners	Damage the ozone layer	700 μ g/L	1000 μ g/L

2.4 Removal Technologies

As the levels of mono-aromatic compounds rise in the environment, there is a continuous search within the scientific community for effective and sustainable approaches to address this pollution. As result, numerous of methods that can be used to treat water that is contaminated with BT compounds. These methods include physical methods, such as filtration and air stripping, chemical methods, such as oxidation and ozonation, and biological methods, such as biodegradation using microorganisms [6,61,62]. The best method for treating BT-contaminated water will depend on the specific source of contamination and the level of contamination.

2.4.1 Adsorption by AC

This method involves passing contaminated water through a bed of activated carbon, which adsorbs the organic pollutants. The activated carbon has a high surface area and porosity, which enables it to trap organic compounds as well as taste and odor from water. The adsorption process is reversible, and the activated carbon can be regenerated and reused [19]. A mean removal effectiveness exceeding 90% was observed when the contact duration was 72 hours and the initial BT concentration was 100 mg/L [6]. However, as phase separation its effectively used for reducing the contamination but not completely eliminate them, also, some organic adsorbents can get drown by absorb water molecules as much as absorbing pollutants [8].

2.4.2 Biological Treatment

This method involves using microorganisms such as yeasts, bacteria, algae and fungi to degrade the BT pollutants. The microorganisms break down the BT compounds into less harmful substances, such as carbon dioxide and water. This method can be cheap and sustainable, but it requires careful management to ensure optimal conditions for the microorganisms to function [61,63,64]. The BT remove/degrade with initial concentration (up to 50 mg/L of) can reach more than 90% in 25 h [6]. For a higher initial concentration (<5000 mg/L) the degradation of BT can reach 100% but in nearly seven months [8].

2.4.3 Air Stripping (aeration)

This physical method involves exposing the contaminated water to air, which causes the BT compounds to evaporate (volatilize contaminants). The BT vapors are then collected and treated using another method [16]. This method is effective for treating water with BT concentrations of 1500 mg/l and with removal efficiency can reach more than 90% of BT at temperature system of 50 °C and an air-water ratio of 100. However, it requires significant energy to operate [6,62].

2.4.4 Advanced Chemical Oxidation

This method involves using oxidizing agents such as hydrogen peroxide or ozone to break down the BT compounds into less harmful substances. This method can be effective for treating water with low to moderate BT concentrations, but it can be expensive and produce waste products that require further treatment [65]. Ozonation processes removal bout 90%, of BT concentrations from 1 to 10 mg/L [6]. Furthermore, Homogeneous photocatalysis using Fenton reaction can remove 80% of monoaromatic components hydrocarbons of initial concentrations 10 mg/L in 150 min, and this can be enhanced by using heterogeneous photocatalysis with TiO2 semiconductor to reach degradation efficiency more than 90% of BT pollutants with concentration ranging from 1 to 20 mg/L in just a few minutes [6].

2.4.5 Membrane Filtration

This method involves passing contaminated water through a membrane that selectively filters out the BT compounds. The size and shape of the membrane pores can be adjusted to targeted compounds. This process requires a driving force (concentration, electrical potential gradients, or pressure,) to separate the desired molecules based on the membrane pore size [66]. This method can be effective for treating water with low to moderate BT concentrations, but it can be expensive and requires regular maintenance due to membrane fouling and need secondary treatment of wastewater [8,66,67]. The processes removal bout 60-70% of BT [66]. Combination with UV light irradiation can enhance removal efficiency of organic contaminants ranging from 85% to complete removal [68].

Overall, the choice of BT removal method depends on the specific contaminants, their concentrations, the available resources, and the desired outcomes. A combination of methods may be necessary for effective treatment in some cases. Table 2.3 summarizes the major advantages and disadvantages of the above treatment methods for BT removal from wastewater.

Table 2.3: Major advantages and disadvantages of treatment methods for BT pollutants removal from wastewater [8,69].

Treatment Method	Advantages	Disadvantages
Activated Carbon Adsorption	-Highly effective in BT removal -Wide availability and applicability - Can remove other organic contaminants	- Adsorption capacity affected by other dissolved organic compounds - Costly regeneration and waste stream generation
Biological Treatment (Bioremediation)	-Environmentally friendly approach - Cost-effective and sustainable -Can treat large volumes of wastewater	-Biodegradation rates dependent on microbial activity and environmental conditions - Longer treatment times - Production of sludge
Air Stripping	- Effective for volatile BT removal - Simple and straightforward process - Can be used for vapor-phase emissions	- Energy-intensive process -Management of off-gas emissions - Limited efficiency for non-volatile compounds
Advanced Oxidation Processes (AOPs)	-Highly effective in degrading BT compounds -Targets a wide range of pollutants	-Higher cost compared to conventional methods and high reactant consumption -Requires skilled operation and maintenance - Byproduct generation
Membrane Filtration	-Efficient removal of particulate matter, suspended solids, and certain organic compounds -Possibility of removing other pollutants simultaneously with no byproducts - Low/no reactant consumption	-Membrane fouling requiring regular cleaning or replacement -Costly equipment and maintenance

2.5 Adsorption and its Mechanisms

Adsorption is a well-established and effective method for the removal and recyclability of BT from various sources [70]. Adsorption is a phenomenon in which a solid material, known as an adsorbent, attracts and retains a solute or gas molecule from a liquid or gas phase [71,72]. Adsorption has several advantages for BT removal, including high removal efficiency, low operating costs, and ease of use. It is a physical process that does not require the use of chemicals or the production of harmful byproducts. Adsorbents can also be regenerated and reused, reducing waste and costs [6,69].

As a surface phenomenon, the mechanism of the adsorption process involves the interaction between the adsorbate (the substance being adsorbed) and the adsorbent (the surface on which adsorption occurs). In other word, when the transferred molecules from the fluid reach the solid surface, they tend to accumulate and transfer within the bulk adsorbent [30,73]. Therefore, these molecules or ions adhere to a solid surface or interface, forming a monolayer or multilayer [69]. Although adsorption can vary depending on the specific adsorbate and adsorbent, there are two common mechanisms physical adsorption (physisorption) and chemical adsorption (chemisorption) presented in figure 2.2. Table 2.4 compares the properties of these mechanisms.

Physisorption is a reversible process driven by weak intermolecular forces such as Van der Waals forces, London dispersion forces, and dipole-dipole interactions. The adsorbate molecules are attracted to the surface of the adsorbent through these forces. Physisorption is typically observed at lower temperatures and is characterized by a lower energy of adsorption [74]. The adsorbate can be easily desorbed from the surface through processes like heating or reducing the pressure.

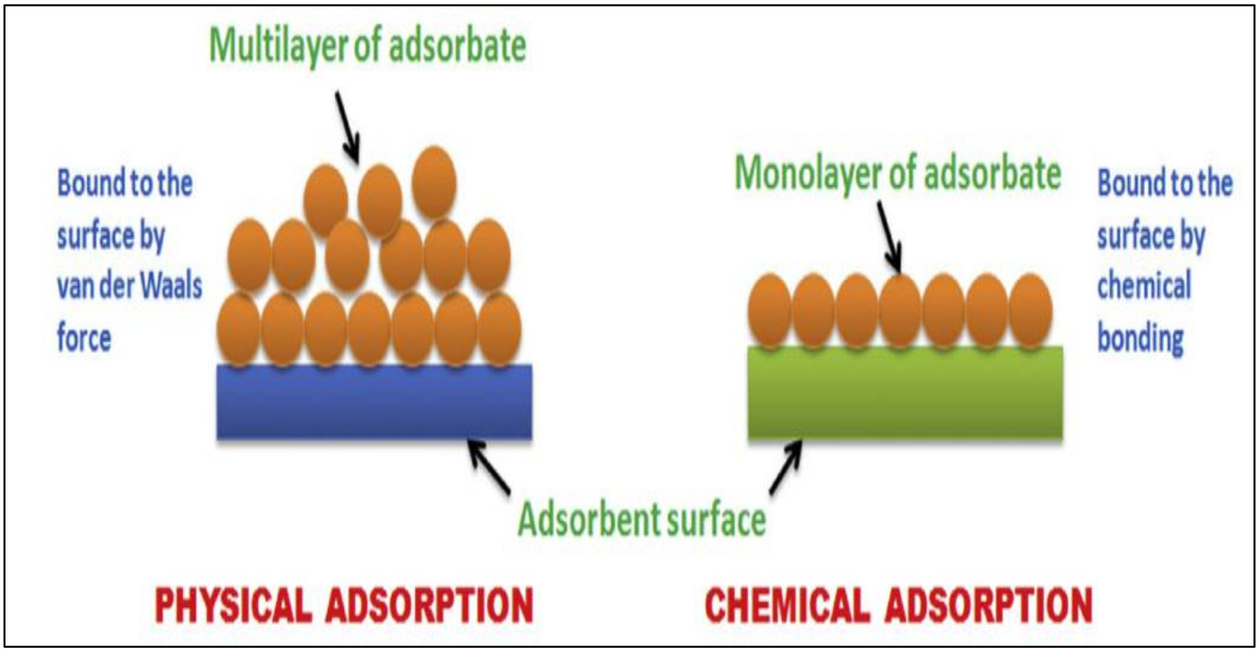

Figure 2. 2: Physisorption phenomenon and chemisorption phenomenon[75].

Chemisorption involving a stronger and more specific interaction between the adsorbate and the adsorbent. It occurs through chemical bonding between the adsorbate molecules and the surface atoms or functional groups of the adsorbent [26]. Chemisorption often involves the exchange or sharing of electrons between the adsorbate and the adsorbent, resulting in the formation of chemical bonds. This type of adsorption is usually observed at higher temperatures and is characterized by a higher energy of adsorption. Chemisorption is typically more difficult to reverse, and desorption may require chemical reactions or severe conditions [74].

Unlike the physisorption, where the one of the diffusion transport steps acts as a rate-limiting step, the chemisorption rate-limiting step is the adsorption step [76]. The specific mechanisms and factors involved in the adsorption process depend on the properties of the adsorbate and the adsorbent, as well as the conditions of the system [70,77]. It's important to note that the adsorption process is often accompanied by other phenomena, such as diffusion of adsorbate molecules into the porous structure of the adsorbent, surface reactions, and competitive adsorption in multicomponent systems. Understanding the adsorption mechanism and its influencing factors is crucial for designing effective adsorption processes in various applications, including wastewater treatment [17,26].

Table 2. 4: Physical and chemical adsorption mechanisms [74,78,79].

Physiosorption process	**Chemisorption process**
Weak van der Waal's force of attraction act to keep the adsorbate on the adsorbent's surface.	A strong chemical bond kept adsorbate on the adsorbent's surface.
New compounds are not created in this phenomenon.	Its involve a formation of new surface compounds.
This mechanism proportion with temperature, decreases with a decrease in temperature.	Increases with an increase in temperature.
reversible process.	irreversible process.
No activation energy is needed.	its required an activation energy.
Low heat of adsorption (20-40 KJ mol^{-1})	High adsorption heat (40-400 KJ mol^{-1})
Can form multilayer of components.	Its form only a monolayer.
The adsorption is effective at low temperatures and high pressure.	The adsorption is effective at high temperatures.
It is not specific in nature.	It is specific in nature.

Its worthily to mention that, physisorption involve three stages as shown in figure 2.3. Where the first stage is the external adsorption and the adsorption rate mainly depend on the specific surface area. The second stage is the particle diffusion and its adsorption rate mainly depend on pore structure and volume. Final stage is equilibrium and its adsorption rate depend on the ratio of meso- and macro-pores to total pore volume. The overall rate is depended on pollutant concentration [80]. The role of specific surface area and pore structure was reviewed and shows that, the large surface specific area and well-developed pore structure especially micropore structure have positive effect on physical adsorption. Also, the shapes and sizes of pollutant molecule can determine the occurrence of adsorption [26].

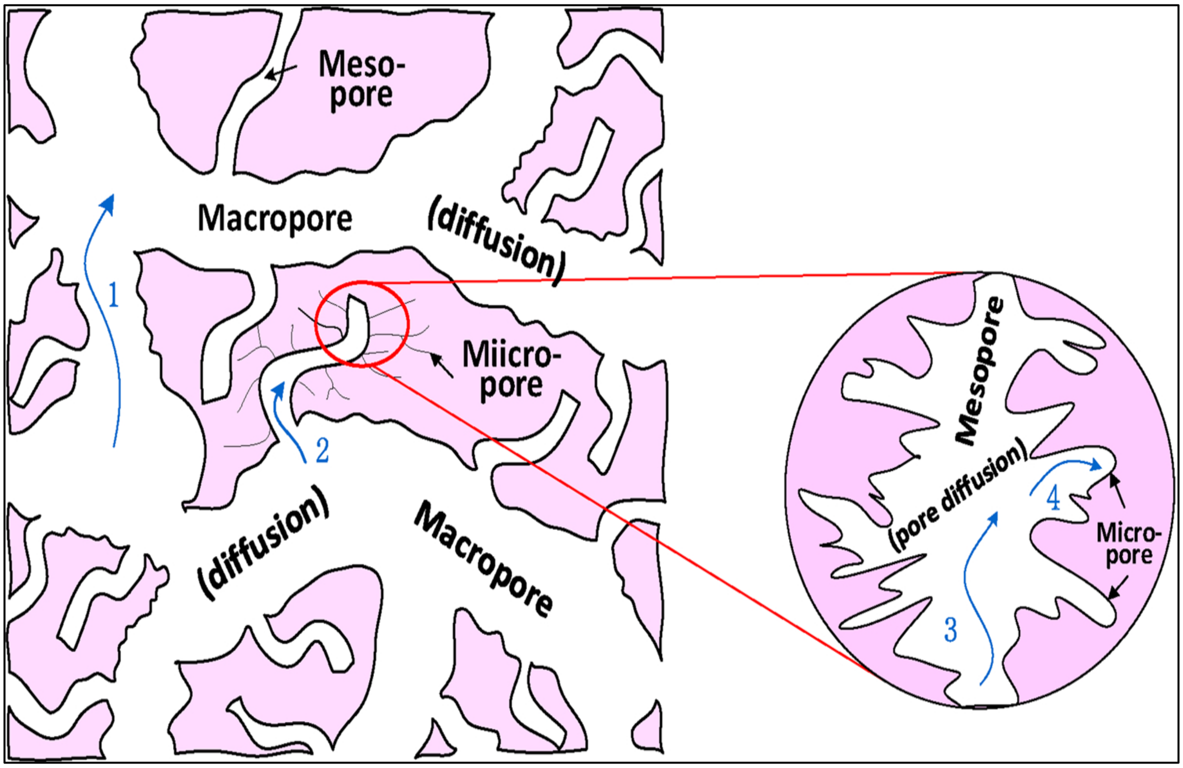

Figure 2. 3: Physical adsorption on the porous adsorbent (1. Convection and dispersion; 2. Convective mass transfer; 3. Pore diffusion; 4. Adsorption on surfaces.) [26].

2.6 Activated Carbon

Activated carbon (AC) as shown in figure 2.4 is a widely used adsorbent material for the removal of toxic pollutants from aqueous solutions , but other materials such as zeolites, silica, and activated alumina can also be used [17,23]. The physiochemical properties and performance of different porous materials for VOCs adsorption are summarized in Table 2.5. The porous of these materials provide internal surface area much higher than the external surface to trappe the molecules [26]. To be considered suitable for commercial applications, an adsorbent should possess several key properties. These include a high surface area per unit volume, excellent selectivity, a substantial adsorption capacity, efficient kinetic and transportation properties, chemical and thermal stability, strong mechanical strength, affordability, the ability to be regenerated, and resistance to fouling, etc.

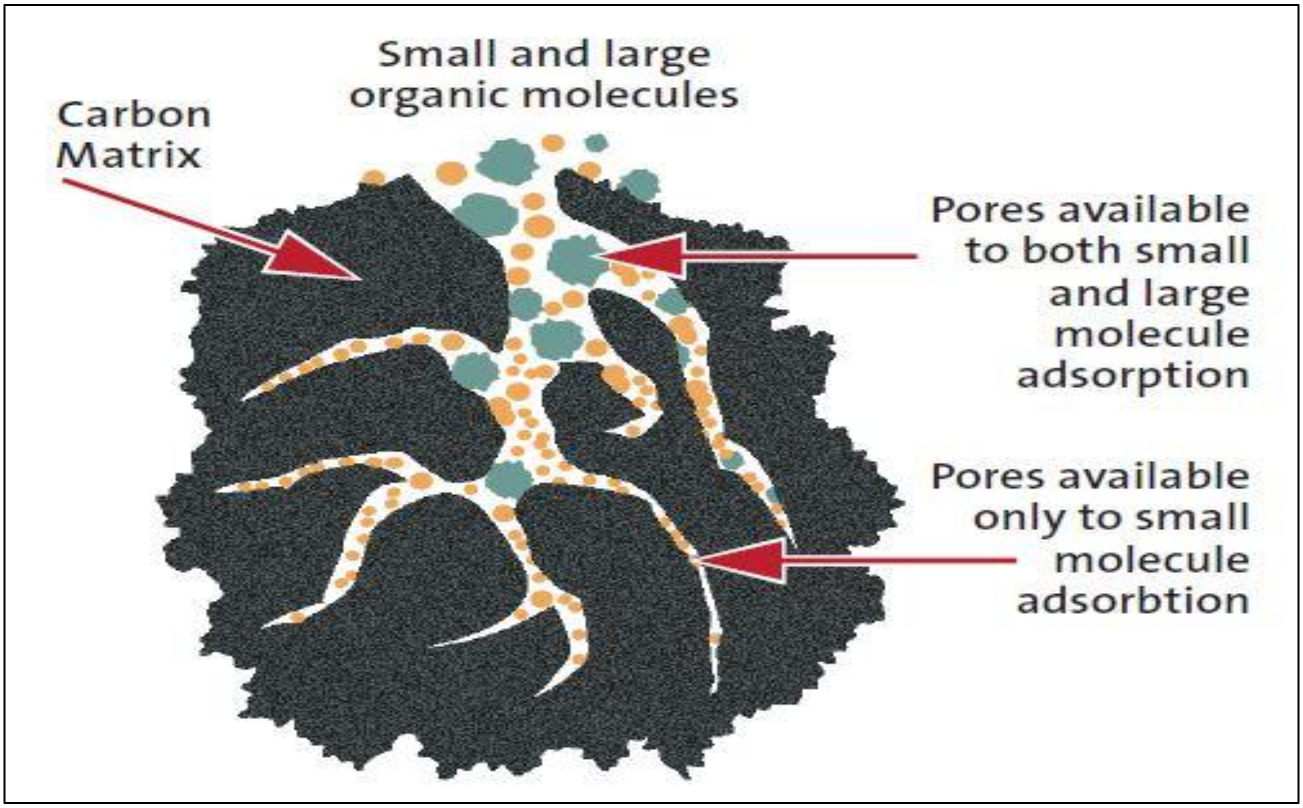

Figure 2. 4: Structure of activated carbon

Table 2. 5: Summary of physiochemical properties and performance of different porous materials

Adsorbent	Specific Surface Area (m^2/g) / (Reference)	Total Pore Volume (cm^3/g) / (Reference)
Activated Carbon	600 – 1400/[26]	0.5–1.4/[26]
Zeolites	250-800/[17]	0.3-0.47/[17]
Clay	14-800/[17]	0.1-0.6/[26]
Metal-Organic Frameworks (MOFs)	1000 – 10,000 / [81]	0.5 - 2.5/[26]
Silica Gel	750–850/[69]	0.444/[26]
Carbon Nanotubes (CNTs)	25 – 650/[17]	0.4 – 0.9/[17]

AC is a form of carbon that has been treated to have a large surface area (500–3000 m^2/g), and microporosity (0.7–1.8 cm^3g^{-1}), which allows it to effectively adsorb a wide range of organic/inorganic pollutants including BT in different environment [15,82,83]. Figure 2.5 shows a common form of activated carbon. AC can be formed in powdered (15 - 25 μm), granular (0.5-100 mm), and fiber form of specific surface of up to 2000 m^2/g [15,84]. AC can be made from various carbonaceous raw materials, such as wood, coal, or coconut shells, which are heated in the absence of air to produce a carbon-rich material [69]. The material is then activated through a process of physical or chemical treatment, which creates a porous structure with a large surface area [73,85]. The effectiveness of activated carbon as an adsorbent for BT removal depends on several factors, including the pH of the solution and characteristics of the carbon, such as its pore size and surface area, and the properties of BT, such as density, and concentration [30,86]. Advantages of using activated carbon as an adsorbent for BT removal include its high adsorption capacity, selectivity for BT pollutants, and compatibility with a wide range of water and soil matrices. Activated carbon is also a commercially available and widely used adsorbent, making it easy to source and use in various applications.

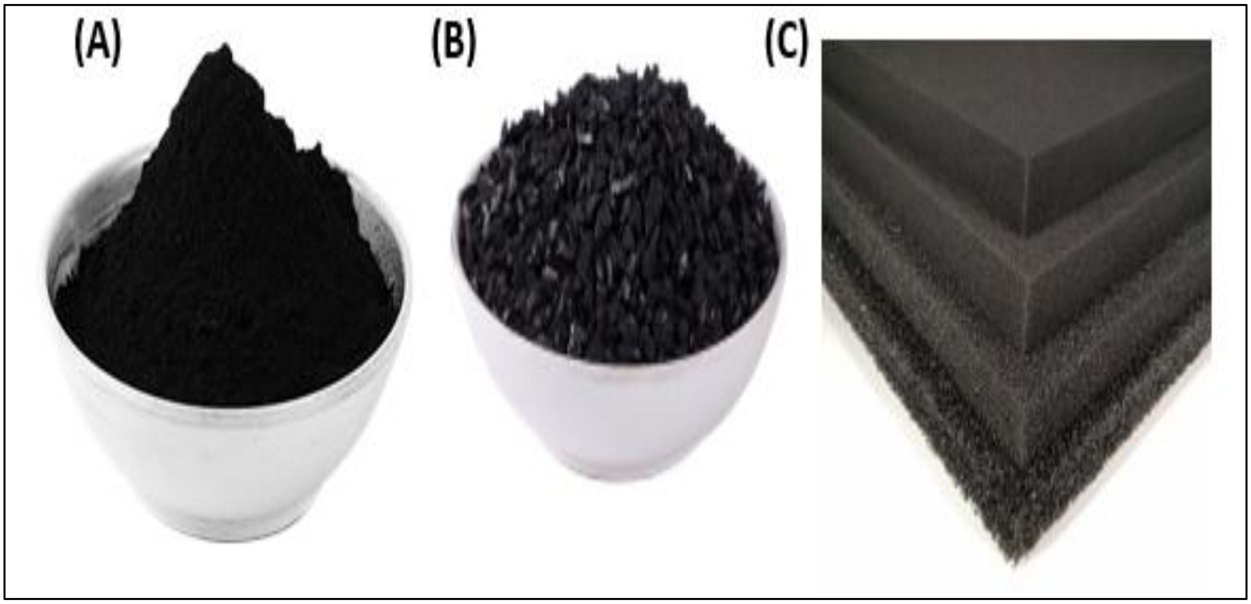

Figure 2. 5: Forms of activated carbon: (**a**) activated carbon powder, (**b**) granular activated carbon, (**c**) activated carbon fabric.

2.6.1 Modification of Activated Carbon

Activated carbon is a remarkably adaptable substance with broad applications for eliminating various types of pollutants from wastewater, including BT. Nevertheless, its surface chemistry and/or morphology can be enhanced through various modification methods. Chemical, physical, electrochemical, and biological treatments are among the techniques used to modify activated carbon [30,87]. Such modifications can lead to improved adsorption properties, expanded surface area, greater selectivity, and improved stability.

Chemical modifications entail incorporating functional groups onto the surface of activated carbon by means of chemical reactions, including oxidation, reduction, and grafting. Chemical activation involves a single carbonization stage where the raw material is impregnated with significant quantities of a chemical agent. This will introduce functional groups onto the surface of activated carbon through various chemical reactions, such as oxidation, reduction, and grafting. The typical ratio of chemical reagent to raw material ranges from 1:4. Subsequently, the impregnated material is heated. After carbonization, the product needs to be thoroughly washed to remove any excess chemical agent. The specific temperature of the thermal treatment varies depending on the choice of chemical agent. Phosphoric acid, $ZnCl_2$ (zinc chloride), and alkaline hydroxides are among the most commonly used chemical agents in this process [88].

The zinc chloride process, which was a widely utilized method of chemical activation in the past, offered several advantages. It primarily employed lignocellulosic materials with high volatile content, such as wood, as precursors. During the process, impregnation with zinc chloride resulted in the weakening of the lignocellulosic structure, leading to increased elasticity and particle swelling. Zinc chloride's presence also prevented tar formation, allowing for the development of activated carbons with wide and open microporosity, comprising both micro- and mesopores. As a result, these activated carbons generally exhibited slightly higher adsorption capacity and wider porosity compared to those produced through thermal activation methods.

However, the zinc chloride process also had its disadvantages. It was associated with low recovery efficiencies and corrosion problems. Additionally, residual zinc could be present in the final carbon product, which required careful control and monitoring. The need for stringent plant emissions controls further contributed to the process being displaced by phosphoric acid as the preferred chemical agent. The drawbacks, along with the demand for improved performance and emissions control, led to the transition away from the zinc chloride process in favor of alternative activation methods [88].

It is noteworthy that the impact of modifications on a material's adsorption capacity can be influenced by several factors, such as the material type, the specific modifications applied, and the properties of the substances being adsorbed. For instance, modifications made to a material through acid and base treatments lead to an increase in its ability to adsorb substances. However, peroxide treatment may not produce the same effect on the material's adsorption capacity [89]. This may be due to the fact that acid and base modifications introduce new functional groups onto the material's surface that can interact with other molecules, increasing the surface area available for adsorption. However, peroxide treatment may have a different effect, such as breaking down or removing some of the functional groups responsible for adsorption [90].

Conversely, physical modifications alter the morphology of activated carbon, such as through pore size engineering, carbonization, and activation techniques [91].

The modification of activated carbon has garnered significant attention in recent times, as it presents opportunities to customize the material for specific applications, thereby increasing its efficiency and effectiveness. Table 2.6 summarizes the advantages and disadvantages of chemical and physical modifications for activated carbon.

Table 2. 6: Advantages and disadvantages of activation techniques [93].

Activation Techniques	**Advantages**	**Disadvantages**	**Activation Agents**	**Functional Groups Introduced**
Physical Activation (e.g.	High surface area, High purity, Low cost	Poor control over pore size and distribution	CO_2, Steam, N_2	N/A

Pyrolysis, Gasification)				
Chemical Activation (e.g. Phosphoric Acid, zinc Chloride)	High surface area, Controlled pore size and distribution, Can introduce specific functional groups	Requires chemical agent, High cost, Presence of impurities, Requires additional washing steps	Phosphoric Acid (acidic functionalization), Zinc Chloride (chlorination)	Phosphoric Acid: Introduces acidic functional groups (carboxylic, phenolic), Controlled pore size and distribution
H_2O_2 Oxidation	Low cost, Mild reaction conditions, Can introduce hydroxyl functional groups	May cause significant loss in BET surface area, Low control over pore size and distribution, Requires additional washing steps	Hydrogen Peroxide (oxidation)	Introduces hydroxyl functional groups

2.7 Corn as A Potential Adsorbent

Corn, also known as maize, is a cereal crop that is widely cultivated around the world for its kernels, which are used for food, feed, and industrial purposes. It is a member of the grass family and can grow up to three meters tall. Corn is a staple food in many cultures and is used to make various food products, including cornmeal, corn syrup, popcorn, tortillas, and corn flakes. It is also used as animal feed and for industrial purposes, such as ethanol production and fertilizer [93,94]. Corn is rich in carbohydrates, fiber, vitamins, and minerals, making it a nutritious food source [95].

Corn biomass, including corn cobs, can be classified as a type of natural organic adsorbent due to its ability to adsorb or remove contaminants from water or other solutions. The cellulose and hemicellulose components of corn biomass provide sites for adsorption, and its abundant availability and low cost make it an attractive alternative to conventional synthetic adsorbents. Additionally, corn biomass can be modified through various chemical and physical treatments to enhance its adsorption properties, making it a promising material for wastewater treatment and other environmental applications. Corncob-based adsorbents has been used in removal of BT from contaminated aqueous and air environments [96]. Corn cobs as low-cost sorbents offer many promising advantages for the removal of BT due to several characteristics:

1. Abundant availability: Corn cobs are an abundant byproduct of the corn industry, making them a low-cost and sustainable option for wastewater treatment [97].
2. High surface area: Corn cobs have a high surface area about is quite high (903.7 m^2/g), due to their porous structure, which provides numerous sites for the adsorption of BT [21].
3. Natural composition: Corn cobs are composed of natural materials, including 39.1% cellulose and 42.1% hemicellulose, which are non-toxic and biodegradable, making them an environmentally friendly option for wastewater treatment [93,98].
4. Modification potential: Corn cobs can be modified through various chemical and physical treatments to enhance their adsorption properties and make them more effective for the removal of BT [99].
5. Effective adsorption: Studies have shown that corn cobs are effective adsorbents for BT removal due to their high adsorption capacity and selectivity [100].

Overall, these characteristics make corn cobs a promising and cost-effective option for the removal of BT in wastewater treatment and other environmental applications.

2.8 Factors Affected the activated carbon Adsorption

Several factors can affect the performance of activated carbon in adsorbing pollutants from aqueous solutions. Some of the key factors include:

2.8.1 Initial Concentration of Pollutants

The concentration of BT pollutants in the adsorption system significantly affects the adsorption process. Higher concentrations generally result in increased adsorption capacity, as more BT molecules are available for adsorption onto the surface of the adsorbent [101,102]. However, there is a limit to the adsorption capacity, and further increasing the concentration may not lead to significant additional adsorption [103]. At higher concentrations, there is also greater competition for adsorption sites, which can slow down the rate of adsorption and decrease overall efficiency. Saturation occurs when all available adsorption sites are occupied, and no further increase in adsorption is observed. Concentration also plays a role in the desorption process, where higher concentrations of desorbing agents can facilitate the release of BT compounds from the adsorbent. It is important to consider the specific adsorbent material, BT compound properties, and treatment objectives to determine the optimal concentration range for effective adsorption while adhering to practical and regulatory limits.

2.8.2 pH Solution

The pH of the solution affects the ionization state of both the BT compounds and the adsorbent surface [103]. The ionization of the compounds and the surface charge of the adsorbent can influence the electrostatic interactions between them. However, the specific pH dependence can vary depending on the nature of the adsorbent. For BT , the increase in pH due to the addition of NaOH leads to decrease their solubility which means increases the adsorption capacity [77].

2.8.3 Temperature

Temperature plays a crucial role in the adsorption process by affecting the rates of adsorption and desorption. Generally, an increase in temperature enhances the adsorption kinetics, as it provides more thermal energy for the molecules to overcome activation barriers and adsorb onto the surface. However, the effect of temperature on adsorption equilibrium can vary depending on the adsorbent and the specific adsorption system. Some adsorption processes may be exothermic, where higher temperatures can reduce adsorption due to decrease affinity and active sites [77]. For BT compounds, an increase in temperature causes a decrease in organic compounds and dissolved oxygen in water and diffusion transfer increases [8].

2.8.4 Contact Time

The contact time refers to the duration for which the BT compounds are in contact with the adsorbent. It affects the extent of adsorption and the achievement of equilibrium. Initially, the adsorption rate is high, and more compounds are adsorbed onto the surface. As time progresses, the rate decreases, and eventually, adsorption reaches equilibrium. Longer contact times generally lead to higher overall adsorption capacities. However, it's important to optimize the contact time to balance efficient adsorption and practical considerations such as process efficiency and cost [77,103].

2.8.5 Bed Height

The height of a bed in adsorption processes affects the overall performance in several ways. A taller bed increases contact time between the adsorbent and adsorbate, improving adsorption efficiency. It can enhance mass transfer by promoting better fluidization but may also cause channeling or uneven flow distribution. A taller bed generally provides a higher adsorption capacity due to containing more adsorbent material. However, it can result in increased pressure drop and energy requirements. Uniform bed height is crucial to avoid uneven flow paths and maximize adsorbent utilization. Increase in the drag force and requires increasing minimum fluidization velocity [104].

2.9 Adsorption Modeling

Adsorption isotherms are mathematical equations that describe the relationship between the concentration of adsorbate and the amount of adsorbent at a constant temperature. These isotherms help in understanding and characterizing the adsorption process. The most commonly type of adsorption isotherms used are Langmuir isotherms. However, for dynamic system different dynamic models have been used to analyzed the breakthrough data for attain high practical value information of column design and predicting its dynamic behaviors. These dynamic models based on axial dispersion and nonlinear isotherms, external film resistance, and intraparticle diffusion hypotheses [105]. Dynamic column models including Thomas model and Adams–Bohart model.

2.9.1 Langmuir Isotherm

This model assumes a monolayer adsorption on a homogeneous adsorbent surface with no interaction between the adsorbed molecules. It is based on the assumption that the adsorption sites are equal and independent. The linearized Langmuir isotherm equation is given by[106]:

$$\frac{c_e}{q_e} = \frac{1}{qm\ kL} + \frac{c_e}{q_m} \qquad \text{...eq(2.1)}$$

where C_e is the equilibrium concentration (mg/l) of adsorbate at equilibrium, q_e is the amount of compound adsorbed at equilibrium(mgg^{-1}), qm is Langmuir isotherm constant (mg g^{-1}) theoretical maximum adsorption capacity and $K_L$is the isotherm constant related to the energy of adsorption (l/mg). The Langmuir constants were evaluated from the slope and intercept of the linear plot of $\frac{c_e}{q}$ vs Ce.

2.9.2 Adams-Bohart model

This model basically describing the first part of the breakthrough curve and dose not considering the axial dispersion effects and assumes that equilibrium does not develop instantaneously. Furthermore, the adsorption rate is proportional to initial pollutant concentration and the adsorbent residual capacity [21,107–109].

The model equation as follows Eq. (2.2) [110]:

$$ln\left(\frac{ct}{c0}\right) = k_{AB}C_0t - k_{AB}N_0\frac{z}{v} \qquad \ldots eq(2.2)$$

where kAB represents the kinetic constant (L /(mg. min)), No stands for the concentration at saturation (mg/L), v is the fluid velocity (in centimeters per minute), defined as (volumetric flow rate /bed cross-sectional area), and Z denotes for column bed depth (in centimeters), The time range, denoted as "t," is considered from the initial breakthrough to the end. The values for N_o and kAB constant can be determined by plotting the natural logarithm of (Ct/C0) vs time (t).

2.9.3 Thomas model

This model is a commonly used to study the performance of column system. This model simplified version of Bohart and Adams's irreversible isotherm model and neglected mass transfer resistance from both intraparticle and fluid-film. Thus, this model assumed that surface reaction between ion molecules and unoccupied sites controlled the adsorption rate [107–109,111]. The model equation as follows Eq. (2.3) [110] :

$$ln\left(\frac{c0}{ce}-1\right)=\frac{q_0wk_{Th}}{Q}-k_{Th}C_0t \qquad \text{…eq (2.3)}$$

where qo is the adsorption capacity (mg/g), k_{Th} is model constant (L /(min mg)). Thuse parameters can be obtained from plot of ln[($C0/Ct$) − 1] vs t.

2.10 Adsorption Treatment System

Adsorption treatment systems are liquid–solid interaction process that can be designed to as batch or continuous reactors, depending on the specific application and requirements.

Batch adsorption reactors are used for small-scale water treatment applications or for treating water with low levels of contaminants. In a batch reactor, a fixed amount of adsorbent material is added to the water to be treated and allowed to adsorb the contaminants for a set period of time. Once the adsorption is complete, the water is separated from the adsorbent material and discharged. The data provided can be utilized in multiple ways for biosorption analysis, such as selecting the suitable biosorption isotherm for process data modeling and determining the maximum capacity of the tested material. Additionally, it can aid in determining kinetic parameters and the corresponding model for evaluating the rate-controlling process step, calculating thermodynamic parameters to establish the spontaneity and thermic effect of the biosorption process, and identifying the most probable biosorption mechanism [105].

Continuous adsorption reactors are used for large-scale water treatment applications or for treating water with high levels of contaminants. In a continuous reactor, the water containing the adsorbates (pollutant molecules or ions) flows continuously through a bed of adsorbent material, allowing for continuous adsorption of contaminants. The adsorption capacity increases as a function of time. When the adsorptive capacity is approached, the adsorbent material is periodically replaced or regenerated to maintain its effectiveness [107].

There are several types of continuous adsorption reactors, including [69,72,113,114]:

1. Fixed-bed reactors: In a fixed-bed reactor, the adsorbent material is contained in a fixed bed through which the water flows. As the water flows through the bed, contaminants are adsorbed onto the surface of the adsorbent material.
2. Fluidized-bed reactors: In a fluidized-bed reactor, the adsorbent material is fluidized by a continuous flow of water or air, allowing for better mixing and more efficient adsorption.
3. Moving bed: a type of bed where solid particles are continuously introduced at one end and removed from the other end while fluid is passed through the bed in the opposite direction.
4. Pulsed bed: a type of bed where the particles are intermittently pulsed with a fluid (usually gas) to enhance the mixing and mass transfer between the particles and the fluid.

The selection of the type of adsorption reactor depends on the specific application, the required flow rate, and the type and level of contaminants present in the water.

2.11 Fluidization and Fluidized Beds

The performance of adsorbents for removing adsorbates and determining maximum adsorption capacity is typically evaluated through batch adsorption studies [115,116]. However, in water treatment systems, bed adsorption is often preferred from an industrial perspective due to its ease of operation, reasonable capital and operating costs, and scalability from laboratory processes. Industrial processes for removing contaminants from aqueous solutions have extensively tested column bed adsorption using activated carbon (AC) [116]. Due to the vigorous movement within a fluidized bed, the distribution of solids more even compared to a fixed bed. This characteristic is particularly significant in various chemical and catalytic processes. Furthermore, the particle size in a fluidized bed is typically smaller than that in a fixed bed, resulting in reduced resistance to diffusion through the particles. This property is advantageous for many chemical and catalytic reactions. Another benefit of fluidization is the ease of adding or removing solids from the bed, which is particularly advantageous in situations where rapid activity losses occur. In many cases, fluidization also leads to lower pressure drops compared to operation in a fixed bed [117].

2.11.1 Breakthrough curve

To design a successful fluidized bed adsorption system, it is necessary to analyze the breakthrough curve for specified operating conditions [114]. The breakthrough curve in a fluidized bed refers to a graphical representation of the concentration of BT components in the effluent stream over time. It provides valuable insights into the adsorption behavior of BT components and helps determine the point at which breakthrough occurs. Figure 2.7 and Table 2.7 show characterization of Breakthrough curve.

Initially, when the fluidized bed column is fed with BT-containing wastewater, the effluent concentration of BT components is relatively low. As time progresses, the concentration gradually increases until it reaches the breakthrough point. The breakthrough point signifies the moment when the concentration of BT components in the effluent stream surpasses a predefined acceptable limit or regulatory threshold. The breakthrough curve typically exhibits the following key features specific to BT components:

1. Adsorption Capacity: Initially, the effluent concentration of BT components remains low as the activated carbon efficiently adsorbs these compounds.

The adsorption capacity of the activated carbon determines the amount of BT components it can effectively remove from the wastewater.

2. Adsorption Zone: As the adsorption capacity of the activated carbon approaches its limit, the effluent concentration of BT components starts to rise. This zone represents the gradual saturation of adsorption sites on the activated carbon.
3. Breakthrough Point: The breakthrough point occurs when the concentration of BT components in the effluent stream exceeds the desired limit. At this point, the activated carbon becomes saturated and is no longer able to effectively adsorb all the BT components, resulting in their presence in the effluent stream.
4. Breakthrough Zone: Beyond the breakthrough point, the effluent concentration of BT components continues to increase significantly. The breakthrough zone represents the period when the activated carbon is fully saturated and unable to adsorb any more BT components.

Analyzing the breakthrough curve provides important information, such as the breakthrough time (the time at which breakthrough occurs), the adsorption capacity of the activated carbon, and the efficiency of the fluidized bed system in removing BT components from wastewater. These insights are crucial for optimizing the design and operation of fluidized bed adsorption processes targeting BT removal.

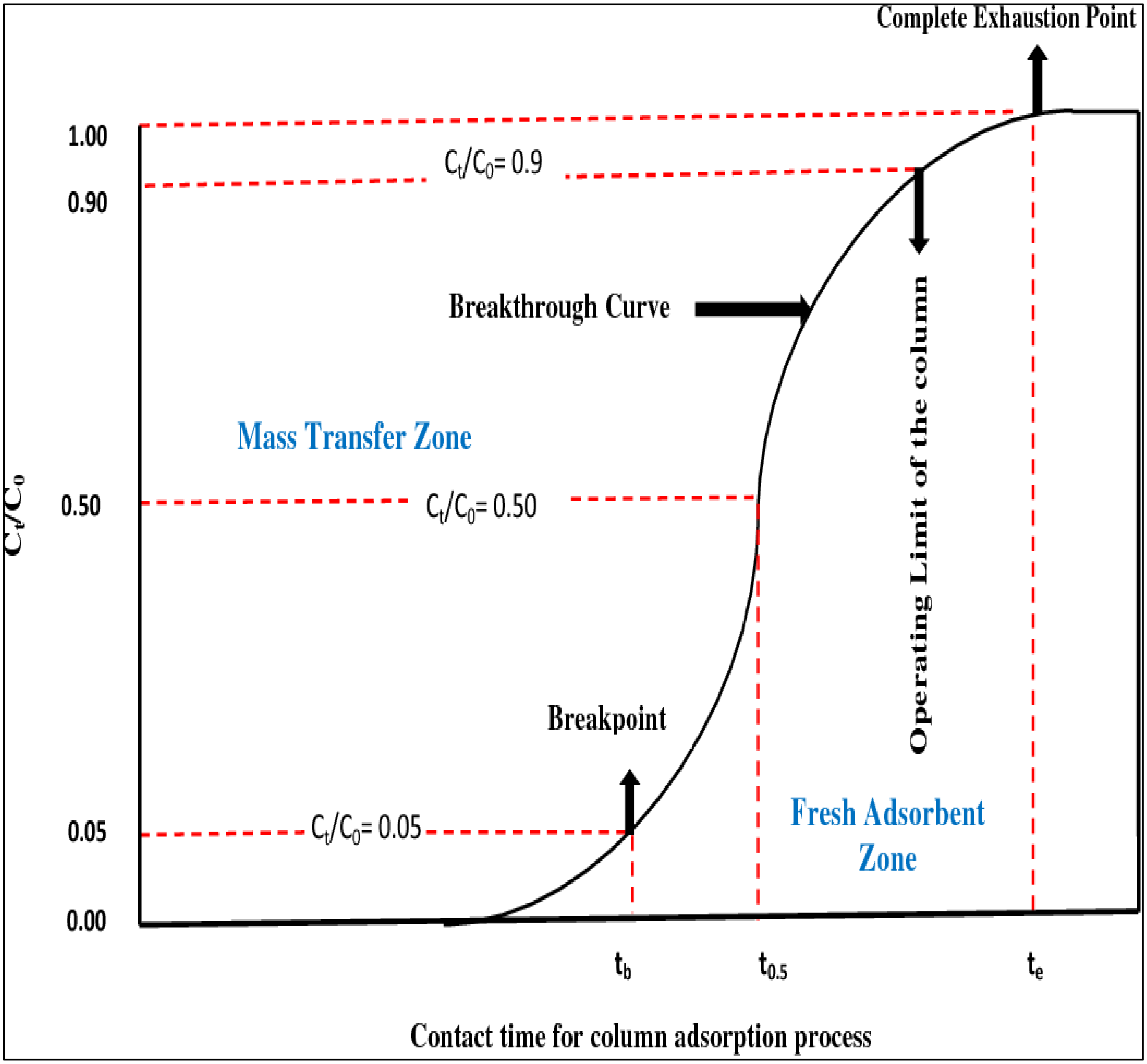

Figure 2. 6: Breakthrough curve[118].

Table 2. 7: Characteristic parameters of the breakthrough curves [106].

Parameters	**Description**	**Formula**
Breakthrough time (t_b), min	The time it takes for the solute to first appear at the outlet of the porous media.	t_b can determine at C_b= 0.1 C_0
Saturation (exhausted) time (t_s), min	The time to achieve saturation concentration of solute at the outlet of the porous media.	t_b can determine at Cs= 0.9 C_0
Breakthrough concentration (C_b), mg/ml	The concentration of solute at the outlet of the porous media at breakthrough time.	C_b=0.1C_0
Saturation concentration (C_s), mg/ml	The maximum concentration of solute observed in the effluent	Cs=0.9 C_0
qb, mg	The adsorption capacity at breakthrough.	qb=C_0 Q $\int_0^{tb}\left(1-\frac{c}{c0}\right)dt$
qs, mg	The adsorption capacity at at saturation, also denoted as qe representing equilibrium adsorption capacity (mg/g),	qs=C_0 Q $\int_0^{ts}\left(1-\frac{c}{c0}\right)dt$
m_{total}, mg	Total amount of pollutant entering the column.	m in = $CoQt_s$
m out, mg	The amount of BT that left the column unadsorbed at saturation.	m out $= C0\ Q\int_0^{ts} C/C0\ \ dt$
m adsorbed , mg	The amount of BT adsorbed in the column at saturation.	*m ads, = m in – m out*
Removal percentage (RE%)	Total adsorbed molecules in the column to the total amount of molecules sent to the column	RE (%) = m ads/ m in × 100

2.12 Previous works

Kulkarni et al (2013)[117]**,** explores the application of coconut shell activated carbon (CCAC) in a fluidized bed setup for the elimination of phenol from wastewater. The researchers established that CCAC proficiently eliminates phenol from wastewater, showcasing an adsorption capacity of up to 8.57 mg/g. The study also delved into the influence of various operational factors on phenol adsorption, including flow rate, initial phenol concentration, bed height, and particle size. The outcomes demonstrated that elevated bed height correlated with prolonged breakthrough times and heightened adsorption capacity, whereas escalated flow rates, inlet phenol concentrations, and particle sizes were associated with decreased breakthrough time and adsorption capacity.

Yakout et al. (2014) [119]**,** investigated the adsorption of benzene and toluene from an aqueous solution using rise husk (AC) with a surface area of (965.5 m^2/g). The results show that, at optimum conditions the removal of toluene (33%) was higher than benzene (22%).

S. Jodeh et al (2015) [77]**,** investigated the adsorption of benzene and toluene from an aqueous solution using date palm seeds (AC) with a surface area of (800 m^2/g). The results show that, at optimum conditions the removal of toluene (72%) was higher than benzene (68%).

Aghdam et al (2015) [120]**,** investigated the use of AC derived from paper mill sludge to remove benzene and toluene from water. The AC has a surface area of (613 m^2/g) and activation by $ZnCl_2$ creates more pore structure. The results show that, at optimum conditions the removal efficiency of toluene was higher and faster than benzene as a result of their chemical and physical properties and less hydrophobicity of benzene (2.13) compared to toluene (2.69).

Kamravaei et al (2017) [24], investigated the effect of fluidization on the adsorption of volatile organic compounds (VOCs) by beaded activated carbon (BAC). The authors found that fluidization can significantly improve the adsorption capacity of BAC for VOCs. They also found that the adsorption capacity of BAC increased with an increase in the fluidization velocity. The authors concluded that fluidization is a promising technique for improving the efficiency of VOC removal by BAC. The improvement in adsorption capacity is due increases the surface area of the BAC particles that are exposed to the VOCs. Fluidization enhances the mass transfer of the VOCs from the gas phase to the solid phase. Fluidization helps to prevent the formation of a stagnant layer of liquid on the surface of the BAC particles, which can reduce the adsorption capacity.

M. Eić et al (2018) [121], investigated the adsorption of toluene from an aqueous solution using peanut shell (AC) activated with $ZnCl_2$. The derived AC has a surface area of (1025 m^2/g). The results showed that, at optimum conditions the toluene shows higher removal capacity of (4 mmol/g) compared to other volatile organic compounds.

P. Stähelin et al (2018) [122], investigated the adsorption of mono- and bicomponent of benzene and toluene using coconut shell-based activated carbon. The results show that the higher surface area favor the adsorption process. Although both component show the same capacity 2.04 mmol/g in mono system, the capacity of bicomponent system is higher for toluene as result of polarity and molar mass.

Zhu et al (2018) [100], investigated the use of $ZnCl_2$ as activating agent for corncob-based activated carbons to remove toluene from waste gas. The authors found that the best adsorption capacity is obtained when the carbon is prepared with a 1:1 impregnation ratio, a carbonization temperature of 550 °C, and a carbonization time of 1.0 h. The best adsorption capacity of 414.6 ± 13.0 mg g^{-1} at initial toluene concentration 3000 mg m^{-3}. The adsorption capacity of the carbon depends on its textural characteristics and functional groups. Corncob-based activated carbon has a heterogeneous surface.

Marlina et al (2019) [123]**,** investigated the feasibility of producing activated carbon from agricultural waste corn cobs. The results showed that the optimum conditions for the preparation of activated carbon from corn cobs are a pyrolysis temperature of 290 °C for 1 hour using a 4N $ZnCl_2$ activator with 24 hour immersion. The resulting activated carbon had a BET surface area of 924.9 m2/g, a total pore volume of 0.37 cm3/g, and a pore size distribution of 2-50 nm.

C. C. Obi et al (2021) [21], examined the application of activated carbon derived from corn cobs (CCAC) to eliminate phenol from water. The researchers concluded that CCAC is efficient in removing phenol from water, demonstrating an adsorption capacity of up to 8.57 mg/g. The investigation also explored the impact of different operational variables on phenol adsorption, such as flow rate, initial phenol concentration, bed height, and particle size. The results indicated that higher bed heights correlated with longer breakthrough times and increased adsorption capacities, while elevated flow rates, inlet phenol concentrations, and particle sizes led to reduced breakthrough time and adsorption capacity.

K. Melaphi et al (2023) [41], investigated the adsorption of benzene and toluene from an aqueous solution using macadamia nut shell (AC) with a surface area of (405 m^2/g). The results showed that, at optimum conditions the removal of toluene (70.4%) was higher than benzene (58.9%). Moreover, the researcher concluded that, a higher specific surface area not mainly result in higher removal percentages. Table 2.8 shows a summary of the studies for BT adsorption by different AC-agriculture base.

Table 2. 8: Summarize the studies for BT adsorption of by AC- agriculture base.

Adsorbent	Adsorbate	Modification	Surface area (m2/g)	Pore volume (cm3/g)	Temp. (°C)	%R	Ref
Date pits (AC)	BT	Modified	800	0.58	20	B = 68 T = 72	Jodeh et al. (2015)
Rise husk (AC)	BT	Modified	965.5	0.726	-	B = 22 T = 33	Yakout et al. (2014)
Macadamia nut shell (AC)	BT	Unmodified	405	0.205	25	B = 58.90 T = 70.4	Melaphi et al (2023) [41]
corn cob (AC)	T	Modified	1501	0.742	25	74	Zhu et al (2018) [103]
coconut shell-based AC	BT	Modified	758.5	0.4	25	B= 36 T=16	P. Stähelin et al (2018) [122]
Paper mill sludge (AC)	BT	Modified	613.38	0.64	25	92	Aghdam et al (2015) [120]

CHAPTER THREE

Experimental Work

3.1 Introduction

This chapter aims to prepare AC using naturel material (corn cobs). Experimental work on activated carbon involves conducting characterization tests to evaluate its properties and performance. These experiments aim to characterize the surface area and porosity of activated carbon. Furthermore, investigate it performance and removal efficiency of two types of important pollutants (benzene and toluene) in continues flow system.

3.2 Chemicals Components

The chemicals utilized in this study are outlined in Table 3.1. All chemicals were of analytical quality and were employed in the experiments without any additional purification.

Table 3. 1: Chemicals used in the present study.

NO	Compound	Purity	Chemical Formula	Supplier
1	Zinc chloride	98%	$ZnCl_2$	Thomas baker
2	Distilled water		H_2O	Iraq
3	Benzene	99.7%	C_6H_6	Alpha chemika, India
4	Toluene	99.9%	$C_6H_5CH_3$	Alpha chemika, India

3.3 Apparatuses

3.3.1 Drying Oven

A drying oven shown in figure 3.1, also known as a drying chamber or drying cabinet, is a piece of laboratory equipment used for drying, sterilizing, or removing moisture from various substances or samples. It provides a controlled environment of elevated temperature to facilitate the drying process and activating adsorbents. Temperature Range: up to 200-300°C.

Figure 3. 1: Drying Oven

3.3.2 Muffle Furnace

A muffle furnace shown in figure 3.2 is a type of high-temperature laboratory furnace that is designed to provide controlled heating in an enclosed chamber known as a muffle. It is commonly used for various applications, including high-temperature material testing, ashing, calcination, activation, and heat treatment processes. Insulated oven with maximum Temperature up to 1100°C.

Figure 3. 2: A muffle furnace

3.3.3 Digital Balance

A digital balance shown in figure 3.3, also known as an electronic balance or precision balance, is a measuring instrument used to determine the mass or weight of an object (adsorbents and other substances) with high accuracy and precision. It utilizes electronic components and sensors to provide a digital readout of the measured weight. Weight capacity of 0.01-300 g.

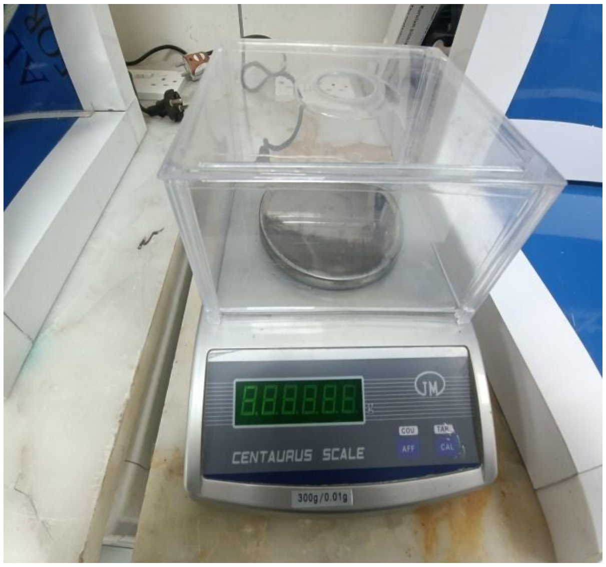

Figure 3. 3: Digital Balance

3.3.4 Thermometer

A thermometer shown in figure 3.4 is a measuring instrument used to measure temperature. It provides a numerical reading that represents the intensity of heat or coldness of an object or environment. Temperature Range: up to 100°C.

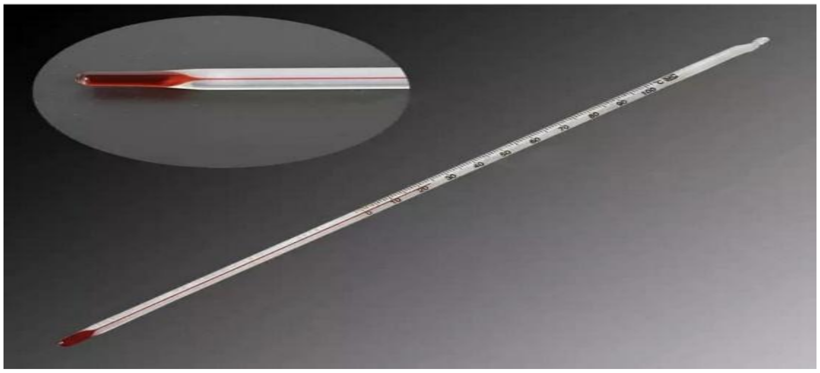

Figure 3. 4: Thermometer

3.3.5 Glassware

Various types of glass containers, such as beakers, flasks, separating funnel, pipettes, and test tubes, used for mixing, heating, and storing adsorbents.

3.3.6 Water Bath

A water bath shown in figure 3.5 is a laboratory equipment used for incubation, heating, or cooling of samples in a temperature-controlled water-filled chamber. It consists of a container or tank that holds water and a heating or cooling element to regulate the temperature. Temperature Range: up to 100°C.

Figure 3. 5: Water Bath

3.3.9 Sieves

Sieves are standardized tools or devices used for particle size classification and separation of adsorbents. They consist of a frame or container with a mesh or perforated plate that allows particles of certain sizes to pass through while retaining larger particles. Mesh size can determine by using conversion formula 25.4 / (particle size in millimeters).

3.4 Materials

3.4.1 Preparation of the adsorbent

Corn cobs used in this study are directly obtained from local farmers' homes. The central section of the corn cobs is selected for sample collection. To reduce moisture, recently harvested corn cobs are naturally sun-dried on the ground. Once sufficiently dried, they are placed in plastic bags and transported to the laboratory, where they are stored in desiccators. The preparation procedures was follow the studies of [123–125].

In the laboratory, the samples of corn cobs undergo washing process with distilled water to remove any remaining debris, dirt, or dust and followed with naturally drying under sunlight for 48h and then heated in a hot air furnace at 110 °C for 2 h to ensure the elimination of any moisture content. After drying, the samples are carbonized in oven at 300 °C for 1h. The samples then crushed in a grinder and sieved into three sizes 0.2, 0.4, and 0.6 mm. All samples can be utilized as a substrate in the subsequent experiments.

Next, the carbonized corn cob samples went through activation process. Detailed procedures are described as follows. The carbonized samples (50g) are immersed in 300 ml of saturated Zinc chloride, $ZnCl_2$ for 8h, under simple stirring. Then the samples recovered by filtration and washed with distilled water at room-temperature. In order to ensure the zinc chloride was completely removed, the samples were through three stages of washing and filtration at 50 °C. The recovered AC was dried in an oven at 150 °C for 2 h, then stored in an airtight container before use. Manufacturing steps of AC are illustrated in figure 3.6 and final product of each step is presented in figure 3.7.

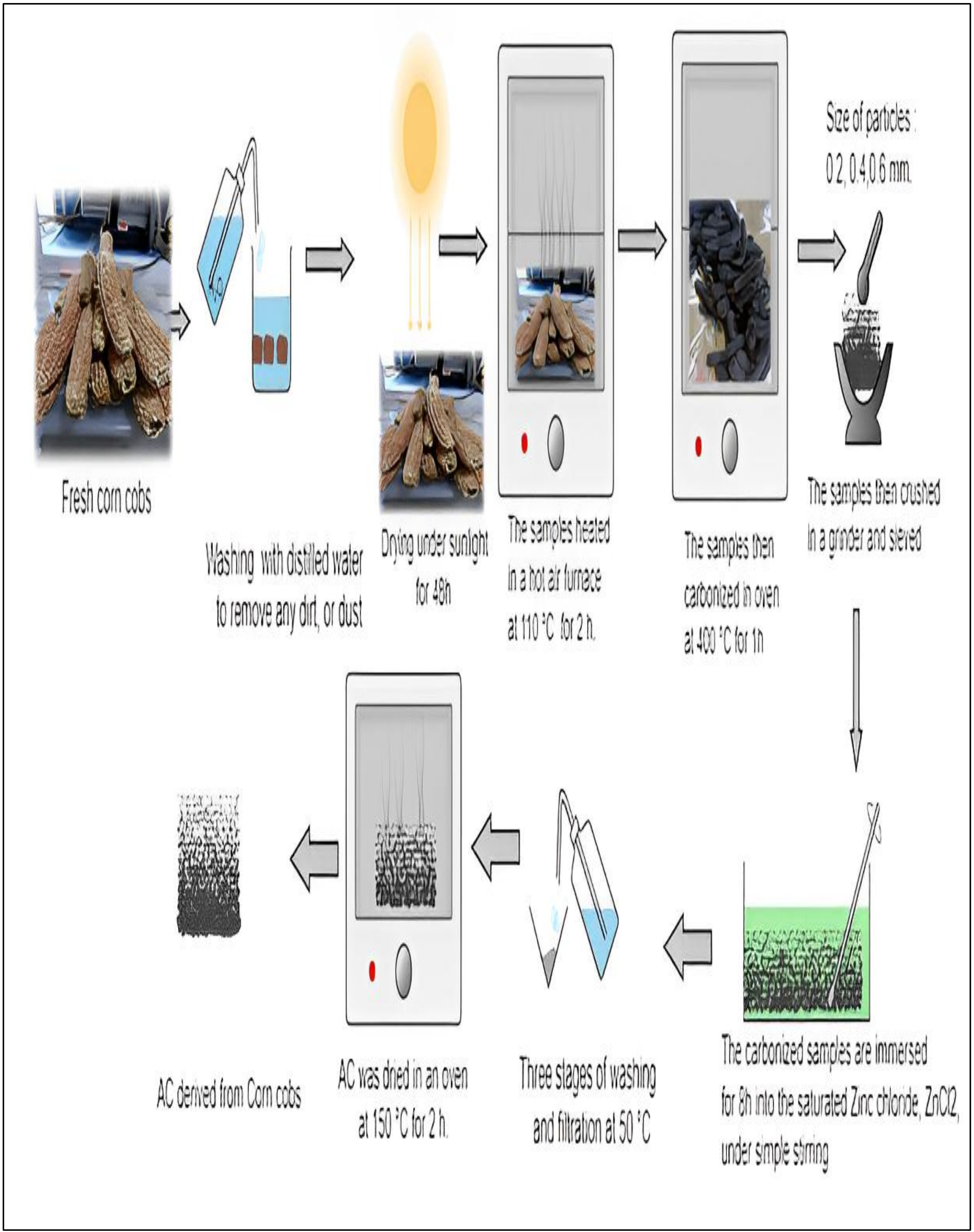

Figure 3. 6: Preparation steps of AC.

Figure 3.7: Macrostructural images of corn cob in different forms (a) dried-bulk corn cobs; (b) carbonized corn cob at 400 ^{o}C; (c) ground carbonized corn cobs; and (d) activated carbon from carbonized corn cob.

3.4.2 Preparation of Adsorbate

A stock solution of Benzene and Toluene was prepared by dissolving a measured amount of organic pollutants in distilled water. Concentrations of 70 mg/ml was prepared and used for the column experiments.

3.5 Column adsorption setup and studies

Fluidized bed column was employed to perform biosorption experiments. The schematic diagram of the apparatus and the setup are illustrated in figure 3.8. The setup has a 70 L feed tank to store the prepared stock solution contaminated with pollutants at a specific concentration for the intended experiment. A PVC pipe lines were used to connect the system and to deliver the wastewater solution. The column was made from Perspex material with a height of 80 cm and a 5 cm internal diameter. A stainless sieve of 1 mm was fixed at the column center to keep constant bed height, support the bed during the continuous operation process. The stock solution was introduced into the column with the aid of a pump (MARQUIS-MQS128, China). The flow rate was regulated with the aid of valve and measured with a rotameter (Platon, France). In addition, a second container of 30 L was used to collect the effluent solution.

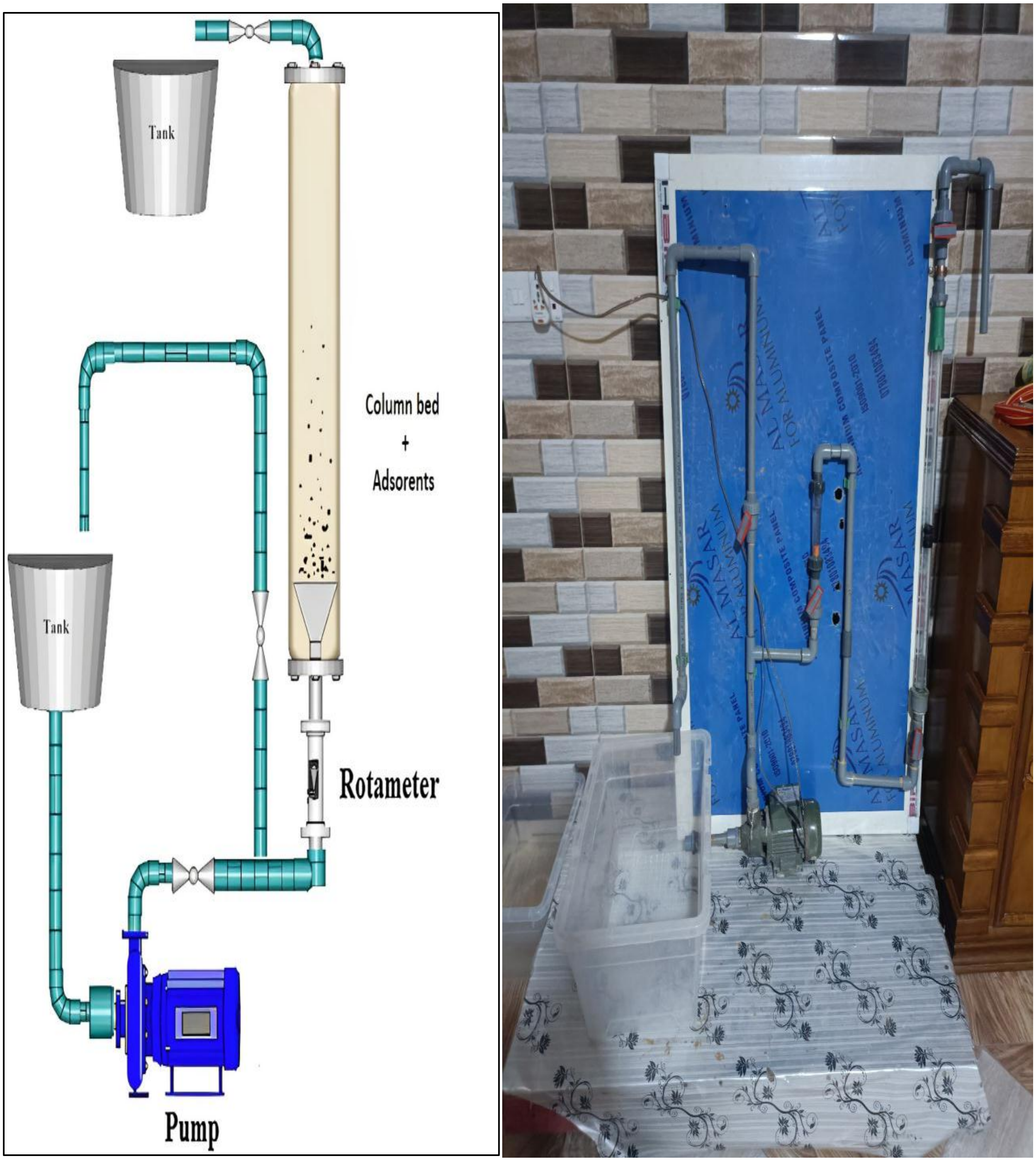

Figure 3.8: The schematic diagram and the setup of the adsorption system

The breakthrough curves' characteristics were examined under various operational conditions by gathering samples every specific period, until the adsorbents reached saturation. The column study was conducted at different process variables, including flow rates (Q), bed heights (Z), and Temperature (T). The effect of particles size was investigated separately at the optimum condition with a range of (0.2-0.6 mm). Table 3-3 shows the set of experiments under different conditions.

Table 3. 2: Set of experiments and conditions of each experiment.

No	**Temp, C**	**Flow rate, (l/hr)**	**Bed depth, cm**
1	30	15	6
2	30	20	8
3	30	25	10
4	35	15	8
5	35	20	10
6	35	25	6
7	40	15	10
8	40	20	6
9	40	25	8

3.6 Characterization and Analytical Measurements

Characterization methods used for activated carbon can include various techniques to evaluate its physical, chemical, and adsorption properties.

2.6.1 Brunauer-Emmett-Teller Analysis (BET)

BET analysis was carried out in order to study a specific surface region of interest by determine the specific surface area and pore volume.

The BET analysis is based on the adsorption of gas molecules onto the surface of a solid material. The method utilizes the principle that as a gas is adsorbed onto a solid, a monolayer of the gas molecules forms on the surface. By measuring the amount of gas adsorbed at different pressures, the specific surface area of the porous material can be determined. BET analysis is conducted at Ministry of Science and Technology-Building Research Center. BET was accomplished using a fully automated system of Quantachrome Autosorb- 6Isa, USA.

3.6.2 Analytical Measurements

The concentration of BT in an effluent after the experiment was measured using Gas Chromatography (GC), shown in figure 3.9. This technique is commonly used in the analysis of volatile and nonpolar substances. To measure the concentration of the desired compound, a calibration curve is usually created. This involves evaluating a range of standard solutions containing known concentrations of the compound under investigation. The standards should cover a range of concentrations that are relevant to the expected concentrations in the effluent. The detector response, typically in the form of peak area or peak height, is recorded for the compound of interest in the effluent sample. The response is compared to the calibration curve obtained to determine the concentration of the compound in the effluent. GC analysis was conducted at Ministry of Science and Technology-

Building Research Center. The device model is (FOCUS GC, Thermo Scientific, United States).

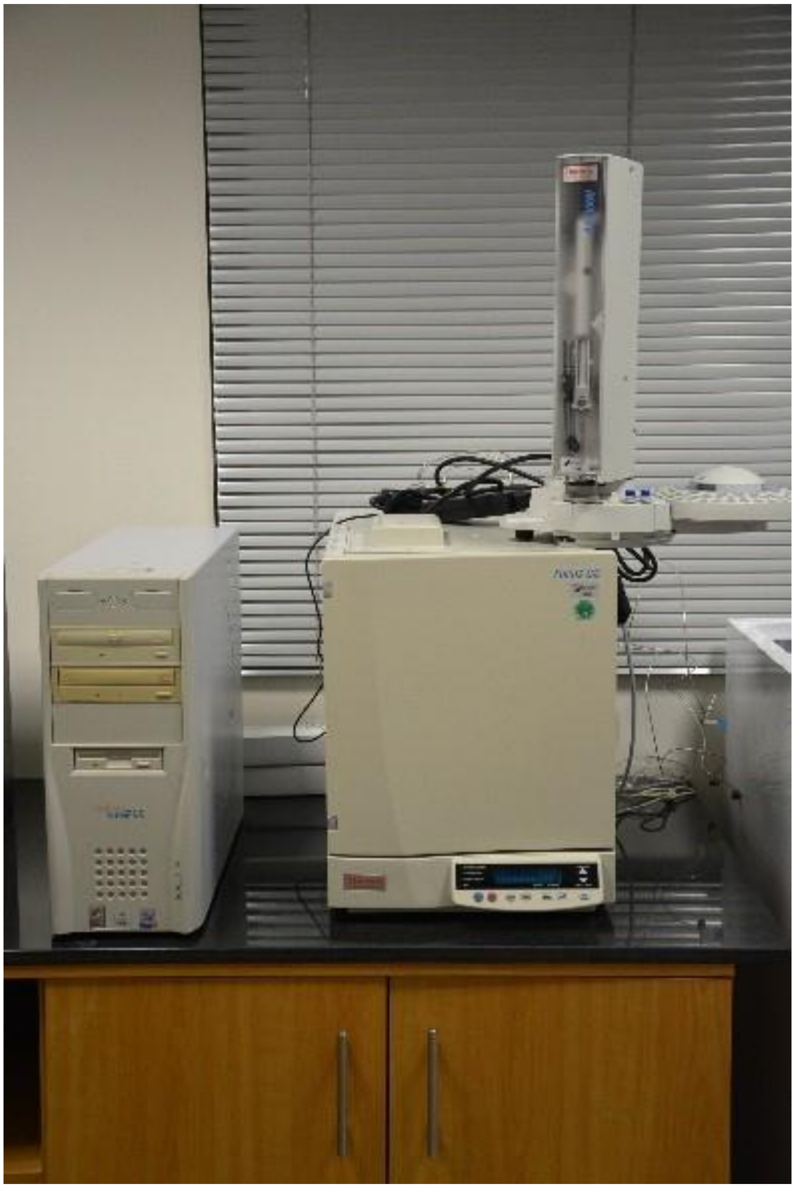

Figure 3. 9: Gas Chromatography

CHAPTER FOUR
RESULTS AND DISCUSSION

4.1 Introduction

This chapter presents and discuss the results of activated carbon derived from corn biomass (corn cobs) with the aim to remove BT pollutants by adsorption using continues flow system. The results of characterization will focus on shape and amount of surface area available for adsorption process and show the effect of modification process using zinc chloride on the generated AC. The results will discuss the removing of benzene and toluene from water in term of their removing efficiency under various operational conditions and determine the optimum conditions by using DOE- Taguchi method. The discussions delve into the factors influencing the adsorption process and potential applications of these natural adsorbents in water treatment for removing hazardous organic pollutants. Equilibrium studies were investigated to indicate the suitable adsorption isotherm that fit the experimental data and providing insights into the adsorption capacity and mechanisms of the AC adsorbents.

4.2 Brunauer–Emmett–Teller (BET) Analysis

BET analysis was used to determine the textural properties of the adsorbents (specific surface area and pore volume), the results presented in table (4-1). The surface areas for raw corn cobs were 24, 21, and 6 m^2/g for particles size of 0.2, 0.4, and 0.6 mm, respectively. Furthermore, the results of pore volume recorded 0.0031, 0.0014, and 0.0012 cm^3g^{-1} for particles size of 0.2, 0.4, and 0.6 mm, respectively.

However, compared to raw corn cobs, the activated corn cobs show higher surface area and recoded 245.12, 210.25, and 96.34 m^2/g for particles size of 0.2, 0.4, and

0.6 mm, respectively. This indicates that the activation process has successfully enhanced the surface area of the adsorbents, making them more effective in adsorption applications compared to their raw counterparts.

The enhanced surface area as a result of increasing temperature (carbonized corn cob at 400 ^{o}C) was attributed to loss and volatilization the organic compounds which results in pore fabrication [100,126]. This observation indicates that the carbonization temperature has a substantial impact on the textural properties of the activated carbons (ACs) [100].

The addition of $ZnCl_2$ during the activation process plays a crucial role in restricting tar formation [88]. By inhibiting tar production, the contraction of the particle is prevented, leading to the formation of a wide and open microporosity, with the presence of border micro-mesopores [88]. The microstructure enhances the pore volume and surface area of the AC derived from corn cobs, making it more efficient in adsorption processes. The wider and open micro-mesoporous structure provides ample active sites for contaminants removing via adsorption, further improving the capacity of adsorption and overall performance of the adsorbents in water treatment applications. The adsorption capacity of adsorbents materials primarily relies on its surface area and porous structure. A dehydrating agent such $ZnCl_2$ will effectively eliminating volatile compounds from the AC adsorbents. Additionally, it facilitates bond cleavage reactions through dehydration and condensation processes [14]. For the following experiment the particles with size of 0.2 mm were used.

Table 4. 1: BET analyses of adsorbents.

Adsorbent	Particles size, mm	Surface area, m^2 /g	Pore volume, cm^3/g
Raw corn cob	0.2 0.4 0.6	24 21 6	0.0031 0.0014 0.0012
Activated corn cob	0.2 0.4 0.6	245.12 210.25 96.34	

4.3 Optimization of the Process Variables

4.3.1 Taguchi Analysis

The experiments were designed and analyzed using the Taguchi approach which presented in appendix B, and MINITAB 2021 was utilized for this purpose. Understanding the impact of each input parameter on the system output is crucial. Statistical analysis was performed to investigate the impact of various factors on the adsorption process. These factors include flow rates, bed depth, and temperature. The Taguchi method employs an orthogonal array, which efficiently provides comprehensive information about all the factors influencing the response variable. Compared to classical design of experiment methods, the Taguchi design method requires a minimal number of tests to achieve reliable results [127].

Table (4-2) displays the experimental conditions along with the corresponding responses, which represent the adsorption removal for benzene and toluene. Additionally, figures 4.1 and 4.2 illustrate the Taguchi Analysis of benzene and toluene removal % versus temperature, feed flow rate, and bed depth.

In this analysis, the 'Signal' term refers to the average for the wanted value (mean) for the response, while 'Noise' refers to value that undesired (standard deviation). The S/N ratio, which is the mean to standard deviation ratio, was used for further justification [12]. The analysis followed a "larger the better" approach since higher BT adsorption is constantly desirable. S/N ratio of largest value indicates the optimum characteristics [13].

Table 4.3 shows the control factors and their levels on the S/N ratio. It is evident that the optimal conditions are a temperature of level 1 (30°C), flow rate of level 1 (15 l/hr), and bed depth of level 3 (10 cm). Among these factors, the bed depth has the most significant influence on the response (removal). Which is indicates the largest difference in delta (table 4.3). Where the adsorption capacity of any adsorbent in this case activated carbon depends largely on the amount of adsorbent used. Adding more amount of adsorbent material in the column enhances the surface area for adsorption, leading to a higher adsorption capacity for BT removal. Figure 4.2 illustrates how increasing the bed depth creates more surface area, contributing to higher S/N ratio and greater BT adsorption.

The second important factor was flow rate which significantly influence the response. A higher flow rate means higher velocity that introduced the system and affects the retention or residence time of the BT polluted solution, decreasing the surface contact of the adsorbates (BT) with the AC adsorbents, leading to increase the concentrations of pollutants in the effluent stream. Based on the results obtained, it can be concluded that a higher feed flow rate will negatively impact the adsorption performance of the adsorbents.

On the other hand, changing the temperature shows the lowest impact on the S/N ratio, the temperature S/N ratio show a decreasing rate as the level of temperature increases from 30°C to 40°C, indicating a decrease in adsorption performance and its capacity.

Table 4. 2: Experimental conditions and response by Minitab

No	Temp, C	Flow rate, (l/hr)	Bed depth, cm	Removal of benzene %	Removal of toluene %
1	30	15	6	66.8	70.2
2	30	20	8	66.5	74.0
3	30	25	10	69.8	78.5
4	35	15	8	69.5	76.0
5	35	20	10	72.1	80.3
6	35	25	6	42.8	56.5
7	40	15	10	74.1	81.2
8	40	20	6	52.8	58.2
9	40	25	8	54.5	63.0

Table 4. 3: Response for Signal to Noise Ratios

Level	Temp	Flow rate	Bed depth
1	36.99	37.23	35.08
2	36.16	36.45	36.47
3	35.98	35.45	37.58
Delta	1.01	1.78	2.50
Rank	3	2	1

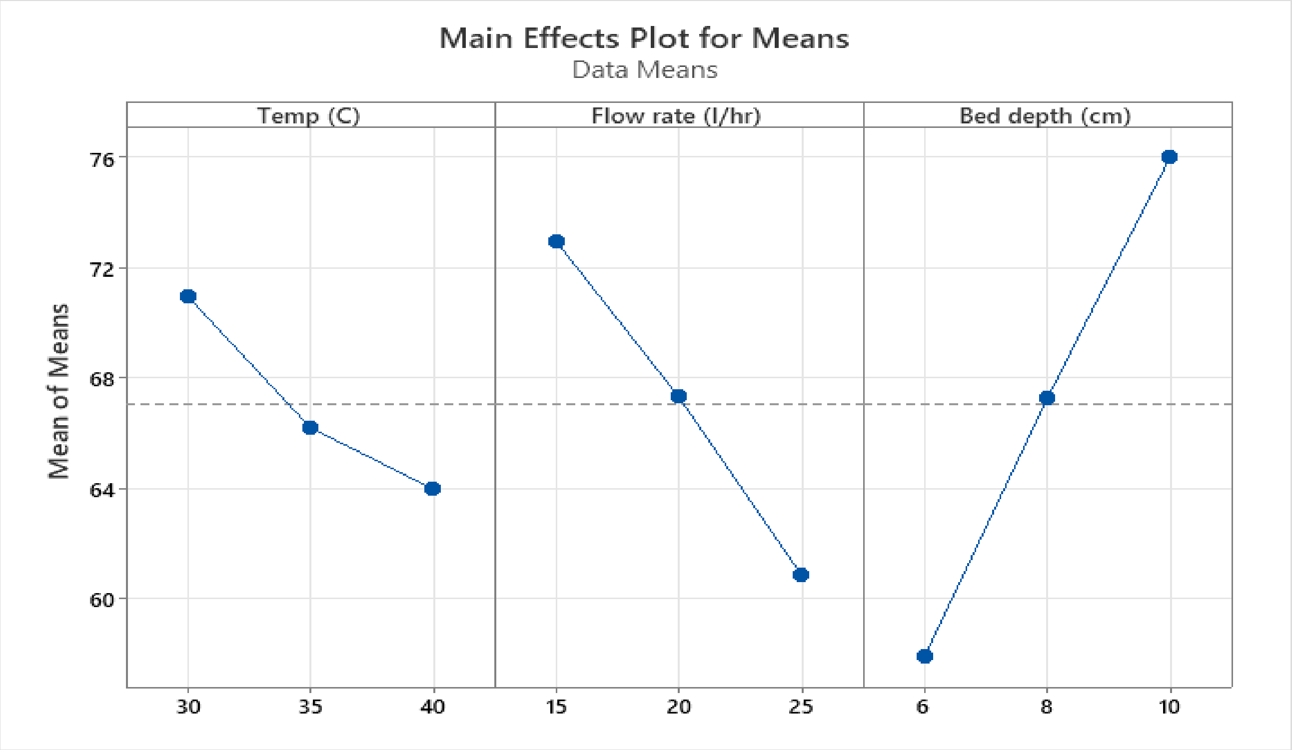

Figure 4. 1: Mains effects plot for means

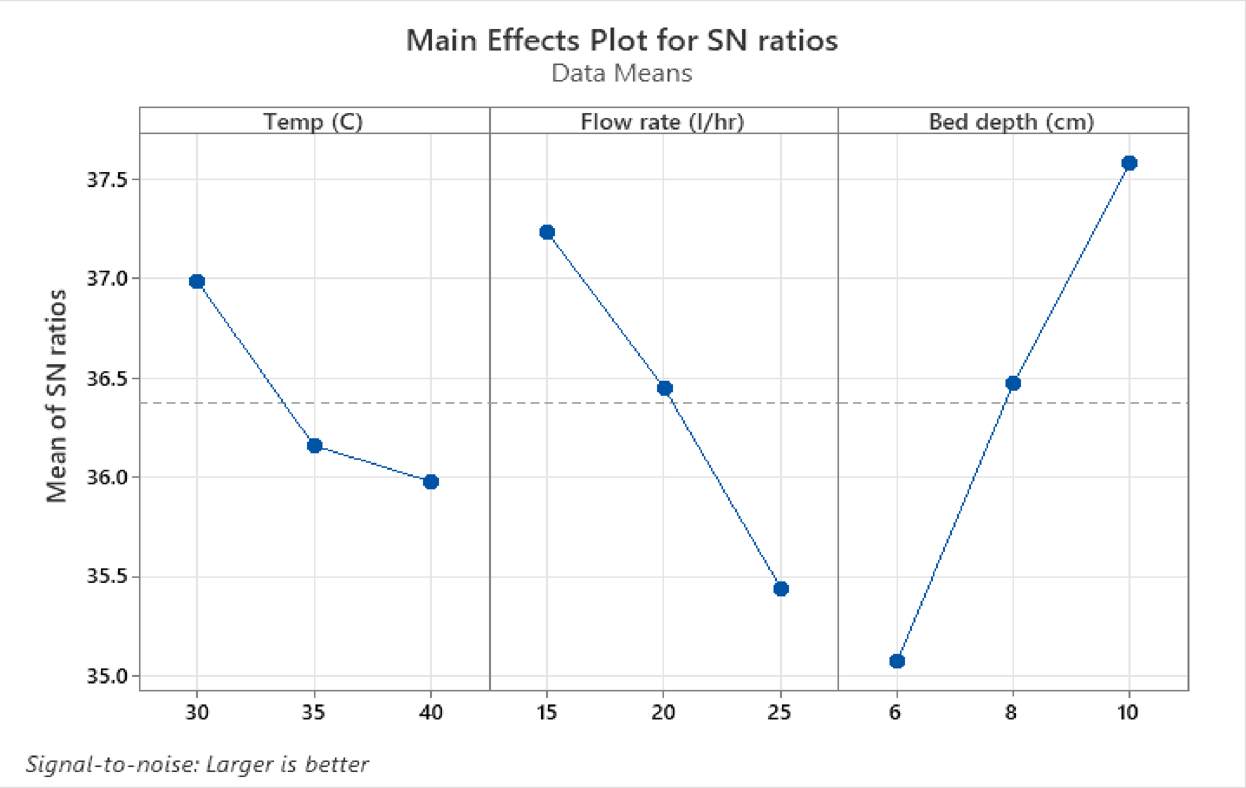

Figure 4. 2: Main effects plot for S/N ratios.

4.3.2 ANOVA Analysis

The ANOVA tables (4.4 and 4.5) analysis indicate that the regression equation successfully captures the response variable and the independent variables relationship. Furthermore, the variables included in the equation demonstrate statistical significance in explaining the variations observed in the response variable. By examining the F-values and p-values, the variables with higher F-values and p-values less than 5% identify as the key contributors in this relationship.

For benzene adsorption, the bed depth has the most impact (52.90%), followed by the feed flow rate influence of (34.52%), and finally, the temperature has low impact (8.67%). Moreover, table 4.5 for toluene adsorption shows that, the bed depth has the most impact (70.34%), followed by the flow rate influence of (20.03%), and finally, the temperature has lowest impact of (9.55%).

Table 4. 4: Analysis of Variance for benzene removal

Source	**DF**	**Seq SS**	**Contribution**	**Adj SS**	**Adj MS**	**F-Value**	**P-Value**
Regression	3	869.79	96.10%	869.79	289.930	41.02	0.001
Temp	1	78.48	8.67%	78.48	78.482	11.10	0.021
Flow rate	1	312.48	34.52%	312.48	312.482	44.21	0.001
Bed depth	1	478.83	52.90%	478.83	478.827	67.75	0.000
Error	5	35.34	3.90%	35.34	7.068		
Total	8	905.13	100.00%				

Table 4. 5: Analysis of Variance for toluene removal

Source	DF	Seq SS	Contribution	Adj SS	Adj MS	F-Value	P-Value
Regression	3	718.743	99.91%	718.743	239.581	1894.75	0.000
Temp	1	68.682	9.55%	68.682	68.682	543.18	0.000
Flow rate	1	144.060	20.03%	144.060	144.060	1139.31	0.000
Bed depth	1	506.002	70.34%	506.002	506.002	4001.77	0.000
Error	5	0.632	0.09%	0.632	0.126		
Total	8	719.376	100.00%				

The experiential relation between the response, which is the removal percentage and the independent variable is shown in table 4.6. The positive terms show the synergistic effect of variables and the negative terms represent the antagonistic effect. For regression equation of benzene removal, R^2 value is the variability between the predicted data and the experimental data. Here, the attained R^2 is 96.1%, which explained that 96.1% of experimental data agreed well with the predicted data. Furthermore, the predicted R^2 is in reasonable agreement with the adjusted R^2; i.e., the difference is less than 20%. According to model equations, the removal efficiency is directly proportional to the bed depth and it was inversely proportional to the temperature and feed flow rate. Same behavior can be observed for toluene regression equation.

Table 4. 6: Regression equations and values of R^2

	Response (%)	Regression Model	R^2	Adjusted R^2	Predicted R^2
Benzene	Removal of benzene %	81.66 - 0.723 Temp - 1.443 Flow rate + 4.467 Bed depth	96.1%	93.73%	84.83%
Toluene	Removal of toluene %	77.43 - 0.6767 Temp - 0.9800 Flow rate + 4.5917 Bed depth	99.9%	99.86%	99.66%

4.4 Parametric Effect on BT Adsorption

4.4.1 Effect of Feed Flow Rate

Figure 4.3 shows the effect of feed flow rate on the adsorption of benzene and toluene. The change in flow rate can significantly affect the continuous adsorption process in the fluidized column. The adsorption experiments were conducted at a range of flow rates (15-25) l/hr. The results reveled that, the lower flow rate (15 l/hr) has the best performance for both benzene and toluene with removal of 70.13% and 75.8% respectively. However, increasing the flow rate to 20 ml/min cause a reduction in removal of the benzene and toluene and recorded 63.8% and 70.83% respectively. Furthermore, the higher flow rate (25 l/hr) shows the lowest removal performance with 55.7% for benzene and 66% for toluene. This behavior can be explained by the fact that at higher rates, The flow takes less time to penetrate the pores of the adsorbent material and lower the mass transfer and inter-particle diffusion. In other word, the higher feed flow rate affected the retention time of BT pollutant in the aqueous phase, causing a reduction of interaction of the adsorbates surface and the adsorbents, thereby resulting in higher effluent concentrations before equilibrium is reached.

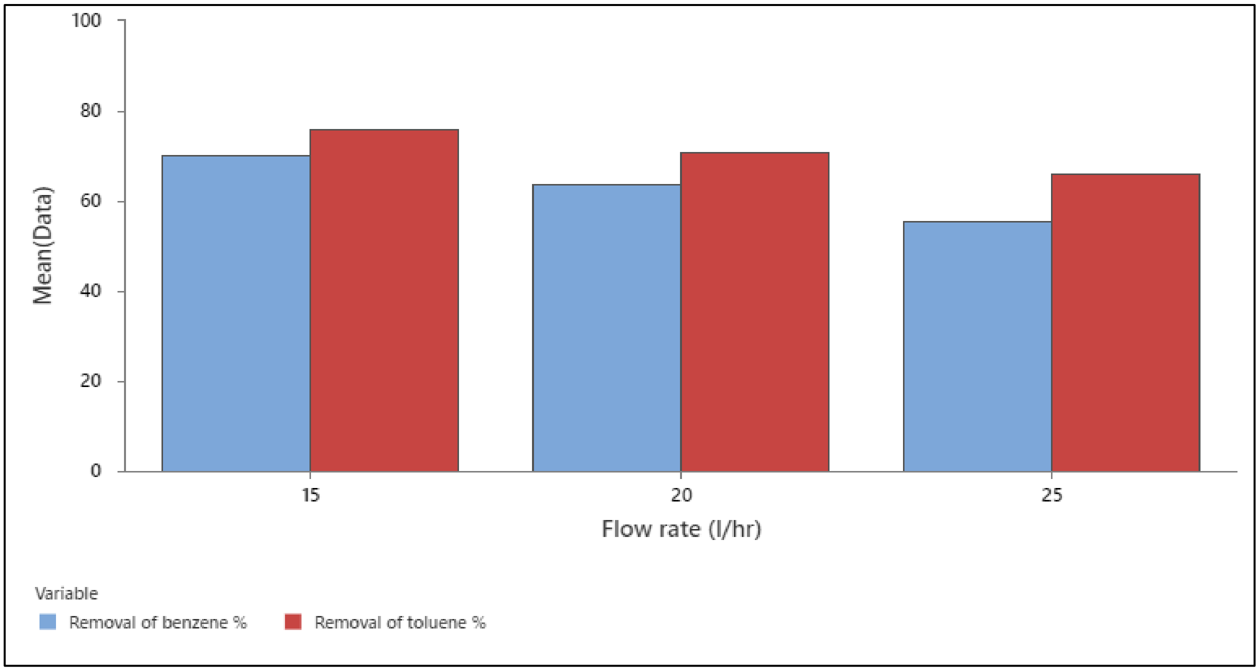

Figure 4. 3: Removal of benzene and toluene with respect to feed flow rate using particle size of 0.2 mm.

4.4.2 Effect of Temperature

Figure 4.4 shows the effect of temperature on the adsorption of benzene and toluene. The change in temperature can significantly affect the continuous adsorption process in the fluidized column. The adsorption experiments were conducted at a range of temperature (30-40 ^{o}C). The results reveled that, the higher temperature (40 ^{o}C) has the lowest performance for both benzene and toluene with removal of 60.4667% and 67.4667% respectively. However, the adsorption of benzene and toluene at (35 ^{o}C) was increased to 61.4667% and 70.933% respectively. Furthermore, the lower temperature (30 ^{o}C) shows the best removal performance with 67.6% for benzene and 74.2333% for toluene.

Although, an increase in temperature enhances the adsorption kinetics, as it provides more thermal energy for the molecules to overcome activation barriers and adsorb onto the surface. The experimental results show that, a reduction in the performance upon increasing temperature indicates that the adsorption processes may be exothermic nature. In exothermic processes, heat is released as a byproduct of the adsorption reaction. This means that with increasing temperature, the adsorption process becomes less favorable, and the adsorptive forces weaken. Additionally, at elevated temperatures, the thermal energy can disrupt the attractive forces between the BT molecules and the active sites on the adsorbent surface. The weakening of these adsorptive forces leads to a reduced interaction and lower adsorption capacity.

Furthermore, as hydrophobic compounds both benzene and toluene tend to have lower solubility in the aqueous phase at higher temperatures. The decreased solubility can promote the release (desorption) of BT back into the liquid phase. As a result, the overall adsorption capacity of the adsorbent for BT may be reduced. Also, as BT becomes less soluble, other solutes might have a higher chance of adsorbing onto the active sites of the adsorbent. Such competing interactions can be result from water molecules, where organic adsorbents tend to absorb water as much as absorbing BT and the absorbent will drown eventually.

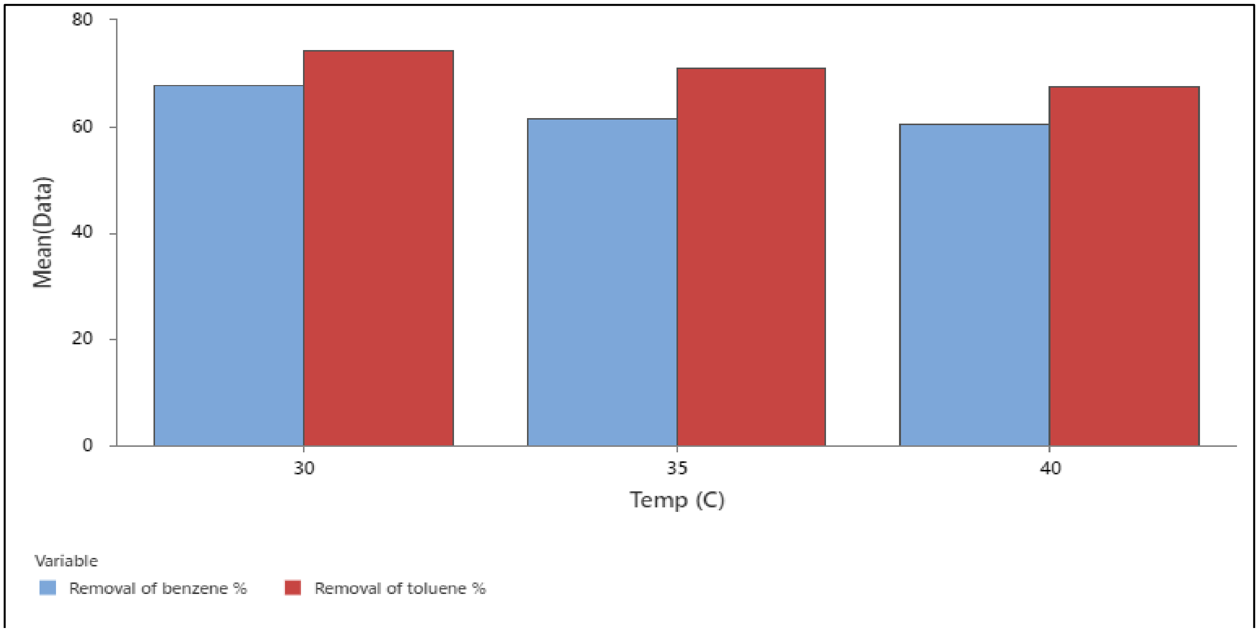

Figure 4. 4: Removal of benzene and toluene with respect to temperature change using particle size of 0.2 mm.

4.4.3 Effect of Bed Depth

Figure 4.5 shows the effect of bed depth (amount of AC filled in the column) on the adsorption of benzene and toluene. The change in bed depth can significantly affect the continuous adsorption process in the fluidized column. The adsorption experiments were conducted at bed depths of (6, 8, and 10 cm) which are equivalent to (52.98, 68.65, and 89.30 g) of AC.

The results reveled that, the lower bed depth (6 cm) has the lowest performance for both benzene and toluene with removal of 54.13% and 61.633% respectively. However, increasing the bed depth to 8 cm cause an increasing in removal of the benzene and toluene and recorded 63.5% and 71% respectively. Furthermore, the higher bed depth (10 cm) shows the highest removal performance with 72% for benzene and 80% for toluene.

This behavior can be explained by the fact that, a taller bed increases contact time between the adsorbent and adsorbates, improving adsorption efficiency. therefore, mass transfer can be enhanced by promoting better fluidization. In other word, the deeper bed provides a larger surface area by holding more adsorbent material which is translated to a higher adsorption capacity to remove a larger quantity of benzene and toluene before the adsorbent material becomes saturated. A deeper bed increases the contact time and extends the residence time, allowing more time for benzene and toluene molecules to interact with the adsorbent's active sites. Longer contact time can lead to more comprehensive adsorption. Similar observation was reported by [21].

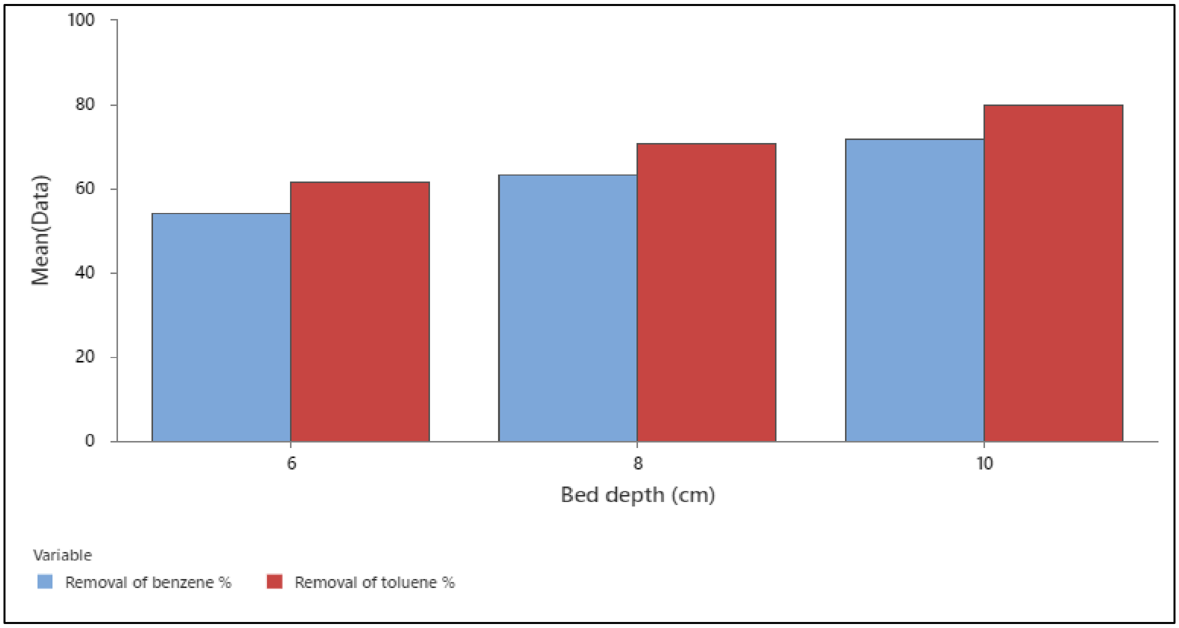

Figure 4. 5: Removal of benzene and toluene with respect to bed depth change using particle size of 0.2 mm.

4.5 Column performance

The breakthrough curves of benzene and toluene were used to determine the column performance. The adsorbent column's breakthrough capacity, exhaustion capacity, and column utilization were assessed to comprehend how the column affects the adsorbent's adsorption capability. To determine changes to the breakthrough curve (plots of C/Co versus time), three particle sizes were used (0.2, 0.4, and 0.6 mm). The experiment conducted at optimum conditions flow rate 15 l/hr, temperature 30 ^{o}C, and bed depth 10 cm.

Figures 4.6 and 4.7 Present the breakthrough curves derived from the column tests for benzene and toluene, respectively. The breakthrough point on the curve is identified as the moment when the effluent concentration (Ct) reaches approximately 10% of the influent concentration (Co). The time at which this breakthrough happens is termed the breakthrough time (tb). The saturation time (ts) is defined as the point when the effluent concentration reaches 90% of Co.

Once can observe the behavior of breakthrough curve shown in figures 4.6 and 4.7 and conclude that, both the particles size of (0.4 and 0.6 mm) has affected the time needed to achieve breakthroughs and cause a reduction in saturation time. However, the lowest particles size (0.2 mm) shows the best performance and may extend the saturation time. These behaviors are a result of low surface for both 0.4 and 0.6 mm which shown 210.25 and 96.34 m^2/g respectively as indicated by BET analysis. Therefore, both sizes have less active site for sorption as a result of the reduced surface area of the adsorbent. Furthermore, particles size of 0.2 mm depicts an enhanced surface area (245.12 m^2/g) available for the interaction of the adsorbate and the adsorbent. As a result, time required to achieve the total capacity of the column was extended and led to higher adsorption capacity during breakthrough and saturation, increased removal efficiency, and a larger volume of effluent treated at saturation.

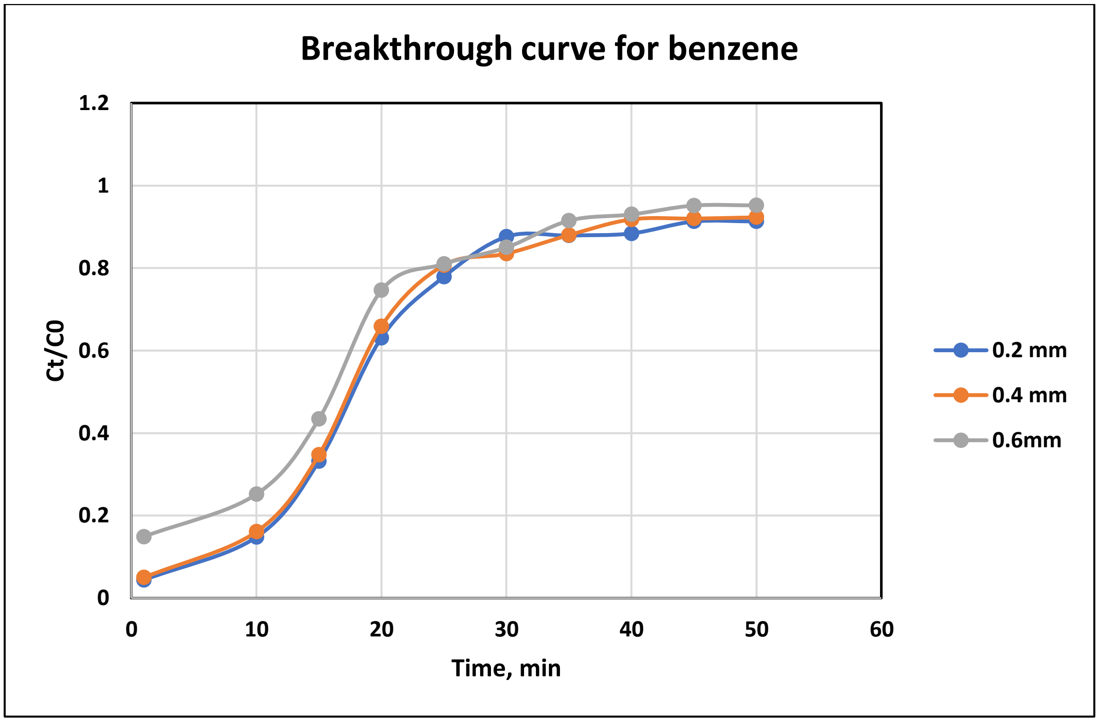

Figure 4. 6: Effect of particle size on breakthrough curve for benzene removal by corn cobs AC adsorbent in continuous fluidized bed column –bed depth: 10 cm, influent concentration: 70 mg/m^3; feed flow rate: 15 l/hr; temperature: 30 °C.

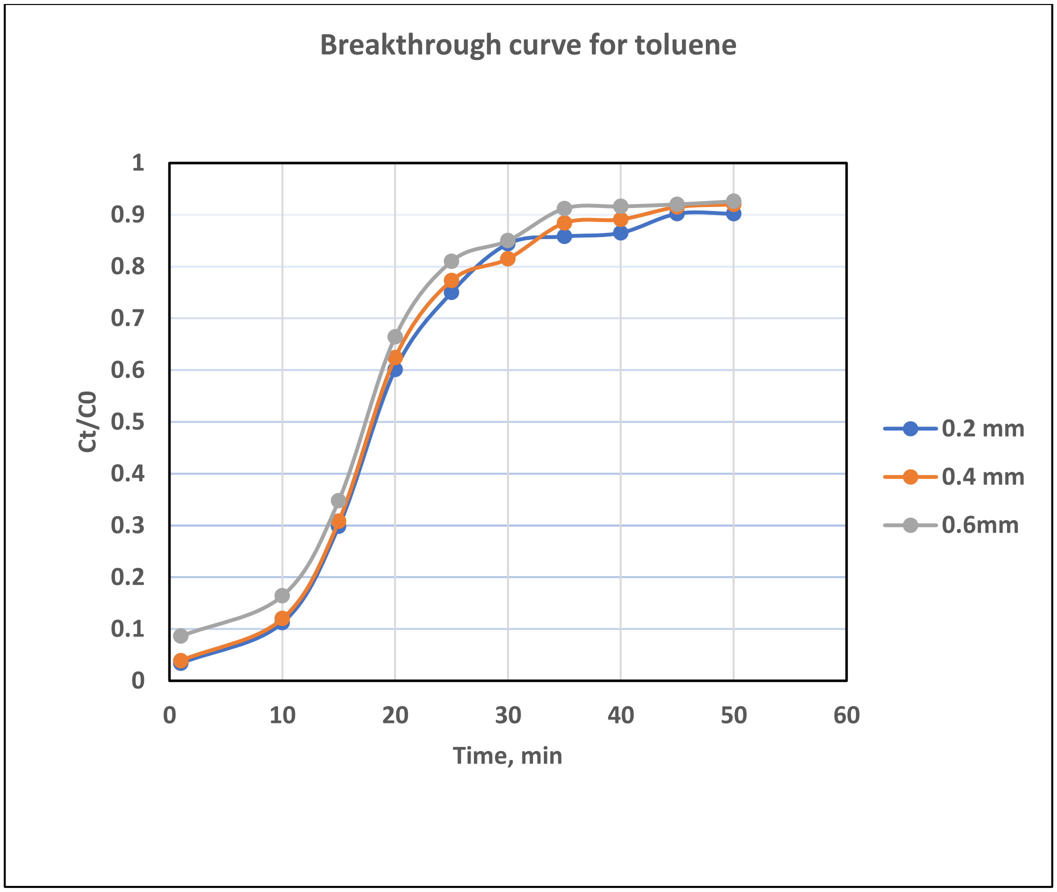

Figure 4. 7: Effect of particle size on breakthrough curve for toluene removal by corn cobs AC adsorbent in continuous fluidized bed column –bed depth: 10 cm, influent concentration: 70 mg/m^3; feed flow rate: 15 L/hr; temperature: 30 ^{o}C.

In figure 4.8, the breakthrough curves of benzene and toluene adsorption at their optimum conditions are presented and depicted the concentration of these compounds in the effluent stream over time during the adsorption process. Notably, the curve reveals that benzene experiences breakthrough earlier than toluene, indicating that benzene molecules appear in the effluent stream at an earlier stage of adsorption compared to toluene.

The solubility of benzene and toluene in the liquid phase significantly influences this behavior when present in aqueous phase. Generally, benzene has a higher solubility in the liquid phase (1.79 g/L). Hence, a larger fraction of the compound may remain dissolved in the liquid, reducing the available concentration for adsorption onto the solid adsorbent. As a result, the effective adsorption of benzene onto the adsorbent may be hindered, leading to a more rapid breakthrough of benzene in the effluent stream. On the other hand, toluene has a lower solubility in the liquid phase (0.52 g/L). Hence, a greater proportion of it may be available for adsorption onto the adsorbent material, delaying its breakthrough. Other attributed factors that can explain this behavior included faster adsorption kinetics, higher affinity to the adsorbent, and variations in the adsorbent's pore structure determine the type of molecules that access and occupy the active sites of adsorbent.

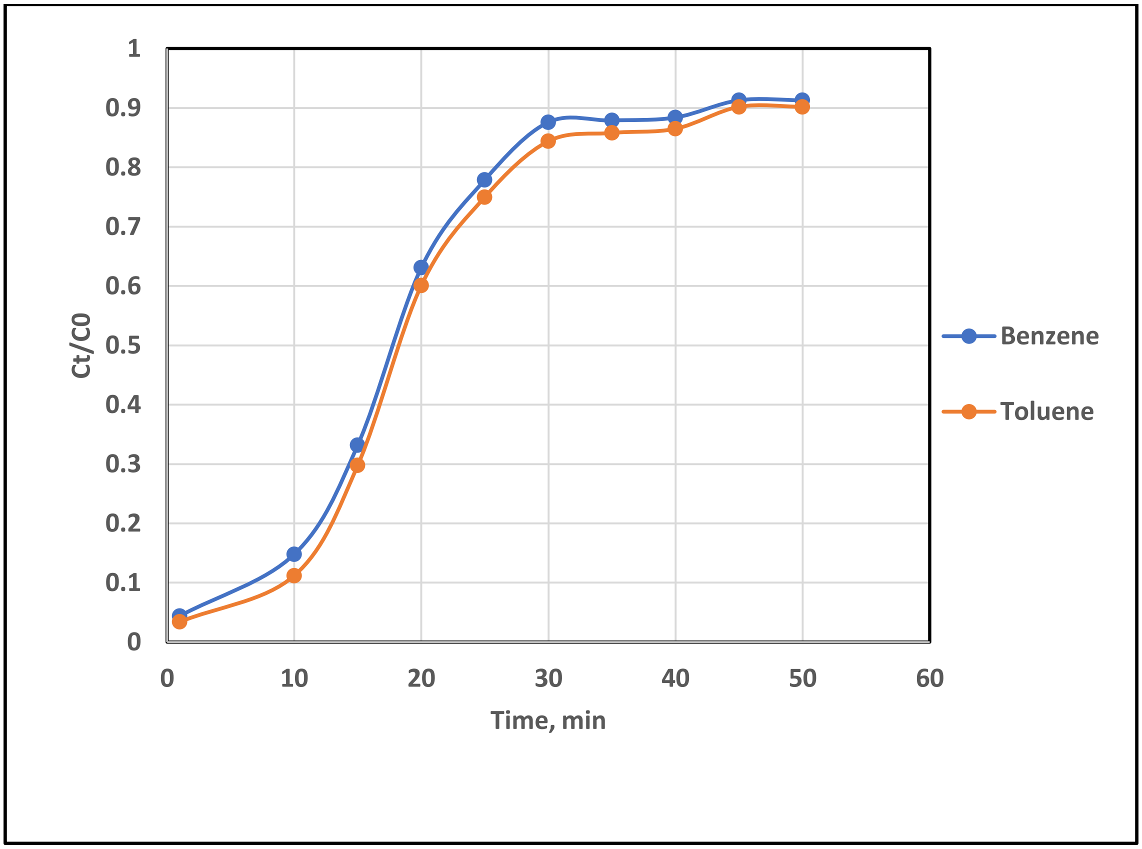

Figure 4. 8: Breakthrough curve for benzene and toluene removal by corn cobs AC adsorbent in continuous fluidized bed column –bed depth: 10 cm, influent concentration: 70 mg/m^3; feed flow rate: 15 l/hr; temperature: 30 ^{o}C; particles size: 0.2 mm.

Table 4.7 show the parameters observed from breakthrough curve for corn cobs AC adsorbent. The 0.2 mm particles size corn cobs AC has much adsorption capacity for toluene than benzene.

Table 4. 7: Parameters determined from breakthrough curve for 0.2 mm AC particles.

Component	**C_b (mg/m^3)**	**Cs (mg/m^3)**	**tb , min**	**ts, min**	**Re%**
Benzene	10.36	63.91	10	45	46.72
Toluene	7.84	63.14	10	45	44.894

4.6 Adsorption Modeling

Adsorption models played a vital role in comprehending and predicting the behavior of adsorption processes, particularly in designing these processes through precise alignment with experimental data [91]. In this study, adsorption isotherms employed to characterize the adsorption capacity of benzene and toluene on the surface of activated carbon derived from corn biomass. Figures 4.9-4.14 show the adsorption models for benzene and toluene.

The Langmuir Adams-Bohart, and Thomas were utilized to describe the adsorption behavior. The Langmuir isotherm, assuming a uniform and consistent binding of the adsorbate on the absorbent surface, was fitted to the experimental data with value of R^2 were found to be > 0.97 for both pollutants. This model suggests that the adsorption occurs in a monolayer on a homogeneous adsorbent surface, with no interaction among the adsorbed molecules. The model is based on the assumption of equal and independent adsorption sites.

In practice, the Langmuir constant must always be positive. The positive value Langmuir constant related to the affinity between the adsorbate and the adsorbent. A larger value Langmuir constant indicates a stronger affinity between the two, which means higher adsorption capacity. Hence, to accurately model dynamic sorption processes, it is essential to consider dynamic isotherms instead of the commonly used batch isotherms. Dynamic isotherms more effectively represent the equilibrium conditions in dynamic systems [128].

The experimental data were fitted to dynamic isotherms mathematical models to describe the breakthrough curve for bed column design, using Adams-Bohart, Thomas then evaluated using linear regression methods.

The linearized calculated parameters of Adams-Bohart, Thomas kinetic models for BT adsorption. By examine the R^2 values for both models for adsorption experimental data of BT adsorption they exhibited good agreement with the Thomas model (R^2>0.89) for benzene as shown in figure 4.11 and R^2>0.89 for toluene as shown in figure 4.13. In this regard, the Thomas model is the closest to the experimental values, hence it is supposed that the adsorption mechanism was a Langmuir type adsorption followed by a pseudo-second-order chemical sorption [105,129].

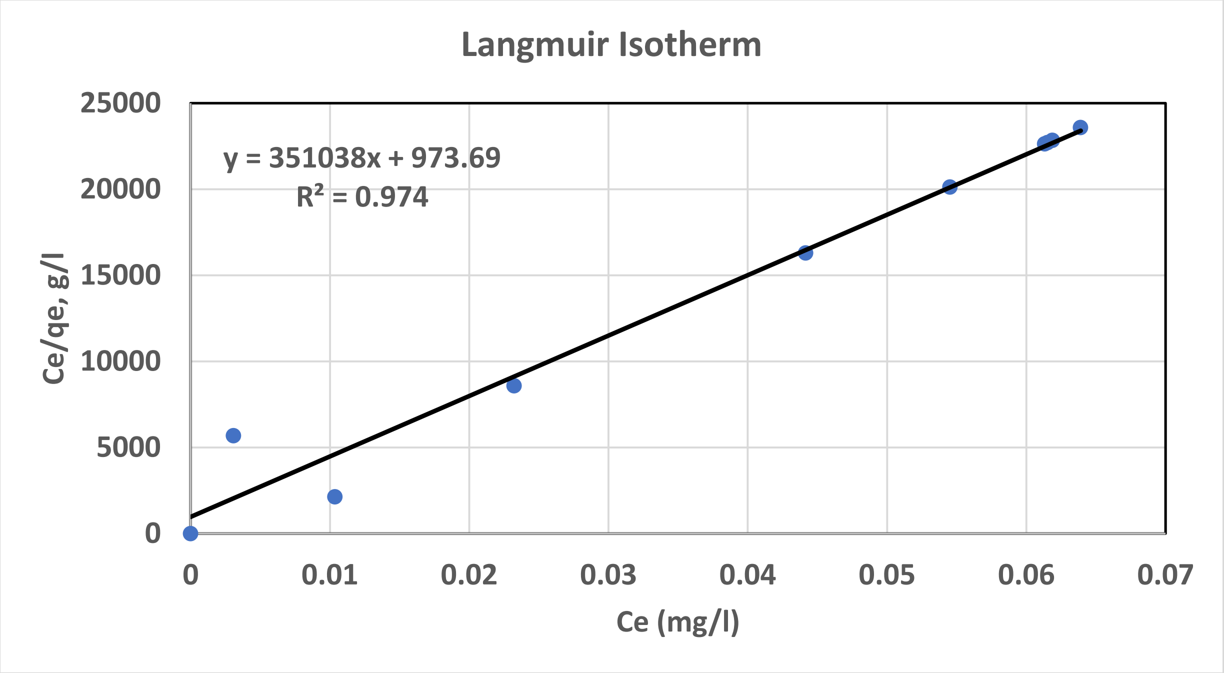

Figure 4. 9: Langmuir isotherm model for continuous benzene adsorption

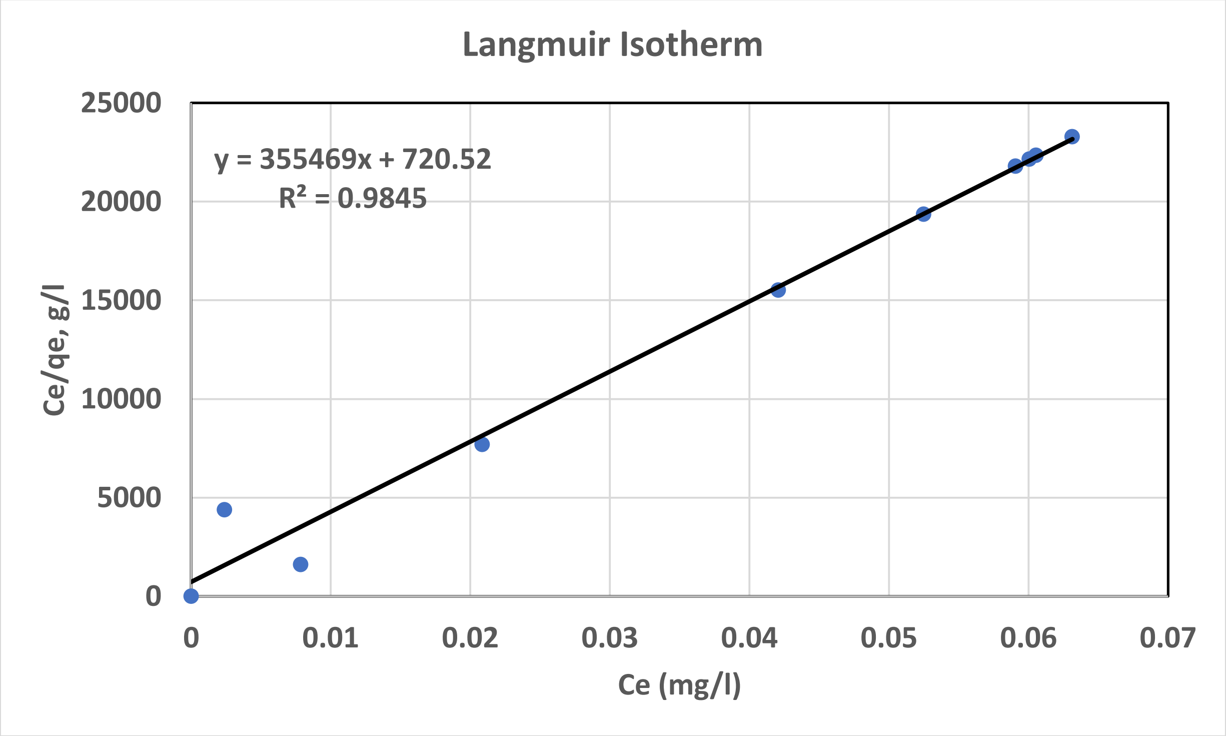

Figure 4. 10: Langmuir isotherm model for continuous toluene adsorption

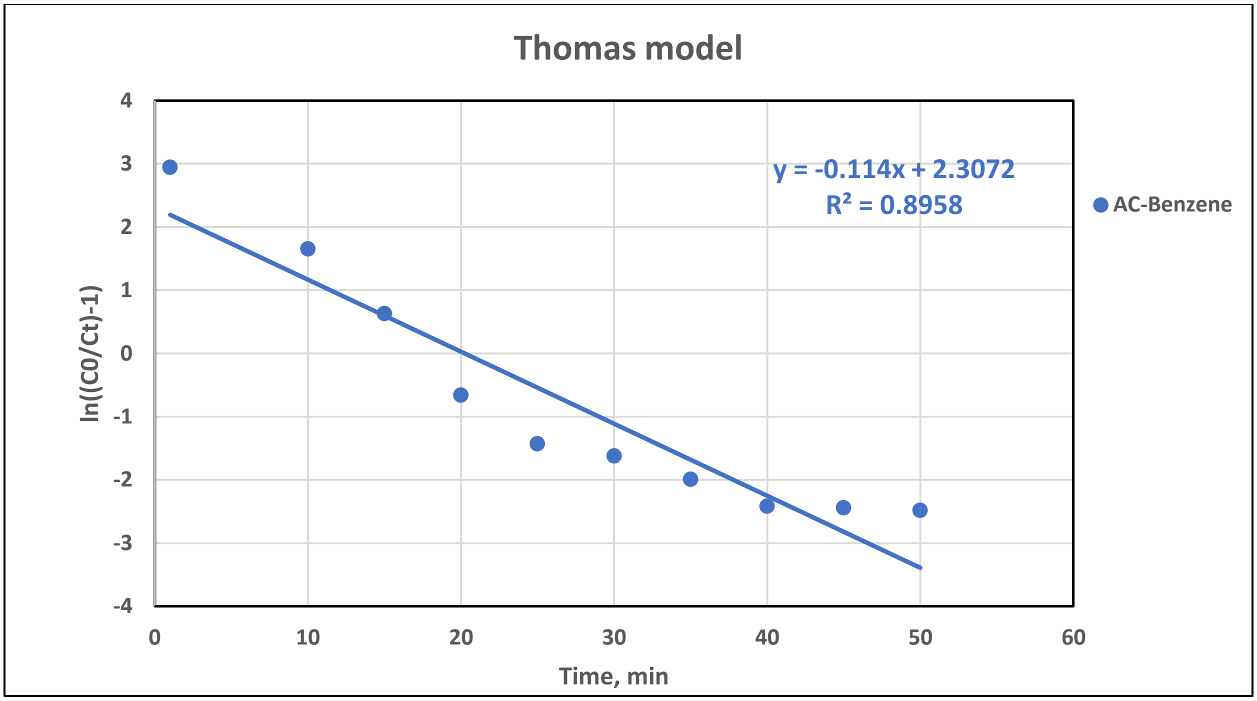

Figure 4. 11: The plot of the measured breakthrough curves according to the linear form of Thomas model for benzene

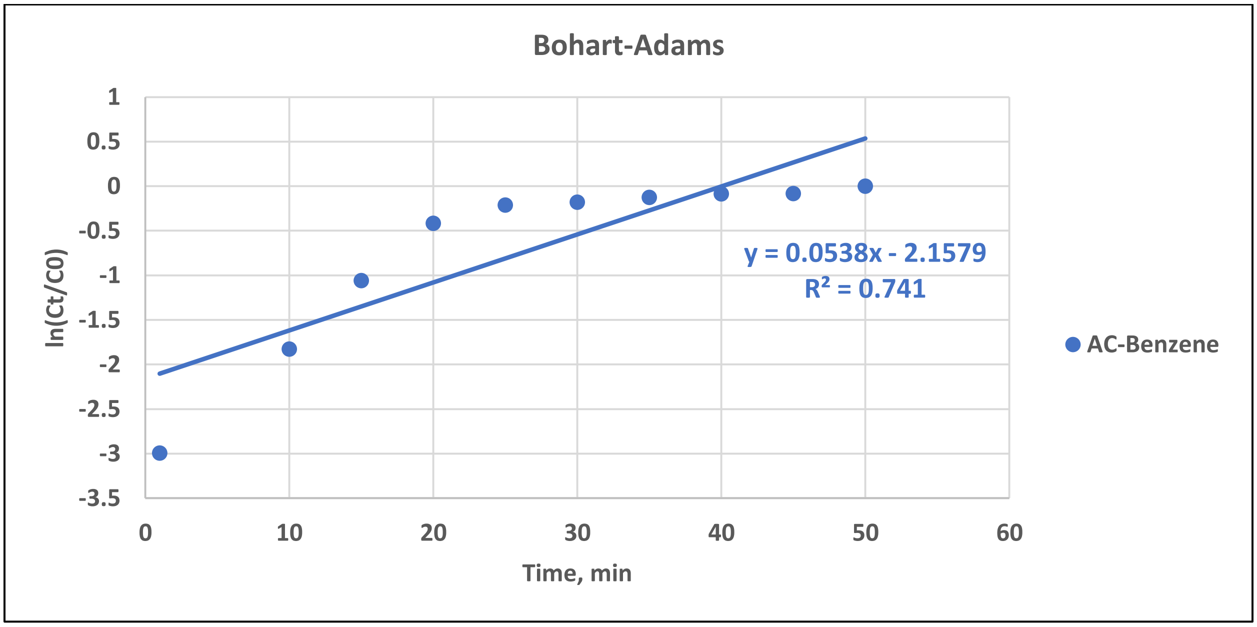

Figure 4. 12: The plot of the measured breakthrough curves according to the linear form of Bohart-Adams model for benzene

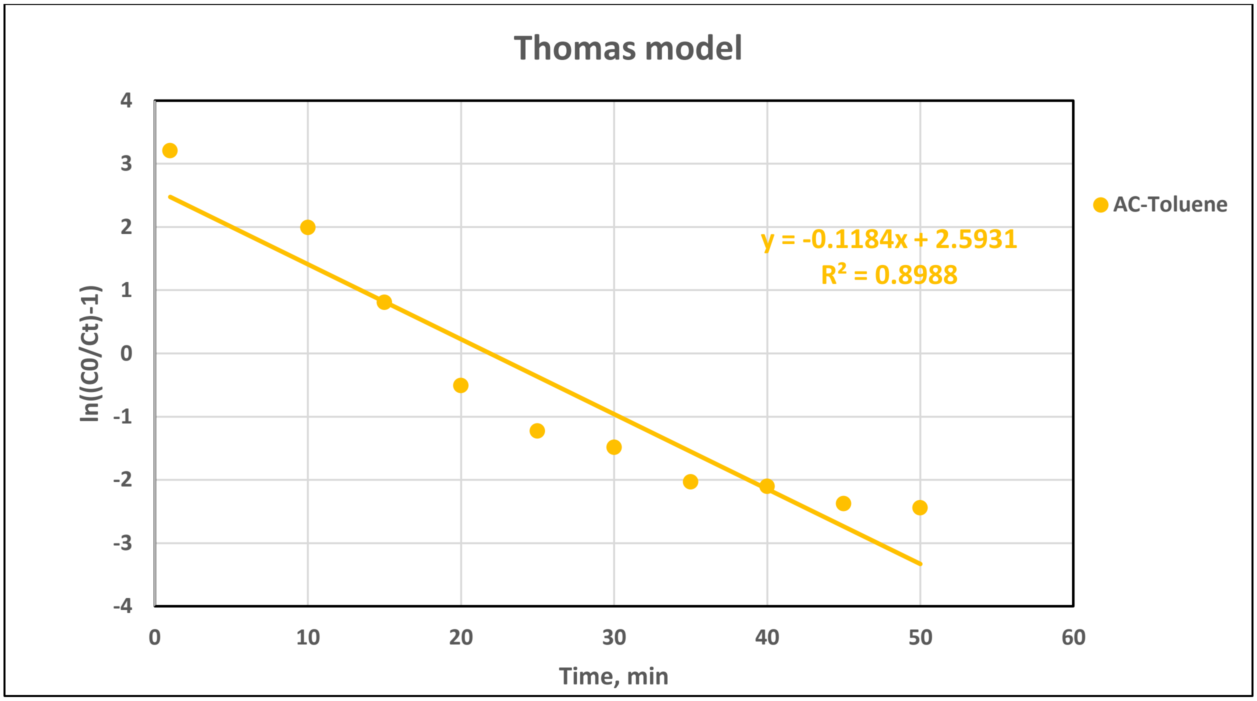

Figure 4. 13: The plot of the measured breakthrough curves according to the linear form of Thomas model for toluene

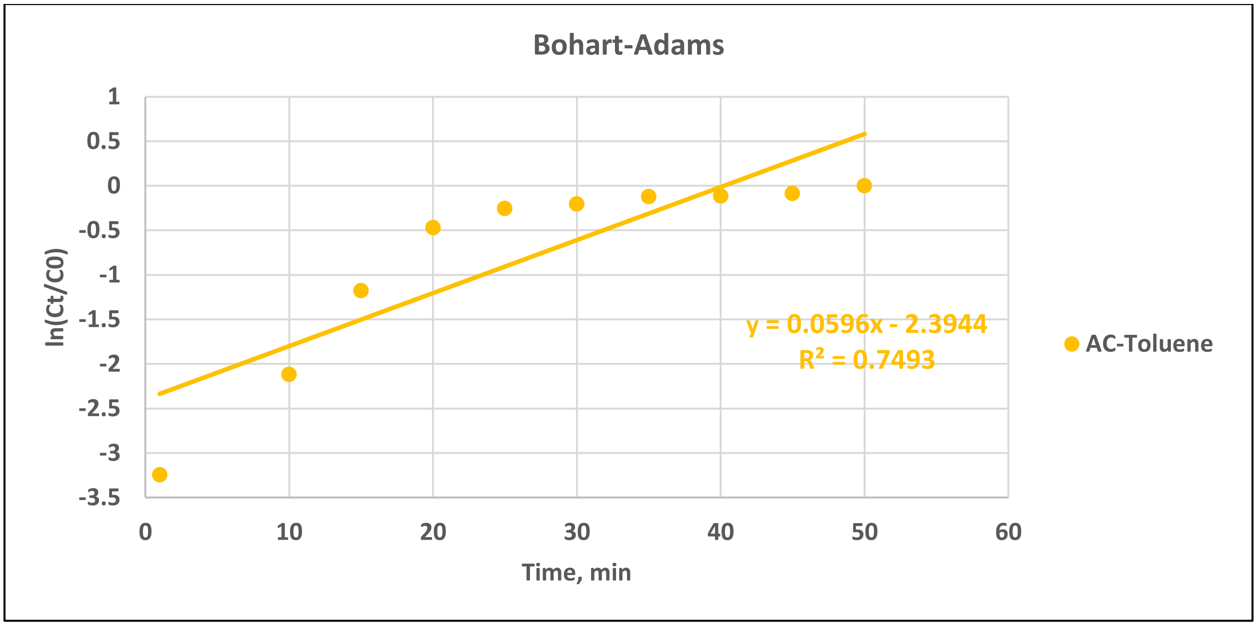

Figure 4. 14: The plot of the measured breakthrough curves according to the linear form of Bohart-Adams model for toluene

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study looked to the removing effectiveness of corn cob- activated carbon from water contaminated with benzene and toluene using a fluidized bed dynamic mode. The research investigated the influence of flow rate, bed height, and temperature on the adsorption process. The findings are listed below.

1- The adsorption capacity and removal efficiency were positively influenced by reducing the flow rate and temperature and increasing both bed height.

2- The particles size 0.4 and 0.6 mm were break earlier compared to the particles size of 0.2 mm as a result of their surface area.

3- The breakthrough curves of benzene and toluene adsorption at their optimum conditions reveals that benzene experiences breakthrough earlier than toluene due to it higher solubility, faster adsorption kinetics, higher affinity to the adsorbent, and variations in the adsorbent's pore structure. The maximum adsorption capacity was 0.1447 and 0.15643 (mg/g) with total removal efficacies of 46.72% and 44.894% for benzene and toluene, respectively

4- The study derived essential parameters for designing a successful dynamic adsorption column, such as adsorption capacity at breakthrough and saturation, from the experimental data. Additionally, the data were subjected to adsorption isotherm models to gain further insights into the adsorption process.

5.2 Recommendations

Despite the extensive research on AC adsorption, several research gaps and uncertainties remain unexplored and not fully addressed. The current study's findings highlight the need for further research to fill these gaps and provide additional insights. Consequently, here additional works are recommended to delve deeper into these areas for future investigations;

1- Increasing the surface area of the adsorbent can potentially improve adsorption capacity. Further research is needed to explore surface modification methods and investigate their effectiveness.

2- Investigating the use of other agricultural substrates, such as lignocellulosic materials and grape wastes, as potential sources for adsorbent synthesis is crucial.

3- Testing the biomass-derived activated carbon at a pilot scale using real wastewater from industrial activities to assess feasibility.

4- Comparing the activity of biomass-derived activated carbon with other types of adsorbents like Graphene, Alumina, or zeolite to understand its performance.

5- Exploring different types of adsorption columns, such as moving bed and Packed-bed reactors, can provide valuable insights into the adsorption process and the suitability of biomass-derived adsorbents for specific applications.

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APPENDICES

Appendix A

Experimental data of breakthrough curve of BT in fluidized bed columns:

Table A - 1: Experimental data of BT breakthrough curve

			CT/C0 Benzene			CT/C0 Toluene		
NO	time, min	c0 (mg/ml)	0.2 mm	0.4 mm	0.6mm	0.2 mm	0.4 mm	0.6mm
1	1	70	0.05	0.044	0.149	0.039	0.034	0.086
2	10	70	0.161	0.148	0.252	0.12	0.112	0.164
3	15	70	0.347	0.332	0.434	0.308	0.298	0.348
4	20	70	0.659	0.631	0.746	0.624	0.601	0.664
5	25	70	0.807	0.779	0.81	0.773	0.75	0.81
6	30	70	0.835	0.876	0.85	0.815	0.844	0.85
7	35	70	0.88	0.879	0.915	0.884	0.858	0.912
8	40	70	0.918	0.884	0.93	0.891	0.865	0.916
9	45	70	0.92	0.913	0.9516	0.915	0.902	0.92
10	50	70	0.923	0.913	0.952	0.92	0.902	0.926

Table A - 2: Operational conditions.

C 0 - Feed concentration of adsorbate (mg /ml)	70
Weight of the adsorbent (g)	89.3 g (10 cm of bed depth)
Temperature (^{o}C)	30
Feed Flow rate	15 l/hr (250 ml/min)

Capacity of the adsorbent can be calculated from [128]:

$q=C_0\,Q\int_0^t\left(1-\frac{c}{c0}\right)dt$

q= Capacity of the adsorbent(mg);

C=Concentration of BT in the outlet of the column (meq/L);

$C\ 0$ -Feed concentration o(mg/mL);

Q -Volumetric flow rate (ml/min);

t-time (min);

The capacity of the adsorbent was calculated from the area determinate by term $(1-\frac{c}{c0})$ calculate by experimental breakthrough curve, illustrated in figure A-1. The integral $\int_0^t\left(1-\frac{c}{c0}\right)dt$, calculated by trapeze method.

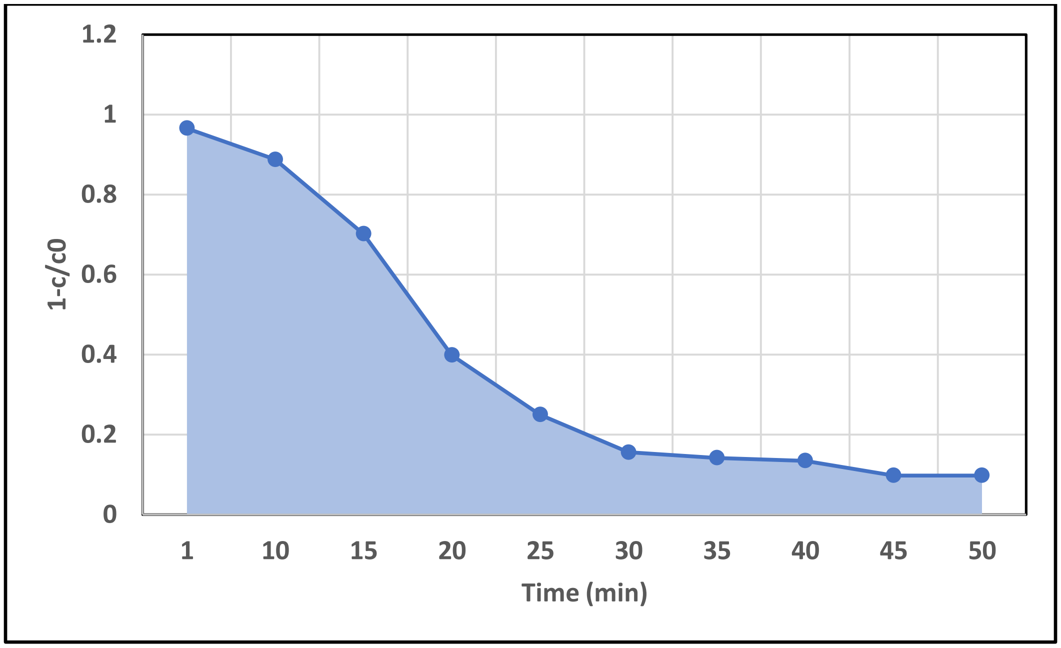

Figure A- 1: Area of curve $(1-\frac{c}{c0})$ of toluene with 0.2 mm particles

Appendix B

The Taguchi method, developed by Japanese engineer and statistician Genichi Taguchi, is a robust optimization technique widely used in experimental design and quality engineering. The main goal of the Taguchi method is to optimize the performance of a system or process while minimizing the effects of variation and external factors.

The basic mathematical equations of the Taguchi model involve the Signal-to-Noise (S/N) ratio, which is used to quantify the performance of a system in the presence of noise or variability. There are different types of S/N ratios depending on the type of response (e.g., smaller-the-better, larger-the-better, nominal-the-best), and the specific objectives of the experiment.

1. Smaller-the-better S/N ratio:

$$S/N = -10 \log_{10} (1/n) \sum_{i=1}^{n} \left(\frac{yi-\bar{Y}}{s}\right)^{2})$$

where:

- n is the number of experimental runs.
- Y_i is the observed value in the (i)-th run.
- $\bar{Y}$) is the average of all observed values.
- s is the standard deviation of the observed values.

2. larger-the-better S/N ratio:

$$S/N = -10 \log_{10} (1/n) \sum_{i=1}^{n} \left(\frac{yi}{\bar{Y}}\right)^{2})$$

where the terms have the same meanings as in the smaller-the-better case.

3. Nominal-the-best S/N ratio:

$$S/N = -10 \log_{10} (1/n) \sum_{i=1}^{n} \left(\frac{yi-\bar{T}}{s}\right)^2)$$

where: (T) is the target or nominal value.

Standard Deviation (S): The standard deviation is a measure of the variability or dispersion of the observed responses. It is often used in the calculation of S/N ratios and is given by: $s = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (Y - \bar{Y})^2}$

This organization highlights the mean response, S/N ratio, and standard deviation, along with their respective equations, providing a structured overview of these key components in Taguchi experiments.

The Taguchi method involves conducting a series of experiments with different factor levels, and the goal is to find the factor levels that maximize the S/N ratio. This is often done by creating an experimental matrix using orthogonal arrays, which efficiently explore the factor space with a relatively small number of experimental runs.

It's important to note that the specific application of the Taguchi method may involve additional considerations and adjustments based on the nature of the problem and the goals of the experiment.

الخلاصة

البنزين والتولوين (مركبات BT) عبارة عن هيدروكربونات توجد بشكل متكرر في الماء بسبب الأنشطة البشرية المختلفة والأحداث العرضية مثل انسكابات النفط. يمكن أن تسبب مشاكل صحية، بما في ذلك تهيج الجهاز العصبي، وآفات الكبد، والسرطان. تهدف هذه الدراسة إلى تطوير تقنيات امتزاز فعالة من حيث التكلفة باستخدام المواد الماصة المصنوعة من الكتلة الحيوية للذرة لإزالة مركبات BT من الماء. تم اختبار الكربون المنشط المركب من الكتلة الحيوية للذرة مع تعديل سطح كلوريد الزنك والكربنة في عمود طبقة مميعة مستمرة. قامت المواد الممتزة بإزالة مركبات BT بشكل فعال، حيث تم امتصاص التولوين بشكل أكثر كفاءة من البنزين بسبب انخفاض قابليته للذوبان في الماء. يصف تساوي حرارة الامتزاز لانجميور سلوك الامتزاز بشكل أفضل. تم فحص المادة الممتزة المشتقة في ظل معلمات التشغيل المتغيرة بما في ذلك معدلات التدفق (Q) (15-25 لتر / ساعة)، وارتفاعات السرير (Z) (6-10 سم)، ودرجة الحرارة (T) (30-40 درجة مئوية) لتحديد تأثيرها على كفاءة الامتزاز BT. تظهر النتيجة الرئيسية أن زيادة معدل التدفق ودرجة الحرارة قللت من إزالة BT بينما أدت زيادة ارتفاع السرير إلى تحسين كفاءة الإزالة. ومع ذلك، أظهر امتزاز العمود فعالية أقل بسبب الوصول المحدود للمواد الممتزة إلى المواقع السطحية على الممتزات بسبب انخفاض أوقات الاستبقاء داخل العمود. تم تحديد الظروف المثلى للامتزاز: ارتفاع السرير 10 سم، ودرجة الحرارة 30 درجة مئوية، ومعدل تدفق المياه الملوثة 15 لتر / ساعة. وفقًا لمنحنى الاختراق لجزيئات التيار المتردد 0.2 مم، كانت سعات الامتزاز القصوى 0.1447 و0.15643 (مجم/جم) مع كفاءة إزالة إجمالية تبلغ 46.72% و44.894% للبنزين والتولوين، على التوالي. بشكل عام، أظهرت هذه الدراسة إمكانات الكربون المنشط المركب من الكتلة الحيوية للذرة باعتباره مادة ماصة فعالة لإزالة BT من المياه الملوثة باستخدام عمود الطبقة المميعة المستمر.

جمهورية العراق
وازره التعليم العالي والبحث العلمي
جامعة بابل كلية الهندسة
قسم الهندسة الكيمياوية

إزالة البنزين والتولوين من مياه الصرف الصناعي في الطبقة المميعة عن طريق الامتزاز

الرسالة

مقدمة الى كلية الهندسة -جامعه بابل وهي جزء من متطلبات نيل الماجستير في الهندسة\ الهندسة الكيمياوية

من قبل

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2023