OPTIMIZATION OF METHYLENE BLUE DYE FROM AQUEOUS SOLUTION USING ACTIVATEDD CARBON OBTAINED FROM COCONUT SHELLS

BY

EWERE ALBRIGHT OSAIGBOKAN

ENG1602597

DEPARTMENT OF CHEMICAL ENGINEERING

FACULTY OF ENGINEERING

UNIVERSITY OF BENIN

BENIN CITY

NIGERIA

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CERTIFICATION

This is to certify that EWERE ALBRIGHT OSAIGBOKAN carried out the project work contained in this thesis, in the Department of Chemical Engineering, University of Benin, Benin City.

_____ _____

ENGR. PROF. (MRS) C.O OKIEIMEN **DATE**

PROJECT SUPERVISOR

_____ _____

ENGR. DR. E.O OYEDOH **DATE**

HEAD OF DEPARTMENT

_____ _____

EXTERNAL SUPERVISOR **DATE**

DEDICATION

This project work is dedicated to God Almighty for giving me the strength and grace to complete the project. Also, to my parents Mr. Gabriel and Mrs. Christiana Ewere.

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First and foremost, I give my profound gratitude to God who sailed me through the waves of challenges and difficulties that I encountered during the course of my work. Therefore, glory to God for what he has done for me.

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ABSTRACT

The influence of dye concentration, adsorbent dosage, and contact time on the % removal of methylene blue dye (textile effluent) from aqueous solution was optimized and evaluated using a three-variable Box-Behnken design (BBD) in combination with response surface methodology (RSM). Coconut shell was utilized to make the adsorbent, which was then activated with H3PO4 after being carbonized at 600°C for an hour. Three variables—dye concentration (50–200 mg/l), adsorbent dosage (g/100 ml), and contact time (10–60 mins), were varied to treat the dye solution. The responses of the linear and quadratic models that were developed for % dye removal from aqueous solution were significantly influenced by all three parameters, according to a statistical analysis of the data with $p < 0.0001$, the models were significant and demonstrated a strong fit with the experimental data. The adsorbent dosage and contact time had a positive impact on the percentage of dye removal. The process was optimized, and the maximum dye removal of 82% was attained at optimum dye concentration, adsorbent dosage, and contact time of 125 mg/l, 0.55 g/100 ml, and 35 min.

Keywords: Activated Carbon, Water treatment, Methylene blue, Coconut shell, Response surface methodology.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND TO THE TOPIC

In recent decades, industrial wastewater has been regarded as one of the main environmental contaminants. Different industries such as paper, paints, mineral extraction, mining, leather, food, cosmetics, plastic, automobile, paper, printing, pharmaceutical, chemical process, petroleum, textile, nuclear, and leather can produce wastewater, also drinking water, industrial wastewater and urban wastewater may contain and produce wastewater that needs to be properly, continuous and effectively purified (zhouY; Liu J. 2019). According to a WHO survey from 2018, the percentage of potable water on earth is between 4 and 4.8%, and the observed turbidity for dangerous substances present in industrial effluents is around 0.05 mg/lit. The pH limit for **Effluent Treatment Plants** or (ETPs) of industries should be neutral but recent studies have shown that the observed pH is 6-6.3 which is still quite acidic. Advancement in industrial activities has brought about growth to many industries and one very notable industry is the textile industry, which focuses primarily on the development, manufacture, and distribution of yarn, fabric, and apparel. According to research, the textile industry is one of the leading wastewater generators, polluting both surface water and groundwater, based on the depth of the underground water (Hettige and Mowjood, 2015; Wang et al., 2007). The activities of the textile industry require significant amounts of water and chemicals, and in the majority of situations, the effluents are released into the environment, particularly into water bodies. The presence of dyes

in water bodies, even in little amounts due to their brilliance, can make them easily visible (Pang and Abdullah, 2013; Robinson et al., 2001). Dyes constitute a significant).

As a result of their chemical makeup, they are resistant to biodegradation, fading when exposed to light, oxidizing agents, water, and numerous chemicals due to the presence of refractory organic molecules. Their presence in waterbodies decolorizes them and makes it difficult to be decolorized once it is released into water bodies. Most organic dyes are very hazardous and if released into waterbodies can affect aquatic life and also cause a serious environmental impact on man. The introduction of these colors of effluent into the water bodies is unsightly and has major environmental consequences. The release of these colorful effluents poses a significant environmental concern for developing countries due to their toxic and cancer-causing impacts on living things (B. Acemioglu 2004). Acidic, reactive, direct, basic, and other types of dyes are commonly utilized in most textile industries.

Different techniques have been used to remove the color from textile effluent, including biological processes, ozonation, chemical coagulation, flocculation, chemical precipitation, photolysis, ion-pair extraction, and ozonation, For instance, the biodegradation process necessitates the maintenance of exacting conditions and can occasionally be challenging to operate on a big scale. Many of these are highly expensive and include major start-up costs. Previous research has shown that dyes from textile wastewaters can be removed using activated carbon sorption because of its simplicity and efficiency, low energy requirements, cost effectiveness, a very straightforward technological procedure, non-corrosiveness to equipment, and the capacity to remove contaminants over a reasonably large temperature and pressure range that are too stable for biological methods. Some of the adsorbents used for activated carbon include peat, bentonite, fly ash, natural zeolite, sawdust, charcoal, silica, agricultural waste, and

lignocellulosic materials. Many of these carbonaceous materials are utilized to make commercially available activated carbons. Because of its porous structure, activated carbon is commonly utilized as an adsorbent. Because a larger surface area allows for more adsorption and a higher porosity allows for greater diffusion.

Adsorption is a method that, in addition to being commonly utilized for dye removal, has many different applications in wastewater treatment. This procedure is being employed in this investigation because it is a very low-cost and easy method for containing harmful contaminants.

1.2 PROBLEM STATEMENT

The effect of pollution as regard textile wastewater during dye the removal process is increasing on a global scale particularly in developing nations. This is because the chemicals and dyes employed in the commercial textile sector do not biodegrade very well, promoting toxicity, mutagenicity, and carcinogenicity, they may also contain elevated levels of heavy metals, grease, wax, and suspended solids. A significant portion of the dye used in the coloring process is lost to the wastewater stream because it does not adhere to the fabric. The effluent is brightly colorful and unappealing because about 10-15% of dyes are released into the environment during the dyeing process. Adsorption techniques including coconut shell biomass are expected to be relatively successful in removing wastewater dye. Due to the low biodegradation of these dyes, the typical biological treatment procedure is ineffective in treating effluents. It is critical to research environmentally friendly and low-cost treatments to address these issues. Adsorption techniques including coconut shell biomass are expected to be relatively successful in removing wastewater dye.

1.3 AIM AND OBJECTIVES

The purpose of this study is to create a modified adsorbent (activated carbon made from coconut shells) from agricultural waste for the best possible dye removal (optimal) from an aqueous dye solution. (textile wastewater) obtained by preparing stock solution of methylene blue dye, with a view of obtaining optimized efficiency of adsorptive treatment with Chemically activated carbon using H3PO4 chemical reagent and the specific objectives are to:

- To produce char from coconut shells by carbonization in a muffle furnace.
- To produce activated carbon from H3PO4 reagent
- Characterize the adsorbent prepared;
- Optimize the process variables (Dye concentration, Adsorbent dosage, and Contact time) to ensure the best possible dye removal using Response Surface Methodology.
- Determine the adsorptive ability of coconut shells to absorb colors from an aqueous dye solution (textile wastewater).

1.4 RELEVANCE OF STUDY

The importance of activated carbon in recent decades cannot be overstated, with applications ranging from purifying liquids and gases, treatment of food and drink, the removal of odors, and industrial pollution management. Textile wastewater presents an environmental issue because it is a liquid waste with a diverse variety of dyes and chemical additives. About 70% of the pollution produced by diverse activities in the textile sector comes from chemical processing. Water consumption by cotton mills for various operations like size, de-sizing, bleaching, dyeing,

mercerization, printing, scouring, washing, finishing, etc. Large amounts of wastewater containing numerous contaminants are released as a result of the nature of the various chemical processes used to prepare textiles. Special consideration must be given because these water streams have a variety of negative effects on the aquatic ecosystem, including lowering the level of dissolved oxygen and settling suspended materials in anaerobic environments. Despite being an eco-friendly fabric, more than 50% of cotton is colored with reactive dyes during production. The textile sector produces effluents that are highly colored, have high salt concentrations, and have high biological oxygen demand (BOD) values. If discarded without treatment, these dyes pose a risk to the environment. Biotechnological techniques including biodegradation and ordinary biological processes were used before the creation of low-cost agricultural and high-carbon biomass.

Advances in research have led to significant breakthroughs in the treatment of water-related issues, and ongoing research into more carbon-rich materials is being conducted to eliminate all wastewater concerns for a fast-industrializing world.

Apart from water treatment problems, studies have shown that activated carbon can be useful in other areas, some of which include

1. Kidney health

By removing medications and poisons that haven't been properly digested, activated carbon may be able to support renal function.

Animal studies suggest that activated charcoal may assist people with chronic renal disease improve kidney function and lessen gastrointestinal harm and inflammation, but more research is

required in this area. Activated charcoal may also be used by medical professionals in the emergency room to treat overdoses and poisoning

2. Skin infection

Many practitioners of traditional medicine use activated charcoal powder manufactured from coconut shells to treat soft tissue disorders like skin infections all around the world. By absorbing dangerous germs from wounds, activated carbon may exert an antibacterial effect.

3. Skincare

According to research, activated charcoal can facilitate the removal of microparticles from the skin by attracting them to the skin's surface, including bacteria, chemicals, toxins, dirt, and dust.

4. Deodorant

There are several different activated charcoal deodorants on the market. The ability of charcoal to absorb odors and toxic gases makes it the perfect deodorant for shoes, underarms, and refrigerators. According to reports, activated charcoal can also absorb surplus moisture and regulate humidity levels at the microscopic level.

CHAPTER 2

LITERATURE SURVEY

2.1 WATER POLLUTION

A wide range of contaminants, including dyes, medications, fluoride, phenols, insecticides, detergents, pesticides, and heavy metals detergents, are contaminating water sources as a result of industrialization and human activities (Khatri and Tyagi, 2015). Every day, new chemical compounds or categories of chemical compounds are produced and put on the market; eventually, they will end up in the environment. Water-borne pathogenic microorganisms are also widespread around the planet. These dangerous microorganisms enter waterways through untreated sewage, septic tanks, storm drains, runoff from farms, and several industries, including meat packaging and tanning. Emerging contaminants found in water might negatively affect aquatic ecosystems and human health. Human health depends on having access to clean water that is devoid of pathogens and hazardous chemicals (Nadal M, et al, 2015).

2.1.1 SOURCES OF WATER POLLUTION

2.1.1.1 Point Source Pollution

Point source pollution occurs when the cause of the water pollution is known or when the pollutants entering the water are coming from an identifiable source, such as a ditch, a pipe industry, an oil spill from a petroleum tank, a storm drain, or a sewage treatment plant (EPA 2021). It can be kept isolated from other contaminating factors. Additionally, municipal and industrial wastewater effluent as well as storm sewer discharge are point sources of pollution that primarily influence the vicinity (Aziz, R.A. and Ab Jalil, M.F. 2011).

2.1.1.2 Non-point Source Pollution

Pollution that cannot be ascribed to a single discrete source or whose origin is unclear is known as non-point source pollution (arrive from different sources of origin). It is extremely challenging to control and can be caused by a range of things, including pesticides, fertilizers, industrial waste, runoff from agricultural areas, and urban garbage (EPA 2021)

Table 2.1 Characteristics of point and nonpoint sources of chemical inputs to receiving water (adapted from Carpenter et al., 1998)

Point Sources	Nonpoint Sources
Wastewater effluent (municipal and industrial)	Runoff from agriculture (including runoff flow from irrigated agriculture)
Runoff and leachate from waste disposal sites	Runoff from pasture and range
Runoff and infiltration from animal feedlots	Urban runoff un-sewered and sewered areas with a population <100,000
Storm sewer outfalls from cities with a population >100,000	Septic tank leachate and runoff from failed septic systems Runoff from construction sites

Overflows of combined storm and sanitary sewers	Runoff from abandoned mines
	Atmospheric deposition over a water surface

2.1.2 Other Forms of Water Pollution

2.1.2.1 Organic Water Pollution

Examples of organic water pollutants include pesticides and herbicides, organo halides and other kinds of chemicals, microorganisms from sewage and animal farms, food processing wastes, volatile organic compounds, pathogens, etc. (Noshin Mashood, 2021).

2.1.2.2 Inorganic Water Pollution

They may be brought on by chemical waste from industrial effluents, slash-and-burn practices, heavy metals from acid mine drainage, logging, silt from surface run-off and land infill, as well as fertilizers from agricultural run-off, including nitrates and phosphates, etc (Holm, J.V., Rugge, k., Bjerg, P.L. 1995).

2.1.2.3 Ground Water Pollution

Groundwater contamination results from pollutants from the earth's surface getting into underground water sources. It becomes unsafe to drink when fecal water containing pathogens travels deep underground. Groundwater that has been contaminated by pathogens may contain bacteria, viruses, protozoa, and, sporadically, helminth eggs. Consuming this water can result in cholera and diarrhea (Emmanuel, E., Pierre, M.G. and Perrodin, Y, 2009).

Groundwater contamination is brought on when pollutants from the earth's surface get into underground water sources. Fecal water becomes unsafe for drinking when it travels beneath the earth and contains pathogens. Groundwater that has been contaminated by pathogens may also contain bacteria, viruses, protozoa, and, sporadically, helminth eggs. Consuming this water can result in cholera and diarrhea. Nitrates also contribute to groundwater pollution, which can lead to blue baby syndrome in children. Blue baby syndrome risk rises when groundwater nitrate concentrations are more than 10 mg/L (10 ppm). Since relatively little nitrate is used by plants and the majority accumulates in the soil, over use of nitrate fertilizers can also harm groundwater by allowing nitrate to leak into the water supply. Dental and skeletal issues result from fluoride contamination in groundwater (Giri, S and Singh, A.K., 2015).

2.1.2.4 Urban Storm Water Runoff

It is a result of densely crowded cities. It originates in homes and workplaces. In suburban and metropolitan settings, buildings and pavement cover a large portion of the land surface, preventing rain and snowmelt from penetrating the ground. These stormwater runoffs immediately pollute rivers and streams by transporting a variety of contaminants like soil, oil, lawn fertilizer, and chemicals (Gobel P; Dierkes C; Coldway WG, 2007).

2.2 METHYLENE BLUE DYE EFFLUENT

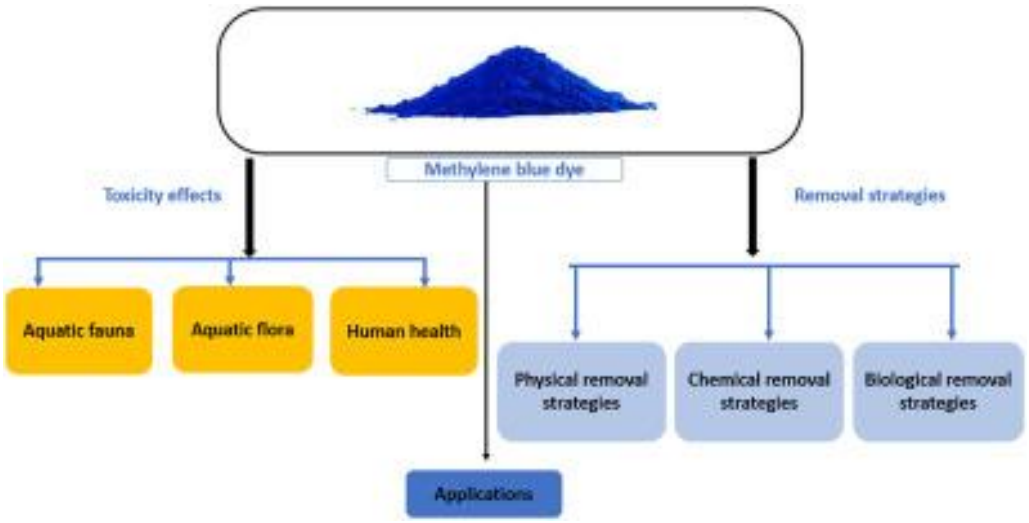
Methylene blue (MB) dye is one of the widely used cationic dyes that are environmentally persistent, poisonous, carcinogenic, and mutagenic. It is frequently used as a synthetic dye to color fabrics in the apparel and textile industries, as well as to color papers and leather (Allen

and Koumanova, 2005). A significant amount of wastewater containing the dye (methylene blue) is released into groundwater and surface waters as a result of the industrial scale of consumption. Considering both volume discharge of dye effluents, the wastewater from the textile industry is rated as the most detrimental among all industrial sectors (Mckay et al., 1981). In addition to endangering aquatic environment species, the monoamine oxidate inhibiting properties of MB dye can cause deadly serotonin poisoning in humans at concentrations more than 5 mg/kg, MB dye can cause several diseases in humans, including cyanosis, tissue necrosis, the formation of Heinz bodies, vomiting, jaundice, shock, and an increased heart rate. Therefore, it is crucial to eliminate MB dye from wastewater. From literature it has been found that several procedures can be used to remediate wastewater containing methylene blue.

The evaluation of elimination techniques found that whereas biological procedures are characterized by an enzyme's sensitivity to pH, chemical removal techniques (both photochemical and non-photochemical) have the potential to produce secondary contaminants.

Their industrial full-scale applications are constrained by these flaws, but adsorption technology has been discovered to have advantages over others (R.G. Prashant, S.D. Jyothi, 2010).

Figure 2.1: Graphical Abstract of Methylene Blue



2.2.1 STRUCTURE AND COMPOSITION OF METHYLENE BLUE

The chemical substance known as methylene blue dye has the molecular formula C16H18N3SCl and a molecular weight of 319.85 g/mol. This dye is a common blue, cationic, and thiazine type that has been widely used in medicine as a staining agent, as well as for prophylactic and therapeutic measures, and in the textile industry as a fiber coloring agent.

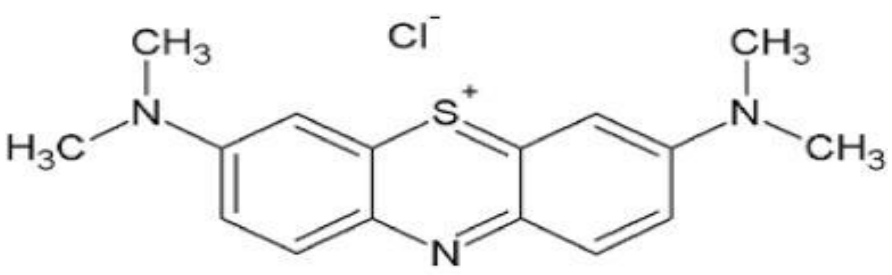


Figure 2.2: Methylene Blue Molecular Structure

Table 2.2: Some physio-chemical properties of Methylene Blue.

Entry	Variable	Names/value
1.	Maximum wavelength of absorption (nm)	664 nm
2.	Degree of solubility (%)	3.55%
3.	Ionization	Basic
4.	Other names	Swiss blue, cationic dye
5.	Aqueous Ph	Strongly acidic between Ph 2.0–3.5
6.	Color index number	52015
7.	Color index name	Basic Blue 9

2.2.2 APPLICATIONS OF METHYLENE BLUE DYE

- Patients with both pediatric and adult methemoglobinemia are recommended to employ methylene blue, which is extensively used in medicine (a blood disorder in which an abnormal level of methemoglobin is produced).

- Methylene blue also has therapeutic uses against hypoxia and hyperdynamic circulation in liver cirrhosis, among other clinical uses, which relieve hypotension associated with various clinical conditions.

- In the industrial setting, MB is predominantly used in the garment and textile sectors to dye a variety of textiles [22]. Additionally, it is utilized to color leather and paper
- It acts as a sensitizer when organic molecules are photo-oxidized in the disciplines of medicine, microbiology, and diagnostics.

  Based on some of the mentioned uses of methylene blue it is undeniably a pertinent dye. However, MB's severe toxicity and refractory nature make it a possible threat to the ecology and human health at a certain concentration, according to reports.

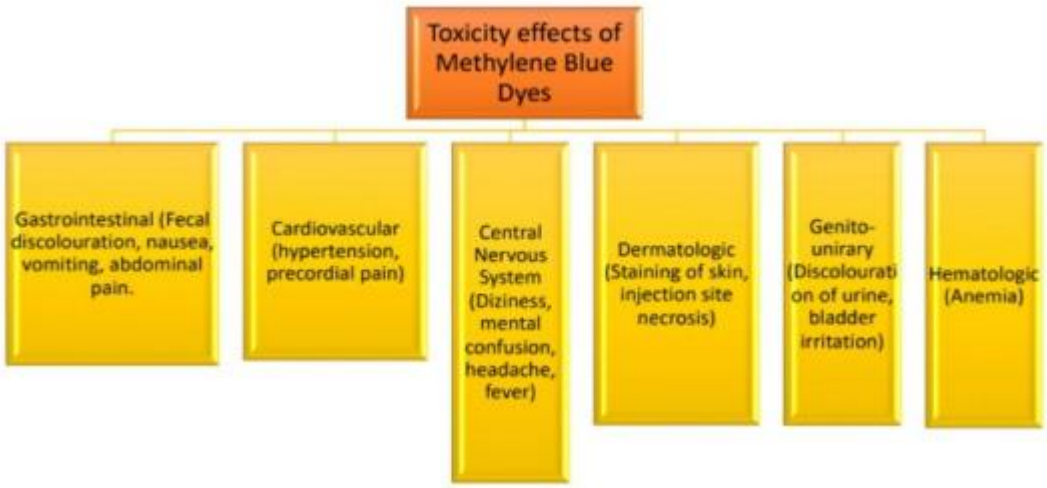
2.2.3 Toxicity Effects of Methylene Blue Dye.

MB is useful in many different industries, but if it is not adequately controlled in an environmentally sustainable way, it could constitute a serious hazard to both the environment and human health (O.S. Bayomie, H. Kandeel, 2020).

- GI upset, headaches, and vertigo are potential side effects.
- By directly oxidizing hemoglobin, high dosages of methylene blue (7 mg/kg) can lead to methemoglobinemia. Hemolysis is linked to doses greater than 15 mg/kg, especially in a baby.
- Prolonged dosage may cause noticeable anemia.

- Local tissue necrosis could be caused by extravasation (the death of body tissue occurs when too little blood flows to the tissue.)
- Potential eye damage and eye discomfort. Skin: Irritates the skin. Cyanosis may result from absorption into the body (bluish discoloration of the skin due to deficient oxygenation of the blood). When consumed, certain foods may irritate the stomach, resulting in nausea, vomiting, and diarrhea.

Figure 2.3: Toxicity effects of methylene blue dye. (A. Krishna Moorthy, B. Govindarajan Rathi, 2021).



2.2.4 REMOVAL STRATEGIES FOR METHYLENE BLUE

Methylene blue is very soluble in water at room temperature and is notoriously difficult to biodegrade and extract from wastewater using conventional, simple treatment methods. As a result, industrial wastes and effluents are the primary targets of the removal procedures. (Hameed, 2009; sallel et al., 2011)

2.2.4.1 PHYSICAL REMOVAL METHODS

The removal of dyes from their effluent discharges can be accomplished physically in several ways. Some of which include filtration methods (ultra/microfiltration, membrane, nano-filtration), reverse osmosis, irradiation, coagulation-flocculation, ion exchange, electrolysis, and adsorption methods are some of the most widely employed (S. Dutta, A. Bhattacharyya, 2011).

2.2.4.2 ADSORPTION TECHNOLOGY

Solid sorbents were used in the adsorption process for the removal of dyes like MB. The method has been successfully applied to remove MB from wastewater on a large scale. Many adsorbents have been investigated and effectively used to lower dye concentrations in aqueous solutions. Many adsorbents have been investigated and effectively used to lower dye concentrations in aqueous solutions (Patel and Suresh, 2008; Gupta and Bhattacharyya, 2006; Salleh et al., 2011).

Some examples of low-cost adsorbents are

- pomegranate peel biochar
- Ava bean peel waste
- Coconut shell-activated carbon
- Cashew nut shells
- Chitosan lignin membrane

- Granular waterworks sludge-biochar composites
- African almond
- Pomegranate peels etc.

2.2.4.3 MEMBRANE TECHNOLOGY

Membrane technology has been cited as an eco-friendly and sustainable technique and as an efficient method for extracting dyes from wastewater, including methylene blue dye (M. Bielska, J. Szymanowski, 2006). Although membrane separation has been praised as a better method for removing dyes, it has been noted that using this procedure is expensive. As a result, researchers are constantly looking for techniques that are more dependable and successful, particularly when it comes to the use of renewable membrane materials. Studies have concentrated on developing hybrid nanomaterials that blend the qualities of inorganic and carbonaceous substances to produce affordable, usable, and equally effective materials. Reverse osmosis and ultrafiltration techniques are thought to be among the most efficient membrane processes for getting rid of many hazardous dyes completely (A.L. Ahmad, S.W. Puasa, 2007).

The main components of the membrane material are polymeric sheets, solvent diluents, non-solvent liquids, and other additives and extracts. For the manufacture of membranes, good polymeric materials include polyvinylidene fluoride and any of its copolymers.

Despite being widely applicable, membrane technology has a significant drawback known as membrane fouling. Once it becomes polluted or overloaded, the membrane needs to be replaced regularly. Therefore, the cost effects and sustainability of the type of membrane to be used must

be taken into account for it to be considered as a feasible alternative strategy for the removal of methylene blue dye. (Z.L. Cheng, Y.X. Li, Z. Liu, 2017).

2.2.5 CHEMICAL REMOVAL METHODS (PHOTOCHEMICAL AND NON-PHOTOCHEMICAL METHODS)

2.2.5.1 NON-PHOTOCHEMICAL METHODS (OZONATION)

Water contaminated with dyes has been treated using extremely reactive ozone. It is useful since it enhances the water's color and flavor. Ozone, however, has a limited range of applications due to its instability and poor solubility (J. Zhang, K.-H. Lee, L. Cui, T.-s. Jeong, 2009).

Other materials are regularly used to enhance the application of ozone for the purification of MB in water, examples of materials that have been utilized for this include titanium oxide and activated carbon. When these materials and ozone were applied together, it was observed that the effectiveness of MB elimination increased. (J. Zhang, K.-H. Lee, L. Cui, T.-s. Jeong, 2009). It was observed that to produce peroxone, which degrades MB, hydrogen peroxide and ozone were used.

2.2.5.2 PHOTOCHEMICAL METHODS (UV light-assisted advanced oxidation process)

UV radiation helps to create highly reactive radicals like hydroxyl radic als and sulfates, which then attack the methylene blue dyes and cause the development of non-toxic or less toxic compounds (D. Wen, W. Li, J. Lv, Z. Qiang, M. Li, 2020). The elimination of methylene blue

dyes by conventional UV radiation is restricted in acidic and natural conditions, so to help other techniques or reagents, UV light has therefore been employed. Methylene blue has been known to degrade when hydrogen peroxide and UV radiation are used. According to research, this procedure decolorized more than 90% of the methylene blue in just one hour. However, depending on the initial methylene blue dye concentration, the decolorization time varies (H.A. Mohammed, S.A. Khaleefa, 2021).

The effectiveness of this approach is also impacted by an increase in hydrogen peroxide concentration, which may be connected to hydrogen peroxide's capacity to scavenge free radicals. As a result, researchers have looked into further UV-assisted techniques (H. Masoumbeigi, 2015).

One approach for the breakdown of the methylene blue dye that has been helped by UV radiation is plasma technology. In a study, the role of UV in plasma technology's operation in the methylene blue deterioration process was investigated. Because the configuration without UV light degraded methylene blue dye less than the setup with UV light, it is clear that the inclusion of UV light in plasma technology is essential for the proper degradation of methylene blue dye (T. Maehara, 2010).

2.3 ACTIVATED CARBON

Activated carbon is powdered, refined charcoal. It undergoes physical or chemical treatment to produce micro fissures that significantly enhance the surface area available for absorption. Numerous polar chemicals can be successfully adsorbed due to the substantial surface area (500–1500 m2/g). Activated carbon (AC) is one of the adsorbents that are most commonly used in the water and wastewater treatment industry globally. Charcoal. There are many carbonaceous

materials that can be used to make AC, including coconut shells, wood, tar, lignite, etc. AC is a flexible material with numerous applications in many fields, but primarily in the environmental sphere. This is because of its high surface area, well-developed internal pore structure composed of micro-, meso-, and macropores, massive porosity, and wide range of functional groups present on the surface. The ability of carbon surfaces to remove particular pollutants from the aqueous process is being greatly improved by the use of various chemicals or appropriate treatment procedures, allowing AC to expand its potential for the removal of particular pollutants from the aqueous phase. The physical and chemical composition of carbon can be changed by several processes, including activation factors processes (various agents, temperature, and time of the process), precursors, compounds, and others. A variety of methods for altering AC surfaces have been described in the literature, which sheds some light on the chemistry and mechanism of the treatment methods that make it possible for AC surfaces to absorb specific contaminants. Typically, the activation phase is followed by the surface modification of AC. Three types of alteration exist chemical, physical, and biological. Activation is mainly created through either physical or chemical activation (Bhatnagar et al., 2013). Physical activation uses hot gases such as steam or CO2 as the activating agent to turn raw material into activated carbon without producing any wastewater, while for chemical activation the carbon-based materials are chemically activated by being impregnated with specific chemicals, often an acid, a strong base, or a salt. Due to lower temperatures, higher quality consistency, and quicker activation times, chemical activation is preferred to physical activation (Ahmad, Syahidah, and Bello, 2015).

2.3.1 CLASSIFICATION OF ACTIVATED CARBON

Based on their behavior, surface properties, and other basic criteria, activated carbons are complicated compounds that can be challenging to categorize. However, a general classification is formed based on factors such as size, preparation techniques, mention of certain physical and chemical qualities, and industrial applications (Afr and Mcdougall, 1991).

The physical and chemical characteristics of the finished product might vary greatly depending on the raw material and the processing techniques employed to create it.

Major types of AC, includes;

- Powdered Activated Carbon (PAC) and Granular Activated carbon (GAC)
- Particle Activated Carbon/Powdered Activated Carbon (PAC)
- Extruded Activated Carbon (EAC)
- Bead Activated Carbon (BAC)
- Woven carbon

2.3.1.1 Powdered Activated Carbon (PAC) and Granular Activated carbon (GAC)

Granular activated carbon (GAC) and powdered activated carbon (PAC) both come from raw materials such as high-quality coal, wood, or coconut shell. PAC is frequently thought to have particles that are smaller than the 80 mesh (0.180 mm) requirement used in the United States, which makes it perfect for water treatment. granular activated carbon (GAC) has a smaller outer surface than powdered activated carbon. Therefore, the absorbate's diffusion is a crucial element. Granulated carbons are used in quick-mix basins as well as for flow system component deodorization, separation, and treatment. The activated carbon that may be kept on a 50-mesh screen is known as granular activated carbon (GAC). Granular activated carbon is excellent for

eliminating a wide range of pollutant from water, air, liquids, and gases. (Randtke and Snoeyink, 1983)

2.3.1.2 PARTICLE ACTIVATED CARBON

The material used in PAC is finer. 95–100% of the crushed or ground carbon particles that makeup PAC will pass through a specific mesh screen. Particle AC is typically produced as powders or tiny granules with an average diameter between 0.15 and 0.25 mm that are smaller than 1.0 mm in size. They thus have a low diffusion distance and a high surface-to-volume ratio. Particle-activated carbon refers to the activated carbon particles that are retained on a 50-mesh screen (0.297 mm). 2019 (Huang et al.).

2.3.1.3 EXTRUDED ACTIVATE CARBON (EAC)

Extruded Activated Carbon (EAC) is made of a binder and activated carbon powder that is fused and formed into cylindrical blocks with diameters ranging from 2 to 4 mm. It is primarily utilized for gas absorption and the recycling of organic solvents such as acetone, toluene, and xylene. This is required for recycling by the oil refining sector, gas stations, and oil refineries. They have highly active characteristics and highly developed surface area, better shape

uniformity, high hardness and low dust, and higher recycling rates. They can be applied in VOCs, gas phase absorption, odor removal, and treatment. (Acrochem., 2022).

2.3.1.4 BEAD ACTIVATED CARBON (BAC)

Highly spherical activated carbon known as BAC is produced from petroleum pitch. Small bead-shaped activated carbon with a diameter of 0.35 to 0.80 mm is known as bead activated carbon (Acrochem., 2022). It has a lower pressure drop and higher hardness, low dust, and a tiny appearance.

2.3.2 SOURCES OF GENERATING AC

Charcoal-containing carbon compounds are commonly referred to as "activated carbon," also known as "activated charcoal" or "activated coal." Because of its thin structure, AC has high adsorptive capabilities due to its pores' enlarged surface area (>1000 m2/g). Powder, granular,

and pellet are the three basic forms of carbon that are available. However, granular and powdered AC is most usually utilized (Tadda et al., 2016).

It was stated that the raw materials used for the synthesis of AC were inexpensive ones with high carbon concentrations and low inorganic contents. A variety of basic materials that could be utilized to make AC was discovered by numerous studies. Agro-industrial byproducts, which have low ash concentrations, are abundant, inexpensive, and renewably produced, they also have excellent mechanical strength. Studies have shown that agricultural wastes and biomass residues are used in the production of air conditioners. Examples include the use of palm shells, jujube seeds, coconut shells, tropical wood, rice husk as coal, sawdust, durian peel, corn cobs, walnut shells, watermelon, hazelnut shells tobacco stems, bean husks, banana peels, and many more (Fazal-ur-Rehman and Husk, 2018). Even non-agricultural items like used automobile tires were discovered to be inexpensive sources of air conditioning. The structure of the raw materials and the manufacturing techniques heavily influence the maximal adsorptive capacity of AC (Tadda et al., 2016).

2.3.3 METHODS OF GENERATING AC

The production of AC, which has been studied extensively, can be divided into four basic processes: pyrolysis (Jianzhong Zhu and Zhu, 2009); physical and chemical activation; carbonization; and steam/thermal activation. In the adsorption procedure for pollutant removal, the preparation of the adsorbent plays a vital role. Dehydration and carbonization are the procedures that are most frequently used for preparing an adsorbent. In the absence of air, the adsorbents are slowly heated to temperatures between 600°C and 800°C then, to open the pore

diameters the carbonized products are activated chemically or physically (Sulyman, Namiesnik, and Gierak, 2017).

In physically activated carbon, hot gases are used to transform the source material into the activated carbon substance. This is typically accomplished by using one or more carbonization processes to convert the organic precursor into primary carbon, which is a mixture of ash, amorphous carbon, tars, and crystalline carbon, and activation/oxidation, where the high temperature in the presence of carbon dioxide and steam is necessary. In chemical activation, the carbonized products are heated to between 450°C and 900°C before being washed with phosphoric acid (H3PO4), potassium hydroxide (KOH), sodium hydroxide (NaOH), or zinc chloride (ZnCl2) (Sahu and Singh, 2019)

2.3.3.1 PYROLYSIS PROCESS

Pyrolysis is the term for the thermochemical process that transforms organic material into gaseous or/and liquid fuels at extremely high temperatures without the presence of halogens (mostly oxygen). Pyrolysis is an irreversible simultaneous process that alters the chemical structure and physical state of materials.

The pyrolysis process is more frequently observed when materials are heated to higher temperatures. Temperature has a major impact on pyrolysis properties, followed by retention time, heating rate, and nitrogen flow rate. In most cases, increasing the reaction temperature causes a reduction in the production of AC and char, whereas increasing the pyrolysis temperature causes a reduction in the yield of solids and an increase in the output of gases and liquid fractions. On the other hand, raising the temperature raises ash and AC% while lowering

volatile matter. As a result, AC of higher quality is produced at higher temperatures. 2016 (Tadda et al).

2.3.3.2 PHYSICAL ACTIVATION PROCESS

There are two steps involved in physical activation. Carbonaceous materials must first be carbonized before the char is activated at high temperatures while being exposed to CO2, steam, air, or three mixes acting as oxidizing gases. CO2 is typically employed as an activation gas because it is simple to handle, hygienic, and has a slow response rate at a temperature of about 800°C. This property makes it easier to manage the activation process. It was discovered that the carbonization temperature ranged between 400°C and 850°C, while it might occasionally reach 1000°C, and the activation temperature ranged between 600°C and 900°C. The AC made by the physical activation process has some shortcomings that make it unsuitable for use as a filter or an adsorbent. Several agricultural biomass residues, including mango pits, rice husks, rice hulls, sawdust, sunflower shells, corncobs, olive pits, pine cones, wood scraps, corn hulls, cotton residues, oak, tobacco stems, corn Stover, coconut coir pith, almond shells, and peanut hulls, can be used for physical activation (Do and Words-coal, 1996). (Tadda et al., 2016).

2.3.3.3 CHEMICAL ACTIVATION PROCESS

The precursor is mixed with the chemical activating agents in the form of oxidants and dehydrates through several simultaneous steps of the chemical activation process. Even while concerns about environmental protection may restrict the use of chemical activators, activation and carbonization performed concurrently during the chemical activation process at lower

temperatures leads to superior porosity architectures of AC. Additionally, phosphoric acid (H3PO4), potassium hydroxide (KOH), Phosphorus trioxide (P4O6), zinc chloride (ZnCl2), and potassium carbonate (K2CO3) are among the substances that are frequently utilized as activation agents. In addition, the agricultural wastes that are being decreased by the aforementioned chemicals include rice husks, rice straw, cassava peel, hazelnut shells, maize cobs, olive seed, peanut hulls, pecan shells, almond shells, and coconut shells (Do and Words-coal, 1996). (Tadda et al., 2016).

2.3.3.4 STEAM PYROLYSIS

In this process, the raw agricultural waste materials are either heated at a lower temperature range of 500–700 °C under a flowing stream of pure steam or heated at a higher temperature range of 700–800 °C under a flowing stream of steam. Numerous types of agricultural waste biomass, including rice husk, jujube seed, sawdust, tropical wood waste, palm shells, durian peel, maize cobs, coconut shells, tobacco stems, hazelnut shell, banana peel, and mangosteen shells, have been effectively processed using steam pyrolysis (Tadda et al., 2016). However, it was generally reported that AC produced by steam pyrolysis was less efficient, except those produced from cherry stones, apricot, and almond shell (Budinova et al., 2006).

2.3.4 FACTORS AFFECTING AC PRODUCTIONS

The following are the variables that influence the production of activated carbon.

2.3.4.1 TEMPERATURE

The activation temperature is a key factor in determining how the AC is formed and how it will behave. According to research, the surface area and production yield of AC are significantly influenced by the activation temperature. The temperature of activation ranges from 200 to 1100 °C. However, prior research claimed that a temperature range of 400 to 500°C should be taken into account for a variety of raw materials, regardless of the time required and the impregnation ratio. As a result, raising the activation temperature always reduces the amount of AC produced, which simultaneously raises the amount of volatile chemicals emitted.

2.3.4.2 RAW MATERIALS

The parameters below can be taken into account to create a porous carbon structure.

1. High carbon content
2. Low inorganic content (i.e., low ash)
3. The potential extent of activation
4. Low degradation upon storage
5. High density and sufficient volatile content
6. Stability of supply in the countries
7. Inexpensive materials.

Obtaining materials with low inorganic content is crucial if AC with low ash content is to be produced. A moderately high volatile content is necessary for complete control of the production process. The most popular raw materials are fruit stones and coconut shells. This may be due to

their relatively high density, volatile content, and hardness, which make them best suited for the formation of hard GAC (Tadda et al., 2016).

The table below shows the characteristics of some raw materials used in AC production.

Raw material	Carbon (mass %)	Volatiles (mass %)	Density (cm^3g^{-1})	Ash (mass %)	Texture of AC
Soft wood	40 – 45	55 – 60	0.4 – 0.5	0.3 – 1.1	Soft, large-pore volume
Hard wood	40 – 42	55 – 60	0.55 – 0.8	0.3 – 1.2	Soft, large-pore volume
Lignin	35 – 40	58 – 60	0.3 – 0.4	-	Soft, large-pore volume
Nutshells	40 – 45	55 – 60	1.40	-	Hard, large micro-pore volume
Lignite	55 – 70	25 – 40	1.0 – 1.35	5 – 6	Hard, small-pore volume
Soft coal	65 – 80	20 – 30	1.25 – 1.5	2 – 12	Medium-hard, medium-pore volume
Petroleum coke	70 – 85	15 – 20	1.35	0.5 – 0.7	Medium-hard, medium-pore volume
Semi-hard coal	70 – 75	10 – 15	1.45	5 – 15	Hard, large-pore volume
Hard coal	85 – 95	5 – 15	1.5 – 1.8	2 – 15	Hard, large-pore volume

2.3.4.3 ACTIVATION TIME

In addition to the activation temperature, the activation time has a bigger impact on the characteristics of AC as well as the carbonization process. A few decades ago, it was determined that the typical activation times for palm fruit bunches, banana peels, and coconut shells ranged from one to three hours (Tadda et al., 2016).

2.4 ADSORPTION THEORY

Adsorption is the accumulation of any material that results in a larger concentration of molecular species on the surface of another substance than in the bulk. When a gas or liquid is introduced to a solid surface, molecules from the gas or the solution phase gather or concentrate there.

Adsorption is the process of a gas or liquid's molecules gathering at a solid surface. For the treatment of domestic and industrial effluents, "adsorption" is a tried-and-true and effective method. The most popular technique for treating water is "adsorption" on the surface of activated carbon. Adsorbates are affixed to the surface of the adsorbent as films. A substance used for adsorption is known as an adsorbent (Sahu and Singh, 2019).

2.4.1 MECHANISM OF ADSORPTION

The surface particles of the adsorbent are not in the same environment as the bulk-level particles, which leads to adsorption. All of the forces between the particles inside the adsorbent are equal and balanced, but on the surface, where the particles are not surrounded by other particles of the same sort, they are subject to residual or unequal attractive forces. Particles from the adsorbate are drawn to their surface by these adsorbent forces. The amount of adsorption rises with an increase in the surface area of the adsorbent per unit mass at a particular temperature and pressure. Another crucial component of adsorption is heat of adsorption. Surface residual forces, or surface energy, which is visible as heat, constantly diminish after adsorption. The reaction of adsorption is always exothermic, in other words, the ΔH of adsorption is always negative. The molecules' ability to move freely is constrained when a gas is adsorbed. This corresponds to a decrease in the entropy of the gas following adsorption, i.e., ΔS is negative. Thus, the enthalpy and entropy of the system both drop in response to adsorption.

Adsorption has several benefits, including low space requirements for batch and continuous fixed bed systems, ease of design and operation, no water pollution, no odor emissions, and low cost of the adsorbent (Pan et al., 2019). Physical adsorption and chemical adsorption are the two

main categories of the adsorption process. Physical adsorption is achieved by Van der Waals forces, dipole interactions, and hydrogen binding. There is no electron exchange between adsorbent and adsorbate, since there is no activation energy required for physical adsorption, the time needed to reach equilibrium is very short. The process of physical adsorption is non-specific and reversible. While Chemical bonds can be either covalent or ionic, chemical adsorption results from the chemical link between adsorbent and adsorbate molecules. Weak chemical adsorption refers to the covalent link between the adsorbent and adsorbate, and strong chemical adsorption refers to the ionic bond.

The following four processes are used to explain how the adsorbate molecules move from the bulk liquid phase into the solid (adsorbent) phase:

- The mass transfer of the adsorbate molecules across the external boundary layer toward the solid particle.
- Adsorbate molecules are transported from the particle surface into the active sites by diffusion within the pore-filled liquid and migrate along the solid surface of the pore.
- Solute molecule adsorption on the active sites on the interior surfaces of the pores.
- The molecule gets approached inside the pores of the adsorbent as presented by

2.5 RESPONSE SURFACE METHODOLOGY

Instead of the traditional one-factor-at-a-time trial, which is time-consuming, a computational framework of experiments is utilized to explore the human and interaction influence of the specified effluent parameters on the chosen answers (Uwadiae and Ihaza, 2018). To overcome the conventional one–factor–at–a–time trial, the use of multivariate statistical methods can be used

to optimize methodological procedures. The objective of using RSM is to simultaneously optimize the levels of these process variables, the process parameters are to attain the best system performance. Experimental design is a specific set of experiments defined by a matrix composed of the different level combinations of the variables studied (E.g Box–Behnken). This design defines a specific set of combinations for the levels of variables that must be applied experimentally to obtain the responses. Factors or independent variables are experimental variables that can be changed independently of each other <overview of rsm>. In this experiment, the independent variables are dye concentration (mg/l), adsorbent dosage (mg/l), and contact time (minutes). Levels of a variable are different values of a variable at which the experiments must be carried out. The variable Adsorbent dosage, for example, 1g, 3g, and 5g can be investigated at three levels. Responses or dependent variables are the measured values of the results from experiments.

2.6 REVIEW OF EXPERIMENTAL DESIGN IN ANALYTICAL CHEMISTRY

2.6.1 FACTORIAL DESIGNS

Factorial design is an experimental matrix that has limited application in RSM when the factor number is higher than 2 because of the number of experiments required for this design (calculated by expression $N=2^k$, where N is the experiment number and k is the factor number). However, for two variables, the efficiency is comparable with designs such as central composite(Almeida *et al.*, 2008).

Advantages of factorial design experiment

- Factorial designs are used primarily for screening significant factors, but can also be used sequentially to model and refine a process.
- The full factorial experiment is more efficient than one factor-at-a-time experiment because they compare 2 or more factors simultaneously to give responses
- They provide more information at a lower or similar cost to experiment
- Using factorial designs, test a factor against other factors at 2 levels

Disadvantages

- It can only 2 levels for each factor selected in experimenting
- A factorial design has to be planned carefully without any error
- The designs can be misleading when significant two-factor interactions affect the response.

2.6.2 BOX-BEHNKEN DESIGN

Box-Behnken designs are used to generate higher-order response surfaces using fewer required runs than a normal factorial technique. These designs are more efficient and economical than their corresponding 3^k designs, mainly for a large number of variables. In Box–Behnken designs, the experimental points are located on a hypersphere equidistant from the central point. Its principal characteristics are:

- It requires an experiment number according to $N=2k(k-1) + c_p$, where k is the number of factors and (c_p) is the number of the central points;

- All factor levels have to be adjusted only at three levels (−1, 0, +1) with equally spaced intervals between these levels. This experimental design has been applied for the optimization of several chemical and physical processes; however, its application in analytical chemistry is still much smaller in comparison with central composite design(Almeida *et al.*, 2008).

Advantages of Box Behnken Design

- This design is more practical for three-level factorial designs providing a better model of the response variable in the experimental space
- It is used for more than 4 -7 factors required in the experiment
- It tests each factor in combination with other central fixed value factors in a block
- It generates higher-order response surfaces using fewer required runs than the normal factorial technique

Disadvantages of Box Behnken Design

- It has fewer design points than CCD, making it relatively less efficient
- It cannot be used in extreme conditions to get better information
- It only considers the middle point of a design, giving it less leverage to fit the model(Ferreira *et al.*, 2007).

2.6.3 CENTRAL COMPOSITE DESIGN

Box and Wilson introduced the central composite (CC) concept. This design consists of the following parts:

- A full factorial or fractional factorial design
- An additional design, often a star design in which experimental points are at a distance from its center
- A central point.

The Central Composite has three types of designs: circumscribed (CCC), face-centered (CCF), and inscribed (CCI).

Full uniformly routable central composite designs present the following characteristics:

A. require an experiment number according to $N=k2+2k+cp$, where k is the factor number and (cp) is the replicate number of the central point;
B. α-values depend on the number of variables and can be calculated by $\alpha=2(k-p)/4$. For two, three, and four variables, they are, respectively, 1.41, 1.68, and 2.00;
C. all factors are studied in five levels ($-\alpha, -1, 0, +1, +\alpha$).

Advantages of central composite design

- This design is more practical for three-level factorial designs providing a better model of the response variable in the experimental domain, and also outside the boundary of the design
- Each factor requires five levels per factor
- This design makes it possible to leave the boundary of the design

- It is very efficient to get higher surface responses

Disadvantages of central composite design

- The trials of the experiment become too many to carry out
- It is more costly to experiment with this design
- It is almost as time taking as the one-at-a-time factor (OATF) experiment

A. (Ahmad, Syahidah and Bello, 2015)(Rakic and Stojanovic, 2014).

Response surface methodology has been proven to be very effective for optimizing multivariable systems using statistically produced research. Box–Behnken design (BBD) has been used in this study to find the best combination of adsorbent dosage, contact time, and dye concentration to obtain the optimal removal of dye from an aqueous solution. Table - displays the parameter ranges for the variables that were optimized. Using Design Expert 7.0.0 (Almeida et al., 2008), the 17-run experimental design was created (Kleijnen, no date). Based on preliminary trials, the levels of the independent variables as displayed in Table - were chosen.

Table 2.3 Experimental range and levels of independent variables

Independent variables	Symbols	Coded and Actual levels		
		Low (-1)	Middle (0)	High (1)
Dye Concentration (mg/l)	X_1	50	125	200

Adsorbent Dosage (g/l)	X_2	0.1	0.55	1
Contact time (minutes)	X_3	10	35	60

CHARPTER THREE

MATERIALS AND METHODS

3.1 MATERIALS

Activated carbon used in this study was prepared from waste coconut shells obtained from Oka Community in Benin City, while the Methylene blue was purchased from Luco Chemical Laboratory Limited in Edo state Nigeria. Other materials used for this study include;

- Phosphoric acid
- Carbonaceous material (Coconut shells)
- Distilled water
- Iodine pellets

- Hydrochloric acid
- Tetra-oxo-sulphate (xi) acid
- Sodium thiosulphate
- Starch solution
- Methylene blue dye
- Filter paper

3.2 EQUIPMENTS

- Furnace crucibles
- Muffle furnace
- Crucibles
- Petri dish(s)
- PH meter
- Orbital shaker
- Measuring cylinder
- Conical flask with stopper
- Mesh sieve
- Dropper

- Electric weighing balance
- Drying oven
- Mortar and piston
- Centrifuge
- UV-Vis spectrophotometer

3.3 METHODOLOGY

3.3.1 Sample Collection and Pretreatment

Coconut shells agricultural waste is used for this study due to its high carbon content, easy availability, low ash content, and good mechanical strength. Coconut shells were obtained from Oka Community in Benin City.

3.3.2 Preparation of Activated Carbon

The coconut shells were collected and then cut into small pieces, followed by washing with water to remove the dust particles that adhered to the surface. Then the material was dried in sunlight for about 2 days. Later the dried material was kept inside the oven for 5 hours at 80°C to remove the moisture content. The precursor (dried coconut shells) was carbonized at 600°C for 1 hour in the absence of air in a muffle furnace. After carbonization, the burnt coconut shells turned to charcoal (char) and were ground using a mortal and piston and sieved to sizes of approximately 0.5 mm. Chemical activation was adopted to develop the pore structures and surface area by using Phosphoric acid (H3PO4). 250g of the carbonized sample was activated in 500 ml of 3M H3PO4 for 24 hours. The prepared sample was then washed several times with distilled water to obtain activated carbon of almost neutral pH (6.5-7.0) followed by heating in

an oven at 110º C. The sample was weighed and sent for characterization and batch studies were carried out.

3.4 CHARACTERIZATION OF ACTIVATED CARBON

3.4.1 Proximate Analysis:

Proximate analysis is a method used to determine the distribution of products when the samples are heated under specific conditions. A typical proximate analysis includes moisture content, ash content, volatile matter, and fixed carbon content.

3.4.2 Moisture content:

2g of activated carbon sample (coconut shell) was placed in a petri dish. On the dish, it was nicely spread. Then, it was heated in an oven at 105º C for 1.5 hours. The petri dish was not covered or kept closed while being heated. The petri dish was heated, then taken out and allowed to cool in a desiccator. The dried product's weight was determined after cooling. The sample's moisture content is defined as the weight difference expressed as a percentage.

Moisture content $M=100(B-F)/(B-G)$

B = weight of petri dish +original sample

F = weight of Petri dish+ dried sample

G = weight of petri dish

3.4.3 Volatile matter content:

A small quantity of the sample was collected in a cylindrical closed crucible. It was then subjected to a precise 7-minute 925°C heating in a muffle furnace. Then the crucible was cooled in a desiccator and weighed.

Volatile matter on a dry basis

$$VM=100[100(B-F)-M(B-G)]/[(B-G)\ (100-M)]$$

B=Mass of crucible, lid, and sample before heating

F=Mass of crucible, lid, and contents after heating

G=Mass of empty crucible & lid

M=% of moistures determined above

3.4.4 Ash content:

A small quantity of the sample was collected in a silica crucible. It was heated in a muffle furnace to 750˚C for 1.5hr. During this heating process, the crucible was left open. After the required heating, the crucible was cooled in a desiccator and then the weight of the ash was measured.

Ash content $A=100(F-G)/(B-G)$

G=Mass of empty crucible

B=Mass of crucible + sample

F=Mass of crucible+ ash sample

3.4.5 Fixed carbon:

Fixed carbon is a calculated value and it is the resultant of the summation of percentage moisture, ash, and volatile matter subtracted from 100.

Fixed carbon (%) = 100 – (moisture, % + ash, % + volatile matter, %)

3.4.6 Bulk Density:

Bulk density is defined as the weight of a material per unit volume. It mostly uses materials in powder form. This bulk density test gauges the sample's flow quality and packing capacity. The unit of measurement is kilograms per cubic meter (kg/m3).

The mass of the measuring cylinder used for this experiment was determined first, then the given sample of activated carbon was placed into this cylinder and reweighed. Then it was transferred into a petri dish and then oven-dried at a temperature of 110˚C for 60mins. After drying the weight of the dry sample was measured.

DB= (m2- m1)/v

M1= mass of measuring cylinder in grams

M2= mass of measuring cylinder + its contents

V= volume of the measuring cylinder in liter

3.4.7 pH:

The ASTMD 3838-80 standard method was used to calculate pH. 100ml of distilled water and 1g of coconut shell activated carbon was added to a conical flask, then the mixture was stirred for 1 hour. A pH meter was used to take the readings of the pH of the activated carbon.

3.4.8 IODINE VALUE/SURFACE AREA DETERMINATION

The iodine value is the amount of iodine that 1 gram of activated carbon may absorb from a standard 0.1N iodine solution when the equilibrium iodine concentration is precisely 0.02N. The amount of micropores in the activated carbon is determined by the iodine number. The sample has more microporosity when the iodine number is higher.

The standard method for determining the iodine number of activated carbon is provided in ASTMD4607-94(2006).

PROCEDURE

1g of dried activated carbon was mixed with 10 ml of 5% by weight of hydrochloric acid in a conical flask. The activated carbon was wetted after swirling the nit. The conical flask was heated for 30 seconds not directly but by placing it on a hot plate. After being cooled to room temperature, the flask's contents were added along with 100ml of 0.1N iodine solution. The flask was shaken vigorously for 30 secs and then its contents were filtered through a filter paper. 20 to 30 ml of the filtrate were initially discarded and the remaining filtrate was collected in a clean beaker. 50 ml of this filtrate was then titrated against a 0.1 N sodium thiosulphate solution until the yellow color just disappeared. Then 1 ml of starch solution was added, and the titration was continued until the blue color completely disappeared.

The iodine value is determined using the relation

Iodine value (iv) = 12.69(B-S) N / W

12.69 = milli-equivalence of iodine * 100 to adjust for percentage

B = volume of thiosulphate used for blank solution

S = volume of thiosulphate used for sample-free aliquot

W = weight of the sample

N = concentration of sodium thiosulfate

3.5 PREPARATION of AQUEOUS SOLUTION OF METHYLENE

3g of methylene blue were dissolved in 1000 ml of distilled water to create the methylene blue solution, it was vigorously shaken for five minutes to ensure thorough dissolution and homogeneity. This makes the stock solution of concentration 1000 mg/L.

Different concentrations were prepared by serial dilution. The effects of dye concentration, contact time, and adsorbent dose were studied using a batch adsorption method.

3.6 BATCH EXPERIMENTAL STUDIES

The batch experimental studies were conducted by mixing 100 ml of methylene blue with varying initial concentrations. The batch experimental studies were conducted by mixing 100 ml of methylene blue at different contact times (10-60 mins), adsorbent dosage (0.1-1 g/100ml), and initial dye concentrations (50-200 mg/l) in a set of 250 ml flasks. The different combinations resulted in 17 batches of experimental runs as determined by the design of the experiment using

design expert software. The mixture was agitated with the orbital shaker maintaining a speed of 150 rpm at room temperature on reaching equilibrium conditions the mixture was filtered using a membrane filter and the filtrate was analyzed for the extent of dye removal using a UV-Vis spectrophotometer at an absorbance of 730nm.

The amounts of dye adsorbed at equilibrium q_e and at time qt, and the percentage removal of methylene blue (%MB) was calculated using the following equations

$$qe\ (mg/g) = \frac{(C_o - C_e)V}{M} \quad (1)$$

$$qt\ (mg/g) = \frac{(C_o - Ct\ ))V}{M} \quad (2)$$

$$\%\ (MB) = \frac{(C_o - C_e)}{C_o} \times 100 \quad (3)$$

Where q_e is the amount of dye adsorbed at equilibrium (mg/g), qt is the amount of dye adsorbed at time t. C_o and C_e are the initial and equilibrium liquid-phase concentrations of dye (mg/g), respectively. V is the volume of the solution, and m is the weight of the sorbent used (g).

Figure 3.1: Orbital shaker agitating MB samples

Figure 3.2: Using membrane filter for filtering MB solution at equilibrium.

Figure 3.3: The UV-Vis spectrophotometer

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 CHARACTERISTICS OF CHEMICALLY ACTIVATED CARBON

Table 4.1: Results of chemically activated carbon

PROPERTY OF AC	RESULT
Moisture content (%) dry basis	4.31
Volatile matter content (%)	6.8
Ash content (%)	1.4
Fixed carbon (%)	87.5
Bulk Density (g/ml)	0.62
Ph	7.12
Iodine value/surface area (m^2/g)	780

4.2 DESIGN OF EXPERIMENTS

The design of experiments comprising the studied factors, their ranges, and the response (dye removal efficiency) is presented in Table 4.2. The response in terms of dye removal efficiency was in the range of 14.7 % to 82 %

Table 4.2: Three-level factorial Box–Behnken design matrix and the experimental responses.

STD	RUN	Factor 1 A: Dye Conc. (mg/l)	Factor 2 B: Adsorbent Dosage (g/100ml)	Factor 3 C: Contact time (minutes)	Response Dye Removed (%)
6	1	200	0.55	10	20.0157
3	2	50	1	35	25.5388
13	3	125	0.55	35	82.1418
8	4	200	0.55	60	46.5214
16	5	125	0.55	35	73.6037
9	6	125	0.1	10	46.7721
7	7	50	0.55	60	23.1509
10	8	125	1	10	59.2807
14	9	125	0.55	35	72.1418
5	10	50	0.55	10	24.1061
15	11	125	0.55	35	72.1418
17	12	125	0.55	35	72.1418
11	13	125	0.1	60	67.1591
4	14	200	1	35	59.5916
1	15	50	0.1	35	30.7174
12	16	125	1	60	64.6756
2	17	200	0.1	35	14.6756

The experimental data were analyzed using BBD and the final empirical model equations showing the relationship between the adsorption process variables and the response was developed as shown in the equation below

Percent Dye Removal =

-42.76551

+1.34828	Dye Conc (A)
+8.37851	Adsorbent Dosage (B)
+1.05432	Contact Time (C)
+0.371071	Dye Conc * Adsorbent Dosage (AB)
+0.003661	Dye Conc * Contact Time (AC)
-0.333158	Adsorbent Dosage * Contact Time (BC)
-0.006473	Dye Conc^2 (A^2)
-26.61720	Adsorbent Dosage^2 (B^2)
-0.015316	Contact Time^2 (C^2)

The developed polynomial model equation shows that the dye conc (A), adsorbent dosage (B), and contact time (C) have a positive influence on the removal of dye from the aqueous dye solution onto the activated carbon from the coconut shell. It also reveals that the interactions of the dye conc and adsorbent dosage (AB), and dye conc and contact time (AC) have a positive influence on the absorbance. Of all the terms in the model, only BC and B^2 have a negative influence on the adsorption of dye on the activated carbon. The adequacy and significance of the

developed model were evaluated using the F-test and analysis of variance (ANOVA) as shown in Table 4.4. From the Table, the terms A, B, C, AB, AC, A^2, and C^2 were found to be the significant model terms while BC and B^2 were insignificant for the dye removal model. A good correlation existed between the experimental and predicted data with the **Predicted R^2** of 0.7720 which is in reasonable agreement with the **Adjusted R^2** of 0.9485; i.e., the difference is less than 0.2. This shows that the developed model is reliable.

4.3 Fit summary

Table 4.3: Response 1. Percent Dye Removal

Source	**Sequential p-value**	**Lack of Fit p-value**	**Adjusted R^2**	**Predicted R^2**	
Linear	0.7072	0.0012	-0.1099	-0.5385	
2FI	0.7289	0.0008	-0.2744	-1.6402	
Quadratic	**< 0.0001**	**0.2645**	**0.9485**	**0.7720**	**Suggested**
Cubic	0.2645		0.9633		**Aliased**

4.4 ANOVA for Quadratic model

Table 4.4: Response 1. Percent Dye Removal

Source	**Sum of**	**df**	**Mean**	**F-value**	**p-value**	

	Squares		**Square**			
Model	8092.32	9	899.15	33.76	< 0.0001	Significant
A-Dye Conc	173.83	1	173.83	6.53	0.0378	
B-Adsorbent Dosage	309.54	1	309.54	11.62	0.0113	
C-Contact Time	329.38	1	329.38	12.37	0.0098	
AB	627.37	1	627.37	23.56	0.0018	
AC	188.52	1	188.52	7.08	0.0324	
BC	56.19	1	56.19	2.11	0.1897	
A^2	5582.87	1	5582.87	209.63	< 0.0001	
B^2	122.32	1	122.32	4.59	0.0693	
C^2	385.81	1	385.81	14.49	0.0067	
Residual	186.42	7	26.63			
Lack of Fit	110.56	3	36.85	1.94	0.2645	not significant
Pure Error	75.86	4	18.97			

Factor coding is **Coded**.

Sum of squares is **Type III - Partial**

The **Model F-value** of 33.76 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case, A, B, C, AB, AC, A^2, and C^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The **Lack of Fit F-value** of 1.94 implies the Lack of Fit is not significant relative to the pure error. There is a 26.45% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Table 4.5: Fit statistics

Std. Dev.	5.16	**R^2**	0.9775
Mean	50.26	**Adjusted R^2**	0.9485
C.V. %	10.27	**Predicted R^2**	0.7720
		Adequate Precision	14.1197

The **Predicted R^2** of 0.7720 is in reasonable agreement with the **Adjusted R^2** of 0.9485; i.e. the difference is less than 0.2.

Adeq Precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. Your ratio of 14.120 indicates an adequate signal. This model can be used to navigate the design space.

Table 4.6: Final equations in terms of coded values

Percent	=

Dye Removal	
+74.43	
+4.66	A
+6.22	B
+6.42	C
+12.52	AB
+6.87	AC
-3.75	BC
-36.41	A^2
-5.39	B^2
-9.57	C^2

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

4.5 Response Surface Plots

Figure 4.1: Response surface plot showing the effect of dye conc and adsorbent dosage on dye removal

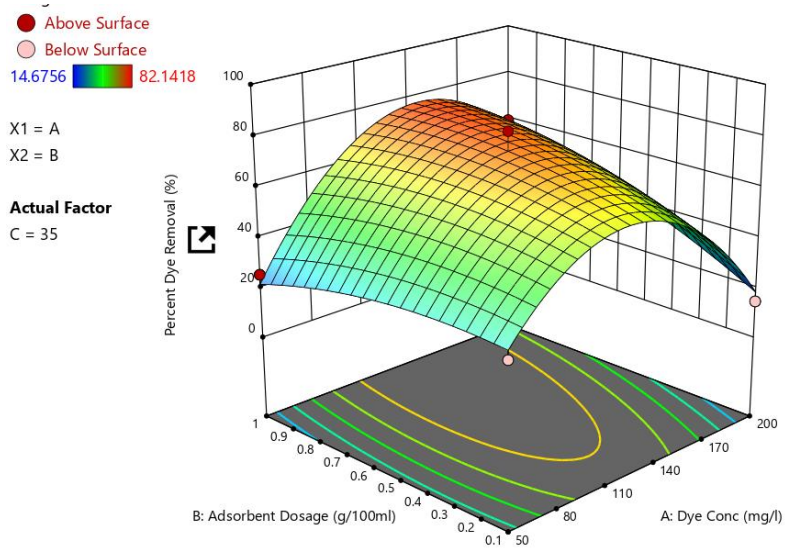


Figure 4.1 shows that the percentage dye removal of MB increased with decreasing dye concentration (200-130 mg/l) to an optimum of about 80% and subsequently decreased to 20% while increasing the adsorbent dosage (0.1-0.55 g/100ml) of activated carbon. This can be attributed to the aggregation of the adsorbent due to its increasing amount, and therefore decreasing the surface area (active sites) of contact between the adsorbate and adsorbent. There was a high statistical influence of adsorbent dosage on MB compared to dye conc. This is also corroborated by the fact that adsorbent dosage had a much smaller p-value (0.0113) than dye conc (0.0378).

Figure 4.2: Response surface plot showing the effect of dye conc and contact time on dye removal

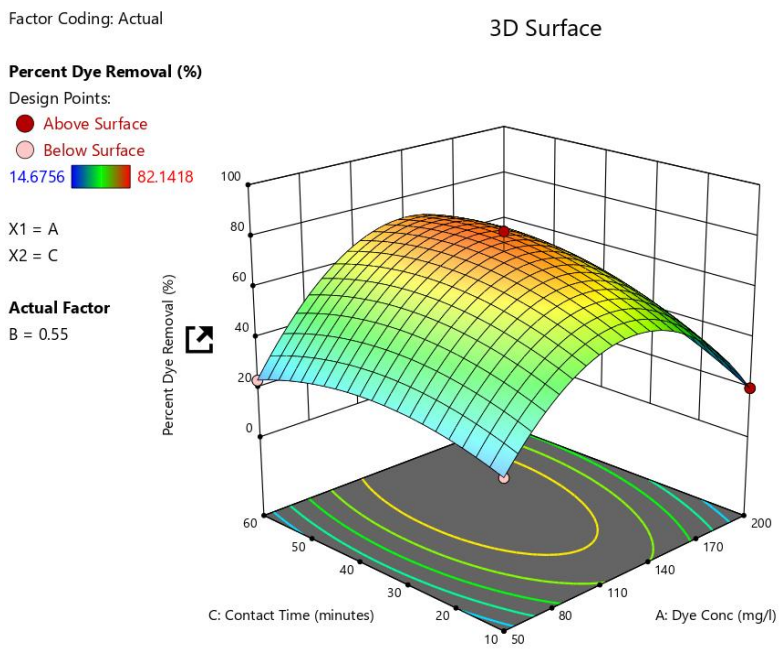


Figure 4.2 shows that the percentage of dye removal of MB increased with decreasing dye concentration (200- 130 mg/l) to an optimum of about 80% and subsequently decreased to 20% while increasing the contact time (10-35 mins) of activated carbon. The decrease in percentage removal of MB can also be attributed to the fact that an increase in contact time between the adsorbate and adsorbent can only be effective for dye percentage removal when there are enough active sites available for the adsorption, but with aggregation of the adsorbent continuous increase of contact, time will only result in a decrease of the percentage removal of MB from the aqueous dye solution. There was a high statistical influence of contact time on MB compared to dye conc. This is also corroborated by the fact that contact time had a much smaller p-value (0.0098) than dye conc (0.0378).

Figure 4.3: Response surface plot showing the effect of adsorbent dosage and contact time on dye removal.

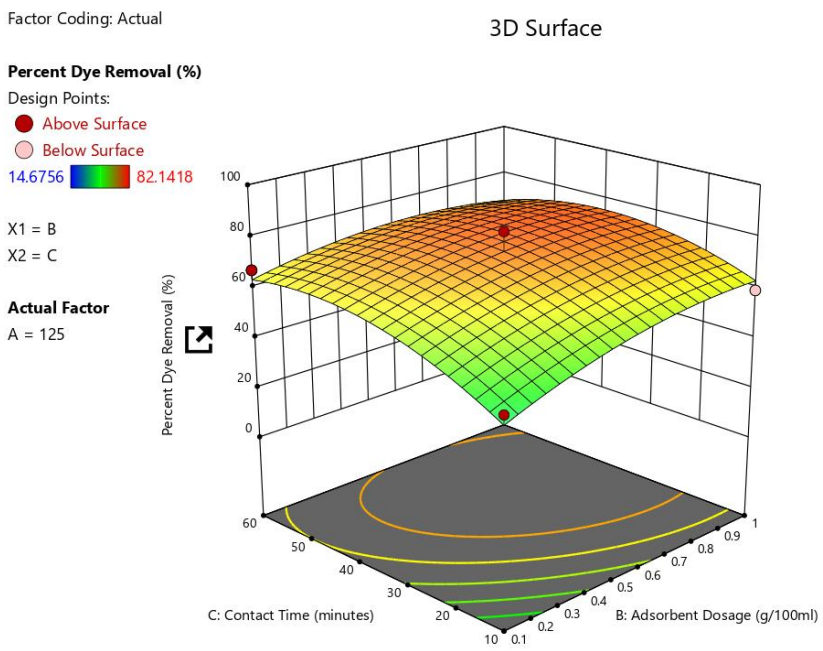


Figure 4.3 shows that the percentage of dye removal of MB increases with increasing adsorbent dosage (from 0.1-0.55 g/100ml) and increasing contact time (10-35 mins) resulting in an optimum of about 80% of dye removal. This can be attributed to the increase in surface area and the number of active sites, but with further increase in adsorbent dosage (0.55-1 g/100ml) and contact time (35-60 mins), there was an observed fall in the percentage removal (from about 80% -60%) of dye due to an increase in adsorbent dosage beyond maximum adsorption capacity which might be as a result of the overlapping of the adsorption sites due to aggregation of adsorbent particles beyond the optimum dose. It is also seen that there was a high statistical influence of contact time on MB compared to adsorbent dosage. This is also corroborated by the fact that contact time had a much smaller p-value (0.0098) than adsorbent dosage (0.0113).

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

The activated carbon prepared from coconut shells showed significant adsorption capacity for the removal of dyes from aqueous dye solution (textile effluent) under suitable experimental conditions. The process was optimized, and the maximum dye removal of 82 % was achieved at optimum conditions of 125 mg/l for dye conc, 0.55g/100ml for adsorbent dosage, and 35 mins for contact time respectively. The ANOVA response shows the reliability of the data with a good

Adjusted R^2 of 0.9485 with the **Predicted R^2** of 0.7720. It was also observed that the adsorption capacity of the coconut shells depends greatly on the conditions of adsorbent dose and contact time with small p-values of 0.0098 and 0.0113 for contact time and adsorbent dosage respectively. Coconut shell is readily available at negligible cost and hence will serve as a useful low-cost and environmentally benign adsorbent. The result will be useful for designing and fabricating an economically cheap treatment process plant for the removal of dyes from industrial effluents.

5.2 RECOMMENDATIONS

- The manufacturing of locally generated activated carbon should be carried out under favorable and desired conditions such as the temperature of carbonation so as to obtain activated carbon within the required specification.
- Future studies should concentrate on improving the quality of activated carbon made from coconut shells by adjusting the reagent type and concentration to meet industrial specifications.

- Activated carbon should be ground in a way to obtain particles of the required mesh size for the desired adsorption.
- When analyzing experiment results, caution should be taken because errors might occur and can generate noise when performing an ANOVA and fitting a response model.
- Textile industries should apply extra wastewater treatment techniques that take advantage of activated carbon's adsorptive capacity.

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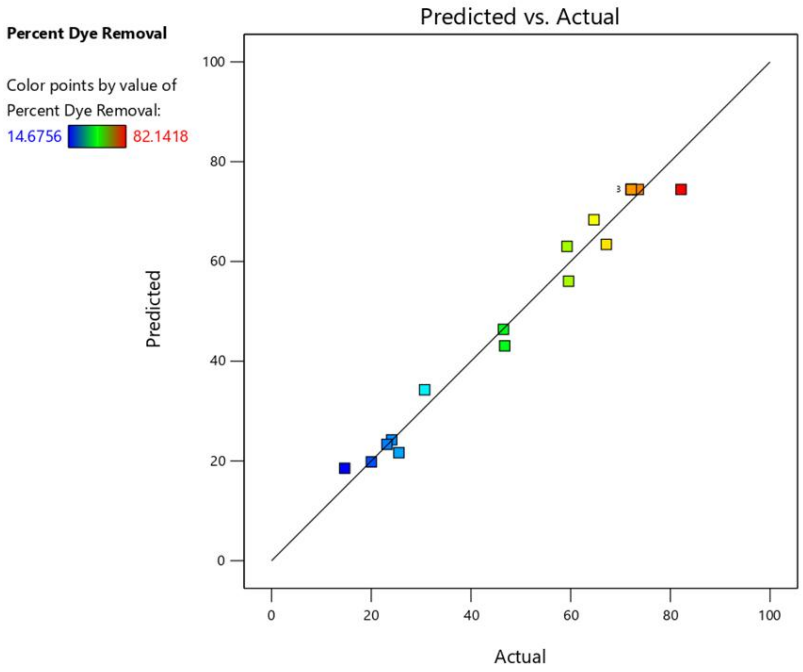
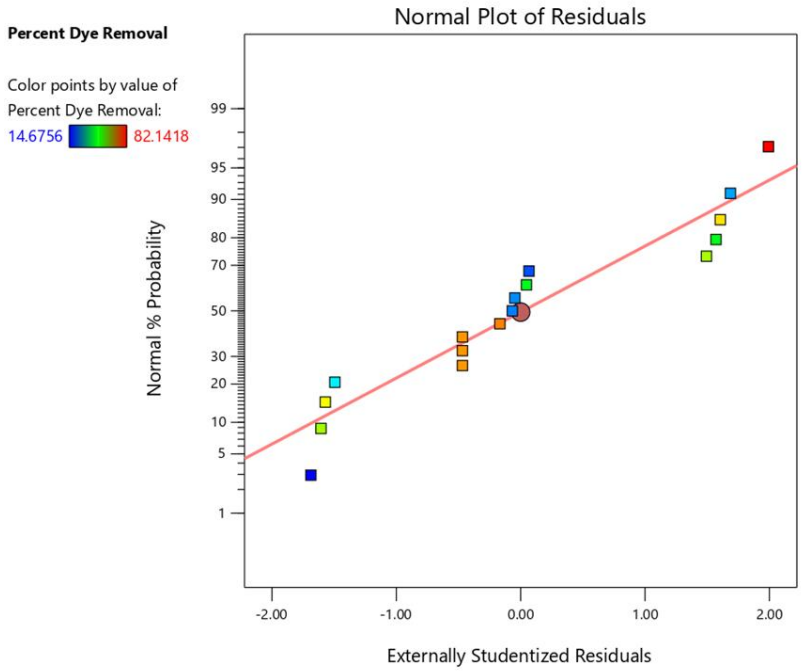
APPENDIX

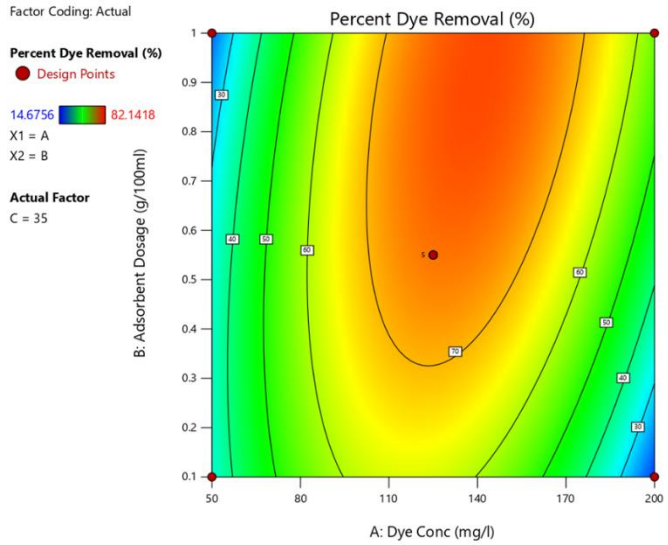


Predicted vs Actual plot for methylene blue removal

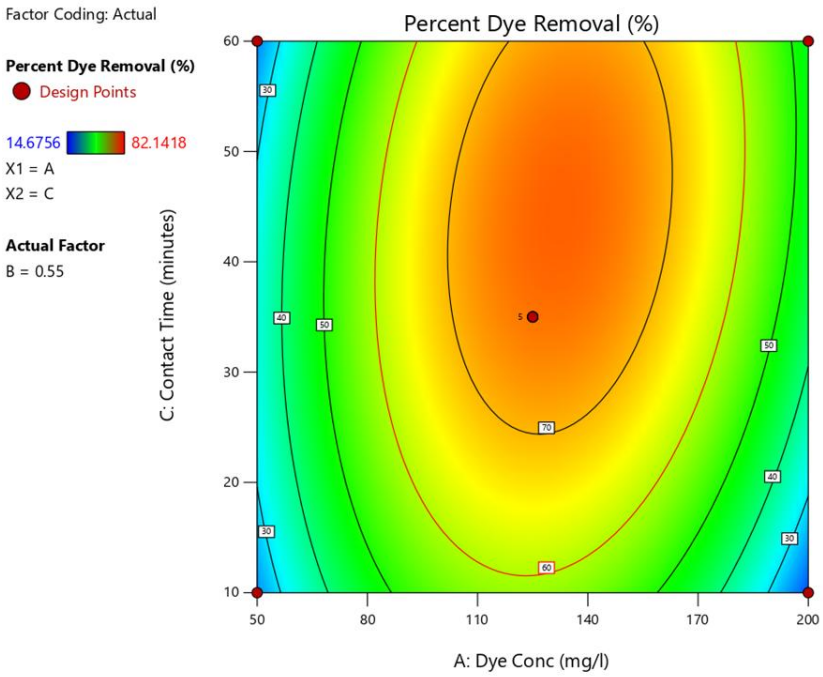


Normal plot of residuals

Contour

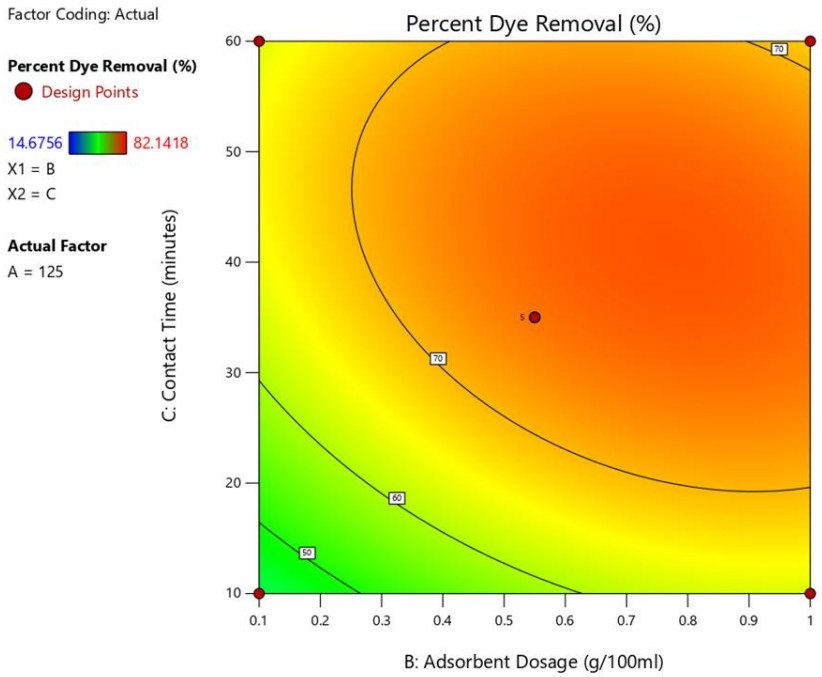


Response surface plot showing predicted percentage removal of methylene blue as a function of dye conc and contact time with fixed adsorbent dosage of 0.55 g/ml.

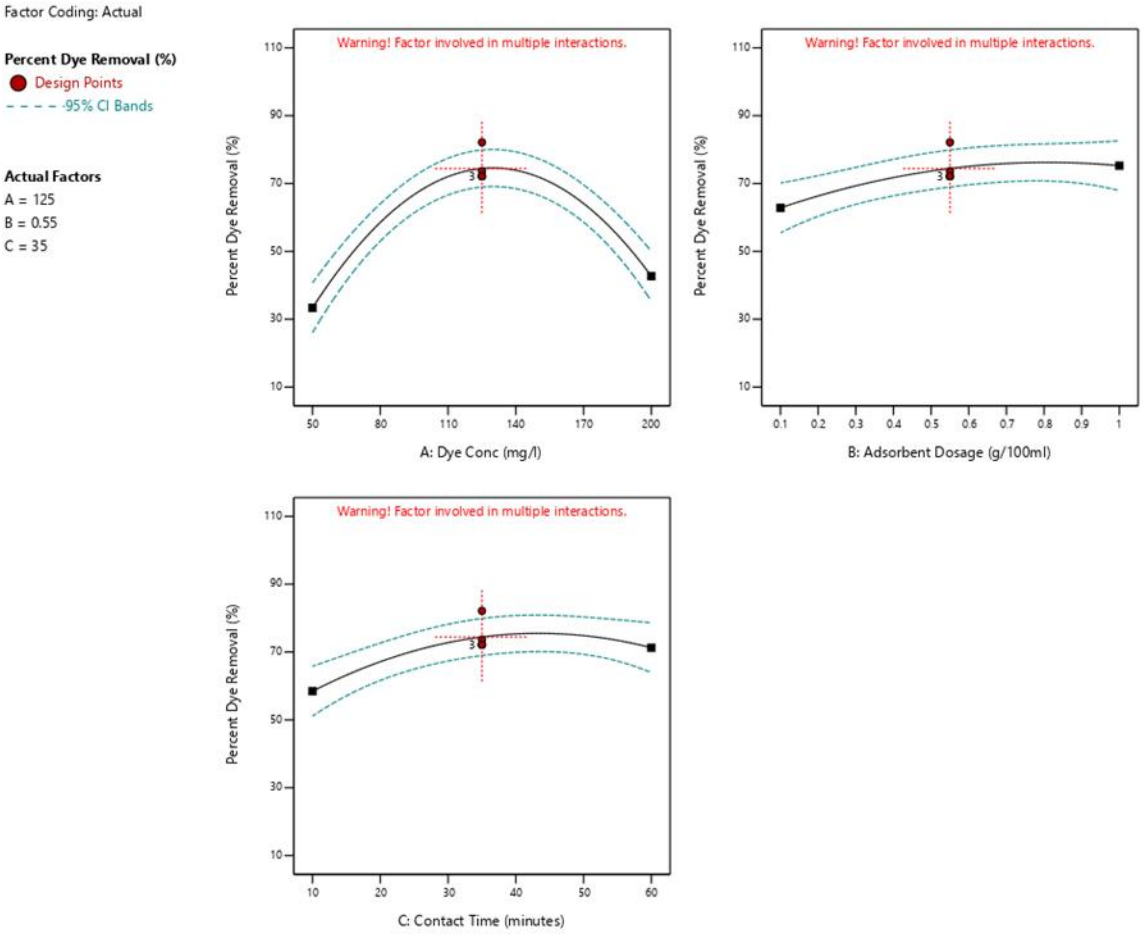


Response surface plot showing predicted percentage removal of methylene blue as a function of

dye conc and contact time with fixed adsorbent dosage of 0.55 g/ml



Response surface plot showing predicted percentage removal of methylene blue as a function of adsorbent dosage and contact time with fixed dye conc of 125 mg/l.



Model graphs: All factors

N,