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Contribution of activated carbon derived from pomegranate peel to the adsorption of methylene blue dye

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إهداء

الحمد لله الذي بنعمته تتم الصالحات في طياتها الكثير من الصعوبات و المشقة و التعب

اليوم أقطف ثمرها و أهديها الى معلم البشرية أجمعين الهادي الأمين

صلى ال هوله عليه وسلم

أهدي ثمرة جهدي المتواضع إلى من وهبوني الحياة الأمل و النشأة على الشغف الإطلاع و المعرفة ومن

علموني أن أرتقي سلم الحياة بحكمةوصبرا و برا و إحسانا و وفاء لهما لهما إلى الغالي

على قلبي أبي وإلى امي الحبيبة

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Abstract

This research aims to convert pomegranate peel (PP) into microporous activated carbon (PPAC) using a microwave-assisted K_2CO_3 activation method. The optimal activation conditions were determined to be a 1:2 PP/K_2CO_3 impregnation ratio, 800 W radiation power, and a 15-minute irradiation time. The statistical Box–Behnken design (BBD) was employed to effectively optimize the factors influencing the adsorption performance and removal of methylene blue (MB) dye. The RSM-BBD results indicated a 93.3% removal of 100 mg/L MB under the following conditions: a PPAC dose of 0.1 g, solution pH of 7, process temperature of 50°C, and a contact time of 18 minutes. The pseudo-second order (PSO) kinetic model accurately described the contact time required for MB adsorption. At equilibrium, the Freundlich adsorption isotherm effectively described the adsorption process, with the maximum adsorption capacity of PPAC for MB dye being 291.5 mg/g. This study supports the utilization of biomass waste from pomegranate peels for conversion into renewable and sustainable adsorbent materials, contributing to both biomass waste management and water pollutant sequestration.

Keywords: Activated carbon, Adsorption, microwave, pomegranate peel, methylene blue dye.

الملخص

يهدف هذا البحث إلى تحويل قشور الرمان إلى كربون منشط باستخدام طريقة التنشيط بمساعدة الميكروويف مع كربونات البوتاسيوم (K_2CO_3). تم تحديد الظروف المثلى للتنشيط بنسبة نقع 1:2 لقشور الرمان وكربونات البوتاسيوم، وطاقة إشعاع 800 واط، ووقت تشعيع 15 دقيقة. تم استخدام تصميم الإحصائي (BBD) لتحسين العوامل المؤثرة على أداء الامتصاص وإزالة صبغة الميثيلين الزرقاء (MB) بشكل فعال. أظهرت نتائج RSM-BBD إزالة بنسبة 93.3٪ من 100 ملجم/لتر من MB تحت الظروف التالية: جرعة PPAC 0.1 جم، ودرجة حموضة المحلول 7، ودرجة حرارة العملية 50 درجة مئوية، ووقت التلامس 18 دقيقة. وصفت نموذج الحركية من الدرجة الثانية الزائف (PSO) بدقة وقت التلامس المطلوب لامتزاز MB. عند التوازن، وصفت إيزوثيرم الامتزاز لفريدليش عملية الامتزاز بفعالية، مع سعة امتزاز قصوى للكربون المنشط من قشور الرمان لصبغة MB بلغت 291.5 ملجم/جم. يدعم هذا الدراسة استخدام نفايات الكتلة الحيوية من قشور الرمان لتحويلها إلى مواد ماصة متجددة ومستدامة، مما يساهم في إدارة نفايات الكتلة الحيوية وعزل ملوثات المياه.

الكلمات المفتاحية: الكربون المنشط، الامتزاز، الميكروويف، قشور الرمان، صبغة الميثيلين الزرقاء.

CONTENTS

BIBLIOGRAPHY

LIST OF TABLES

LIST OF FIGURES

LIST OF Abbreviations

SEM	Scanning electron microscope
EDX	Energy- dispersive x-ray spectroscopy
FTIR	Fourier Transform Infrared
MB	Methylene Blue
RSM	Response Surface Methodology
BBD	Box Behnken design
q_e	Adsorption capacity at equilibrium (mg/g)
q_t	Amount of dye adsorbed per unit of adsorbent (mg/g)
R^2	Correlation coefficient
K_L	Langmuir constant (L/mg)
K_f	Freundlinch constant
K_T	Temkin constant
C_O	Initial concentration (mg/L)
C_e	Equilibrium concentration (mg/L)
t	contact time
V	Volume of adsorbate (L)
W	Weight of adsorbent (g)
PFO	pseudo-first-order
PSO	pseudo-second-order

GENERAL INTRODUCTION

- **Background of the study**

Water is the secret to the life of humans and other living beings; it is the essential compound in every living cell, and without it, life is impossible. It has been used in various aspects of daily life. Allah says in the Quran: "And We made from water every living thing" (Al-Anbiya, verse 30).However,(15%) of the world's population lacks access to safe and clean drinking water. This is due to the reckless actions of irresponsible entities that dispose of contaminated liquid waste into water bodies[5] .Pollution occurs in its various forms, whether it is air, water, or soil pollution. This happens due to human interventions or natural phenomena. Water pollution is considered the most dangerous because water plays a significant role in daily life, in addition to being essential in industry, which is regarded as the largest polluter of the environment.

Dyes are among the organic pollutants of water sources due to their significant importance and wide use in various industries. They are used in the textile industries, printing, and as additives in the oil industries, in addition to their countless other applications.In general, the dyes used in the textile industry are disperse, basic, acid, direct, reactive, azo, and others[6].Annually, approximately (5.10^7) tons of these dyes are produced worldwide. Various compounds, whose interfacial behavior is largely unknown, are used in their preparation. About(10-15%) of these dyes are lost as waste in the water from different industries.Otherwise, it can also cause severe damage to humans. Therefore, it is essential to remove the dangerous compounds contained in dyes from liquid waste before it is discharged into the environment. Thus, treating wastewater to remove these pollutants and recover it has become a vital task[7].

Various therapeutic methods have been applied to remove dyes from wastewater. Recently, several specialized treatments for wastewater have been developed, such as chemical precipitation, ion exchange, and membrane filtration. However, these treatment methods either have high operational costs or low efficiency, limiting the effectiveness of the process[8]. It has been proven that the most important technique used is adsorption, due to its high efficiency in this field and the simplicity of the technology used for this purpose compared to other methods, as well as its lower economic cost. In this technique, activated carbon is often used as an adsorbent to remove various types of inorganic pollutants like heavy metals and organic pollutants like different dyes and phenols due to its high adsorption capacity. However, because of its high cost and issues with reuse, as well as the difficulty of separating it from wastewater, there was a need to find alternative, environmentally friendly materials. Consequently, researchers have recently turned to developing new adsorbent materials using some naturally derived materials (such as hardwood sawdust and pomegranate peels).

Activated carbon derived from pomegranate peels is an eco-friendly material used in water treatment due to its high pollutant absorption capacity. It is produced from pomegranate peels, which are abundant agricultural waste, making it a sustainable and economical option.

The production process of activated carbon involves heating the peels in an oxygen-free environment (pyrolysis) and then activating them through physical or chemical methods to increase surface area and porosity. These properties enable activated carbon to effectively absorb methylene blue dye.

Methylene blue dye is a common organic pollutant used in various industries such as textiles. Removing this dye from water is essential to prevent environmental and health damage. Activated carbon absorbs the dye through an adsorption process, where dye molecules accumulate on the surface and pores of the activated carbon, leading to water purification.

By using activated carbon derived from pomegranate peels, multiple benefits can be achieved, including reducing agricultural waste and effectively treating wastewater, thereby promoting environmental sustainability and providing an economical solution to water pollution problems.

- **Problem statement**

With the increasing environmental pollution, the treatment of water contaminated with industrial dyes has become a significant challenge. Among these dyes, methylene blue is a common pollutant widely used in various industries such as textiles and paper. These dyes greatly contribute to water pollution, making the removal of these contaminants using effective and environmentally friendly techniques essential.

Activated carbon is an excellent material for absorbing pollutants from water due to its high porosity and large surface area. However, traditional activated carbon can be expensive. Therefore, searching for low-cost and sustainable alternative sources of activated carbon is a promising area of research.

Pomegranate peels, being largely underutilized agricultural waste, offer a potential alternative source for activated carbon. These wastes can be converted into activated carbon and used to remove methylene blue dye from contaminated water.

Research Question:

How effective is activated carbon derived from pomegranate peels in absorbing methylene blue dye from contaminated water?

- **Objectives**

✍ **a.** To convert pomegranate peels into porous activated carbon using microwave-assisted activation with potassium carbonate (K_2CO_3).

✍ **b.** To assess the activated carbon as an adsorbent, various analytical techniques including Fourier-transform infrared spectroscopy (FTIR), SEM-EDX, and pHpzc tests were employed.

✍ **c.** Response surface methodology was used to optimize the MB removal conditions such as adsorbent dose, solution pH and contact time

- **Significance of study**

Water pollution caused by organic dyes can be reduced using adsorbents, which are known for their porous, insoluble, and sponge-like structures that trap and capture pollutant particles. Adsorbents play a crucial role in the adsorption process. Activated carbon, a widely used adsorbent, can be produced from fruit waste, which contains high levels of carbon, such as fruit peels. Microwave technology is an efficient and convenient method for producing activated carbon from fruit waste.

- **Thesis Layout**

This thesis is organized into :

General introduction encompassing the Background of the study, Problem statement, Objectives, and Significance of the study.

Chapter 1 The discussion encompasses a review of literature pertinent to the current study, including the challenges associated with water treatment, the technique of adsorption, and the application of activated carbon for dye removal.

Chapter 2 This section presents the methodology and procedures employed to remove methylene blue (MB) dye from simulated water meduium.

Chapter 3 This section presents the results of the research, starting with a discussion of the spectroscopic study. It then addresses the characterization, optimization and modeling of the specific adsorbent. In addition, the reaction mechanism is examined in detail.

In conclusion, the study was summarized with key findings and final remarks.

CHAPTER 1

LITERATURE REVIEW

1.1 Introduction

The Creator, glorified be He, has endowed water with numerous physical, chemical, and vital attributes that truly make it the unique fluid of life. Indeed, He has made it the most wondrous and greatest liquid, without which life would not exist on Earth. God, glorified be He, created the earth and the heavens, and He created humans on this earth, providing them with water, the essence of their life and the life of the living beings around them.

As time progressed, humans entered the era of industry and mining, discovering sources of energy such as coal and petroleum, along with the emissions and waste gases they produce, in addition to many chemical compounds introduced by humans that were not naturally[9; 10] present in the environment, such as synthetic dyes and various pesticides. Consequently, a significant problem arose that humanity faced in this modern era: pollution.

1.2 Water

Water or freshwater is the most precious gift bestowed to our planet. It is responsible for maintaining mankind and even other biotas alive [11]. Regrettably, this finite natural resource is threatened due to contamination from agricultural and industrial activities that the modern world is currently witnessing. Alarmingly, increased levels of industrial wastewater and sewage released into rivers or neighboring land will continue owing to increased demand for food and housing . Based on NORMAN Network's report [12], the water bodies have a large number of toxic contaminants such as agrochemicals, heavy metals, oil products, and synthetic dyes [4]. Undoubtedly, these irresponsible actions will be an exorbitant bill for the next and even current generations. The rate of pollution all over the world is projected to continue rising leading to dire consequences . Consequently, the global water demand is expected to exceed 55 % at the end of the next two decades according to United Nations World Water Assessment Programme (WWAP)

Among the important parameters for testing water quality, chemical oxygen demand (COD) is a critical parameter in evaluating water quality, which represents the amount of oxygen required to chemically oxidize organic and inorganic substances in water. High COD levels indicate significant pollution [13], because they reflect the presence of pollutants that consume oxygen, which is essential for aquatic life. When organic matter such as wastewater, industrial effluents, and agricultural runoff enter water bodies, they increase COD, leading to oxygen depletion. This can lead to serious consequences for aquatic ecosystems, including the death of fish and other organisms due to hypoxic conditions. COD monitoring is vital to identify and manage sources of water pollution, ensure healthy aquatic environments, and protect human health, as contaminated water can negatively impact drinking water supplies and recreational water bodies. Effective wastewater treatment and pollution control are essential to reduce COD levels and protect water quality.

1.3 Water pollutant

Water pollution, also known as aquatic pollution, is the contamination of water bodies, negatively impacting their usability. It predominantly results from human activities. Water bodies affected by pollution include lakes, rivers, oceans, aquifers, reservoirs, and groundwater. This contamination occurs when harmful substances mix with these water sources [14].

The main sources of water pollution are sewage discharges, industrial activities, agricultural activities, and urban runoff, including stormwater. Both surface water and groundwater can be affected by this type of pollution.

Water pollution can lead to numerous problems. It degrades aquatic ecosystems, spreads water-borne diseases when polluted water is used for drinking or irrigation, and diminishes ecosystem services, such as the provision of clean drinking water.

1.3.1 Sources of water pollution

There are a variety of sources from which water pollution arises, and in this section, we will limit ourselves to mentioning some of them:

1.3.1.1 Thermal Pollution

Thermal pollution occurs when water temperatures rise due to human activities, such as industrial discharges or power plant cooling processes. Elevated temperatures can harm aquatic organisms and disrupt entire ecosystems. Oxygen-depletion pollution happens when pollutants like organic matter or excess nutrients reduce dissolved oxygen levels in water. Low oxygen levels can be detrimental to fish and other aquatic life. Preventing and combating water pollution involves understanding its sources and implementing effective measures to protect our water resources. By addressing these various types of pollution, we can improve water quality and safeguard our environment [15].

1.3.1.2 Wastewater discharges

Wastewater discharges are a major source of water pollution, originating from domestic, industrial, and agricultural activities. Domestic wastewater includes sewage and household effluents, often laden with harmful bacteria and chemicals. Industrial wastewater, discharged from factories and plants, can contain toxic substances such as heavy metals, solvents, and hazardous chemicals [16]. Agricultural runoff carries pesticides, fertilizers, and animal waste into water bodies, contributing to contamination. These pollutants degrade water quality, harm aquatic ecosystems, and pose health risks to humans. Effective wastewater treatment and management are crucial for mitigating these impacts and ensuring safe, clean water resources .

1.3.1.3 Agricultural Activities

Agricultural activities contribute significantly to water pollution through the use of fertilizers and pesticides on crops. When applied, these chemicals can leach into the soil and contaminate groundwater. Additionally, during rainfall, surface runoff can carry these pollutants into nearby water bodies. This runoff causes nutrient pollution, leading to issues like algal blooms and the degradation of aquatic ecosystems. The presence of pesticides in water sources also poses health risks to humans and wildlife. Overall, agricultural runoff is a major source of water contamination [17]

1.3.1.4 Dyes

The latest appearance of dyes The first dye ever produced was Mauve dye, marking the beginning of the scientific revolution in the dye industry.

These dyes have been applied in all areas of our daily lives, such as dyeing clothes, food, medicines, cosmetics, as well as paper industries, and more. Textile dyes have been produced for over 40,000 years, using natural sources like plants, animals, and minerals[18]. Synthetic dyes were discovered by Perkins. They are aromatic compounds that provide a wide range of vibrant colors. In 1856, Perkin William discovered purple, the first synthetic organic color[19], while attempting to synthesize quinine, a drug used to treat malaria. So, Perkin Henry produced, in his attempt to manufacture quinine, a new substance to generate the dye[20]. In 1871, Woufle prepared picric acid by treating the natural substance indigo with nitric acid, leading to the formation of synthetic organic dye, introducing a large number of new chemical dyes to the list. Synthetic dyes almost entirely replaced natural dyes at the beginning of the twentieth century[21].

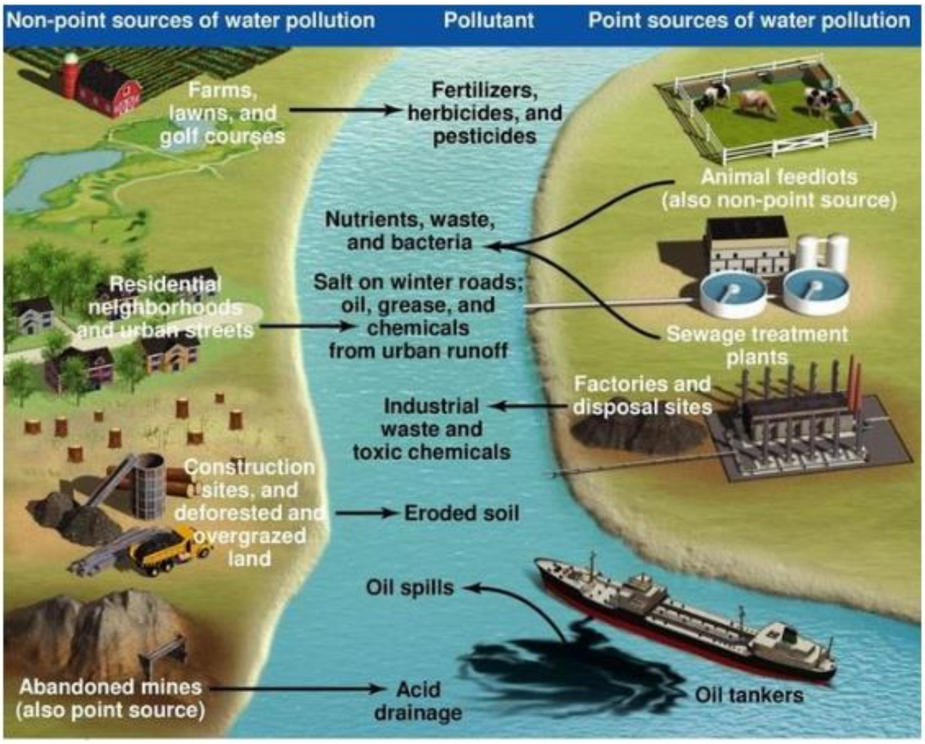


Figure 1.1: Sources of water pollutant [2]

✍ a. Definition of dyes

Dyes chemically are organic or inorganic compounds used to impart color to various materials such as food, walls, fabric, and paper. They exist in liquid or powder form and are widely used in various industries for coloring materials. They rely on the absorption and reflection of light to produce different colors, usually consisting of small particles capable of penetrating the surface being dyed[8; 22]. Dyes are characterized by their ability to absorb radiation ranging from 4000 to 7000 (nm) in the visible spectrum[23].

✍ b. Classification of dyes

Generally, all dyes consist of two main components: chromophores and auxochromes [24].

Chromophores are groups of atoms responsible for the dye's color and act as electron-withdrawing groups. Common chromophores include C=C, C=N, C=O, N=N, NO_2, and NO.

Auxochromes are electron-donating constituents that intensify the color of chromophores, enhance solubility, and help the dye adhere to fibers, often with the aid of a mordant. Common auxochromes include $NH_2, NR_2, COOH, SO_3H, andOH$.

Dyes can be classified in several ways, including their solubility in water, molecular structure, and particle charge upon dissolution in an aqueous medium. For instance, acid, basic, reactive, and direct dyes are soluble in water, whereas vat and disperse dyes are not as illustrated in Table: 1.1 . Additionally, dyes can be categorized based on their particle charge in solution,

Table 1.1: Different types of dyes and their main applications[1]

Type	Water Solubility	Applications	Common Application Method	Example
Acid	*Soluble*	Cosmetics, food, leather , modified acrylics, nylon , paper, printing ink , silk and wool	In dye baths with neutral to acidic conditions	Acid Yellow 36
Azo	*Soluble/insoluble*	Acetate, cellulose, cotton , rayon and polyester	Coupling component used to impregnate fiber and a solution of stabilized diazonium salt is used for treatment	Bluish Red azo dye
Basic	*Soluble*	Inks, medicine, modified nylon, modified polyester , paper, polyacrylonitrile, polyester	In dye baths with acidic conditions	Methylene Blue
Direct	*Soluble*	Cotton, leather, nylon, rayon, silk and paper	In dye baths with neutral or slightly alkaline conditions with additional electrolyte.	Direct Orange 26
Disperse	*Insoluble*	Acetate, acrylic fibers, cellulose, cellulose acetate	Padded on cloth and either baked or thermo-fixed at high pressure and temperature or low temperature carrier methods	Disperse Red 4
Reactive	*Soluble*	Cellulosic, cotton, nylon, silk and wool	reactive group on dye. Covalently bonding under heat and alkaline pH	Reactive Blue 5
Solvent	*insoluble*	Fats, gasoline, inks, lacquers, lubricants, oils, plastics, stains, varnishes and waxes	Substrate dissolution	Solvent Red 26

such as anionic and cationic dyes [25].

Methylene blue dye, also known as methyl thioninium chloride (tetramethyl thionine chloride), is a cationic dye and an aromatic chemical compound with the chemical formula $C_{16}H_{18}ClN_3$. It is a solid, dark green powder that is odorless. When dissolved in water, it produces a blue solution [26; 27]. The distinctive formula includes three water molecules associated with one molecule of methylene blue at room temperature. This dye has various applications across chemical and biological fields.

Heinrich Caro first synthesized methylene blue in 1876. The compound can also be prepared by reacting dimethyl-4-phenylamine with hydrogen sulfide in a hydrochloric acid medium, followed by oxidation with ferric chloride. Table: 1.2 Elucidates some Physical and chemical properties of MB dye.

Figure 1.2: Methylene blue dye powder

Table 1.2: Physical and chemical properties of MB dye.

Name	**Properties**
Chemical name	Methylene Blue
Abbreviation	MB
Melting point	100-110°C
Molar mass (g/mol)	319.85
Solubility	Water (20°C)
Chemical formula	$C_{16}H_{18}ClN_3S$

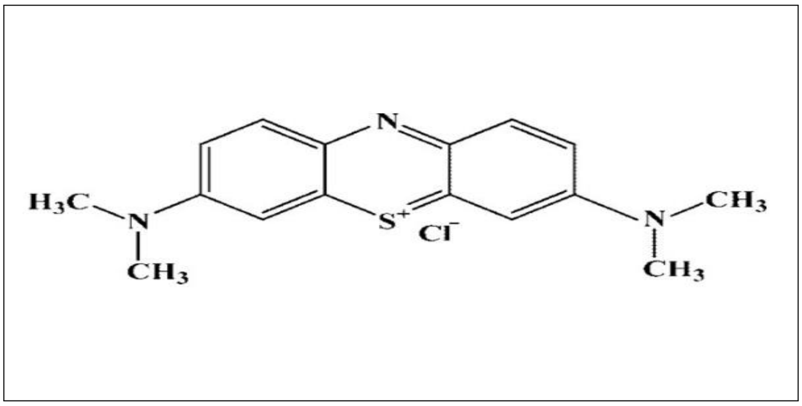


Figure 1.3: Chemical structure of Methylene Blue (MB) dye [3].

✍ c. Toxicity of dyes

We face many environmental problems, among which is the discharge of wastewater loaded with dyes into aquatic environments. These substances are known for their toxicity[20], which is related to their complex molecular structures and large molecular weights, giving them resistance to biodegradation in addition to their accumulation. It is believed that diazo dyes are the most toxic. Several studies have shown that azo dyes have carcinogenic effects on humans. The impact of these dyes on us occurs due to the chemical or enzymatic breakdown of azo bonds, leading to the generation of aromatic amines. These aromatic amines are absorbed by the body through the lungs and cause harm to animals, plants and other microorganisms living in these waters, leading to a decrease in oxygen levels in these environments. This toxicity is associated with varying levels of harmful effects, allowing these compounds to persist in the environment for extended periods. This results in significant disruptions to the natural processes that govern plants and animals by destroying certain species of fish and microorganisms[28].

1.4 Adsorption

Over the past years, numerous technologies and techniques have been developed to remove pollutants from water bodies. The removal of dyes from polluted water has been achieved through various methods, including sedimentation, ion exchange, and biological and physical processes

Adsorption is considered one of the best techniques for pollutant removal due to its numerous advantages, such as High Efficiency, Simplicity, Reusability and so forth.

1.4.1 Definiton of adsorption

Adsorption is the collection of substances at an interface between two phases. The substance that gathers on the interface is referred to as the adsorbate and the solid material used is called the adsorbent.

Adsorption can occur through various mechanisms, including physical adsorption (physisorption) and chemical adsorption (chemisorption), depending on the forces involved between the adsorbate (the substance being adsorbed) and the adsorbent (the surface to which the adsorbate adheres).

1.4.1.1 physisorption

It's the adsorption resulting from electrostatic forces between the mixture and the surface. It involves weak energies, making it suitable for temperature reduction as it reflects quickly[29]. These weak interactions between molecules are known as van der Waals forces, playing a role in attracting and stabilizing species released onto solid bases. If the adsorption process is fast, it occurs instantly[30].

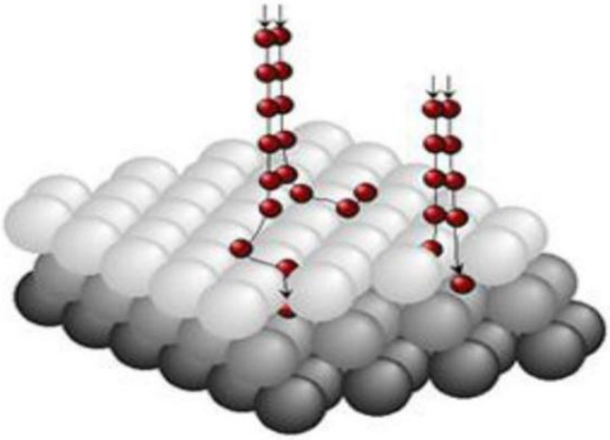


Figure 1.4: physical adsorption

1.4.1.2 chemisorption

It's adsorption based on the bonding forces of a chemical substance. Often involving sharing, donating, or transferring charges[30], which makes chemical adsorption opposite to physical adsorption because of the large amount of energy involved[29].

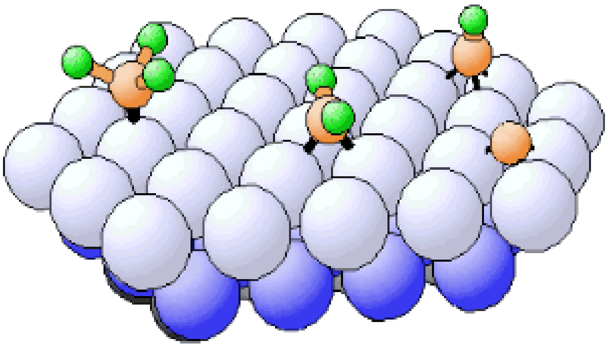


Figure 1.5: Chemical adsorption

The following Table: 1.3 shows the difference between chemisorption and Physisorption.

Table 1.3: The difference between chemisorption and Physisorption

Properties	**Chemisorption**	**Physisorption**
bonding type	chemical bonds	van der Waals bond
layer kind	mono layer	mono, or multi layers
	slowly and irreversibly	rapid and reversibly
adsorption heat	more than 10 K Cal/mol	less than 10 KCal/mol
	needs to an activation energy	does not need to an activation energy

1.4.2 The Factors Influencing Adsorption

Several principal factors affect the effectiveness of adsorption, including the initial dye concentration, temperature, pH, contact time, adsorbent dosage, and adsorbent particle size [31]. Optimizing these conditions is crucial for developing an industrial-scale dye removal treatment process. The next section will discuss some of these factors in detail.

1.4.2.1 The temperature

The effect of temperature is a significant physico-chemical parameter, as it can alter the adsorption capacity of the adsorbent. If adsorption increases with rising temperature, the process is endothermic. This increase may result from the enhanced mobility of dye molecules and the availability of more active sites on the adsorbent. Conversely, if adsorption capacity decreases with increasing temperature, the process is exothermic [32]. This decrease may occur because higher temperatures weaken the adsorptive forces between the dye molecules and the active sites on the adsorbent, leading to reduced adsorption.

1.4.2.2 The initial dye concentration

The effectiveness of dye removal through adsorption is highly dependent on the initial dye concentration. This effect is influenced by the immediate relationship between the dye concentration and the available adsorption sites on the adsorbent surface. Generally, the percentage of dye removal decreases as the initial dye concentration increases, likely due to the saturation of adsorption sites. However, an increase in initial dye concentration can also enhance the adsorption capacity of the adsorbent, attributed to a higher driving force for mass transfer at elevated dye concentrations [33].

1.4.2.3 pH

One of the most important factors affecting the capacity of adsorbents in wastewater treatment is the solution pH. The efficiency of adsorption is highly dependent on the pH, as changes in pH can alter the degree of ionization of the adsorptive molecules and the surface properties of the adsorbent [34].

1.4.2.4 Contact time

The longer the contact time, the more complete the adsorption process will be. However, this also necessitates larger equipment. Increased contact time reduces boundary layer resistance, enhancing the rate of adsorption and improving the mobility of dye molecules during the process.

1.4.2.5 The amount of adsorbent

Adsorbent dosage is a crucial process parameter for determining the capacity of an adsorbent under specific operating conditions. Generally, the percentage of dye removal increases with a higher adsorbent dosage, as the number of available sorption sites on the adsorbent surface increases. Understanding the effect of adsorbent dosage is essential for optimizing dye adsorption efficiency, allowing for the assessment of how effectively dyes can be removed with minimal adsorbent usage. This optimization is important from an economic perspective, ensuring cost-effective treatment processes[35].

1.4.3 Adsorption models

1.4.3.1 Langmuir model

The Langmuir adsorption isotherm was initially developed to describe the adsorption of gases onto solid surfaces. This empirical model assumes that adsorption occurs in a monolayer at specific homogeneous sites on the adsorbent surface. Consequently, the process is often referred to as homogeneous adsorption [36]. The Langmuir isotherm model can be expressed in both linear and nonlinear forms, as shown in equations: 1.1 ,: 1.2 :

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max}K_L}.\frac{1}{C_e} \tag{1.1}$$

$$q_e = \frac{q_{max}K_L C_e}{1 + K_L C_e} \tag{1.2}$$

Where :

q_{max}: The maximum adsorption capacity (mg/g)

K_L: Langmuir constant(l/mg)

C_e:equilibrium concentration of the adsorbate (mg/l)

q_e: the amount of adsorbate at equilibrium (mg/g)

1.4.3.2 Freundlich model

The Freundlich isotherm is one of the earliest models describing non-ideal and reversible adsorption processes. This empirical model is applicable to multilayer adsorption, where there is a non-uniform distribution of adsorption heat and affinities across a heterogeneous surface [37]. The Freundlich isotherm assumes heterogeneous surface energies and is widely used in heterogeneous systems, particularly for highly interactive species or organic compounds on molecular sieves and adsorbents. The Freundlich isotherm model can be expressed in both nonlinear and nonlinear forms, as shown in equations: 1.3 , : 1.4

$$q_e = K_F C_e^{1/n} \tag{1.3}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{1.4}$$

Where :

q_e:The amount of adsorbed material(mg/g)

C_e:Focus on balance (mg/l)

K_F, n are constants of Freundlich

1.4.3.3 Temkin model

This model relies on the enabling temperature, assuming an increase in the recovery rate of the solid surface, which leads to a linear decrease in the heat of adsorption. It was developed into an enabling equation for the case of gas and solid adsorption and then applied to the liquid phase [28]. The model is expressed by the following nonlinear equation equations: 1.5 :

$$q_e = \frac{RT}{b_T} ln(K_T C_e) \tag{1.5}$$

Where :

q_e: Equilibrium amount adsorbed (mg/g)

C_e:Equilibrium adsorption concentration (mg/l)

R: Gas constant (kj/mol.K)

T: Temperature (k)

b_T and K_T : Characteristic constants of the adsorbent/adsorbate system (j/mol), and (l/mg), respectively.

1.4.4 Adsorption kinetics

Adsorption kinetics are understood through the evolution of the amount of adsorbate and the time required to reach adsorption equilibrium. Adsorption kinetics refer to the rate at which a solute is adsorbed from a solution, providing insights into the adsorption mechanism and the transfer pattern between the liquid and solid phases. This has led to the development of kinetic properties and the application of several models to describe adsorption kinetics and determine the nature of the interactions at the liquid-solid interface [29].

Three types of adsorption kinetics can be distinguished: pseudo-first-order (PFO), pseudo-second-order (PSO), and intraparticle diffusion (IPD).

1.4.4.1 PFO

Typically, the pseudo-first-order kinetic model is used to predict adsorption kinetics. This model assumes that the rate of change of solute uptake over time is directly proportional to the difference between the current solute concentration and the saturation concentration [38]. The rate constant for adsorption is determined using the pseudo-first-order equation, as described by. equations: 1.6 :

$$q_t = q_e(1 - exp^{K_1 t}) \tag{1.6}$$

Where:

q_t: The amount of adsorbate at time t and its unit (mg/g)

q_e: Adsorption capacity at equilibrium per gram of adsorbent (mg/g)

K_1: the rate constant of adsorption (min^-1)

1.4.4.2 PSO

In chemical research involving chemical bonding between metal ions and functional groups, Mackay and Ho proposed in 1999 the second-order pseudo-dynamic reflection, also known as the second-order kinetic model. This model is represented by the following equations: 1.7 :

$$q_t = \frac{q_e^2 K_2 t}{1 + K_2 t} \tag{1.7}$$

Where:

K_2:The rate constant of adsorption for the second-order pseudo-dynamic model (min mg/g)

1.4.4.3 IPD

IPD means Intraparticle diffusion model, the adsorption process is controlled by the diffusion within the particles, which quickly reaches an equilibrium state and continues for long periods for small adsorbates due to the slowdown. The diffusion of particles in these structures has dimensions close to the diameter of the liquid particles[38]. Instead of contact time, the adsorption changes approximately in proportion to $t^{1/2}$ [39], and its equations are of the following form equations: 1.8

$$q_t = K_i t^{1/2} + C \tag{1.8}$$

Where:

The intraparticle diffusion rate constant, K_i (mg/gůmin$^{-1/2}$), can be calculated from the slope of the linear segment of the plot of q_t versus $t^{1/2}$.

1.5 Activated carbon

The term "activated carbon" (AC) refers to carbonaceous materials characterized by high porosity, physicochemical stability, adsorptive capacity, mechanical strength, and a large surface area. These properties distinguish activated carbon from elemental carbon through the oxidation of carbon atoms on its outer and inner surfaces [40]. Also known as activated charcoal, activated coal, or solid sponge, Thus, activated carbon can be made in two easy steps, firstly by using carbonaceous raw material which is carbonized in an inert environment at 1000°C, and carbonized material is activated with chemical activators

This process results in a highly adsorptive material used in various applications, including water and air purification, medical treatments, and industrial processes.

Figure 1.6: Activated carbon [4]

1.5.1 Preparation of Activated carbon

Two methods for producing activated carbon were established in this study: physical activation, chemical activation, and microwave activation.

1.5.1.1 physical activation

Physical or "direct thermal" treatment involves the use of nitrogen, steam, carbon dioxide, nitrogen with plasma heating, and carbon dioxide alone for the activation process, including pyrolysis. In direct thermal treatments, ion exchange sites and functional groups can often be more crucial than surface area, especially for dye removal. Certain pollutants are sensitive to specific elements, which can enhance adsorption capacity. For example, an increase in nitrogen content has been reported to significantly boost the adsorption of phenol.

Pyrolysis is also employed to modify the surface chemistry of activated carbon, increasing surface acidity and decreasing basicity. This occurs because volatile basic compounds are removed during the process, potentially attaching to the material's surface. Additionally, pyrolysis at temperatures above 100 °C increases the carbon content by eliminating volatile components and water, which can initially decrease phenol recovery due to water loss. At higher temperatures, such as 250°C, phenol recovery further decreases due to lignocellulose depolymerization [41].

Moreover, physical activation involves two main steps: carbonization and activation. This process is often referred to as dry oxidation. Carbonization typically occurs at temperatures ranging from 400°C to 850°C, while activation usually takes place between 600°C and 900°C.

The primary goal of carbonization is to reduce the volatile content of the precursor material, resulting in char with a higher fixed carbon content suitable for activation. The subsequent activation step aims to develop additional porosity and order within the structure, producing a highly porous solid form of activated carbon.

1.5.1.2 chemical activation

Chemical activation, also known as wet oxidation, requires that a catalyst be oxidized into the precursor and then washed to generate activated carbon. Chemical activation has traditionally been carried out at temperatures ranging from 450 °C to 600 °C. The activating agents used in this process are essentially dehydrating agents and oxidants that influence the decomposition of pyrolytic material. They may also reduce the development of tar or ash, thereby increasing carbon yield.

Common chemical catalysts or oxidizing agents include potassium sulfide (K_2S), nitric acid (HNO_3), hydrogen peroxide (H_2O_2), potassium permanganate ($KMnO_4$), sodium hydroxide ($NaOH$), potassium hydroxide (KOH), and potassium carbonate (K_2CO_3). When the precursor reacts with these activating agents, oxygen functional groups can be introduced to the carbon surface. Furthermore, the final stage in the preparation of activated carbon through chemical activation is always the washing step.

Activated carbon is typically washed with acid or alkali, depending on the chemical reagents used during its preparation, and then rinsed with water. This washing step removes the chemical components from the activated carbon. The chemicals initially occupy the pores within the carbon structure, so the washing step is crucial for developing porosity in the activated carbon. As a result, this stage is one of the most important in the chemical activation process.

1.5.1.3 microwave activation

Previously, conventional heating methods such as tube furnaces and fluidized bed reactors were widely used for biomass pyrolysis. However, these methods required long heating times, which resulted in lower quality products due to secondary reactions. Other drawbacks included the increased energy required for the heating process, heat transfer resistance, and heat losses to the surroundings. Additionally, conventional heating methods could take several hours or even up to a week to achieve the desired level of activation, leading to rapid firing. Consequently, the slow thermal process increased the overall cost. These issues can be addressed by using the microwave heating method.

The microwave method is a non-contact technique in which heat is transferred to the product via electromagnetic waves. This allows large amounts of heat to be transmitted to the interior of the material, reducing the impact of different synthesis processes and overcoming the problems associated with conventional fast firing. Moreover, microwave radiation is both volumetric and internal, creating a large thermal gradient from the interior of the sample to the cooler surface. This enables microwave-induced reactions to proceed more rapidly and effectively at a lower bulk temperature, resulting in reduced processing time and energy savings [42].

Additionally, the process of producing activated carbon can be conducted in a microwave. This was done in a fabricated microwave using 300 W of power at a frequency of 2450 MHz. The fruit peel waste sample was placed in a reactor, and the microwave irradiation was carried out with nitrogen gas as an inert atmosphere. The final temperature of the sample was measured using a type-K thermocouple during the pyrolysis process. Condensable volatile matter was collected using a condenser with cooling water at a temperature of 0-5°C.

The solid and liquid fractions were determined by measuring the weight changes before and after the process, while the gas fraction was calculated by difference. According to Jamaluddin et al. (2013), to ensure accuracy and calculate the range and deviation of the results, all experiments were performed in duplicate.

1.5.2 Use of activated carbon for the removal of dyes

∗ In 2011, Maysam Farhani and others conducted a study on the use of activated carbon made from sugarcane bagasse to remove cationic dyes present in wastewater. This study also showed that it is a cheap and highly effective adsorption agent in removing dyes present in solutions. It can be used as an easy and inexpensive means of removing dye from wastewater in either stirred or batch tank reactors. Through the data collected, an ideal production system can be designed that uses one of these reactors to remove cationic dyes from industrial liquid waste. This study predicts the effect of activated carbon made from sugarcane bagasse on the adsorption of cationic dyes[43].

∗ Mohammad Arifur Rahman and his group removed methylene blue dye from water in 2012 by using activated carbon from rice husks as an adsorbent. By using sulfuric acid and zinc, chloride activation was used as an absorbent to remove a basic dye (methylene blue) from aqueous solutions. The effects of various experimental parameters, such as adsorbent dosage, particle size, initial dye concentration, pH and flow rate in the column process, were studied. Maximum absorption of methylene blue by rice husk activated carbon under ideal conditions. The results indicate that activated carbon from rice husk can be used as low-cost alternatives to commercial activated carbon in wastewater treatment. Removal of basic dyes. This efficient and low-cost removal method may provide a promising solution for methylene blue dye removal[44].

∗ In 2018, Ali Jawad et al. where they studied Pomegranate (Punica Granatum) peels were utilized as precursors to prepare mesoporous activated carbon (PPAC) viaH_3PO_4 -activation method. The surface characterization of PPAC was achieved using Fourier Transform Infrared (FTIR), Scanning Electron Microscopy (SEM), N2 adsorption/ desorption, X-Ray Diffraction (XRD), and the point of zero charge (pHPZC) method. It was found that PPAC a large surface area The adsorption properties of PPAC with methylene blue (MB) was conducted at different adsorbent dose , solution pH , initial dye concentrations , contact time using batch mode operation. The kinetic uptake profiles are well described by the pseudo-second-order model, while the Langmuir model describes the adsorption behaviour at equilibrium[45].

∗ In this work, where they did Al-Heetimi, Dhafir and conducted study in 2019 orange (Citrus sinensis) peels biochar (OPBC) were prepared by one-step H_2SO_4 activation for Methylene Blue (MB) adsorption from aqueous solution. The physicochemical properties of OPBC were characterized using instrumental analyses such as CHNS-O analyzer, Fourier Transform InfraRed (FT-IR) spectroscopy, Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), and point-of-zero charge (pHpzc) analysis. Batch mode adsorption study was conducted by varying operational parameters such as adsorbent dosage , solution pH , initial MB concentrations , and contact time . The equilibrium data was found to better fit with the Langmuir isotherm model compare to Freundlich and Temkin models. The maximum adsorption capacity, qmax of OPBC for MB adsorption[46]

$*$ To study the removal of Methylene Blue dye(MB) from aqueous solutions,Mohd Azmier Ahmad and his colleagues used activated carbon derived from peanut shells(PSAC). Sodium hydroxide $NaOH$ and carbon dioxide CO_2 were employed as a chemical agent and gasification agent, respectively, to prepare PSAC through both physical and chemical activation. In their investigations, they evaluated various effects including the initial concentration of the MB dye, solution temperature, and pH level. Isotherm and kinetic studies revealed that the adsorption system of MB-PSAC fitted best with the Freundlich model and the pseudo-second-order kinetic model, respectively. Thermodynamic studies demonstrated that the adsorption of Methylene Blue on PSAC was effectively controlled and was endothermic in nature.

CHAPTER 2

METHODOLOGY

2.1 Introduction

The research methodology utilized in this study encompassed several key stages, which included the collection and initial preparation of raw biomass materials. This initial phase involved meticulous gathering and processing of the biomass materials. Following this, the materials underwent an activation process, subsequent screening, and optimization, focusing particularly on precursors such as pomegranate peels.

To produce the desired adsorbents, a chemical activation method was employed, resulting in activated carbons denoted as pomegranate peels-based activated carbon (PPAC). Subsequently, these activated carbons underwent further modification through impregnation with potassium carbonate, enhancing their adsorption properties.

Following the preparation and modification stages, the adsorbents were subjected to rigorous characterization using techniques such as SEM/EDX (Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy), FTIR (Fourier Transform Infrared Spectroscopy), and BET (Brunauer Emmett Teller analysis). These analyses provided comprehensive insights into the structural, morphological, and chemical properties of the prepared adsorbents, facilitating a thorough understanding of their potential applications and effectiveness in adsorption processes.

2.2 Materials and Chemical Reagents Used

The raw materials and chemicals utilized in this study include Potassium carbonate (K_2CO_3: chemical activator), methylene blue dye $C_{16}H_{20}ClN_3SO$, ultrapure water, hydrochloric acid, and sodium hydroxide, as summarized in (Table: 2.1)

Table 2.1: physico-chemical properties for materials and chemical reagents used.

No	Name	Chemical formula	Properties	Company
1	*Potassium carbonate*	K_2CO_3	Solid	Sigma Aldrich
2	*Methylene blue dye*	$C_{16}H_{20}ClN_3SO$	Powder, MW= 373.9 g/mol, λ_{max} = 592 nm	Sigma Aldrich
3	*Ultrapure water*	H_2O	Liquid	
4	*Hydrochloric acid*	HCl	Liquid	Fluka
5	*Sodium hydroxide*	NaOH	pellets	Fluka

2.3 Preparation of Adsorbate (Stock Solution MB Dye)

A 1000 mg/L stock solution of MB was prepared by dissolving 1.0 g of MB powder in ultra-pure water within a 1 L volumetric flask. Subsequently, this stock solution was diluted to achieve an initial dye concentration ranging from 30 to 300 mg/L, which was consistently utilized throughout the adsorption process[47].

Figure 2.1: Stock Solution MB Dye

2.4 Preparation of Adsorbent

2.4.1 Preparation of Pomegranate peels (PP)

Pomegranate peels (PP) were collected from a farm near GUEMAR - EL OUED city. We washed them with Ultrapure water before drying to remove soluble impurities. They were dried in the oven overnight at a temperature of 105°C. Finally, they were crushed to convert them into very fine particles.

2.4.2 Preparation of Pomegranate peels activated carbon (PPAC)

A dried sample of pomegranate peels was immersed in a potassium carbonate (K_2CO_3) solution at a carefully optimized absorption ratio of 1 part pomegranate peels to 2 parts potassium carbonate (w/2w), which is considered an ideal mixing ratio. Following this, the activation process was carried out in a quartz cell, maintaining pure nitrogen conditions, within a microwave oven operating at 800 watts input power for a duration of 15 minutes. Subsequently, the activated products underwent thorough washing with Ultrapure water followed by 0.1 M hydrochloric acid until the pH of the washing solution reached a desired range of 0.6 to 0.7. The resulting activated carbon derived from K_2CO_3 treatment was designated as PPAC,as illustrated in (figures : 2.2, and 2.3)

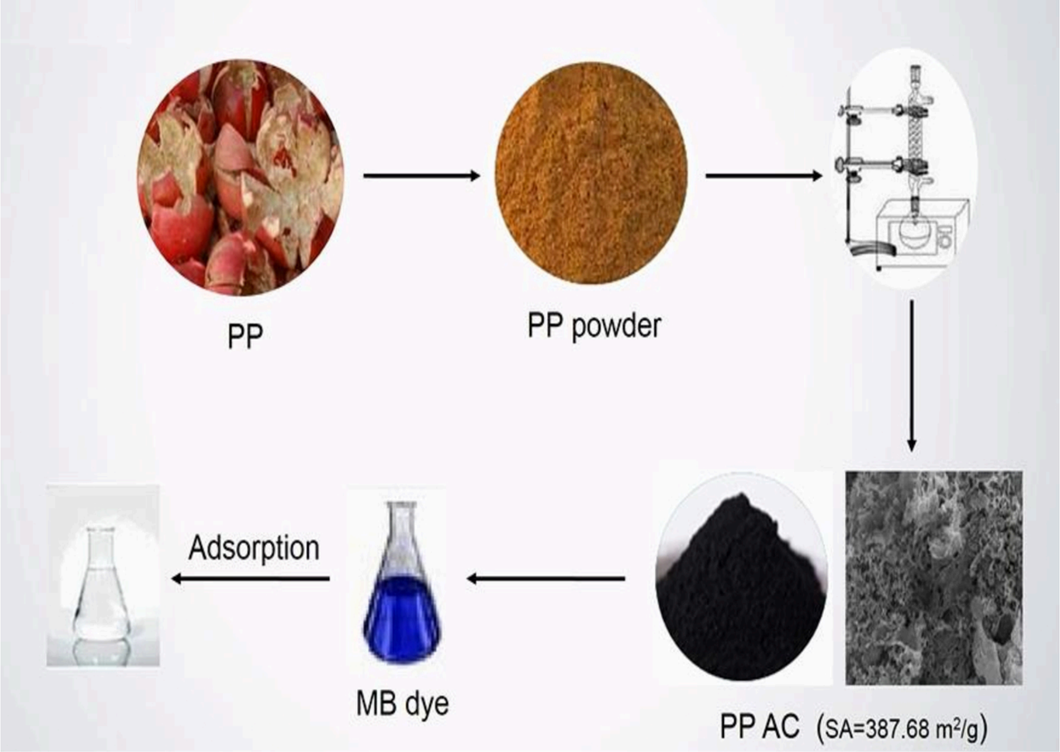


Figure 2.2: Steps preparation of PPAC

Figure 2.3: Illustrative Scheme of the Activation Process of PP

2.5 Adsorbent Characterizations

Various analytical techniques were employed in this study to investigate the morphology, functional group chemistry, and surface properties of the optimally prepared PPAC (Pomegranate Peel Activated Carbon). The properties and conditions of the adsorbent (PPAC) were thoroughly investigated and characterized. Detailed explanations of the equipment names, brands, and models used for the characterization study are provided below

2.5.1 Visible Spectroscopy Analysis

This device is one of the most important instruments used in the fields of chemical and biological analysis to measure concentrations of various substances in aqueous solutions and other materials. The visible device is distinguished by its high accuracy, dual-beam optical path, minimal stray light, stronger stability and reliability, and ease of use. It features a high-brightness 6-inch liquid crystal display screen with a resolution of 240x320 pixels, providing clear and comprehensive information. The device consists of several main components, including the light source, optical arrangement, detector, and computer. The basic principle of operation of this device relies on the transmittance of light at different wavelengths by various substances, each having its own absorption characteristics. Thus, when the dispersed light spectrum passes through a particular solution, the solution absorbs specific wavelengths of light at a certain wavelength, and the concentration of the substance in the solution is fundamentally related to the attenuation of the light energy. After the light source passes through the selected sample, a portion of the light is absorbed, and the absorbance value of the sample is calculated. The concentration of the sample is proportional to its absorbance. The Visible device presents in (figure: 2.4)

Figure 2.4: Visible device

2.5.2 Scanning electron microscopy (SEM-EDX)

Is a type of electron microscope that produces images by scanning the surface with a focused electron beam. The SEM consists of main components including magnetic lenses, a display screen (which includes a computer for data collection and data analysis software), and the electron source. This device operates by interaction of electrons with atoms in the sample, producing various signals containing information about the surface topography and composition of the sample. The electron beam is scanned in a raster pattern, and the position of the beam is combined with the intensity of the detected signal to generate an image. SEM images provide extremely detailed information about the surface of the sample.

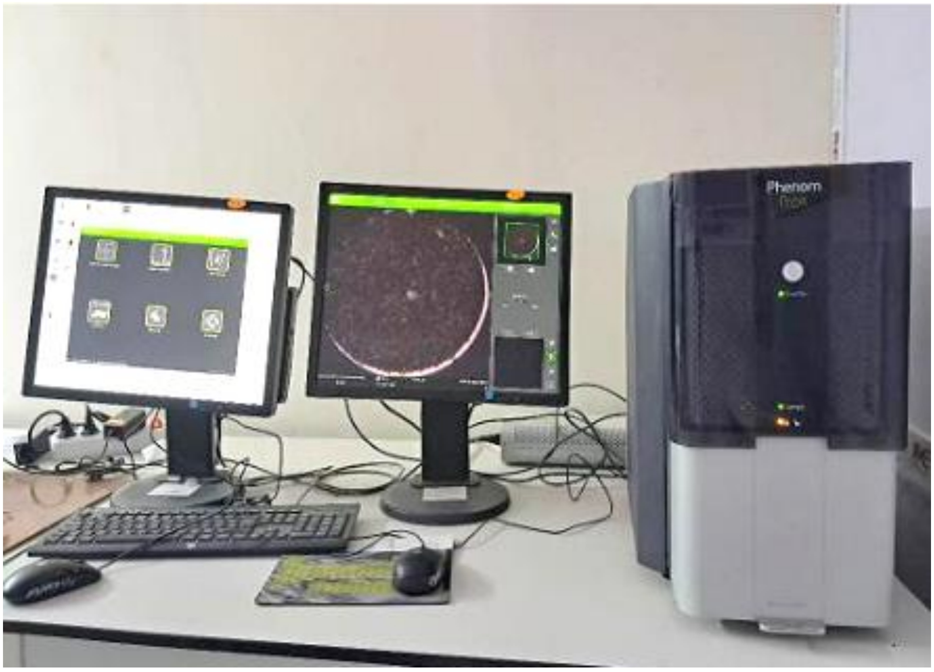


Figure 2.5: SEM-EDX device

2.5.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR stands for Fourier Transform Infrared Spectroscopy, which is used to analyze the chemical composition of materials by examining their infrared absorption or emission spectra. This method is commonly used to identify organic and polymeric substances, as well as some inorganic materials. It is employed to determine and describe unknown materials such as films, solids, powders, or liquids, identify contaminants within a substance, detect additives extracted from polymer matrices, and ascertain oxidation, degradation, or unidentified monomers in failure analysis investigations.

FTIR is a widely utilized technique in the pharmaceutical industry due to its speed, non-destructive nature, and minimal sample preparation requirements. Recently, it has also been applied in the cosmetics industry for product characterization, stability assessment, contaminant identification, and forensic analysis of crime scene samples.

In summary, FTIR is an applied method for analyzing both organic and inorganic materials by examining their chemical structure through the study of chemical bonds and compositions. It is useful for identifying functional groups in substances and is based on the absorption of light by molecules as they interact with infrared radiation to determine the structure of the analyzed material. This method is also known as Fourier-transform infrared spectroscopic analysis and is applied in various ways.

Figure 2.6: FT-IR device

2.5.4 BrunauerEmmett Teller (BET)

Measuring surface properties has become more important for a variety of materials. Therefore, the BET instrument is considered a primary tool used by engineers and scientists to analyze the surface of different materials and evaluate their physical and chemical properties.This device consists of three main parts: the main part of the tools (the furnace, vacuum pump, electrical circuit, and electronic measuring device), the drainage cells, and the control system.The operation of this device relies on the adsorption of nitrogen gas on the surface to be measured. When activated, gas flows into the analysis cell, and excess molecules are removed until reaching a very low pressure inside this cell. Since nitrogen has a high affinity for the solid surface of small pores, it adsorbs onto the sample surface material over a short period. By analyzing the electronic signal, the amount of nitrogen adsorbed on the surface is measured, and the actual surface area can be calculated. When activated, gas flows into the analysis cell, and excess molecules are removed until reaching a very low pressure inside this cell. Since nitrogen has a high affinity for the solid surface of small pores, it adsorbs onto the sample surface material over a short period. By analyzing the electronic signal, the amount of nitrogen adsorbed on the surface is measured, and the actual surface area can be calculated.

2.5.5 pHpzc test

pHpzc means pH at a point of zero charge, it is an important parameter for determining the pH range at which it contains either a positive or negative surface charge. At the pHzpc, the surface of the material is neutral. above this value, the surface is positively charged, and Below this value, it becomes negatively

Figure 2.7: BET device

2.6 Optimization by Box-Behnken design method

An initial test was conducted to identify the primary influencing factors and assess their impact. Subsequently, a design implementation approach was employed within the Box-Behnken Design (BBD) framework, coupled with Response Surface Methodology (RSM) as a powerful statistical and mathematical tool. This method enables the optimization of adsorption performance parameters such as the dosage of the adsorbent material, solution acidity, temperature, and contact time for dye uptake, with MB as the response variable.

The statistical analysis of the BBD experimental data was performed using Design-Expert 13.0 software (Stat-Ease, Minneapolis, USA), which offers robust capabilities for experimental design, model development, and examining parameter interactions. The software serves as a valuable resource for both statistical and mathematical aspects of this study. The corresponding results are summarized below: (Table: 2.2). Then, the official stamp is added to the multivariate quadratic that links the influencing factors and the adsorption performance of the dye MB in equation: 2.1

$$Y = \beta_0 + \sum \beta_{ii} X_i^2 + \sum \sum \beta_{ij} X_i X_j \tag{2.1}$$

where (Y , X_i and X_j) represent the response of MB dye removal (%); and coded independent factors. β_0 is constant, whereas, β_i, βii, and βij signify the linear, quadratic, and interactive coefficients of input independent variables, respectively. A total of 29 runs were completed by BBD model to investigate the impacts of 4 independent factors on the removal of MB (%) as presented in Table: 2.3 .

Table 2.2: Experimental levels of independent factors and their codes in BBD

Factor Codes	**Variables**	**Lowest (-1)**	**Level centre (0)**	**Highest (+1)**
A	PPAC dose (g)	0.02	0.06	0.1
B	pH	4	7	10
C	Temperature (℃)	25	37.5	50
D	time (min)	6	18	30

Table 2.3: The four variables BBD matrix and experimental data for MB removal.

Run	A: PPAC Dose	B: pH	C: Temperature	D: time	MB removal (%)
1	0.02	4	37.5	18	25.6
2	0.1	4	37.5	18	51.5
3	0.02	10	37.5	18	32.9
4	0.1	10	37.5	18	87.9
5	0.06	7	25	6	51.2
6	0.06	7	50	6	69.4
7	0.06	7	25	30	84.1
8	0.06	7	50	30	89.3
9	0.02	7	37.5	6	20.9
10	0.1	7	37.5	6	65.6
11	0.02	7	37.5	30	50.1
12	0.1	7	37.5	30	91.5
13	0.06	4	25	18	41.4
14	0.06	10	25	18	83.9
15	0.06	4	50	18	64.8
16	0.06	10	50	18	84.6
17	0.02	7	25	18	23.8
18	0.1	7	25	18	86.1
19	0.02	7	50	18	43.9
20	0.1	7	50	18	**93.3**
21	0.06	4	37.5	6	21.3
22	0.06	10	37.5	6	68.8
23	0.06	4	37.5	30	84
24	0.06	10	37.5	30	64.7

25	0.06	7	37.5	18	78.4
26	0.06	7	37.5	18	85.5
27	0.06	7	37.5	18	80.5
28	0.06	7	37.5	18	77.2
29	0.06	7	37.5	18	76.9

2.6.1 Batch adsorption study

The adsorption experiments were conducted to evaluate the efficiency of PPAC adsorption for (MB) absorption, where a study of MB dye adsorption by PPAC was conducted at different initial concentrations (from 30 to 300 mg/L). The highest MB removal (93.3%) was obtained in experiment number 20 under ideal working conditions, with the following parameters: (PPAC) dose of 0.1 g, solution acidity of 7, operating temperature of 50 degrees Celsius, and contact time of 18 minutes. For this purpose, the ideal operating conditions were examined: 100 mL of MB dye solutions were transferred to a 100 mg/L concentration in a conical flask, and then a certain amount of PPAC was added to the bottles using a water bath (Memmert, 45 WNB7, Germany) with a vibration rate of 100 beats/minute. After the adsorption process, the remaining concentration of MB dye was determined using a spectrophotometric or optical spectrometer (HACH, DR 3900) at a maximum absorption wavelength of 661 nanometers, and then the amount of adsorbed was calculated using the following equation: 2.2

$$q_e = \frac{C_0 - C_e}{W} \times V \tag{2.2}$$

knowing that:

q_e is the adsorption capacity (mg/g)

V is the volume of the dye solution (L)

W(g) is the amount of the adsorbent.

CHAPTER 3

RESULTS AND DISCUSSION

In the concluding chapter, the focus is on analyzing and discussing the results of activated carbon derived from Pomegranate peels (PP). This particular carbon has demonstrated its efficacy in absorbing the MB dye from the aqueous medium. Through thorough examination, this chapter aims to shed light on the performance and potential applications of this innovative material

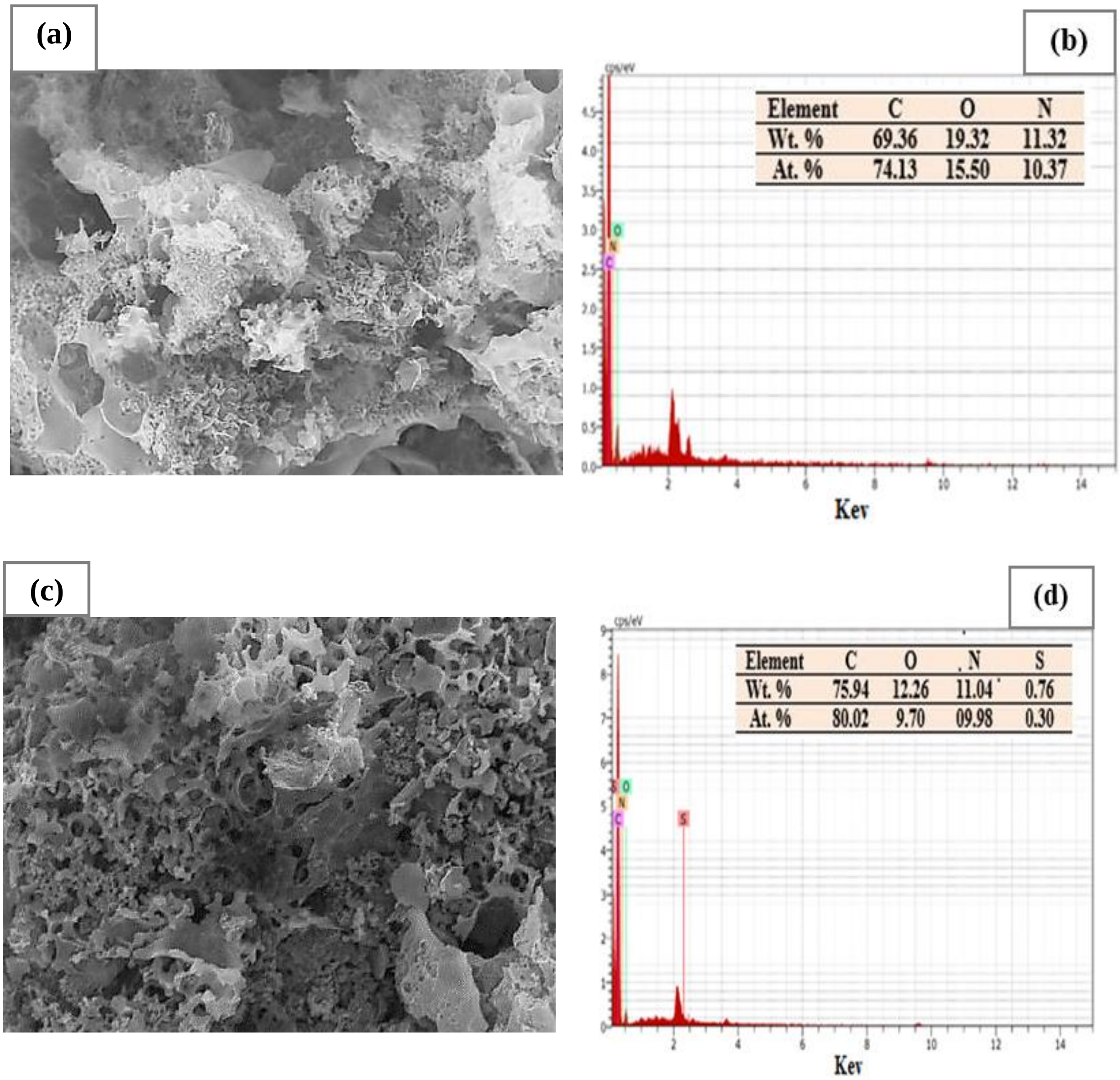
3.1 Results And Discussion Of PPAC

3.1.1 Characterization of PPAC

3.1.1.1 SEM-EDX Analysis

Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray Spectroscopy (EDX) serves as a powerful tool for elucidating disparities in formation, elemental composition, and particle density across various scales. This tandem technique also facilitates the generation of high-resolution images essential for identifying surface fractures, defects, contaminants, or corrosion within a diverse range of materials.

As depicted in (Figure: 3.1,a,b), SEM and EDX spectra of PPAC before and after MB absorption, prepared under ideal conditions, show that the surface of PPAC before absorption (Figure: 3.1,a) is non-homogeneous and irregular with surface features somewhat smooth, including the presence of voids. Meanwhile, EDX spectra applied to PPAC revealed the presence of several elements (carbon, oxygen, nitrogen) and the absence of sulfur, leading to the successful conversion of PP to PPAC via the microwave-assistedK_2CO_3 process. As seen in (Figure: 3.1,c), after absorption, there is a clear change in surface morphology, which was irregular and organized in pores due to the presence of MB dye on its surface. This led to an increase in C content(by weight %) in PPAC, while in the corresponding EDX spectrum, the peaks for sulfur species appeared, indicating the presence of MB dye particles during the absorption process, meaning that the dye can be trapped and absorbed [**?**].



Element	C	O	N
Wt. %	69.36	19.32	11.32
At. %	74.13	15.50	10.37

Element	C	O	N	S
Wt. %	75.94	12.26	11.04	0.76
At. %	80.02	9.70	09.98	0.30

Figure 3.1: SEM and EDX spectra: (a) PPAC, and (b) PPAC after adsorption of MB dye

3.1.1.2 FT-IR spectral results

The FTIR spectral analysis was conducted to delineate the fundamental functional groups within the surface structure of PPAC. The FT-IR spectra of PPAC before and after methylene blue (MB) adsorption are presented in (Figure: 3.2). In (Figure: 3.2,a), the observed IR bands at 3,400 cm^{-1}, 2,827 cm^{-1}, 2,117 cm^{-1}, and 1,015 cm^{-1} correspond to distinct functional groups: the OH stretching vibration [48], CH stretching of an alkane [49], sp or C≡C asymmetric vibrational band [50], and C-O stretching vibrations [51], respectively. Additionally, the IR band at 1,656 cm^{-1} signifies the presence of the C=O group typically found in esters or carboxylic acids [52].

Several functional groups contribute to the adsorption of MB, as evidenced by changes in the intensity of spectral signatures within the wavenumber ranges of 3,569 – 2,450 cm^{-1} and 1,345–1,075 cm^{-1}. Notably, the displacement of the strong band at 1,015 cm^{-1}, along with the band at 1,656 cm^{-1} observed in the IR spectrum of PPAC (Figure: 3.2,a), to 1,550 cm^{-1} in the PPAC+ MB spectrum (Figure: 3.2,b), is likely attributed to C=C and C=O stretching vibrations [53]. These spectral alterations provide compelling evidence that MB adsorption occurs on the surface of PPAC.

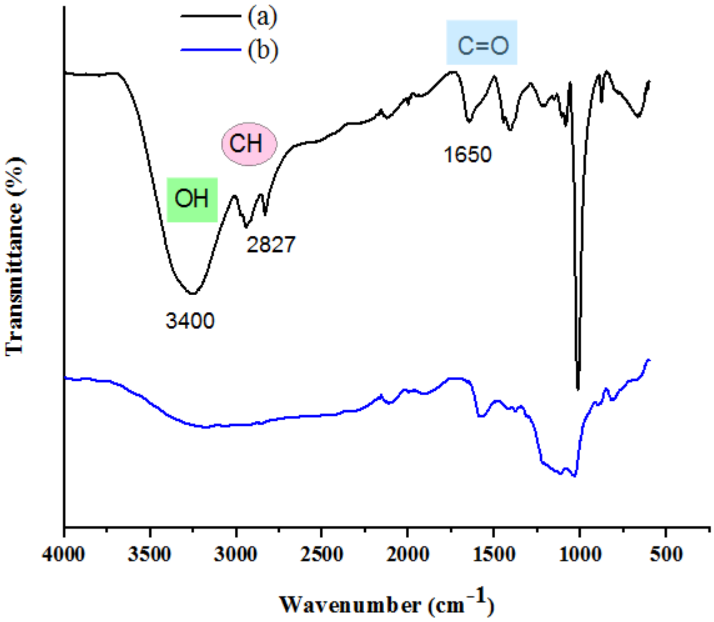


Figure 3.2: FTIR spectra of (a) PPAC, and (b) PPAC after adsorption of MB.

Table 3.1: Distinct Wavenumbers in the PPAC Spectrum.

The function or group	**Wavenumber (cm^{-1})**	**The specific type of bond**	**The appearance of the bond**
O-H	3400	stretching vibration	broad
C-H	2827	stretching of an alkane	medium to wide
$C\equiv C$	2117	asymmetric vibrational	
C-O	1015	stretching vibration	
$C=C$	155O	Stretching Vibration	
$C=O$	165O	Stretching Vibration	

3.1.1.3 BET analysis of PPAC

The N2 adsorption-desorption isotherms and pore size distribution curves, as illustrated in Figure: 3.3 , provide valuable insights into the structural properties of the material under study. Corresponding surface area and pore size parameters are detailed in Table: 3.2 , for comprehensive analysis.

Analysis of Figure: 3.3 reveals a distinctive nitrogen uptake profile characterized as type IV isotherms with a type H4 hysteresis loop. Notably, the P/P0 proximity to 1 suggests the presence of macropores within the samples. These macropores offer a significant advantage for adsorbing large-size adsorbates, as highlighted by [54] .

The obtained BET surface area of 387.7 (m^2/g) surpasses that of various inorganic framework materials, such as kaolin (61.1 m$^2/g), zeolite(24.6$m^2/g), and plasma-surface modified bentonite clay (65.3 m^2/g), as reported by Rida et al [55], and Sÿahin et al. [56]. This substantial surface area underscores the material's potential for efficient adsorption applications, particularly in the removal of MB dye from aqueous media.

Furthermore, the pore diameter of 1.33 nm falls within the lower range of 2 nm, indicating the prevalence of macropores on the surface of the PPAC. This observation holds significant implications for the material's adsorption behavior and its suitability for targeted applications.

Table 3.2: BET properties of the PPAC

Sample	**BET surface area (m^2/g)**	**Langmuir surface area (m^2/g)**	**Total pore volume (cm^3/g)**	**Mean pore diameter (nm)**
PPAC	387.683	478.085	0.128	1.33

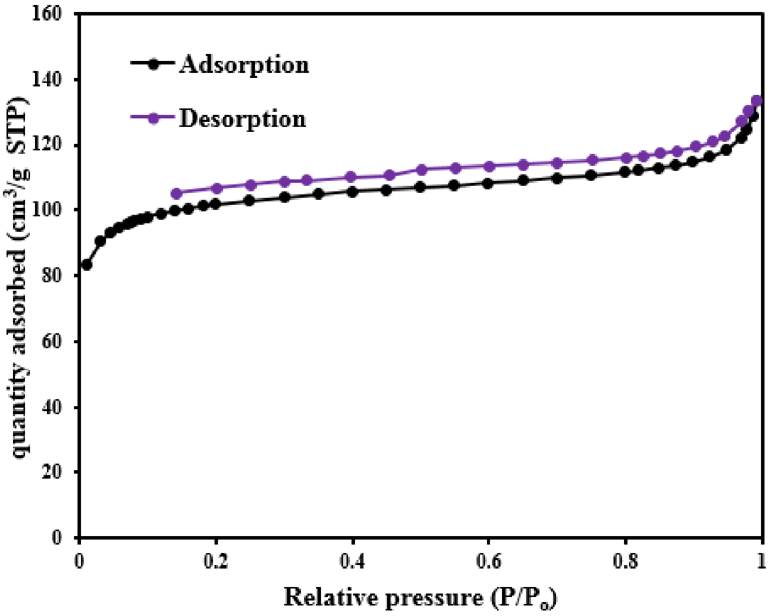


Figure 3.3: Nitrogen adsorption-desorption isotherms of PPAC at 77k.

3.1.2 BBD model analysis

The BBD model analysis was used to remove MB dye from aqueous media and improve it using ANOVA, where individual and interaction effects varied as follows: The dose of coagulant A, pH B, temperature C, and contact time D were simulated in the Box-Behnken design model. Responses to MB dye removal are listed inTable: 3.3 , showcasing various statistical multivariate boundary tests (linear, 2F1, quadratic, and cubic models). This experimental study reveals the relationship between experimental parameters and MB dye removal (response), relying on the sequential P-value for each model (linear $P < 0.0001$, 2F1 $P = 0.2425$, quadratic $P < 0.0001$, and cubic $P = 0.0892$). Additionally, the expected determination coefficients (R^2) pre-linear are 0.5622, pre-2F1 are 0.4948, pre-quadratic are 0.8805, and pre-cubic are 0.8236. The quadratic model was selected as the best model, as shown in equation: 3.1a :

$$\begin{aligned}\text{MB removal }(\%) = &+79.7 + 23.22A + 11.18B + 6.23C + 13.87D + 7.27AB \\ &- 5.67BC - 16.7BD - 17.40A^2 - 12.6B^2 - 6.42D^2 \qquad (3.1\text{a})\end{aligned}$$

Table 3.3: ANOVA analysis of MB removal .

Source	**Sum of Squares**	**Df**	**Mean Square**	**F-value**	**p-value**
Model	15069.10	14	1076.36	42.24	< 0.0001
PPAC-Dose	6472.81	1	6472.81	254.19	< 0.0001
B-pH	1500.80	1	1500.80	58.94	< 0.0001
C-Temp	466.25	1	2310.19	18.31	0.0008
D-time	2310.19	1	2310.19	90.72	< 0.0001
AB	211.70	1	211.70	8.31	0.0120
AC	41.60	1	41.60	8.31	0.2220
AD	2.72	1	2.72	0.1069	0.7485
BC	128.82	1	128.82	5.06	0.0411
BD	1115.56	1	1115.56	43.81	<0.0001
CD	42.25	1	42.25	1.66	0.2186
A^2	1964.79	1	1964.79	77.16	<0.0001
B^2	1032.52	1	1032.52	40.55	<0.0001
C^2	1.22	1	1.22	0.0478	0.8300
D^2	268.11	1	268.11	10.53	0.0059
Residual	306.45	14	25.46		
lack of fit	306.45	10	30.64	2.45	0.2012
Pure error	50.06	4	12.51		
Cor Total	15425.61	28			

3.1.2.1 Parametric optimization of BBD

There is another approach to understanding the combined binary interaction of significant parameters (dose, pH, temperature, and time) [57]. These results are dependent on the graphical representation of three-dimensional (3D) response surfaces, and two-dimensional (2D) contour plots that employ the Design-Expert software (version 13, Stat-Ease, Minneapolis, USA), as illustrated in Figure: 3.4 . The interaction between PPAC dose (A) and working solution pH (B) was a significant function, while the other two parameters (temperature and contact time) were kept constant at 50 °C and 18 min. Referring to Table: 3.3 , the F-value and p-value were estimated at 8.31 and 0.0120, respectively. It is evident from Figure: 3.4,a that the MB dye removal increased from 20.9% to 92.09% with a greater PPAC dose from 0.02 to 0.1 g. This observation returns to the unique surface properties of PPAC that serve to augment the number of active adsorption sites and pores on its surface. The latter was discussed in the above section (BET analysis). The combined interaction of solution pH (B) with temperature (C) was the second statistically significant interaction for the removal of MB (F-value 5.06 with a p-value equal to 0.0411) by keeping the other operation parameters constant (PPAC dose = 0.1 g/100 mL and contact time = 18 min). Figure: 3.4,b shows a 3D response surface graph and the 2D contour corresponding plot that is presented in Figure: 3.4,b* , respectively. It was observed that MB removal (%) increased by raising the solution pH from 4 to 10. This observation can be understood based on the pHpzc results, which provide insight into the surface charge of PPAC. In this regard, the value of pHpzc for the adsorbent was recorded to be 7.6 in Figure Figure: 3.5 . At pH values above 7.6, the surface of PPAC will adopt a negative charge because of deprotonation in basic media. In turn, favorable electrostatic attraction can occur between the negatively charged adsorption sites and dyes with cationic surface charge. Similar results for MB dye uptake by Casuarina empty fruit-based activated carbon were reported by [58]. On the other hand, the greater removal of MB dye by varying the temperature from 25 °C to 50 °C indicates that the adsorption process on the surface of PPAC with MB is endothermic [59].

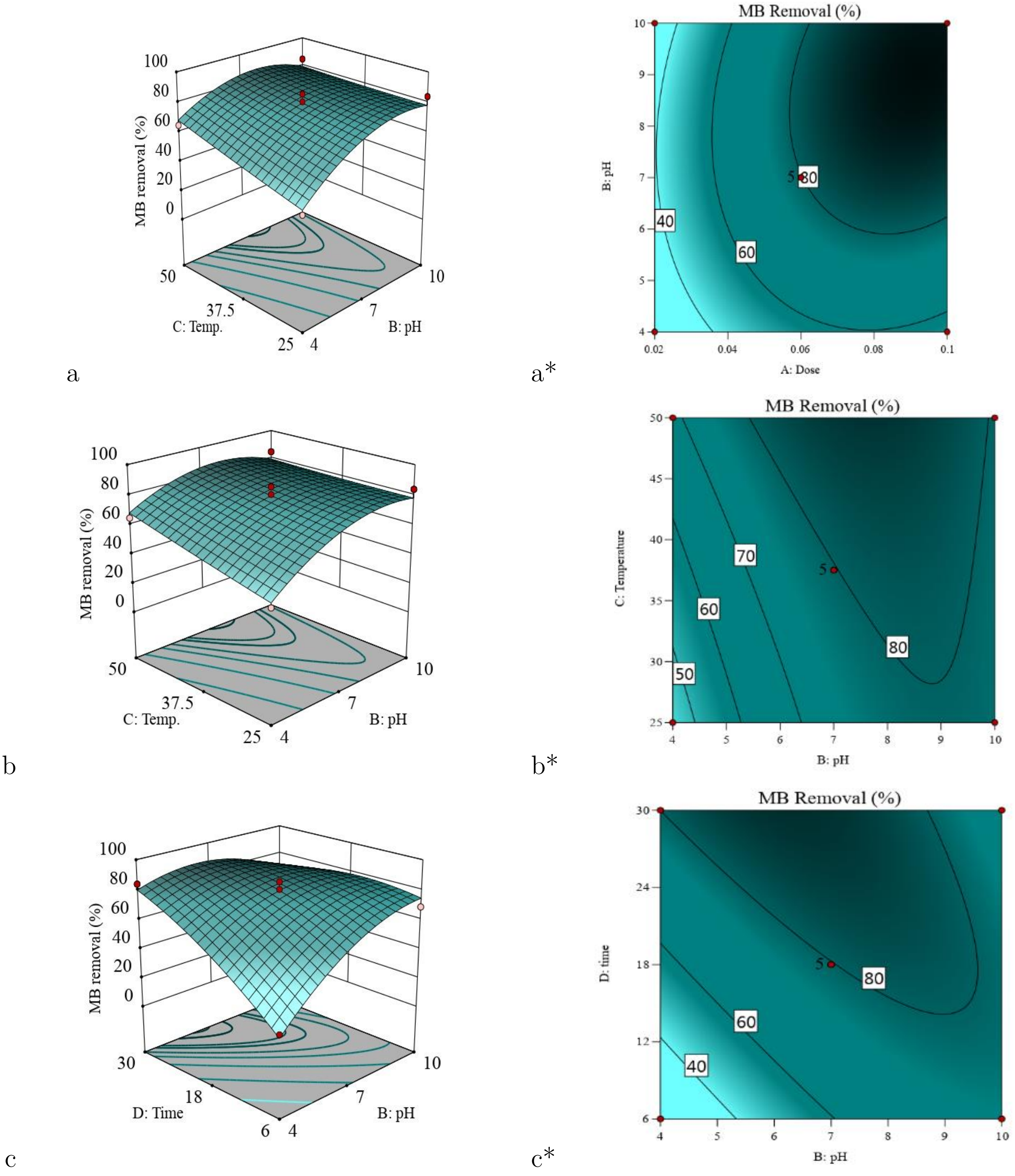


Figure 3.4: (a) 3D plot, and (a*) 2D contour plot of the parametricc interaction between AB, (b) 3D plot, and (b*) 2D contour plot of the parametric interaction between BC, and (c) 3D response surface plot, (c*) 2D contour plot of MB dye removal demonstrating the parametric interaction between BD

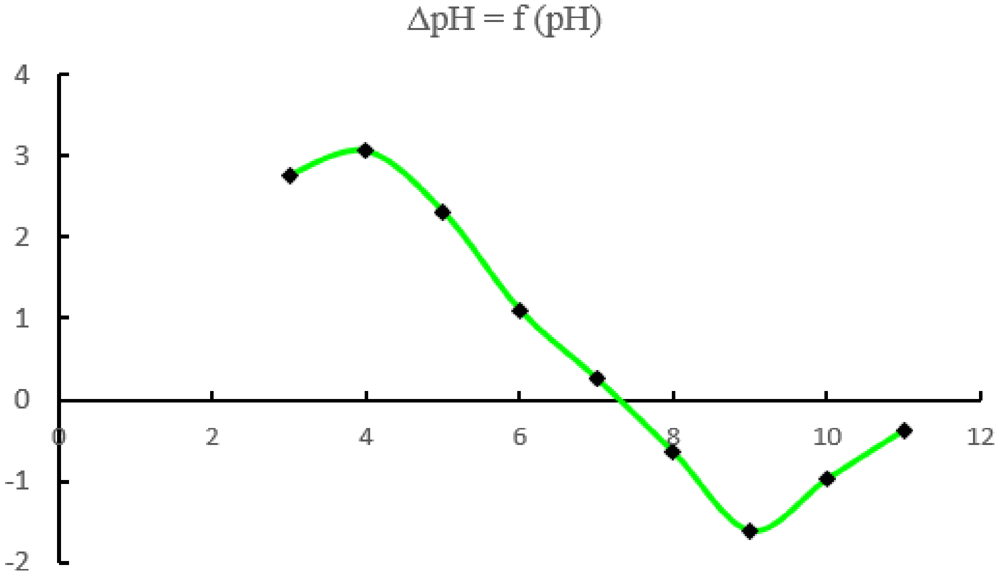


Figure 3.5: pHpzc of PPAC.

3.1.3 Adsorption study

The efficiency of adsorption for PPAC has been evaluated, where the adsorption time was adopted as the minimum level to reach equilibrium point in this study. It was measured at seven different initial concentrations ranging from 30 to 300 mg/l, achieving, as shown in the Figure Figure: 3.6 , that the adsorption process is very rapid, evident within the first few minutes of the treatment process according to the data obtained. Based on concentration analysis, the adsorption rate was recorded in less than five ten-minute analyses as follows: 28.9, 69.7, 89.7, 144.4, 141.6, 173.2, 196.79 mg/l for varying initial concentrations of (30, 60, 100, 150, 200, 250, 300 mg/l), respectively. With increased contact time, the rapid removal of dye for different initial concentrations was characterized by a very rapid and short removal. It was observed that the PPAC material has a porous structure along with numerous active or non-active sites on the surface qualified for dye removal, exhibiting high absorption capacity.

3.1.4 Adsorption kinetics

The pseudo-first-order, pseudo-second-order, and intraparticle diffusion models are three kinetic models used to understand the controlling behavior of the adsorption process of methylene blue (MB) onto porous polymer-activated carbon (PPAC). The first two models are represented by the non-linear equations: 3.2,and 3.3, respectively. In contrast, the intraparticle diffusion model is described by the linear equation: 3.4 equation

The kinetic parameters of the PSO and PFO models are shown in Table: 3.4 . The PSO kinetic model was shown to be more appropriate than the PFO model for explaining MB dye uptake on PPAC, based on the correlation coefficients R^2 that were obtained. Additionally, there was a fair degree of agreement between the experimental results and the theoretical values of qe computed values. These comments suggest that chemisorption defined the behavior of the MB adsorption process onto PPAC.

Table: 3.5 and Figure: 3.7 show the intra-particle diffusion model's computed parameters and plot of qt vs $t^{1/2}$ data, respectively. Figure: 3.7 depicts the two processes that the adsorption process goes through Step 1 spans (0 to 3.87 min), during which the external mass transfer of MB dye onto the porous surface of PPAC caused the intra-particle diffusion to occur quickly [60]. The adsorption system exhibits a slower diffusion in the equilibrium phase for a longer contact period in step 2, which runs from (3.87 to 13.41 min). It is important to notice that boundary layer effects or the presence of external mass transfer resistance are indicated by the plot's minor curvature [61] .

$$q_t = q_e(1 - exp^{-K_1 t}) \tag{3.2}$$

$$q_t = \frac{q_e^2 K_2 t}{1 + q_e K_2 t} \tag{3.3}$$

$$q_t = K_d t^{1/2} + C \tag{3.4}$$

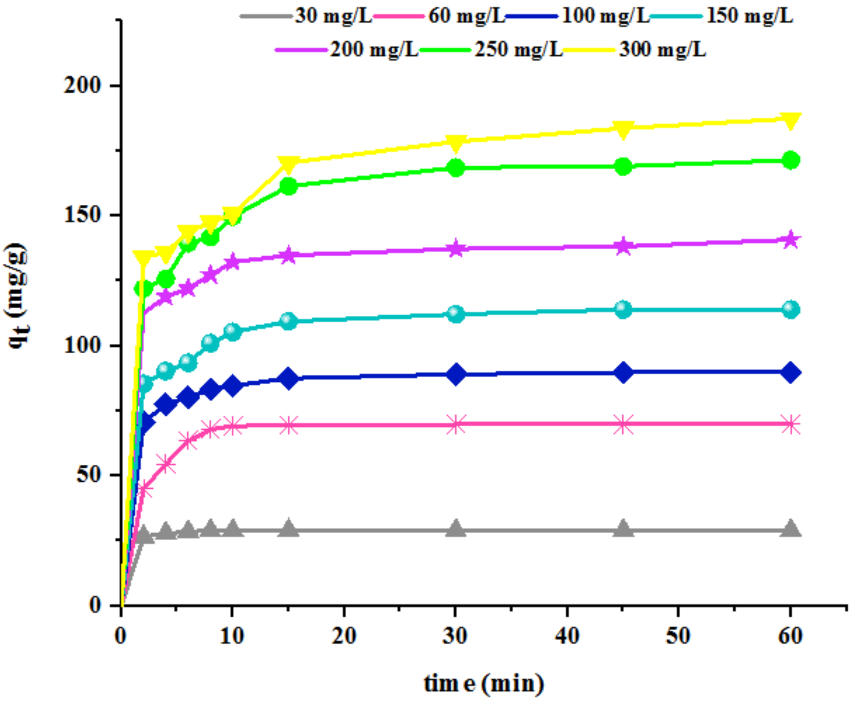


Figure 3.6: Effect of intial MB concentrations vs .contact time.

Table 3.4: PFO and PSO kinetie parameters for MB dye adsorption onto PPAC

MB Concentration(mg/L)	$q_e exp(mg/g)$	**PFO**			**PSO**		
		$q_e cal(mg/g)$	$k_1(1/min)$	R^2	$q_e cal(mg/g)$	$k_2 * 10^{-2}(g/mgmin)$	R^2
30	28.9	28.5	1.32	0.99	28.7	14.07	0.99
60	69.8	68.3	0.79	0.99	70.5	1.832	0.99
100	89.8	85.5	0.77	0.98	90.2	1.550	0.99
150	114.4	108.2	0.62	0.95	114.3	1.181	0.99
200	141.6	134.6	0.61	0.97	140.0	0.996	0.99
250	173.2	164.0	0.46	0.93	172.1	0.500	0.98
300	196.7	180.9	0.39	0.87	190.5	0.358	0.96

Table 3.5: Parameters of intra-particle diffusion model at various initial MB concentrations

MB Concentration		**Intraparticle diffusion model**		
(mg/L)	$K_d(L/g)$	ki $(mg/g.t^{1/2})$	C (g/mg)	R^2
30	**59.41**	11.43	4.42	0.82
60	**12.26**	10.33	26.0	0.62
100	**3.549**	9.823	43.1	0.50
150	**2.413**	6.673	66.2	0.41
200	**2.382**	5.424	93.4	0.31
250	**1.747**	6.015	108.7	0.38
300	**1.570**	6.290	116.5	0.46

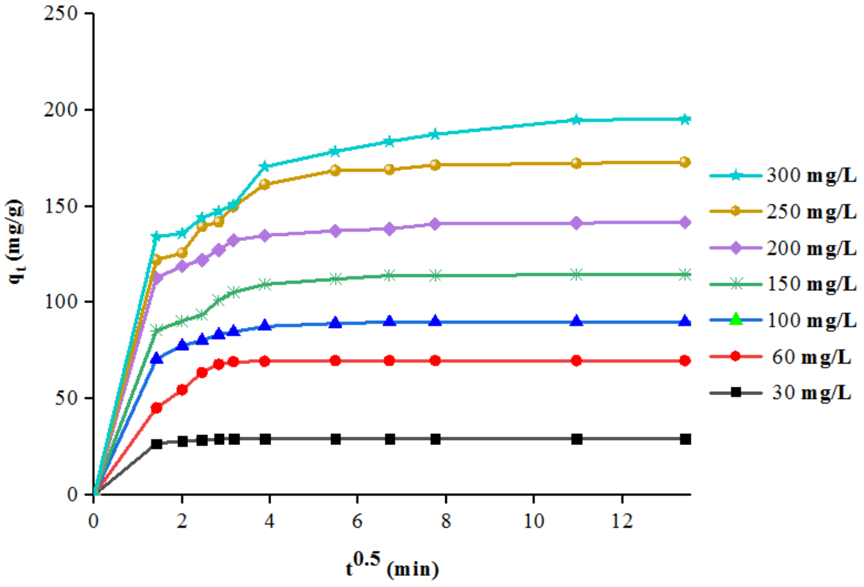


Figure 3.7: q_t vs $t^{0.5}$ data for intra-particule diffusion

3.1.5 Adsorption isotherm

According to the heat of adsorption equilibrium, it is very important to demonstrate the relationship between the concentration of the adsorbate substance and the degree of substance deposition on the surface of the adsorbent material at a constant temperature. Various models of heat of adsorption have been adopted and have included the Langmuir, Freundlich, and Temkin methods, which were simulated in the study of the adsorption mechanism of MB dye on the surface of PPAC, as shown in Figure: 3.7 and Table: 3.6 Lower R^2 values were observed for the Langmuir model, with the following trend: Langmuir ($R^2 = 0.91$) < Temkin ($R^2 = 0.93$) < Freundlich ($R^2 = 0.97$). This indicates that the Freundlich isotherm model provides the most reliable description of the adsorbate distribution on a heterogeneous surface. Additionally, the value of n ($n = 6.10$) lies between 1 and 10, suggesting a favorable physical adsorption process [62]. According to the best fit by the Langmuir isotherm model, the maximum monolayer adsorption capacity was 291.5 mg/g .

In a related study, Jawad et al [63] reported that methylene blue was adsorbed by activated carbon derived from watermelon rind using a microwave-assisted process. Similarly, Salem et al [64] found that walnut shells activated through a microwave-assisted process (producing walnut shell-activated carbon, WSAC) enabled effective cationic dye uptake. The maximum monolayer adsorption capacity was 283.9 mg/g for WSAC and 130 mg/g for untreated walnut shells (WS).

The high q max value for PPAC with MB underscores its potential as a promising adsorbent for removing toxic cationic dyes from aqueous solutions.

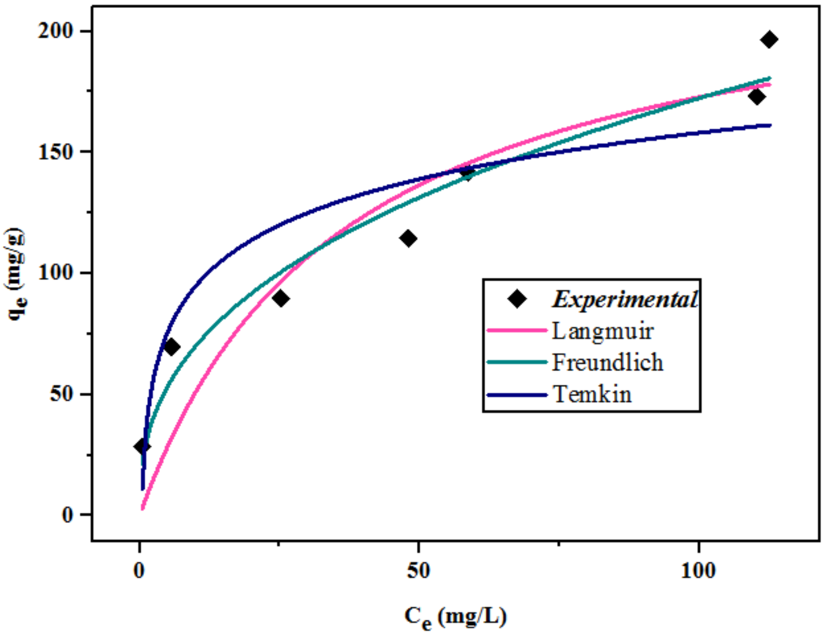


Figure 3.8: Adsorption isotherms of MB onto PPAC

Table 3.6: Calculated adsorption isotherm parameters for MB adsorption onto PPAC

Adsorption isotherm	Parameter	MB
Langmuir	q_{max} (mg/g)	291.5
	K_L (L/mg)	0.67
	R^2	0.91
Freundlich	K_F (mg/g) (L/mg)$^{1/n}$	149.1
	n	6.10
	R^2	0.97
Temkin	K_T (L/mg)	14.82
	b_T (J/mol)	82.2
	R^2	0.93

3.1.6 Adsorption mechanism

To explain the dye adsorption behavior of PPAC, a schematic illustration of the adsorption mechanism is proposed based on the interactions between various surface functional groups of PPAC and MB Figure: 3.9 . Figure: 3.9 suggests that two types of potential interactionshydrogen bonding and electrostatic interactionscontribute to the enhanced adsorption of MB onto the PPAC adsorbent.

Hydrogen bonding interactions occur between the lone electron pairs on nitrogen atoms in MB molecules and hydrogen donor atoms in functional groups on the surface of the adsorbent [65]. Electrostatic interactions become more significant, especially in basic medium, where functional groups such as carboxyl and hydroxyl become more negatively charged due to deprotonation. This facilitates more favorable interactions between ionized OH or COOH groups and the positively charged ammonium groups in the MB dye .

Additionally, it is important to note that the number of active sites, the adsorbent dosage, the temperature of the reaction medium, and the pH of the solution are the main factors influencing the adsorption process between PPAC and MB.

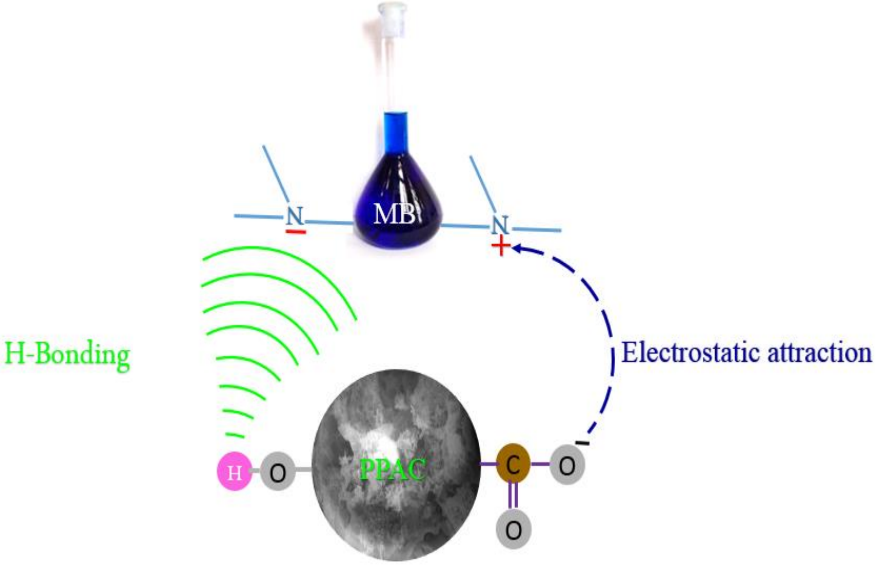


Figure 3.9: Schematic illustration of the possible adsorption mechanism between PPAC and MB dye.

CONCLUSION

In conclusion, biomass waste from pomegranate peel was successfully converted into a more sustainable adsorbent using a microwave-assisted technique, demonstrating fast removal and excellent adsorption capability with methylene blue (MB) as a model dye contaminant through a physical adsorption process. The optimal activation conditions were established as follows: an impregnation ratio of 1:2 (PP/K_2CO_3), radiation power of 800W, and irradiation time of 15 minutes.

The obtained adsorption operation parameters were: a PPAC dose of 0.1 g, solution pH of 7, process temperature of 50°C, and an adsorption time of 18 minutes. These conditions resulted in the highest adsorptive removal efficiency of 93.3% for MB. The Freundlich isotherm model provided the best fit, confirming multilayer adsorption of MB onto the heterogeneous surface sites of PPAC. The maximum monolayer adsorption capacity, according to the Langmuir isotherm model, was computed to be 291.5 mg/g .

In terms of kinetic studies, the pseudo-second-order model was more suitable for describing the adsorption properties of the PPAC/MB system. PPAC represents a renewable, cost-effective, and efficient adsorbent material for capturing MB dye from aqueous media.

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