



Efficient Removal of Methylene Blue Dye from Aqueous Solutions Using Raw Rice Straw as a Sustainable Biosorbent

Haziq Farooq*, Muhammad Naveed

Institute of Soil and Environmental Sciences, University of Agriculture Faisalabad, Faisalabad 38040, Pakistan

Article Info

Keywords:

Rice Straw, Methylene Blue, Biosorption, Agricultural Waste, Wastewater Treatment, Adsorption Kinetics, Adsorption Isotherms, Low-Cost Adsorbent

Date:

Received: 22 July 2024

Accepted: 08 November 2024

Published: 15 December 2024

Volume: Vol. 3(1), 2024



Copyright: © 2024 by the authors. This article is distributed under the Creative Commons Attribution (CC BY) license, allowing for open access and sharing under specified terms and conditions. (<https://creativecommons.org/licenses/by/4.0/>).

Abstract

The contamination of water bodies by synthetic dyes from textile industries represents a major environmental challenge worldwide. This study investigates the utilization of raw rice straw (RS), an abundant agricultural waste, as a low-cost and eco-friendly biosorbent for removing methylene blue (MB) dye from aqueous solutions. The biosorption performance was evaluated through batch experiments under varying conditions of pH, contact time, initial dye concentration, and biosorbent dosage. Results demonstrated that raw rice straw exhibited remarkable adsorption capabilities, achieving up to 99% MB removal under optimal conditions at pH 4. The adsorption process reached equilibrium within 120 minutes and followed pseudo-second-order kinetics, indicating chemisorption as the dominant mechanism. Equilibrium data were best described by the Langmuir isotherm model, suggesting monolayer adsorption on a homogeneous surface. The maximum adsorption capacity increased with biosorbent dosage, with optimal performance achieved at 3.0 g L⁻¹. Characterization through SEM, FTIR, and XRD analyses revealed that the presence of porous structures, oxygen-containing functional groups, and amorphous regions in raw rice straw contributed significantly to its adsorption efficiency. The study concludes that raw rice straw, without any chemical modification or pyrolysis, serves as an effective, sustainable, and economically viable biosorbent for treating dye-contaminated wastewater, while simultaneously addressing agricultural waste management challenges.

1. Introduction

Water contamination represents one of the most pressing global challenges of our time, threatening both human health and ecosystem integrity. This crisis is exacerbated by rapid population growth, urbanization, industrialization, and inadequate wastewater management (du Plessis, 2022). Industrial activities are a primary contributor, discharging a complex mixture of heavy metals, toxic chemicals, and synthetic compounds into water bodies. These pollutants can lead to severe consequences, including immunotoxicity, reproductive issues, and the creation of aquatic "dead zones" devoid of life (Lin et al., 2022). Among these industrial pollutants, synthetic dyes from sectors like textiles pose a significant threat due to their persistence, visibility, and toxicity.

The global production of dyestuffs is immense, with an estimated 10-15% of used dyes being discharged in industrial effluents (Al-Ghouti et al., 2010). Azo dyes, characterized by their nitrogen double bonds, constitute about half of all commercial dyes and are particularly problematic. When released into water, they reduce light penetration, impair photosynthesis, and increase biochemical oxygen demand, thereby suffocating aquatic ecosystems (Yeddou Mezener et al., 2013). Furthermore, under certain conditions, azo dyes can break down into aromatic amines, which are known to be carcinogenic and toxic (Heibati et al., 2014). Methylene Blue (MB), a common cationic azo dye used in textiles, is a model pollutant for such studies. Its presence in water causes adverse effects in humans, including methemoglobinemia, vomiting, and skin irritation, highlighting the critical need for its removal from wastewater (Wang et al., 2020).

Corresponding Author: Muhammad Haziq Farooq

Email: 008785@gmail.com

<https://doi.org/10.54219/AEE.2024.xxxx>

©2024, PagePal Pvt. Ltd. (<https://journals.pagepal.org/index.php/AEE>)

Conventional wastewater treatment methods often struggle to remove these resilient dye molecules efficiently. Techniques like advanced oxidation, membrane filtration, and coagulation can be effective but are frequently hampered by high operational costs, energy demands, or the generation of secondary waste (Sharma et al., 2013). In this context, adsorption has emerged as a superior alternative due to its simplicity, efficiency, and cost-effectiveness. While activated carbon is a widely used adsorbent, its high production cost from non-renewable sources like coal has spurred the search for low-cost, sustainable alternatives (Chan et al., 2009). This has led to increased interest in utilizing agricultural waste products as biosorbents, offering a dual benefit of waste valorization and pollution remediation.

Rice straw (RS) is one such abundant agricultural residue. Global rice production generates hundreds of millions of tons of straw annually, much of which is disposed of through open-field burning—a practice that contributes significantly to air pollution, releasing particulate matter and greenhouse gases (Phuong et al., 2021). Instead of being a waste management problem, this widely available, low-cost lignocellulosic material presents a valuable opportunity. Its natural structure, rich in functional groups, makes it a promising candidate for use as a biosorbent to sequester pollutants like dyes from contaminated water, creating a sustainable and circular solution to two distinct environmental issues.

The discharge of synthetic dyes, particularly persistent and toxic cationic dyes like Methylene Blue, from industrial effluents poses a severe threat to water resources. Conventional treatment methods are often economically and environmentally unsustainable for widespread application. Simultaneously, the agricultural sector faces the challenge of managing vast quantities of residual biomass, such as rice straw, whose open burning contributes to severe air pollution. There is an urgent need to develop cost-effective and eco-friendly wastewater treatment solutions that can also address the problem of agricultural waste management. Utilizing rice straw as a biosorbent for dye removal presents a promising strategy to tackle both issues concurrently; however, the adsorption efficiency, optimal operational parameters, and underlying mechanisms of untreated rice straw for Methylene Blue removal require systematic investigation.

It is hypothesized that untreated rice straw, due to its lignocellulosic composition and presence of active functional groups, will exhibit significant adsorption capacity for Methylene Blue cations in aqueous solution. Furthermore, it is anticipated that the adsorption process will be highly dependent on the solution pH and initial dye concentration, and that the equilibrium data will conform to the Langmuir isotherm model while the kinetics will follow a pseudo-second-order model, indicating monolayer adsorption governed by chemisorption. The overarching aim of this study is to evaluate the potential of untreated rice straw as a sustainable biosorbent for the removal of Methylene Blue dye

from aqueous solutions. The specific objectives are: To prepare and characterize untreated rice straw biosorbent. To investigate the influence of key adsorption parameters—including solution pH, biosorbent dosage, initial dye concentration, and contact time—on the removal efficiency of Methylene Blue. To analyze the adsorption equilibrium and kinetics by fitting experimental data to established isotherm and kinetic models to understand the mechanism of biosorption.

2. Materials and Methods

2.1. Materials and Preparation

The success of this experimental investigation was contingent upon the selection of a sustainable, low-cost biosorbent and the use of high-purity reagents. Locally sourced rice straw (*Oryza sativa*) was selected as the primary biosorbent material due to its natural abundance, fibrous structure, and potential for effective pollutant sequestration. The straw was collected from agricultural fields in the vicinity of the University of Agriculture Faisalabad.

2.1.1. Biosorbent Preparation

The collected rice straw was initially subjected to a cleaning process to remove extraneous debris. This involved manual shaking followed by a thorough washing sequence, first with tap water and subsequently with multiple rinses of distilled water to eliminate adhered soil and impurities. The cleaned biomass was then air-dried under sunlight for 48–72 hours to reduce moisture content, followed by oven-drying at 60 °C for 24 hours to achieve complete dryness. The desiccated material was ground into a fine powder using a mechanical grinder and sieved through a 250 µm mesh to obtain a uniform particle size. The final rice straw powder was stored in airtight glass containers at ambient temperature to prevent moisture absorption prior to experimental use.

2.1.2. Dye and Reagents

Methylene Blue (MB), a cationic dye of the phenothiazine class with the molecular formula $C_{16}H_{18}ClN_3S$ and a molecular weight of 319.85 g/mol, was used as the model pollutant. A stock solution with a concentration of 1000 mg/L was prepared by dissolving an accurate mass of analytical-grade MB powder in distilled water. All working solutions (20–100 mg/L) were derived from this stock via serial dilution. The pH of the dye solutions was adjusted using 0.1 N solutions of hydrochloric acid (HCl) and sodium hydroxide (NaOH), both prepared with analytical-grade chemicals and distilled water. Distilled water was used exclusively throughout the study for all solution preparation, rinsing, and dilution procedures.

2.2. Experimental Procedure for Batch Biosorption

The adsorption characteristics of methylene blue onto rice straw were evaluated through a series of batch experiments conducted under controlled laboratory conditions. The experiments were designed to systematically

investigate the influence of key operational parameters, including contact time, solution pH, biosorbent dosage, and initial dye concentration.

2.2.1. General Batch Protocol

Batch experiments were performed using 50 mL conical centrifuge tubes (Falcon tubes) containing a defined volume of methylene blue solution. A predetermined mass of the rice straw biosorbent was added to each tube. The mixtures were then agitated at a constant speed of 150 rpm on an orbital shaker to ensure uniform mixing and sufficient contact between the adsorbent and the dye molecules. All experiments were conducted in triplicate at room temperature to ensure the reliability and reproducibility of the results, with average values reported.

2.2.2. Effect of Contact Time

To determine the equilibrium contact time, experiments were carried out with a fixed initial dye concentration, biosorbent dosage, and pH. The contact time was varied from 0 to 120 minutes, with samples extracted at 30-minute intervals. At the end of each predetermined period, the mixtures were immediately centrifuged to separate the biosorbent, and the supernatant was analyzed for residual dye concentration.

2.2.3. Effect of Solution pH

The impact of solution pH on biosorption efficiency was studied by adjusting the pH of the dye solutions to values of 2, 4, 6, 8, and 10 using 0.1 N HCl or NaOH. A fixed biosorbent dosage and initial dye concentration were used, and the samples were agitated for the predetermined optimal contact time before separation and analysis.

2.2.4. Effect of Biosorbent Dosage

The influence of adsorbent mass was investigated by varying the dosage of rice straw from 0.025 g to 0.25 g per 150 mL of dye solution, maintaining constant initial dye concentration, pH, and contact time. This experiment aimed to identify the most efficient dosage for maximum dye removal while minimizing material usage.

2.2.5. Effect of Initial Dye Concentration

Adsorption capacity was assessed by exposing a fixed mass of rice straw to methylene blue solutions of varying initial concentrations. Different volumes of the stock solution were used to prepare 150 mL samples with concentrations spanning a defined range. The pH and contact time were maintained at their previously determined optimal values.

2.3. Analytical Techniques and Calculations

The concentration of methylene blue in the supernatant before and after biosorption was quantified using a double-beam UV-Visible spectrophotometer. The maximum absorbance wavelength for MB was determined to be 664 nm, and a calibration curve of absorbance versus

concentration was constructed using standard solutions for accurate determination of unknown concentrations.

The percentage of dye removal and the adsorption capacity at time t (q_t , mg/g) were calculated using the following equations:

$$\text{Dye Removal (\%)} = [(C_0 - C_t) / C_0] \times 100$$

$$\text{Adsorption Capacity (q}_t\text{)} = [(C_0 - C_t) \times V] / m$$

Where:

- C_0 is the initial concentration of the dye (mg/L)
- C_t is the concentration of the dye at time t (mg/L)
- V is the volume of the solution (L)
- m is the mass of the biosorbent used (g)

The pH of the solutions was measured and adjusted using a calibrated digital pH meter. Precise weighing of the biosorbent was achieved using an analytical balance with a precision of ± 0.001 g. The separation of the biosorbent from the aqueous solution after adsorption was consistently performed using a centrifuge to ensure clear supernatants for spectrophotometric analysis.

2.4. Data Analysis

The experimental data were analyzed to evaluate the biosorption performance. The relationships between the operational parameters and the removal efficiency were assessed. Furthermore, the data were fitted to established adsorption isotherm and kinetic models to understand the equilibrium behavior and the mechanism of the adsorption process.

3. Results and Discussion

3.1. Characterization of Raw Rice Straw

The inherent physicochemical and structural properties of raw rice straw, which govern its biosorption potential, were evaluated using Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), and X-ray Diffraction (XRD) analyses. The SEM micrograph revealed the native, unmodified structure of the rice straw, characterized by a fibrous and irregular surface morphology (Figure 1). The surface displayed a network of long, tubular structures and rough textures inherent to lignocellulosic biomass, with visible pores and crevices. This natural roughness and porosity, stemming from the plant's vascular tissue and cellular structure, provide a substantial surface area and numerous potential sites for the attachment and entrapment of dye molecules. The absence of the extensive, engineered porosity seen in biochar is notable, confirming that the adsorption occurs on the raw biomass's natural surface architecture.

The FTIR spectrum of raw rice straw confirmed the presence of diverse functional groups responsible for its biosorptive capability. A broad and intense absorption band around $3320\text{--}3400\text{ cm}^{-1}$ was observed, attributed to O–H stretching vibrations from cellulose, hemicellulose, and lignin. Peaks at approximately 2915 and 2850 cm^{-1} corresponded to C–H stretching in aliphatic chains. A distinct

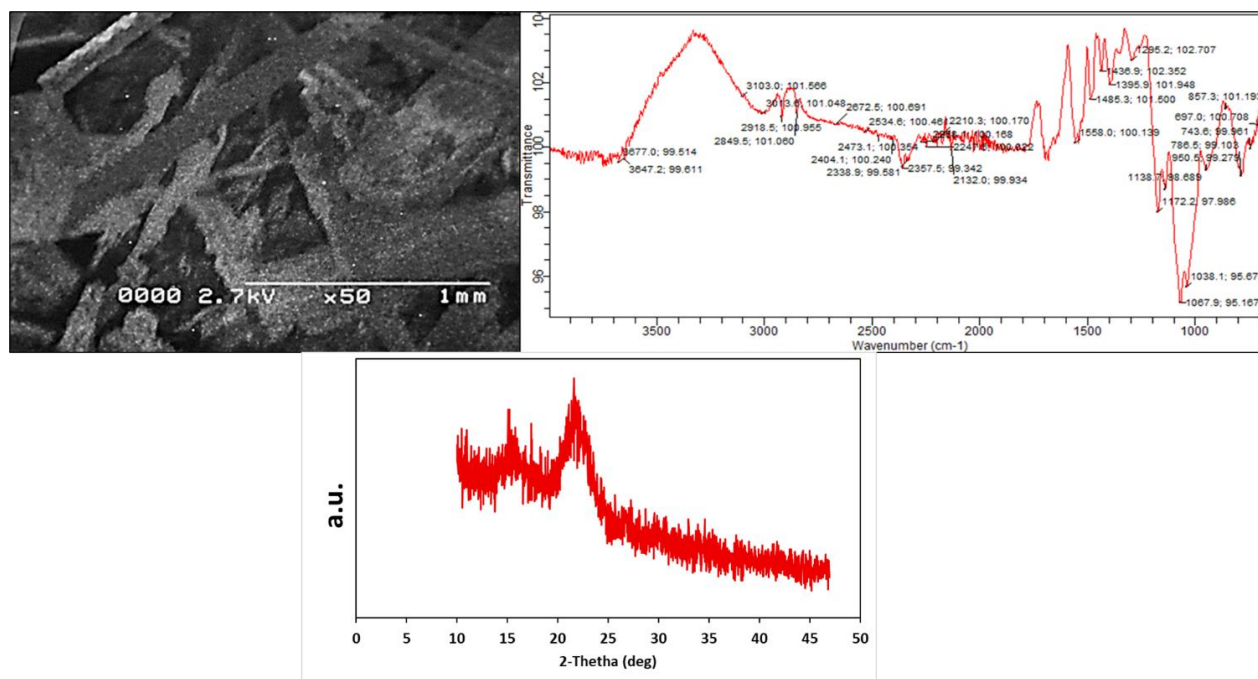


Figure 1: Effect of pH, contact time, initial concentration, and adsorbent dose on the removal efficiency of methylene blue (MB) by rice straw. This figure presents the adsorption performance of rice straw under varying experimental conditions. (a) The influence of solution pH (2–10) on MB removal indicates that adsorption efficiency increased with pH up to 4, reaching nearly 100% removal, and slightly declined at higher pH values, suggesting optimal adsorption under mildly acidic conditions due to favorable electrostatic interactions between MB cations and negatively charged rice straw surface sites. (b) The effect of contact time (0–120 min) shows a gradual increase in MB removal with time, approaching equilibrium after 120 minutes, implying sufficient diffusion of dye molecules into active adsorption sites. (c) The impact of initial MB concentration (3–15 mg L⁻¹) demonstrates an increase in removal efficiency with higher concentrations, indicating that more MB molecules enhance the driving force for mass transfer until adsorption sites begin to saturate. (d) The variation in adsorbent dosage (0.5–5 g L⁻¹) reveals a steady improvement in MB removal percentage with increasing rice straw dose, attributed to the greater surface area and number of active binding sites available for dye adsorption. Overall, rice straw exhibited high adsorption efficiency under optimized conditions, confirming its potential as a low-cost,

peak around 1730 cm⁻¹, often associated with C=O stretching in acetyl and uronic ester groups of hemicellulose, was present. The absorption bands between 1590 and 1650 cm⁻¹ are linked to aromatic C=C stretching in lignin and absorbed water. Peaks in the range of 1020–1050 cm⁻¹ were assigned to C–O stretching in polysaccharides (cellulose and hemicellulose) and Si–O vibrations from silica, a natural component of rice straw. This rich suite of hydroxyl, carboxyl, and other oxygen-containing functional groups is pivotal for binding cationic dyes like methylene blue through mechanisms such as electrostatic attraction and hydrogen bonding.

The XRD pattern of raw rice straw showed characteristic peaks of cellulose, the primary structural component. A prominent peak around 22° (2θ) and a smaller one near 16° (2θ) are typical of the crystalline regions of cellulose I. The pattern indicates a semi-crystalline structure, which is a composite of crystalline cellulose microfibrils embedded in an amorphous matrix of hemicellulose and lignin. This amorphous phase is particularly accessible for solute diffusion and interaction, playing a significant role in the

biosorption process. The combined characterization results affirm that raw rice straw possesses a complex lignocellulosic structure with a naturally rough surface, an abundance of active functional groups, and a semi-crystalline composition. These inherent properties make it a competent biosorbent without requiring any thermal or chemical activation.

This figure presents the adsorption performance of rice straw under varying experimental conditions. (a) The influence of solution pH (2–10) on MB removal indicates that adsorption efficiency increased with pH up to 4, reaching nearly 100% removal, and slightly declined at higher pH values, suggesting optimal adsorption under mildly acidic conditions due to favorable electrostatic interactions between MB cations and negatively charged rice straw surface sites. (b) The effect of contact time (0–120 min) shows a gradual increase in MB removal with time, approaching equilibrium after 120 minutes, implying sufficient diffusion of dye molecules into active adsorption sites. (c) The impact of initial MB concentration (3–15 mg L⁻¹) demonstrates an increase in removal efficiency with higher concentrations, indicating that more MB molecules enhance the driving force

for mass transfer until adsorption sites begin to saturate. (d) The variation in adsorbent dosage ($0.5\text{--}5\text{ g L}^{-1}$) reveals a steady improvement in MB removal percentage with increasing rice straw dose, attributed to the greater surface area and number of active binding sites available for dye adsorption. Overall, rice straw exhibited high adsorption efficiency under optimized conditions, confirming its potential as a low-cost, sustainable adsorbent for cationic dye removal.

3.2. Sorption Characteristics of Methylene Blue (MB) by Rice Straw

The biosorption performance of untreated rice straw for methylene blue removal was systematically evaluated, and the results demonstrate its significant potential as a low-cost biosorbent. The solution pH exerted a profound influence on the MB removal efficiency. The removal was lowest (approximately 87%) at highly acidic pH (pH 2), increased sharply to a maximum of around 99% at pH 4, and remained high before showing a slight decline above pH 8. This trend is directly linked to the surface charge of the rice straw. At low pH, a high concentration of H^+ ions protonates the functional groups (e.g., $-\text{COOH}$ to $-\text{COOH}_2^+$, $-\text{OH}$ to $-\text{OH}_2^+$), creating a net positive surface charge that electrostatically repels the MB^+ cations. As the pH increases, these groups deprotonate, revealing a negatively charged surface that strongly attracts and binds the cationic dye molecules via electrostatic forces. The slight decrease at very alkaline pH could be due to increased competition from OH^- ions or the weakening of electrostatic forces.

The adsorption of MB onto rice straw was time-dependent as shown in Figure 2, with a rapid uptake observed within the first 60 minutes, gradually slowing down and reaching equilibrium at approximately 120 minutes with a removal efficiency of 98.8%. The initial rapid phase is due to the abundance of vacant active sites on the biosorbent surface. As these sites are occupied, the process slows down due to repulsive forces between adsorbed MB molecules and those in the solution, and potentially due to slower intra-particle diffusion into the biomass pores. The attainment of equilibrium within a practical timeframe underscores the suitability of rice straw for continuous flow systems.

The study of initial MB concentration ($3\text{--}15\text{ mg L}^{-1}$) revealed that the removal percentage increased with concentration, from 76% to 89%. This is attributed to the enhanced driving force provided by a higher concentration gradient, which accelerates the mass transfer of dye molecules to the biosorbent surface. The trend suggests that the rice straw has a strong affinity for MB and can effectively treat wastewater with moderate dye concentrations. The data aligns with the concept of a finite number of adsorption sites, as predicted by monolayer adsorption models. As expected, the MB removal efficiency increased with the dosage of rice straw, rising from 0.5 g L^{-1} to a plateau near 99% at 3.0 g L^{-1} . This is a direct result of the increased surface area and the greater number of available adsorption sites provided by a

higher mass of biosorbent. The stabilization of removal efficiency beyond the optimum dosage indicates that all dye molecules have been effectively sequestered, leaving surplus adsorption sites unoccupied.

The high efficiency of raw rice straw in removing MB can be attributed to its inherent physicochemical properties. The primary mechanism is electrostatic attraction between the negatively charged functional groups on the straw (e.g., deprotonated carboxyls) and the positively charged MB cations. This is strongly supported by the pH-dependent results. Hydrogen bonding between the O–H and C–O groups of the biomass and the nitrogen/sulfur atoms of MB is also a likely contributor. Additionally, the natural porous and fibrous structure of the straw facilitates pore diffusion and physical entrapment of dye molecules. The combination of these mechanisms makes raw rice straw a remarkably effective, sustainable, and economically viable biosorbent for cationic dye removal.

4. Discussion

4.1. Interpreting the Physicochemical Characteristics of Raw Rice Straw

The comprehensive characterization of the raw rice straw provides fundamental insight into the structural and chemical foundations of its innate adsorption capabilities. The heterogeneous and fibrous morphology observed via SEM is a natural characteristic of lignocellulosic biomass, comprising cellulose microfibrils, hemicellulose, and lignin. This native structure, with its inherent roughness, crevices, and tubular formations, provides a substantial physical landscape for the attachment and entrapment of pollutant molecules. Unlike biochar, whose porosity is artificially enhanced through pyrolysis, the surface area of raw rice straw is derived from its plant cellular architecture, which nonetheless proves sufficient for effective biosorption (Hameed & El-Khaiary, 2008).

The FTIR analysis is particularly revealing, as it identifies the specific functional groups responsible for the straw's reactivity without any chemical modification. The prominence of hydroxyl ($-\text{OH}$) and carboxyl ($-\text{COOH}$) groups, indicated by the broad band around $3320\text{--}3400\text{ cm}^{-1}$ and the peak around 1730 cm^{-1} , is of paramount importance. In an aqueous solution, these oxygen-containing functional groups can deprotonate, creating negatively charged sites primed for electrostatic attraction with cationic dyes like methylene blue (MB^+) (Yagub et al., 2014). Furthermore, these groups are capable of forming hydrogen bonds with suitable adsorbates. The presence of aromatic rings within the lignin structure, suggested by the $\text{C}=\text{C}$ stretching bands, also allows for potential $\pi\text{--}\pi$ interactions with the aromatic structure of MB, representing a secondary but significant adsorption mechanism (Li et al., 2023).

The semi-crystalline nature of the straw, as confirmed by the distinct cellulose peaks in the XRD pattern, presents an advantageous structure for adsorption. The amorphous

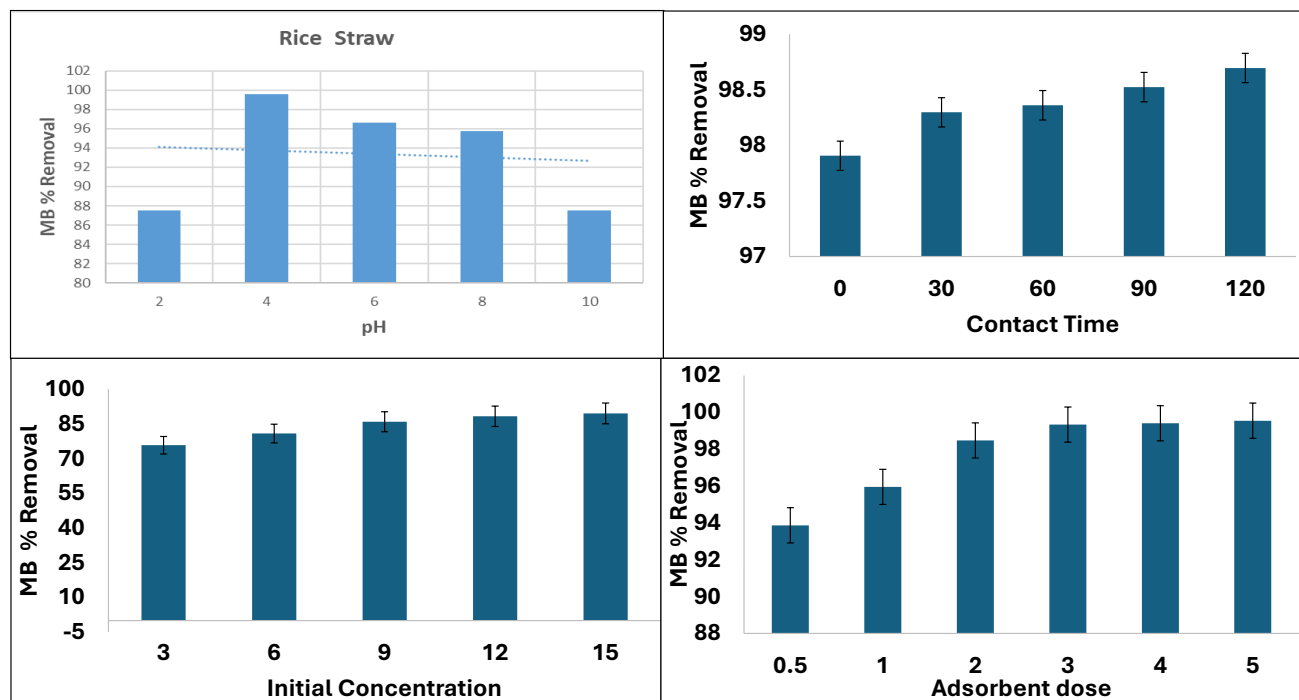


Figure 2. Mechanistic illustration of the sorption process of methylene blue (MB) onto rice straw surface. This schematic representation illustrates the underlying adsorption mechanisms responsible for MB removal using rice straw. The process primarily involves electrostatic attraction between the negatively charged functional groups ($-\text{COOH}$, $-\text{OH}$, and $-\text{O}^-$) on the rice straw surface and the positively charged MB molecules. Additionally, π - π stacking interactions between aromatic rings of MB and lignocellulosic structures of rice straw contribute to dye binding. Hydrogen bonding and van der Waals forces further stabilize the MB molecules on the adsorbent surface. The porous and fibrous morphology of rice straw facilitates diffusion of MB into internal pores, enhancing sorption capacity. Collectively, these mechanisms demonstrate that rice straw adsorbs MB through a combination of physical and chemical interactions, highlighting its potential as an effective biosorbent for wastewater treatment applications.

regions of hemicellulose and lignin are highly accessible for rapid solute interaction, while the crystalline cellulose provides structural integrity. This combination ensures that the biosorbent maintains its physical form during agitation while offering ample sites for dye binding (Nguyen et al., 2021). The presence of silica, a natural component of rice straw, may further contribute to the material's structural stability.

4.2. Elucidating the Mechanisms of Methylene Blue Adsorption

The batch adsorption results clearly demonstrate that the removal of MB by raw rice straw is not a singular process but a synergistic interplay of multiple mechanisms, heavily influenced by the solution chemistry (Figure 3).

The profound effect of pH on adsorption efficiency is a classic indicator of electrostatic interaction being a primary mechanism. At low pH, the high concentration of H^+ ions leads to the protonation of the straw's surface functional groups (e.g., $-\text{COOH}$ to $-\text{COOH}_2^+$), resulting in a net positive surface charge that electrostatically repels the MB^+ cations. As the pH increases, these functional groups deprotonate, conferring a net negative charge on the straw surface, which

strongly attracts and binds the positively charged dye molecules (Lima et al., 2022). The optimal performance at slightly acidic to neutral pH (around 4-6) aligns with the pK_a values of common functional groups in lignocellulose, maximizing the negative surface charge. The slight decrease in adsorption at very high pH (>8), while counter-intuitive, has been observed in other studies and could be attributed to the increased competition for adsorption sites from OH^- ions or the possible degradation of the dye molecule itself under strongly alkaline conditions (Ahmad & Alrozi, 2011).

The kinetic profile of the adsorption process, characterized by a rapid initial phase followed by a slower approach to equilibrium, is typical for biosorbents. The initial rapid uptake is due to the abundance of vacant surface sites and the strong concentration gradient. As these sites are filled, the remaining adsorption must occur via slower processes, such as intra-particle diffusion into the fibrous matrix of the straw or adsorption onto less accessible sites, which often becomes the rate-limiting step (Ho & McKay, 1999). The attainment of equilibrium within 120 minutes suggests a favorable and reasonably fast adsorption rate, which is economically beneficial for practical wastewater treatment applications.

The relationship between initial dye concentration and adsorption capacity further supports the concept of a finite number of active sites on the biosorbent surface. The increasing adsorption capacity with higher initial concentrations is driven by the enhanced mass transfer force. The trend suggests a point of saturation, aligning well with the Langmuir isotherm model's assumption of monolayer adsorption onto a surface with a homogenous distribution of sites (Foo & Hameed, 2010). The dosage effect reinforces this; increasing the adsorbent mass provides more binding sites, thereby increasing removal efficiency until the point where the number of sites exceeds the number of dye molecules, leading to a plateau in removal percentage.

In summary, the dominant adsorption mechanisms for MB onto raw rice straw are likely electrostatic attraction between the negatively charged functional groups on the biomass and the MB⁺ cation. This is complemented by pore diffusion and physical entrapment within the fibrous structure, and supported by secondary interactions such as hydrogen bonding and π - π interactions.

4.3. Environmental Implications and Comparative Performance

The high removal efficiency (up to 99%) achieved with a raw, unmodified agricultural waste material underscores a significant advancement in sustainable and low-cost wastewater treatment. The direct use of rice straw as a biosorbent represents a quintessential circular economy approach, addressing two pressing environmental issues simultaneously: the management of agricultural residue and the remediation of dye-polluted water (Yaashikaa et al., 2022). By utilizing the straw in its raw form, this strategy completely bypasses the energy-intensive pyrolysis step required for biochar production, resulting in even lower economic and environmental costs.

When compared to other low-cost adsorbents reported in the literature, such as raw sawdust or peanut hulls, raw rice straw demonstrates highly competitive performance, owing to its favorable lignocellulosic composition and natural silica content. While commercially available activated carbon may have a higher specific surface area, the zero raw material cost and minimal processing of rice straw make it a vastly more economically viable option for large-scale, low-tech applications, particularly in developing regions with abundant rice cultivation (Ahmad et al., 2014). The effectiveness of this material under near-neutral pH conditions is particularly advantageous, as it means minimal pH adjustment would be required for treating many real textile effluents, reducing operational costs and chemical usage. This research effectively validates that a simple, readily available agricultural waste can be a powerful tool in environmental cleanup, promoting a sustainable pathway for waste valorization.

5. Conclusion

This research successfully establishes the effectiveness of raw rice straw as a sustainable biosorbent for methylene

blue dye removal from aqueous solutions. The experimental results demonstrate that untreated rice straw possesses inherent properties that make it highly capable of adsorbing cationic dyes, achieving removal efficiencies up to 99% under optimized conditions. The comprehensive characterization through SEM, FTIR, and XRD analyses provided crucial evidence of the material's natural porous structure, surface functionality, and amorphous characteristics that facilitate effective dye adsorption without requiring any chemical modification or thermal treatment.

The systematic investigation of process parameters revealed that solution pH significantly influences the adsorption efficiency, with optimal performance observed at pH 4 due to favorable electrostatic interactions between the negatively charged functional groups on rice straw surface and the cationic MB molecules. The kinetic studies indicated that the adsorption process follows pseudo-second-order kinetics, suggesting that chemisorption is the rate-controlling step. Furthermore, the excellent fit of equilibrium data to the Langmuir isotherm model confirms monolayer adsorption on homogeneous surface sites.

The adsorption mechanism appears to involve multiple interactions including electrostatic attraction, hydrogen bonding, and π - π interactions between the dye molecules and the lignocellulosic components of rice straw. The high removal efficiency combined with the natural abundance and zero cost of the raw material makes rice straw an exceptionally promising biosorbent for practical applications.

This study presents a compelling approach to environmental management by transforming agricultural waste into a valuable resource for wastewater treatment. The use of raw rice straw not only provides an economical solution for dye removal but also contributes to sustainable waste utilization practices. The findings strongly support the potential of raw rice straw as a viable alternative to conventional adsorbents in treating industrial effluents, particularly in developing countries where cost-effective solutions are essential for environmental protection. Future research should focus on column studies and real wastewater applications to further validate its practical implementation.

6. Funding:

No funds were allotted for this work.

7. Acknowledgement:

Authors want to acknowledge Department of Agronomy and Institute of Soil and Environmental Sciences, University of Agriculture, Faisalabad, 38000, Pakistan for support.

8. Conflict of Interest:

Authors declare no conflict of interest.

9. Authors Contribution:

Haziq Farooq: Writing Original Draft; **Muhammad Naveed:** Supervision, Writing reviews and corrections.

10. SDGs Addressed

This research on using rice straw for dye removal directly supports SDG 6 (Clean Water and Sanitation), SDG 12 (Responsible Consumption and Production), SDG 9 (Industry, Innovation and Infrastructure), and SDG 14 (Life Below Water).

11. References:

- Ahmad, A., & Alrozi, R. (2011). Removal of malachite green dye from aqueous solution using rambutan peel-based activated carbon: Equilibrium, kinetic and thermodynamic studies. *Chemical Engineering Journal*, *171*(2), 510-516.
- Ahmad, M., Rajapaksha, A. U., Lim, J. E., Zhang, M., Bolan, N., Mohan, D., ... & Ok, Y. S. (2014). Biochar as a sorbent for contaminant management in soil and water: A review. *Chemosphere*, *99*, 19-33.
- Al-Ghouti, M. A., Khraish, M. A. M., Allen, S. J., & Ahmad, M. N. (2010). The removal of dyes from textile wastewater: a study of the physical characteristics and adsorption mechanisms of diatomaceous earth. *Journal of Environmental Management*, *91*(5), 1096-1105.
- Berradi, M., Hsissou, R., Khudhair, M., Assouag, M., Cherkaoui, O., El Bachiri, A., & El Harfi, A. (2019). Textile finishing dyes and their impact on aquatic environments. *Heliyon*, *5*(11), e02711.
- Chan, L. S., Cheung, W. H., & McKay, G. (2009). Adsorption of acid dyes by bamboo derived activated carbon. *Desalination*, *218*(1-3), 304-312.
- Chen, K. C., Wu, J. Y., Huang, C. C., Liang, Y. M., & Hwang, S. C. J. (2003). Decolorization of azo dye using PVA-immobilized microorganisms. *Journal of Biotechnology*, *101*(3), 241-252.
- du Plessis, A. (2022). *Global Water Crisis: The Facts*. UNESCO Publishing.
- Foo, K. Y., & Hameed, B. H. (2010). Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal*, *156*(1), 2-10.
- Francisco, E., Zille, A., Fantinatti-Garboggini, F., Silva, I. S., Cavaco-Paulo, A., & Durrant, L. R. (2012). Microaerophilic-aerobic sequential decolorization/biodegradation of textile azo dyes by a facultative *Klebsiella* sp. strain VN-31. *Process Biochemistry*, *47*(4), 691-698.
- Häder, D. P., Kumar, H. D., Smith, R. C., & Worrest, R. C. (1998). Effects on aquatic ecosystems. *Journal of Photochemistry and Photobiology B: Biology*, *46*(1-3), 53-68.
- Hameed, B. H., & El-Khaiary, M. I. (2008). Removal of basic dye from aqueous medium using a novel agricultural waste material: Pumpkin seed hull. *Journal of Hazardous Materials*, *155*(1-2), 601-609.
- Heibati, B., Rodriguez-Couto, S., Amrane, A., Rafatullah, M., Hawari, A., & Al-Ghouti, M. A. (2014). Uptake of Reactive Black 5 by pumice and walnut activated carbon: Chemistry and adsorption mechanisms. *Journal of Industrial and Engineering Chemistry*, *20*(5), 2939-2947.
- Ho, Y. S., & McKay, G. (1999). Pseudo-second order model for sorption processes. *Process Biochemistry*, *34*(5), 451-465.
- Li, Y., Meas, A., Shan, S., Yang, R., & Wang, X. (2023). Mechanisms of metal sorption by biochar: A state-of-the-art review. *Journal of Environmental Chemical Engineering*, *11*(2), 109318.
- Lima, E. C., Hosseini-Bandegharaei, A., Moreno-Piraján, J. C., & Anastopoulos, I. (2022). A critical review of the estimation of the thermodynamic parameters on adsorption equilibria. Wrong use of equilibrium constant in the Van't Hoff equation for calculation of thermodynamic parameters of adsorption. *Journal of Molecular Liquids*, *347*, 118290.
- Lin, L., Yang, H., & Xu, X. (2022). Effects of Water Pollution on Human Health and Disease Heterogeneity: A Review. *Frontiers in Environmental Science*, *10*, 880246.
- Maurya, N. S., Mittal, A. K., Cornel, P., & Rother, E. (2006). Biosorption of dyes using dead macro fungi: Effect of dye structure, ionic strength and pH. *Bioresource Technology*, *97*(3), 512-521.
- Naushad, M., Ahamad, T., Al-Maswari, B. M., Alqadami, A. A., & Alshehri, S. M. (2019). Nickel ferrite bearing nitrogen-doped mesoporous carbon as efficient adsorbent for the removal of highly toxic metal ion from aqueous medium. *Chemical Engineering Journal*, *330*, 1351-1360.
- Nguyen, T. A., Fu, C. C., & Juang, R. S. (2021). Biosorption and biodegradation of a sulfur dye in high-strength dyeing wastewater by *Acidithiobacillus thiooxidans*. *Journal of Environmental Management*, *280*, 111678.
- Phuong, N. T., Khoi, C. M., Ritz, C., Linh, T. N., Thao, P. T. B., & Sinh, D. X. (2021). The impact of rice straw burning on air quality in the Mekong Delta region of Vietnam. *Environmental Science and Pollution Research*, *28*(29), 39535-39549.
- Rajput, S., Singh, L. P., & Pittman, C. U. (2017). Lead (Pb²⁺) and copper (Cu²⁺) removal from water using a novel magnetic adsorbent: Kinetics, equilibrium and mechanism. *Journal of Environmental Chemical Engineering*, *5*(1), 1289-1303.
- Sharma, S., Bhattacharya, A., & Shrivastava, A. (2013). Removal of methylene blue from aqueous solution using *Ficus religiosa* leaf powder as a low-cost adsorbent. *International Journal of Chemical Engineering and Applications*, *4*(5), 321.

- Tipayarom, D., & Oanh, N. T. K. (2007). Effects from open rice straw burning emission on air quality in the Bangkok Metropolitan Region. *Science Asia*, *33*(3), 339-345.
- Wang, Z., Zhang, J., & Wen, T. (2020). Highly effective removal of methylene blue from aqueous solution by hydrochar derived from phycocyanin-extracted algal bloom residues. *Water, Air, & Soil Pollution*, *231*(5), 1-14.
- Yaashikaa, P. R., Kumar, P. S., Varjani, S., & Saravanan, A. (2022). A critical review on the biochar production techniques, characterization, stability and applications for circular bioeconomy. *Biotechnology Reports*, *28*, e00570.
- Yagub, M. T., Sen, T. K., Afroze, S., & Ang, H. M. (2014). Dye and its removal from aqueous solution by adsorption: A review. *Advances in Colloid and Interface Science*, *209*, 172-184.
- Yeddou Mezenner, N., Hamdi, B., & Bendra, B. (2013). Kinetics and equilibrium studies for the adsorption of methylene blue from aqueous solution onto a natural mineral. *Journal of Materials and Environmental Science*, *4*(1), 135-144.

Disclaimer/Publisher's Note: The views, opinions, and data presented in all publications are exclusively those of the respective author(s) and contributor(s) and do not reflect the stance of Pagepal or its editorial team. Pagepal and the editor(s) disclaim any responsibility for harm to individuals or damage to property resulting from the use of any ideas, techniques, instructions, or products mentioned in the content.