

Chemical Functionalization of Banana Stem Biochar for Enhanced Methylene Blue Removal from Wastewater

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Abstract—Agricultural biomass-derived biochar has emerged as a sustainable and low-cost adsorbent for the treatment of dye-contaminated wastewater. In the present study, banana stem biochar was prepared through pyrolysis and chemically modified using phosphoric acid (H_3PO_4) and alkaline activating agents to enhance its adsorption properties toward methylene blue (MB). The modified biochars were characterized using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and X-ray Diffraction (XRD) to evaluate their surface functional groups, morphology, and crystalline characteristics. Batch adsorption experiments were conducted to investigate the effects of solution pH, adsorbent dosage, and contact time on MB removal efficiency. The H_3PO_4 -modified biochar exhibited abundant oxygen-containing and phosphate functional groups, a highly porous surface, and predominantly amorphous carbon structure, resulting in enhanced adsorption performance. The maximum dye removal efficiency of 86.43% was achieved at pH 6, 1.0 g L^{-1} adsorbent dosage, and 80 min contact time. Adsorption efficiency increased with dosage and contact time until equilibrium was reached, while strongly alkaline conditions reduced dye removal due to competition between hydroxide ions and dye molecules for adsorption sites. The findings demonstrate that chemically modified banana stem biochar is an effective, environmentally friendly, and economical adsorbent for the treatment of dye-containing wastewater and offers significant potential for sustainable wastewater management.

Index Terms—biomass, Scanning Electron Microscopy (SEM), biochar, wastewater

I. INTRODUCTION

Water pollution has emerged as one of the most critical environmental challenges of the twenty-first century, posing severe threats to aquatic ecosystems, human health, and sustainable development [1]. Among the various industrial sectors responsible for water contamination, the textile and dyeing industries are considered major contributors, discharging large volumes of chemically complex effluents into water bodies [2]. These effluents frequently contain synthetic dyes that are highly resistant to conventional treatment processes due to their complex aromatic structures, stability under light and heat, and persistence in aquatic environments [3]. Methylene blue (MB), a cationic thiazine dye, is one of the most widely

used synthetic dyes in textile, paper, leather, and pharmaceutical industries, and has become a representative model pollutant in adsorption and wastewater treatment research [4].

Even at low concentrations, MB causes serious environmental and health concerns, including inhibition of photosynthesis in aquatic plants, depletion of dissolved oxygen, mutagenicity, carcinogenicity, and acute toxicity to aquatic organisms [5]. Therefore, the development of efficient, cost-effective, and environmentally sustainable methods for the removal of MB from industrial effluents is of paramount importance. Various physicochemical and biological methods have been investigated for the removal of synthetic dyes from wastewater, including coagulation, flocculation, membrane filtration, photocatalytic degradation, advanced oxidation processes (AOPs), and biological treatment [6]. However, each of these methods presents notable limitations. Biological treatments are often ineffective against recalcitrant and non-biodegradable dye molecules, while membrane-based processes and AOPs are associated with high operational costs and energy consumption [7]. Adsorption has gained widespread acceptance as one of the most promising methods for dye removal due to its simplicity, operational flexibility, high efficiency, and potential for regeneration and reuse of adsorbents [8]. Among the various adsorbents explored, biochar — a carbon-rich material produced by the thermochemical conversion of biomass under oxygen-limited conditions (pyrolysis) has attracted considerable attention owing to its large surface area, porous structure, diverse surface functional groups, and low production cost from agricultural residues and biomass wastes [9,10]. Despite these advantages, the adsorption performance of raw biochar for cationic dyes such as MB is often limited by its moderate surface area, insufficient surface charge density, and relatively low density of active functional groups [9]. To overcome these constraints, chemical modification of biochar using acidic (e.g., H_3PO_4 , HCl) and alkaline (e.g., KOH, NaOH) activating agents has been widely explored. Acidic modification introduces oxygenated functional groups (carboxyl and hydroxyl groups) onto the biochar surface, enhancing its ion-exchange capacity and electrostatic affinity

toward cationic dye molecules [12]. Alkaline modification, on the other hand, increases the surface area, micropore volume, and basicity of the biochar, which promotes π - π stacking interactions and electrostatic attraction with MB [13]. Several studies have demonstrated that KOH- and NaOH-activated biochar's exhibit significantly enhanced MB removal efficiency compared to unmodified counterparts [14,15]. Despite these advances, adsorption-based systems alone may not meet increasingly stringent effluent discharge standards when dealing with highly concentrated dye wastewater, necessitating the integration of complementary treatment technologies. Electrocoagulation (EC) is an electrochemical treatment process that has gained increasing recognition as an effective, versatile, and relatively low-cost method for the removal of dyes, heavy metals, suspended solids, and other contaminants from wastewater [16]. In the EC process, metal ions (typically iron or aluminum) are generated in situ by the electrochemical dissolution of sacrificial anodes, which subsequently hydrolyze to form metal hydroxide flocs capable of destabilizing colloidal dye particles through charge neutralization, sweep flocculation, and adsorption onto the floc surface [17]. EC offers several advantages over conventional chemical coagulation, including the elimination of chemical dosing, lower sludge production, ease of automation, and compatibility with a wide range of wastewater compositions [18].

Experimental studies have confirmed that EC using iron and aluminum electrodes achieves substantial color and chemical oxygen demand (COD) removal from textile wastewater containing cationic dyes such as MB, through effective destabilization and separation of dye aggregates [19]. However, EC alone may leave residual dissolved dye fractions in solution, particularly under conditions of high dye loading or complex effluent matrices, limiting its standalone performance [20]. In light of the individual strengths and limitations of both modified biochar adsorption and electrocoagulation, there is a compelling rationale for integrating these two processes into a combined treatment system. Hybrid electrocoagulation-adsorption systems have recently been reported to achieve substantially higher pollutant removal efficiencies than either process operated independently, by exploiting complementary removal mechanisms [21]. A sequential approach in which electrocoagulation serves as a primary treatment step to reduce bulk dye concentration and suspended matter, followed by modified biochar adsorption as a polishing stage to capture residual dissolved MB, is expected to deliver superior and more consistent removal performance. The use of biochar derived from agricultural waste further aligns this approach with circular economy principles by valorizing low-cost biomass residues into high-performance adsorbents, reducing both the cost and environmental footprint of the treatment process [22]. The adsorption efficiency of such modified biochar systems for MB has additionally been validated in composite bead configurations, further demonstrating the versatility of functionalized biochar as a treatment material [23]. Despite the growing interest in both EC and modified biochar technologies, studies systematically investigating their combined

application for MB removal remain scarce in the literature. The present study, therefore, aims to investigate the efficiency of acid- and alkali-modified biochars (H_3PO_4 -modified and KOH/NaOH-modified) for the removal of methylene blue from aqueous solution, and to evaluate a combined electrocoagulation-modified biochar system as an enhanced and sustainable wastewater treatment approach. Specifically, the objectives of this work are: (i) to prepare and characterize biochar and its chemically modified forms; (ii) to assess the adsorption performance of modified biochars for MB removal under varying experimental conditions; (iii) to evaluate the MB removal efficiency of the electrocoagulation process; and (iv) to examine the synergistic potential of the combined EC-modified biochar treatment system. The findings of this study are expected to provide valuable insights into the design of hybrid treatment strategies for dye-contaminated industrial effluents and contribute to the advancement of sustainable, low-cost wastewater treatment technologies.

II. MATERIALS AND METHODS

A. Chemicals and Reagents

Methylene blue (MB; molecular weight 319.85 g/mol; $\lambda_{\text{max}} = 664 \text{ nm}$; molecular formula $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$) was selected as the model cationic dye pollutant in this study [4]. The stock solution of MB (1000 mg/L) was prepared by dissolving the weighed quantity of the dye in distilled water and the working solutions of the required concentrations were obtained by serial dilution. For the acid modification of biochar, analytical grade orthophosphoric acid (H_3PO_4 , 1 M) were employed [12, 15]. The electrodes were washed with dilute HCl (5%) before each experimental run [17]. All solution preparations, washing procedures and dilutions were done in distilled water. All chemicals were of analytical reagent grade and used as received.

B. Raw Material Collection and Preparation

Banana stem waste (*Musa* spp.) was selected as the primary source for biochar preparation due to its abundance as an agricultural waste and the presence of high cellulose, hemicellulose, and Lignin content which are rich in functional groups such as $-\text{OH}$ and $-\text{COOH}$ for dye molecules binding [9], [22]. Banana stem was collected from the local market. The collected material was thoroughly washed with tap water to remove adhered soil, dust and surface impurities and rinsed with distilled water. The stems were washed, cut and shredded into small and uniform pieces for uniform drying and carbonization. The chopped material was sun-dried for 48-72 hours until all moisture was removed and stored in sealed polythene bags prior carbonization [9].

C. Biochar Preparation

Biochar was prepared by pyrolysis of the dried banana stem pieces in a muffle furnace under limited oxygen conditions [9], [10]. The dried feedstock was placed in a covered ceramic crucible and carbonized at 400–500 °C for 1–2 hours. The pyrolysis temperature was chosen based on previous protocols

that affect biochar surface area, porosity and functional group density [10], [11]. After carbonization, the muffle furnace was naturally cooled to room temperature. The obtained biochar was placed in a desiccator to prevent re-adsorption of moisture during cooling and stored in sealed containers for subsequent modification. Fig.1 depicts the production of banana stem derived material.

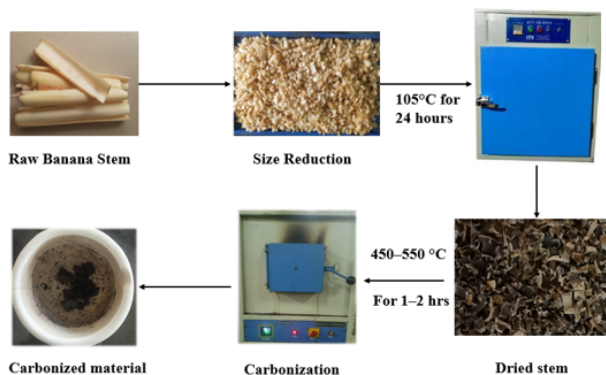


Fig. 1. Synthesis of Banana stem (Musa spp.)

D. Chemical Modification of Biochar

Chemical modification of biochar involves treating the raw material biochar with chemical agents to alter its surface chemistry, functional groups, and adsorption properties. These modifications are employed to enhance the removal efficiency of specific contaminants by tailoring the surface charge, porosity, and reactivity of the biochar.

E. Acid Modification (H_3PO_4 Treatment)

The acid modification was carried out by immersing raw biochar into 1 M orthophosphoric acid (H_3PO_4) solution with solid-liquid ratio of 1:10 (w/v) with continuous shaking for 24 h at room temperature [12], [14]. In the treatment, acidic oxygen-containing functional groups and phosphate-containing groups ($P=O$, $P-O-C$) were introduced to the surface of biochar, and the surface porosity was improved by opening the blocked pores [12], [15]. Consequently, the surface of biochar became acid after the treatment [12].

F. Post-Treatment Process

The biochar was washed several times with distilled (deionized) water to remove activating agents and soluble impurities remaining after chemical modification [13], [15]. The washing was continued until the effluent attained neutral pH of 7 thereby confirming the total removal of excess chemical reagents. Sample was dried in an oven at 105°C for 24 hours to remove moisture and achieve constant weight. Dried biochar was ground using a mortar and pestle to obtain uniform particle size and stored in air-tight containers until use [9]. Fig. 2 illustrates the modification of banana stem-derived material.

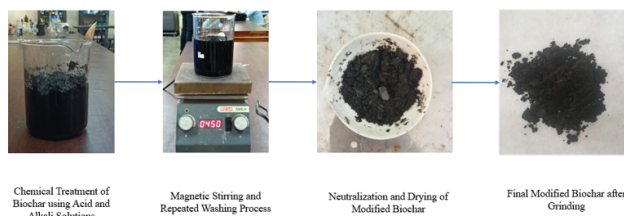


Fig. 2. Modification of biochar (acid treatment)

G. Experimental Configuration

The experimental setup consisted of a laboratory-scale electrocoagulation reactor fitted with aluminium electrodes. The aluminium plates were used as both anode and cathode and were connected to a direct current (DC) power supply as shown in Fig. 3. The DC power supply was used to provide a controlled electric current required for the electrocoagulation process. The reactor was filled with a prepared methylene blue dye solution of known concentration. A measured quantity of modified biochar was added to the dye solution to enhance the adsorption and removal efficiency. During the experiment, electric current was passed through the aluminium electrodes, which resulted in the dissolution of aluminium ions from the anode. These aluminium ions reacted with hydroxide ions formed in the solution and produced aluminium hydroxide coagulants in situ. The freshly formed coagulants helped in destabilizing and trapping the dye molecules present in the solution. At the same time, the modified biochar provided additional active sites for adsorption of methylene blue dye.

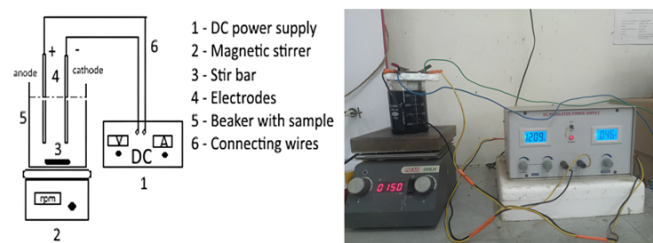


Fig. 3. Schematic diagram electrocoagulation system

III. RESULT AND DISCUSSION

Various analytical methods have been used to characterize the synthesized material and confirm its structural, morphological and Crystallinity features.

A. Fourier transform infrared spectroscopy- acidic treated biochar – H_3PO_4

The FTIR spectrum of H_3PO_4 -treated banana stem biochar showed the presence of important functional groups responsible for methylene blue adsorption. A broad peak at 3849 cm^{-1} indicated O-H groups, while the peak at 1693 cm^{-1} confirmed carbonyl groups. The band at 1575 cm^{-1} represented

aromatic C=C structures, which support π - π interactions with dye molecules. Strong peaks at 1230 cm^{-1} and 988 cm^{-1} confirmed the presence of P=O and P-O-C groups. These peaks indicate the successful modification of banana stem biochar using phosphoric acid. The phosphate and carboxyl groups provide negatively charged active sites on the biochar surface. These sites attract the cationic methylene blue dye mainly through electrostatic interaction. In addition, aromatic structures further enhance dye removal through π - π stacking interactions. Table.1 shows the absorption intensity in relation to the wavelength and functional group of acid treated biochar.

B. SEM analysis - Acid treated banana stem biochar

SEM analysis was carried out to examine the surface morphology of acid- and alkali-treated banana stem biochar. Fig. 6 depicts the surface properties of acid treated biochar at two magnification levels (5KX and 50KX). The H_3PO_4 modified biochar showed a highly porous surface with cavities, cracks, and irregular channels. Acid activation helped remove impurities and opened the blocked pores on the biochar surface. This treatment produced a rough texture with smaller and more uniform pores. The improved pore structure increased the available active sites for dye adsorption. Therefore, the acid-treated biochar showed better surface characteristics for enhanced adsorption efficiency.

C. XRD Analysis- acid treated banana stem biochar

The XRD pattern of acid-treated banana stem biochar showed a broad diffraction hump in the range of $2\theta = 15^\circ$ – 30° , indicating a predominantly amorphous carbon structure. The absence of strong sharp crystalline peaks confirmed the formation of a highly disordered and non-crystalline carbon matrix after acid activation. A small peak around $2\theta \approx 24^\circ$ – 26° may be attributed to turbostratic carbon or graphitic-like carbon layers commonly found in biomass-derived biochar. Minor weak peaks observed in the pattern may indicate trace inorganic mineral residues. However, their low intensity suggests that H_3PO_4 treatment effectively removed ash and mineral impurities. Overall, the XRD results confirmed that acid modification enhanced carbon amorphization, improved surface reactivity, and increased the adsorption potential of banana stem biochar. Fig. 8 represents Crystallinity features of acid treated biochar.

D. ANALYTICAL METHODS

The dye effluent is a mixture of dye compounds, and hence the specific dye concentration cannot be directly obtained. Therefore, the percentage of dye removed was calculated from the Optical Density (OD) values before and after treatment [3], [7]. The OD values at 664 nm were read using an ELISA Microplate Reader. The OD value of dye effluent before treatment was 0.2634. The percentage dye removal was computed by the following formula: Removal = $((A_0 - A_t) / A_0) \times 100$ Where, A_0 = Optical Density value at $t = 0$ (before treatment) A_t = Optical Density value at time “t” (post treatment)

E. H_3PO_4 Modified Biochar

Effect of pH

The effect of pH on methylene blue removal using H_3PO_4 modified biochar was examined at pH 6, 8, and 10. Unlike alkali-modified biochar, the acid-modified variant showed best performance at pH 6 for certain dosage–time combinations, and performance declined consistently as pH increased to 10. At pH 6, removal ranged from 74.43% to 86.43% as indicated in Table 8 and Figure 15. At pH 8, values ranged from 75.84% to 84.51% as indicated in Table 9 and Figure 16. At pH 10, the lowest efficiencies were recorded 65.53% to 79.46% as indicated in Table 10 and Figure 17. The decline at pH 10 is due to modification of the biochar’s surface charge under strongly alkaline conditions and increased competition from OH ions for phosphate-group adsorption sites. The optimum pH for H_3PO_4 -biochar is 6–8, with peak removal of 86.43% at pH 6, 1.0 g/L, 80 min.

Effect of Dosage

The effect of dosage on modified H_3PO_4 biochar was studied at 0.6, 0.8, and 1.0 g/L. As shown in Table 11 and Fig. 18, removal efficiency increased with dosage at all pH levels, though with varying trends. At pH 6, the 80 min contact time showed the steepest dosage-dependent improvement, with removal increasing from 76.94% at 0.6 g/L to 84.66% at 0.8 g/L and further to 86.43% at 1.0 g/L. At pH 8, the removal efficiency at 0.8 g/L was slightly higher at 84.51% than at 1.0 g/L with 84.10% after 80 min, suggesting saturation of adsorption sites at 1.0 g/L. At pH 10, the increase in removal efficiency from 0.8 to 1.0 g/L was negligible, with values of 79.46% and 79.35% at 100 min, respectively, confirming adsorption plateau behaviour under high-pH conditions. These results indicate that 0.8 g/L is the optimum dosage for H_3PO_4 modified biochar.

Effect of Contact Time

The effect of contact time on H_3PO_4 modified biochar was examined at 60, 80, and 100 min. As shown in Table 12 and Fig. 19, removal efficiency increased with contact time across all conditions. At pH 6, 1.0 g/L, removal increased from 81.80% at 60 min to 86.43% at 80 min, then dropped marginally to 82.94% at 100 min, suggesting possible re-desorption at longer contact times under acidic conditions. At pH 8 and 0.8 g/L, values increased from 82.53% at 60 min to 84.51% at 80 min and then slightly decreased to 84.10% at 100 min, indicating equilibrium was approached at 80 min. At pH 10, efficiency improved consistently from 65.53% at 60 min to 79.46% at 100 min at 0.8 g/L, with the largest gain between 60 and 80 min. The increase in removal with time reflects progressive diffusion of dye molecules into the pores of the biochar and their interaction with phosphate and hydroxyl functional groups. The optimum contact time is 80–100 min for H_3PO_4 modified biochar.

IV. CONCLUSION

Banana stem-derived biochar chemically modified with phosphoric acid exhibited excellent potential as a sustainable adsorbent for methylene blue removal from aqueous solution.

FTIR, SEM, and XRD analyses confirmed successful surface functionalization, increased porosity, and the formation of an amorphous carbon structure favorable for adsorption. Batch adsorption studies demonstrated that solution pH, adsorbent dosage, and contact time significantly influenced dye removal efficiency. The highest removal efficiency of 86.43% was achieved at pH 6, an adsorbent dosage of 1.0 g L^{-1} , and 80 min contact time. The enhanced adsorption performance was attributed to the combined effects of electrostatic attraction, π - π interactions, and increased surface active sites introduced through phosphoric acid activation. These findings indicate that chemically modified banana stem biochar is an economical, environmentally friendly, and promising adsorbent for the treatment of dye-contaminated wastewater and offers considerable potential for large-scale wastewater remediation.

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