

Article

Utilization of Chemically Modified Banana Peels as an Eco-Friendly, Cost-Effective and Sustainable Biosorbent for the Efficient Removal of Copper and Manganese from Aqueous Media: A Comparative Analysis

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Abstract

Herein, the adsorption of Cu²⁺ and Mn²⁺ from individual aqueous solutions was investigated using raw banana peels (BP) and H₂SO₄-modified banana peels (mBP-SA) as a low-cost biosorbent prepared from renewable agricultural waste. Through a batch of adsorption experiments, extent to which adsorption efficiency is influenced by pH, exposure time, adsorbent dosage, and adsorbate starting concentration, was consistently examined. The maximum removal percentages of Cu²⁺ ions were 92% and 98% for BP and mBP-SA, respectively. While both BP and mBP-SA achieved a maximum Mn²⁺ removal efficiency of 90% under the optimized experimental conditions, mBP-SA exhibited a higher adsorption capacity (q_{max}), indicating improved adsorption performance, particularly at higher initial Mn²⁺ concentrations. The highest possible effectiveness of removal for Cu²⁺ and Mn²⁺ was achieved at a starting concentration of 5 ppm. Furthermore, the kinetics and isotherms of the proposed adsorption process were investigated. Langmuir and Freundlich isotherm equations were utilized for investigating the equilibrium data in order to appraise the adsorption mechanism. The good conformity of the Cu²⁺ and Mn²⁺ adsorption data with the Langmuir model suggests that the adsorption process predominantly follows monolayer adsorption on relatively homogeneous surface sites. The maximum adsorption capacities (q_{max}) of mBP-SA were 8.70 and 3.38 mg g⁻¹ for Cu²⁺ and Mn²⁺, respectively, compared with 5.29 and 1.86 mg g⁻¹ for BP. Meanwhile, the biosorption process obeys the pseudo 2nd order kinetic model, indicating that both BP and metal ions influence the adsorption process. Meanwhile, the biosorption process obeys pseudo 2nd order kinetic models, indicating that both BP and metal ions influence the adsorption process. This study showed that BP and mBP-SA can serve as efficient and inexpensive adsorbents for the uptake of Cu²⁺ and Mn²⁺ out of their aqueous combinations. Additionally, three green evaluation methods were used to evaluate the environmental impact of our proposed procedure: the Analytical Eco-Scale Assessment (ESA), Green Analytical Procedure Index (GAPI), and the Analytical GREENness metric (AGREE).

Keywords: copper; manganese; banana peel; removal; water pollutants

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1. Introduction

Contaminating heavy metals are identified as a substantial environmental peril affecting water quality and are increasing due to industrialization, urbanization, and anthropogenic activities. Furthermore, the literature lists industrial wastewater, mining, fertilizers, pesticides, and runoff as dominant contributors to the heavy metals that are present and building up in water and soil [1,2]. Mn, Cu, Cr, Fe, Ni, Zn, Cd, Hg, and Pb are among the foremost hazardous and prevalent heavy metals that are environmentally detected at concentrations surpassing allowable limits [3]. Manganese (Mn^{2+}) and copper (Cu^{2+}) are essential trace elements that play critical roles in biological and environmental systems. Mn^{2+} functions as a cofactor for numerous enzymes involved in metabolic pathways, antioxidant defense mechanisms, and photosynthesis, and it is actively bioaccumulated by microorganisms as part of normal cellular processes [4]. Similarly, Cu^{2+} acts as an indispensable component for key enzymes including cytochrome c oxidase and superoxide dismutase, which are essential for cellular respiration and iron metabolism [5].

Despite their biological importance at low concentrations, elevated levels of Mn^{2+} and Cu^{2+} which may arise from mining activities, industrial effluents, and agricultural runoff, pose significant ecological and human health risks. Prolonged exposure to Mn^{2+} is associated with neurotoxicity manifested as impaired perception, memory loss, behavioral alterations, and motor disorders resembling Parkinson's disease—a condition commonly referred to as “manganism” [6]. Excessive Cu^{2+} exposure triggers oxidative stress via stimulating reactive oxygen species generation and strong interactions with cellular macromolecules, resulting in cellular damage and metabolic disruption [5]. Environmentally, elevated Mn^{2+} and Cu^{2+} concentrations pose significant risks, leading to the disruption of aquatic and terrestrial ecosystems expressed in impaired algal photosynthesis, harm to fish and invertebrates, altered microbial activity, and induced phytotoxicity in soils [7].

Considering their potential health risks, regulatory agencies have established guideline limits for both Mn^{2+} and Cu^{2+} in drinking water. For Mn^{2+} , the World Health Organization (WHO) has proposed a guideline value of 0.4 mg/L [8,9], whereas the U.S. Environmental Protection Agency (EPA) recommends a level of 0.05 mg/L [10]. Similarly, for Cu^{2+} , 2.0 mg/L is a standard limit which has been defined by the WHO [8,9], while the U.S. EPA has recognized a secondary standard of 1.0 mg/L [10]. Therefore, several scientific efforts have focused on the development of affordable and eco-friendly adsorbents—especially those sourced from municipal and agricultural wastes—for Mn^{2+} and Cu^{2+} uptake from contaminated environmental matrices.

Various technologies have been employed for the removal of heavy metals from contaminated water, including chemical precipitation, ion exchange, membrane filtration, electrochemical treatment, coagulation–flocculation, and solvent extraction. Although these techniques can achieve high removal efficiency, many are associated with limitations such as high operational costs, substantial chemical consumption, membrane fouling, sludge generation, or complex operational requirements. In contrast, adsorption has attracted considerable attention owing to its operational simplicity, high efficiency, cost-effectiveness, ease of operation, and the availability of low-cost biosorbents derived from agricultural wastes, making it one of the most promising approaches for sustainable wastewater treatment [11,12].

Various agricultural and industrial waste-based adsorbents materials have been investigated for Mn^{2+} remediation, such as *staphylococcus aureus* [4], sugarcane bagasse [13], tea waste [14], kaolinite clay [15], sawdust of deciduous trees [16], iron-ore sludge [17], and biopolymeric materials [18]. Corn-cob-based bio adsorbents were used for the removal of Mn^{2+} and Cu^{2+} [19]. In addition, sawdust [7], wheat straw [20], sugarcane bagasse [13,21], and agricultural grain shells [22] have demonstrated effective Cu^{2+} biosorption. Moreover, biochar derived from municipal solid waste [23], bare and magnetic

biochar from water hyacinth [24] as well as biochars obtained from orange peels [25] and oilseed residues [26] have shown enhanced adsorption performance and operational feasibility. These findings highlight adsorption-based remediation as a promising and economically viable approach for Mn^{2+} and Cu^{2+} removal from environmental samples [26].

The adsorption technique is widely used for the removal of pollutants during the treatment process that occurs for several types of water; this can be attributed to its operational simplicity, great efficiency, high effectiveness, availability, and low cost [27]. Several synthetic adsorbents, like activated carbon or amberlite XAD-4 showed great effectiveness for this purpose, but they are still characterized as highly costly, requiring intensive pretreatment steps, or requiring functionalization to increase effectiveness, which limits their large-scale applications [28]. Therefore, there is a need to use an inexpensive alternative adsorbent that can reduce the cost and enhance the effectiveness of an adsorption system. Several natural materials and agricultural biomass waste are considered promising renewable materials for heavy metal water remediation due to their unique eco-friendly nature, chemical composition, abundance, renewability, biodegradability, low cost, and efficiency [11]. Also, thanks to their biological origin, agricultural wastes are utilized in the production of low-cost biosorbents as well as feedstock for producing biochemicals and biofuels. Therefore, utilizing these wastes to produce valuable compounds can both mitigate environmental pollution and reduce the need for costly solid waste recycling processes [29]. Due to their adsorption capabilities, various agricultural biomasses such as rice husk [30], sugarcane bagasse [12], wheat bran [31], tea waste [32], orange peels [33], coconut shell [34], and several types of agricultural biomass were utilized for the elimination of diverse contaminants.

In the current work, attention was focused on the use of banana peels (BP), which constitutes around 40% of the total weight of the ripened fruits. BP serves multiple purposes, including composting, livestock nutrition, and the manufacture of pectin, proteins, ethanol, methane, and enzymes. BP is primarily composed of cellulose, hemicellulose, chlorophyll, and pectin, along with various low-molecular-weight compounds [35–37]. It was found that ripened BP may contain protein (8%), ether extract (6.2%), soluble sugars (13.8%), and phenolic content (4.8%) among its constituents. Pectins are complex heteropolysaccharides including galacturonic acid, arabinose, galactose, and rhamnose, which bear hydroxyl and carboxyl groups that endow BP with a high affinity for the adsorption of metal ions and organic pollutants. Many chemicals are used for the modification of BP such as H_2SO_4 [38,39], H_3PO_4 [40], KOH [41], Fe_3O_4 [42], surfactants [43], Al_2O_3 -chitosan [44], and others, which act as activating agents that polymerize with BP to increase chelating site density and pore structure, thus promoting more efficient heavy metal removal from wastewater. Under this background, unmodified and modified banana peels were investigated as environmentally sustainable and inexpensive adsorbents for the decontamination of heavy metals-polluted water [37,45,46].

The present work investigates the potential of pristine banana peel (BP) and H_2SO_4 -modified banana peel (mBP-SA) as low-cost biosorbents for the removal of Mn^{2+} and Cu^{2+} ions from aqueous media. The adsorbents were comprehensively characterized using elemental analysis, FTIR, and SEM, and the effects of key operational parameters on adsorption performance were systematically evaluated together with equilibrium modeling using the Langmuir and Freundlich isotherms. Although BP has been investigated previously as a biosorbent, comparatively few studies have systematically evaluated the influence of mild H_2SO_4 surface modification on its adsorption performance toward both Cu^{2+} and Mn^{2+} ions under identical experimental conditions while simultaneously investigating adsorption equilibrium, kinetic behavior, surface characterization, and sustainability using green analytical assessment tools. Accordingly, the present study provides a comprehensive evaluation of mBP-SA as a sustainable biosorbent and offers an integrated

assessment of its adsorption performance, adsorption mechanism, and environmental sustainability. Furthermore, the work integrates conventional adsorption studies with a comprehensive sustainability evaluation based on Analytical Eco-Scale Assessment (ESA), Green Analytical Procedure Index (GAPI), and the Analytical GREENness (AGREE) metrics, providing a balanced assessment of both adsorption performance and environmental compatibility. This combined technical and green analytical approach demonstrates that simple and economically viable surface modification presented in the current article can substantially enhance the practical applicability of banana peel for sustainable wastewater treatment, particularly in large-scale and resource-limited settings.

2. Experimental Section

2.1. Instrumentation

Orbital shaker (Model BT4010, BIOTECH Company (BTC), Giza, Egypt), magnetic stirrer (model ME1, IDL GmbH, Nidderau, Hesse, Germany), shaking standard testing sieves (model RX-29-10, W.S. Tyler, Mentor, Ohio, USA), balance (model ED224S, Sartorius AG, Göttingen, Lower Saxony, Germany), drying oven (model FDL 115 BINDER GmbH, Tuttlingen, Baden-Württemberg, Germany) and domestic blender were used in the successive steps of sample preparation throughout the entire process. CHNS/O analyzer (model CHNS/O 2400 II PerkinElmer Inc., Waltham, MA, USA) was used for elemental analysis. Fourier transform infrared spectroscopy (FTIR, model 7199 (170 SX) Nicolet Instrument Corporation, Madison, WI, USA) was utilized to depict the functional groups existing in BP and *m*BP-SA. Scanning electron microscope (SEM) to analyze the surface morphology of different samples in the current study was achieved using a Jeol Jsm-5500 LVSEM, JEOL Ltd., Akishima, Tokyo, Japan, at an accelerating voltage of 25 kV and a working distance of 50 μ m. All the pH measurements were made using pH Meter HI 2210, Hanna Instruments Inc., Woonsocket, Rhode Island, USA. The pH electrode standardization was executed utilizing calibration buffers at pH 4.01, 7.00, and 9.00.

2.2. Chemicals and Reagents

Throughout this study, all chemicals and reagents were of analytical-reagent grade and were used without further purification. $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, anhydrous CuSO_4 , NaCl , H_2SO_4 , HNO_3 , NH_4Cl , NH_4OH , $\text{NH}_2\text{OH} \cdot \text{HCl}$, and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ were purchased from Fluka Analytical (Buchs, Switzerland), whereas ethylenediaminetetraacetic acid (EDTA) and the indicators murexide and Eriochrome Black T (EBT) were obtained from Sigma-Aldrich (St. Louis, MO, USA). All washing procedures and solution preparations were carried out using bi-distilled water.

2.3. Adsorbent

Banana Peels were collected from local fruit shops located at Dar-Elsalam town, Sohag, Egypt.

2.4. Methodology

2.4.1. Adsorbent Preparation

The adsorbent was extensively washed to remove all external contaminants. Washing occurred in two rounds, initially using regular municipal water and bi-distilled H_2O in the second [38], then spread horizontally on a glass surface to dry naturally overnight. The dehydrated BP was ground and pulverized into a fine powder and subsequently subjected to boiling in bi-distilled H_2O for 10 min. Magnetic stirrer was (100 rpm) utilized during this step to ensure good distribution of the ground BP which was subsequently separated by decantation followed by a single filtration step. Finally, the BP powder was

oven-dehydrated at 70 °C to an unchanging weight and sieved to yield particles with a uniform size of 125 µm and packed in clean, airtight polypropylene plastic bottles. A particle size of 125 µm was selected because fine particles provide a larger external surface area and shorter diffusion pathways, thereby facilitating effective contact between the biosorbent and metal ions during the adsorption process and reducing mass-transfer limitations [37].

2.4.2. BP Powder Modification

H₂SO₄ was used for BP powder modification. BP was dispersed in 0.1 M H₂SO₄ for 30 min at a solid–liquid ratio of 0.003 g/0.1 mL at room temperature. A concentration of 0.1 M H₂SO₄ was selected as a mild acid treatment to modify the surface chemistry of the banana peel by promoting the exposure of oxygen-containing functional groups while minimizing excessive degradation of the lignocellulosic structure, thereby preserving the structural integrity of the biosorbent [36]. Subsequently, the suspension was agitated on a shaker at 100 rpm for 2 h. The acid-treated biomass was repeatedly washed with bi-distilled water until the pH of the washings reached approximately neutral (pH ≈ 7), indicating the effective removal of residual sulfuric acid. The washed material was subsequently oven-dried at 70 °C to constant weight, sieved to obtain a uniform particle size of 125 µm, and stored in clean, airtight polypropylene bottles for further use. From this point forward, the regular and modified BP adsorbent is designated as BP and *m*BP-SA, respectively.

2.4.3. Mn²⁺ and Cu²⁺ Adsorption Study

The sorption process is influenced by several key considerations, encompassing pH, exposure interval, and adsorbent quantity alongside starting concentration of metal ions. These parameters were investigated under controlled circumstances, including ambient temperature, utilizing a particle size of 125 µm, a solution volume of 25 mL, and an agitation speed of 100 rpm while initial concentration of studied metal ions solutions was maintained at 15 mg L^{−1}. On the basis of these preliminary experiments, specific values of pH, exposure time, and adsorbent dosage were adopted for all subsequent experiments. After a defined exposure time under these optimum conditions, the dispersion was filtered, and the resulting filtrate was analyzed for Mn²⁺ and Cu²⁺ using complexometric EDTA titration [13,47–49].

The adsorbed amount of Mn²⁺ and Cu²⁺ onto the biosorbent and the percentage uptake (Removal %) were computed using Equation (1) [13,39,50] and Equation (2) [13,39,50,51], respectively.

$$q_e = \frac{(C_i - C_f)V}{m} \quad (1)$$

$$\text{Removal (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

In the above two equations, q_e denotes the number of milligrams of adsorbed metal ions for each gram of adsorbent (mg/g); C_i and C_f are the starting and finishing metal ion concentrations (mg/L); V is the solution volume (L); and m is how many grams of the utilized adsorbent (g). All adsorption experiments were carried out using separately prepared aqueous solutions of Cu²⁺ and Mn²⁺. No mixed metal solutions of Cu²⁺ and Mn²⁺ were investigated in this study. Therefore, the observed adsorption behavior reflects the intrinsic affinity of the adsorbents toward individual metal ions in the absence of competitive effects. All experiments were conducted in triplicate ($n = 3$), and the results are expressed as mean ± standard deviation (SD). Statistical analysis was performed using one-way analysis of variance (ANOVA) to assess the significance of experimental parameters,

including pH, contact time, adsorbent dose, and initial metal ion concentration. In addition, a t-test was applied to compare the adsorption performance of BP and mBP-SA adsorbents. Differences were considered statistically significant at $p < 0.05$.

2.5. Greenness Assessment Methods

The environmental sustainability of the proposed analytical procedures was evaluated using three complementary greenness assessment tools, namely the Analytical Eco-Scale Assessment (ESA), the Green Analytical Procedure Index (GAPI), and the Analytical GREENness Metric (AGREE). ESA evaluates the environmental impact of an analytical method by assigning penalty points associated with reagent hazards, energy consumption, occupational hazards, and waste generation, with the final Eco-Scale score calculated by subtracting the total penalty points from 100 [52]. GAPI provides a comprehensive qualitative assessment of the entire analytical workflow, from sample collection to final determination, through a multicolored pictogram representing the environmental performance of each analytical step [53]. AGREE is based on the twelve principles of Green Analytical Chemistry and expresses the overall greenness of an analytical procedure as a numerical score ranging from 0 to 1, accompanied by a circular pictogram illustrating the contribution of each principle [54]. The three metrics were applied according to their published methodologies using the experimental conditions employed in the present study.

3. Results and Discussions

3.1. Adsorbent Characterization

3.1.1. Elemental Analysis for BP and mBP-SA

Elemental analysis of BP and mBP-SA reveals they have largely similar compositions, with the main difference being that mBP-SA contains a higher proportion of sulfur than BP, as summarized in Table 1. Elemental analysis revealed an increase in the sulfur content of mBP-SA compared with raw BP (Table 1), confirming that sulfuric acid treatment altered the surface chemical composition of the biosorbent. The higher sulfur content is consistent with the incorporation of sulfur-containing surface functionalities during the acid modification process, which may contribute to the enhanced affinity of the modified biosorbent toward metal ions [38,39].

Table 1. The elemental analysis of BP and mBP-SA.

Sample	Elemental Results (% Dry Basis)				
	H%	C%	S%	O%	N%
BP	5.14	42.55	0.39	41.06	1.14
mBP-SA	3.94	58.14	10.11	35.78	1.75

3.1.2. FTIR Characterization for BP and mBP-SA

FTIR reveals valuable details on the surface functional groups responsible for pollutant uptake utilizing proposed biosorbents. The FTIR of BP confirmed the presence of various surface functional groups, including O–H, N–H, C–H, C=O, C=C, C–N, and C–O, indicating abundant sites available for pollutant interaction. In addition, the FTIR spectrum of BP showed absorption peaks attributable to oxidized carbon-containing materials, which were assigned to C–O and/or C–O–C stretching in acids, alcohols, phenols, ethers and/or esters groups and sulphonic acid groups (–SO₃). Figure 1a exhibits that the FTIR spectrum of BP was characterized by the stretching vibrations of CH, CH₂, and CH₃ (2933 cm^{−1}), together with the C–O stretching vibration (1042 cm^{−1}). A weak absorption band was observed at approximately 3836 cm^{−1}. Because this wavenumber is not characteristic of the broad hydrogen-bonded O–H stretching vibrations typically observed in

lignocellulosic biomass ($3200\text{--}3600\text{ cm}^{-1}$), no definitive assignment is made for this band. The discussion therefore focuses on the more characteristic FTIR bands associated with hydroxyl, carbonyl, and other oxygen-containing functional groups that are relevant to the adsorption process. FTIR analysis of *m*BP-SA (Figure 1b) revealed significant changes in the surface functional groups, including the appearance of a broad absorption band centered at approximately 3275 cm^{-1} , characteristic of hydrogen-bonded hydroxyl groups. These spectral changes indicate that H_2SO_4 treatment modified the surface chemistry of the biomass, resulting in alterations to the surface functional groups that may contribute to metal ion adsorption. The C–O stretching vibration decreased from 1042 cm^{-1} to 1037 cm^{-1} , and the CH, CH_2 , and CH_3 stretching vibrations decreased from 2933 cm^{-1} to 2917 cm^{-1} , indicating that these functional groups were partially oxidized. Furthermore, the tweak being suggested caused the emergence of stretching bands at 1644 cm^{-1} , ascribed to the C=O stretching of ketones, aldehydes, lactones, and carboxyl groups [55,56].

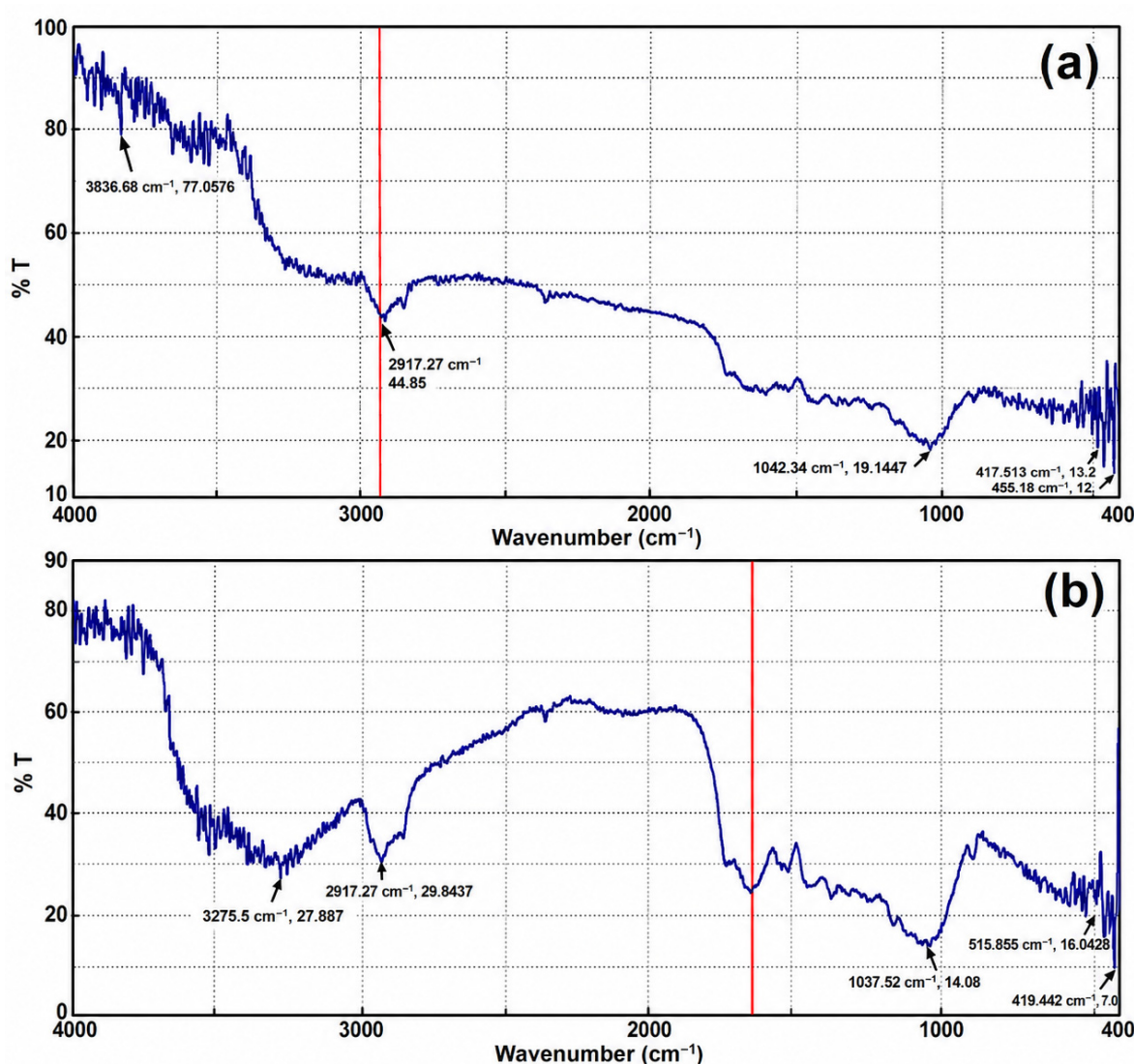


Figure 1. FTIR spectrum of (a) BP and (b) *m*BP-SA samples showing functional group variations as a function of wavenumber (cm^{-1}).

3.1.3. Scanning Electron Microscopy (SEM)

To study how BP modification as well as metal ion adsorption affect BP surface morphology and porosity, SEM analysis was carried out for the BP, *m*BP-SA and *m*BP-SA loaded with adsorbed Cu^{2+} ions (Figure 2). SEM is commonly used to infer surface

characteristics, where the presence of cavities, cracks, and voids reflects improved porosity and promotes adherence of adsorbed metal ions. Figure 2a showed the BP which looks like a heterogeneous, rough surface with crater-like pores. Moreover, Figure 2b showed the *m*BP-SA surface morphology which is a highly porous, irregular, and heterogenous surface compared to the raw BP. The H_2SO_4 treatment appears to alter the surface morphology by generating a rougher and more heterogeneous surface with additional visible cavities and fissures, which may improve the accessibility of adsorption sites for metal ion interaction [31,55,57]. This comes in accordance with SEM results that suggest that H_2SO_4 treatment altered the surface morphology, producing a rougher and more heterogeneous texture that may improve the accessibility of adsorption sites for metal ion interaction. However, SEM provides qualitative morphological information and does not directly quantify specific surface area or pore size distribution. Therefore, the enhanced adsorption performance of *m*BP-SA is consistent with these structural changes and previous reports on acid-treated lignocellulosic materials [31,57]. Figure 2c showed that the surface of *m*BP-SA consists of adsorbed Cu^{2+} which become more smooth, shiny and whitish due to Cu^{2+} adsorption. The results obtained showed that there is a difference in BP surface morphology due to BP surface modification followed by the binding of Cu^{2+} .

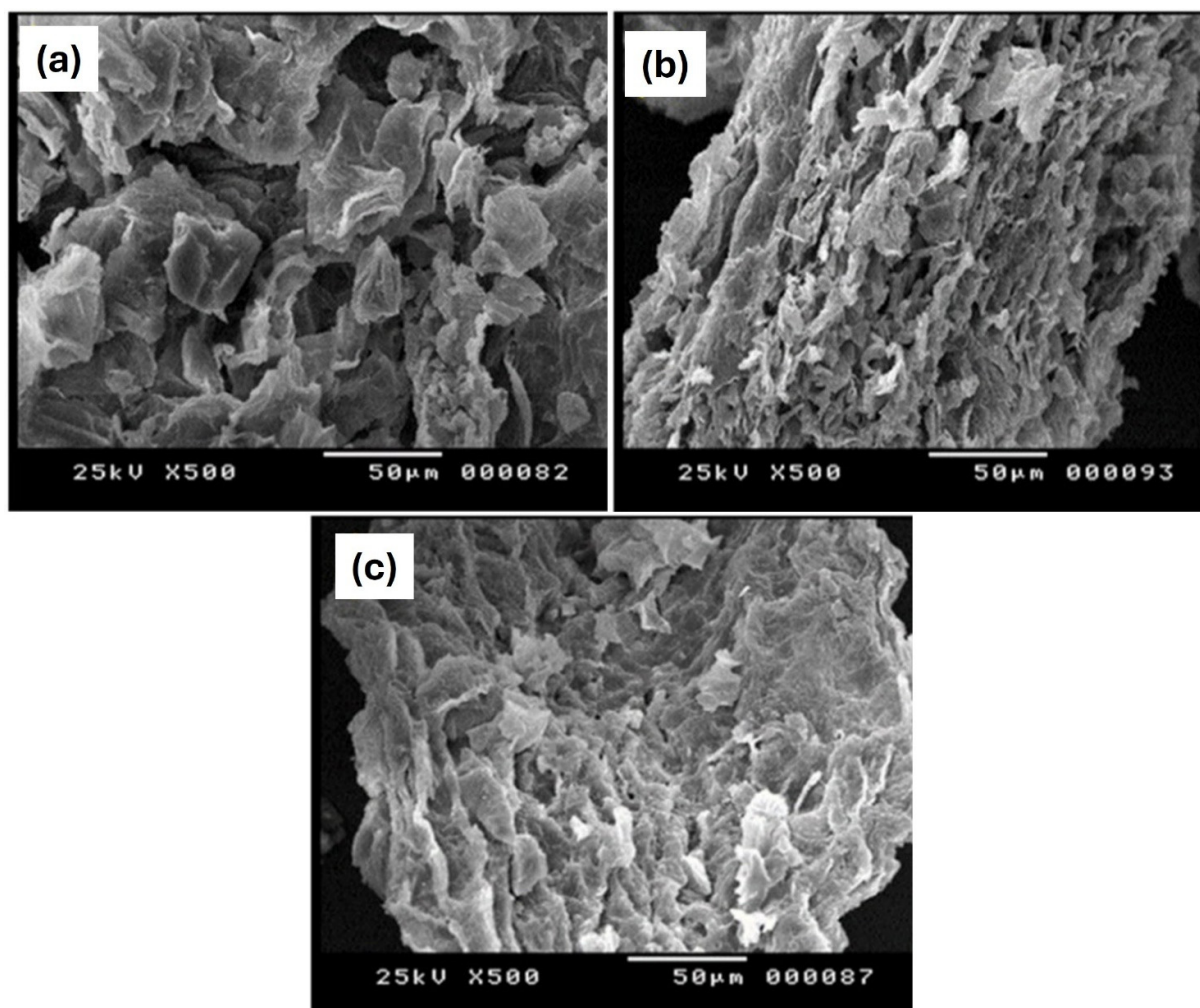


Figure 2. SEM images of: (a) pure BP; (b) *m*BP-SA and (c) *m*BP-SA loaded with Cu^{2+} .

3.2. Adsorption Studies

3.2.1. Effect of pH

The effect of the pH on the removal percentage of Mn^{2+} and Cu^{2+} for BP is shown in Figure 3. Keeping other parameters constant, the pH study outcomes commonly demonstrate that metal adsorption is optimized at higher pH levels. The removal percentage of BP toward Mn^{2+} increases by increasing pH, achieving the highest removal percentage at pH 6.5 with approximate constancy through higher pH values. For Cu^{2+} , its eradication efficiency improves with rising pH up to 5.5, after which it declines at higher pH values. Under acidic conditions, there is an increase in H^+ , which largely occupies the adsorption sites on BP, competing with the metallic adsorption on its substrate, lowering the attraction between them. Conversely, the functioning groups on BP substrate will reveal an increase in the negative charge density at alkaline conditions, achieving more attraction throughout such functioning groups and metal ions [58]. Increasing pH above 7 causes Mn^{2+} and Cu^{2+} to settle out as $\text{Mn}(\text{OH})_2$ and $\text{Cu}(\text{OH})_2$, respectively, which is not acceptable since they cannot be absorbed, and so the adsorption process does not occur [59]. The observed pH dependence suggests that surface functional groups play an important role in the adsorption process and are consistent with mechanisms involving surface complexation and electrostatic interactions.

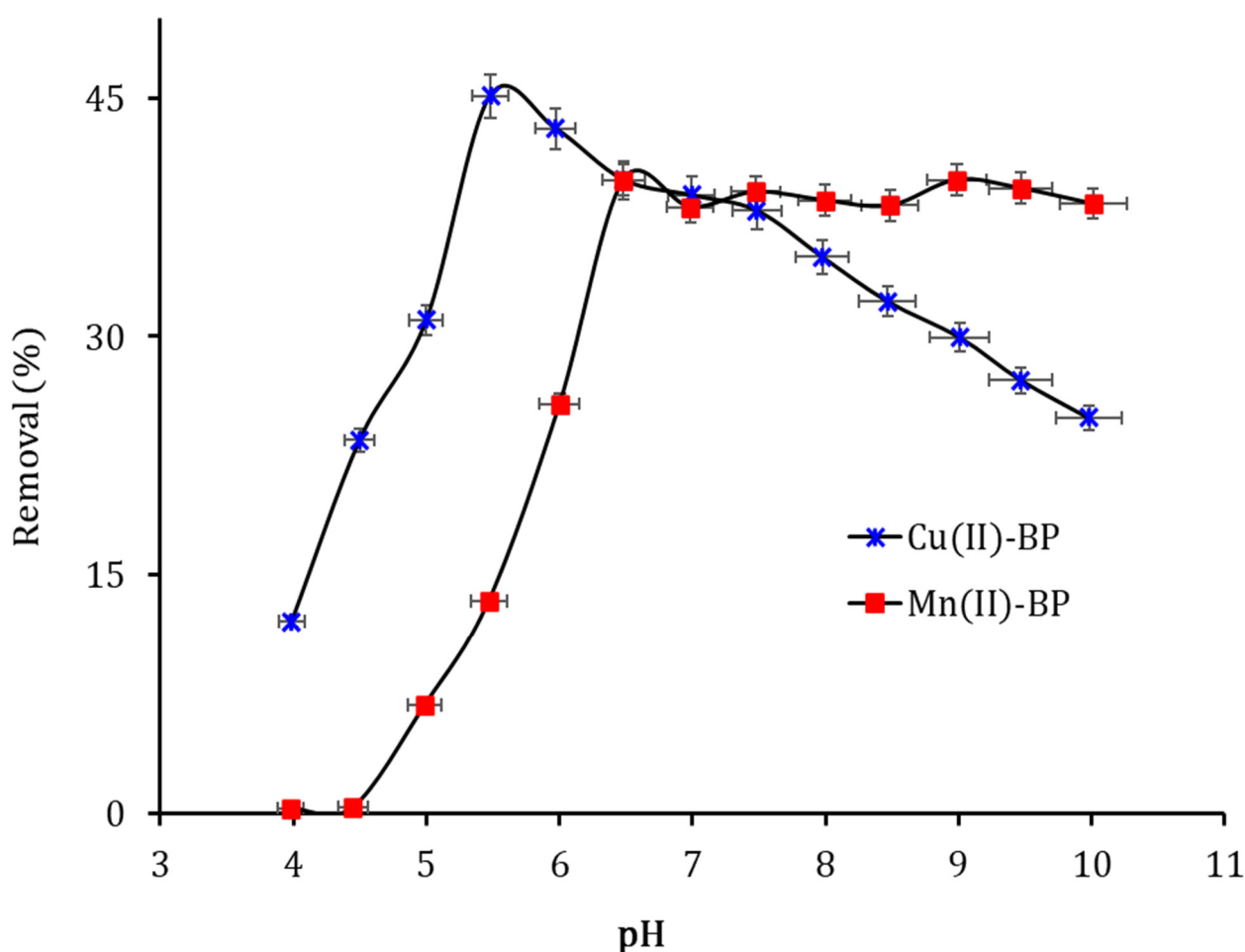


Figure 3. Effect of pH on the removal percentage of Mn^{2+} and Cu^{2+} ions using BP ($n = 3$).

3.2.2. Effect of Exposure Time

Removal percentage of Mn^{2+} and Cu^{2+} gradually increased with increasing exposure time with BP, where saturation and the maximum removal percentage is obtained at exposure time of 40 and 80 min, respectively. Subsequently, it was revealed that elimination percent decreased with prolonged exposure time, eventually attaining an equilibrium status. This phenomenon can be explained by the interactions between BP functional groups and Mn^{2+} or Cu^{2+} , which leads to the adsorption sites being progressively saturated. As a result, the removal efficiency of Mn^{2+} or Cu^{2+} reached a maximum when the adsorption sites and BP functioning groups approached occupancy [60]. The adsorption rate has been elevated during the first 10 min where the adsorption surface area is large and therefore the rate of removal percentage is rapid. Throughout the current investigation, all other adsorption variables were maintained constantly. The percentages of removal of Mn^{2+} and Cu^{2+} ions for initial concentration at the optimum pH value are represented in Figure 4, which illustrates that Cu^{2+} removal percentage was more than that of Mn^{2+} because it has high affinity for the adsorbents. One reason for this high affinity is the low ionic radius of Cu^{2+} . Whenever the ionic radius decreases, the affinity for penetrating smaller pores of the adsorbent becomes greater and consequently leads to the highest removal capacity of the adsorbents which is very important in estimating the metal ion selectivity [61].

The adsorption selectivity of metal ions in multi-component systems is governed by their interaction strength with surface functional groups, electrostatic characteristics, and ionic size [62]. Recent studies have shown that adsorption of heavy metal ions on biomass-derived adsorbents is primarily governed by complexation with oxygen-containing functional groups and chemisorption mechanisms [63]. The strong adsorption behavior of Cu^{2+} and Mn^{2+} compared to common background ions such as Na^+ , Ca^{2+} , and Mg^{2+} can be attributed to their strong chemical interaction toward oxygen-containing functional groups (e.g., $-\text{COOH}$ and $-\text{OH}$) present on the biomass surface [64]. Cu^{2+} are known to form stable inner-sphere complexes and chelates, resulting in stronger binding affinity [65]. Mn^{2+} , although exhibiting a comparatively lower affinity than Cu^{2+} , can still participate in surface complexation and ion-exchange interactions, leading to more effective adsorption than common background ions such as Na^+ , Ca^{2+} , and Mg^{2+} [62]. Studies related to competitive adsorption indicate that Cu^{2+} exhibits higher selectivity and stronger binding among other divalent metal ions, followed by other ions including Mn^{2+} . This can be attributed to its electronic structure as well as its coordination binding ability, which enhances its stronger surface complexation interactions with existing oxygen-containing functional groups and finally resulting in higher adsorption affinity compared to other metal ions such as Na^+ , Ca^{2+} , and Mg^{2+} which remain strongly hydrated and interact mainly through weaker electrostatic mechanisms, which limits their adsorption efficiency [66]. Therefore, the preferential adsorption of Cu^{2+} and Mn^{2+} can be attributed to their greater chemical affinity for surface functional groups and their ability to form more stable surface complexes [62].

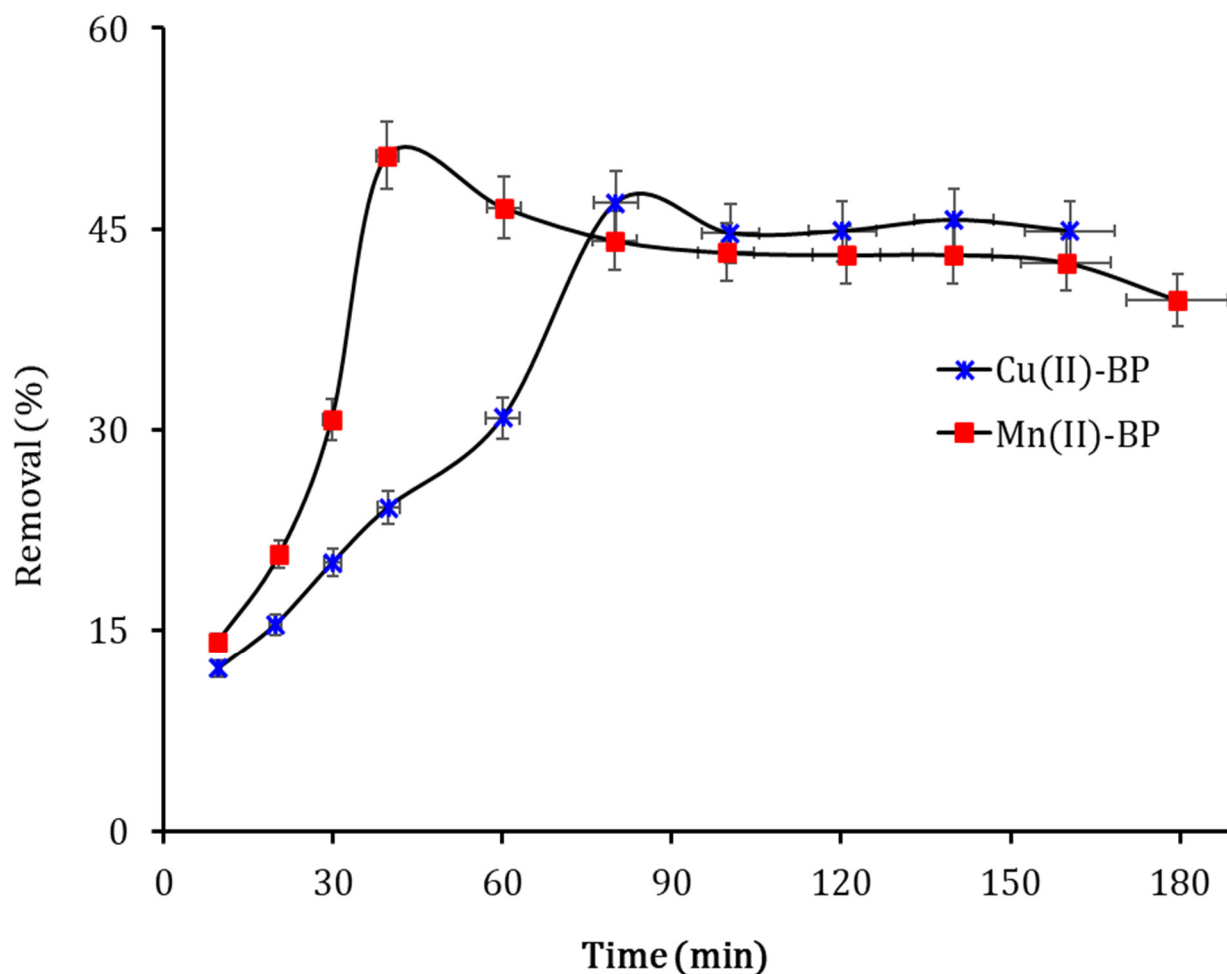


Figure 4. Effect of contact time on the removal percentage of Mn^{2+} and Cu^{2+} using BP ($n = 3$).

3.2.3. Effect of Amount of Adsorbent

According to the data depicted in Figure 5, the removal of heavy metal ions increased with the increasing adsorbent dose until saturation occurred, and using a larger adsorbent amount had no effect on adsorption percentage. The highest removal was obtained at 0.05 and 0.1 g for Mn^{2+} and Cu^{2+} , respectively, as shown in Figure 5. This can be clarified as BP dosages being elevated may result in substantial enlargement of the sorptive surface area as well as a greater number of accessible effective binding positions. The diminution in the eradication efficiency becomes apparent if a further adsorbent dose is applied; this is due to the occurred saturation, which takes place after optimum dose. The diminution may be ascribed to aggregation or overlapping of adsorption positions, which limits the adsorbent's accessible surface area [67].

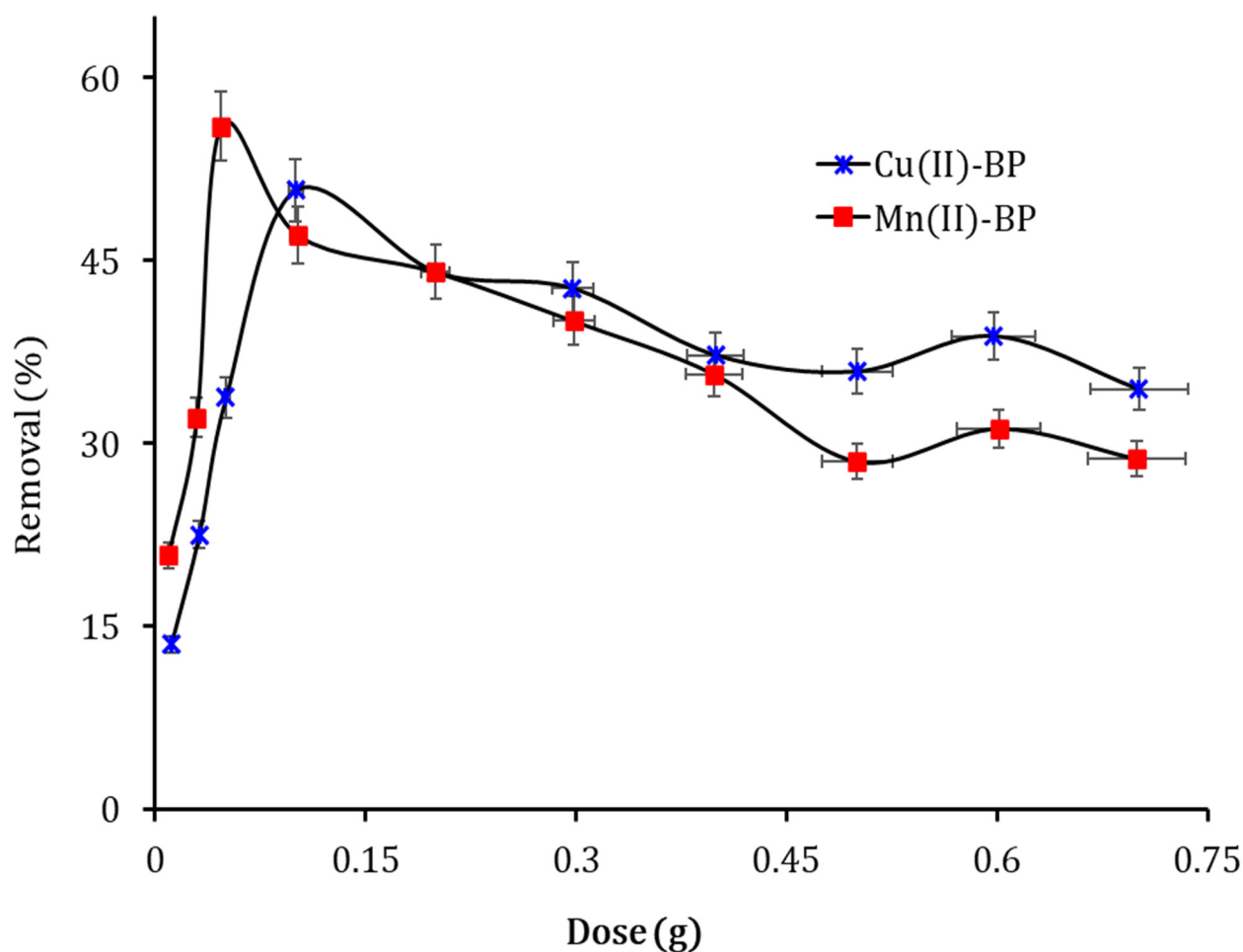


Figure 5. Effect of dose of BP on the removal percentage of Mn^{2+} and Cu^{2+} utilizing BP ($n = 3$).

3.2.4. Effect of Metal Ions Concentrations

A comparative study was conducted to evaluate both BP and mBP-SA adsorption efficiency. The modification impact on Mn^{2+} and Cu^{2+} sorption is shown in Figure 6 where the results with the adsorbents before and after modification are shown. Such a sorption comparative study was accomplished at pH 6.5 and 5.5, exposure time 40 and 80 min respectively and adsorbent doses of 0.05 and 0.1 g, for sorption of Mn^{2+} and Cu^{2+} , respectively. Removal efficiencies of Mn^{2+} and Cu^{2+} declined sharply from 90% to 19%, and from 92% to 21%, respectively, with BP and from 90% to 26% and from 98% to 34%, respectively, with mBP-SA. The best removal occurs at the concentration of 5 ppm. Therefore, higher heavy metal concentrations lead to a decline in removal efficiency, since the sorption sites on a given amount of adsorbent reach saturation.

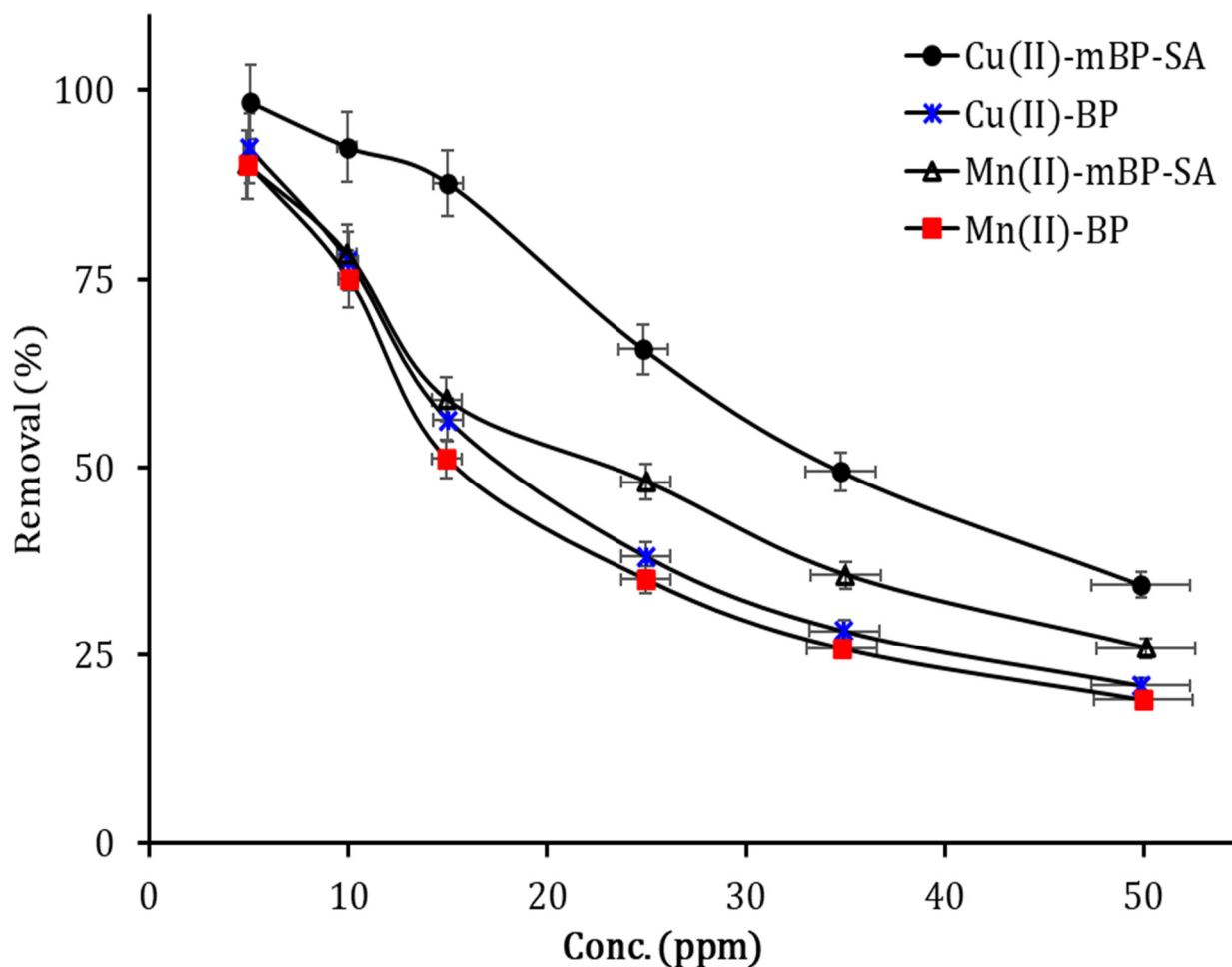


Figure 6. Effect of initial conc. of Mn^{2+} and Cu^{2+} onto BP and mBP-SA adsorbents ($n = 3$).

3.3. Adsorption Isotherms

The experimental data for metal ions were interpreted with the Langmuir and Freundlich isotherms as expressed by Equations (3) and (4), respectively [13,39,50,68–70].

$$q_e = \frac{q_{max} b C_e}{1 + b C_e} \quad (\text{Langmuir equation}) \quad (3)$$

and the in linearized form is:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}}$$

$$q_e = K_f C_e^{1/n} \quad (\text{Freundlich equation}) \quad (4)$$

and the in linearized form is:

$$\ln q_e = \ln K_f + \left(\frac{1}{n}\right) \ln C_e$$

Here, C_e is the metal ion concentration at equilibrium (mg/L), and q_e is the metal amount adsorbed per unit weight of adsorbent (mg/g), q_{max} is the maximum quantity sorbed (mg/g), b is the Langmuir constant, and K_f and n are the Freundlich constants (L/g) that describe adsorption capacity and intensity, respectively. Outcomes related to Langmuir and Freundlich isotherm equilibrium models for the biosorption of Mn^{2+} and Cu^{2+} onto BP and mBP-SA are summarized in Table 2, which highlights the q_{max} values and the maximum sorption capacities of the metal ions on the adsorbents. Table 2 shows that the Langmuir constant (b) for Cu^{2+} exceeds that for Mn^{2+} , implying that Cu^{2+} exhibits higher

adsorption, and its potential to interact with diverse functional groups on the BP surface [71]. Based on the computed correlation coefficients (R^2), the Langmuir isotherm model provided the best fit for the biosorption data, as illustrated in Figures 7 and 8, suggesting that the adsorption process predominantly follows monolayer coverage on relatively homogeneous adsorption sites. The Langmuir isotherm suggests that adsorption predominantly occurs as monolayer coverage on relatively homogeneous surface sites. While the adsorption capacities obtained in this study are moderate compared to some engineered adsorbents, they are comparable to several low-cost agricultural biosorbents reported in recent studies. Importantly, the observed enhancement after acid modification (approximately 65% for Cu^{2+} and 82% for Mn^{2+}) demonstrates the effectiveness of surface activation in improving adsorption performance. This improvement is attributed to increased availability of active binding sites and enhanced surface acidity, facilitating metal ion interaction. The improved adsorption performance after H_2SO_4 treatment is attributed to acid-induced structural and chemical modifications that enhance the accessibility of adsorption sites and increase the availability of oxygen-containing functional groups for metal ion interaction. This interpretation is supported by the combined evidence from FTIR, which indicates changes in surface functional groups, and SEM, which reveals a rougher and more heterogeneous surface morphology. Since the experiments were conducted in single-metal systems, the proposed adsorption mechanism does not account for competitive interactions between Cu^{2+} and Mn^{2+} ions, which may influence adsorption behavior in multi-component systems.

Acid treatment of lignocellulosic biomass can induce partial hydrolysis of cellulose and hemicellulose through cleavage of β -1,4-glycosidic bonds, resulting in structural disruption and increased porosity. It may also lead to the removal or transformation of hemicellulose components and modification of lignin structure, thereby enhancing surface accessibility and exposing internal adsorption sites [72]. In addition, the treatment can enrich the surface with oxygen-containing functional groups (e.g., $-\text{OH}$, $-\text{COOH}$) on the biomass surface, which may serve as active sites for metal ion binding through mechanisms including surface complexation, ion exchange, and possible electrostatic interactions [73]. These structural and chemical changes are likely responsible for the improved adsorption performance observed for the modified biosorbent, in agreement with previously reported studies.

Table 2. Langmuir and Freundlich models of the metal ions adsorption on BP and *m*BP-SA (Experimental data used for isotherm modeling are expressed as mean $\pm$ SD ($n = 3$)).

Metal Ion	Langmuir				
	Adsorbent	$q_{\max}(\text{mg/g})$	$b(\text{L/mg})$	R^2	Equation
Mn^{2+}	BP	1.86	1.00	0.998	$y = 0.40x + 0.67$
	<i>m</i> BP-SA	3.38	0.54	0.998	$y = 0.30x + 0.57$
Cu^{2+}	BP	5.29	0.84	0.998	$y = 0.19x + 0.28$
	<i>m</i> BP-SA	8.70	1.95	0.999	$y = 0.12x + 0.04$
	Freundlich				
	Adsorbent	$K_f((\text{mg/g}) \cdot (\text{L/mg}))$	n_f	R^2	Equation
Mn^{2+}	BP	1.39	6.17	0.917	$y = 0.16x + 0.30$
	<i>m</i> BP-SA	1.45	4.08	0.959	$y = 0.23x + 0.39$
Cu^{2+}	BP	2.94	5.92	0.936	$y = 0.16x + 1.09$
	<i>m</i> BP-SA	4.67	4.59	0.927	$y = 0.21x + 1.55$

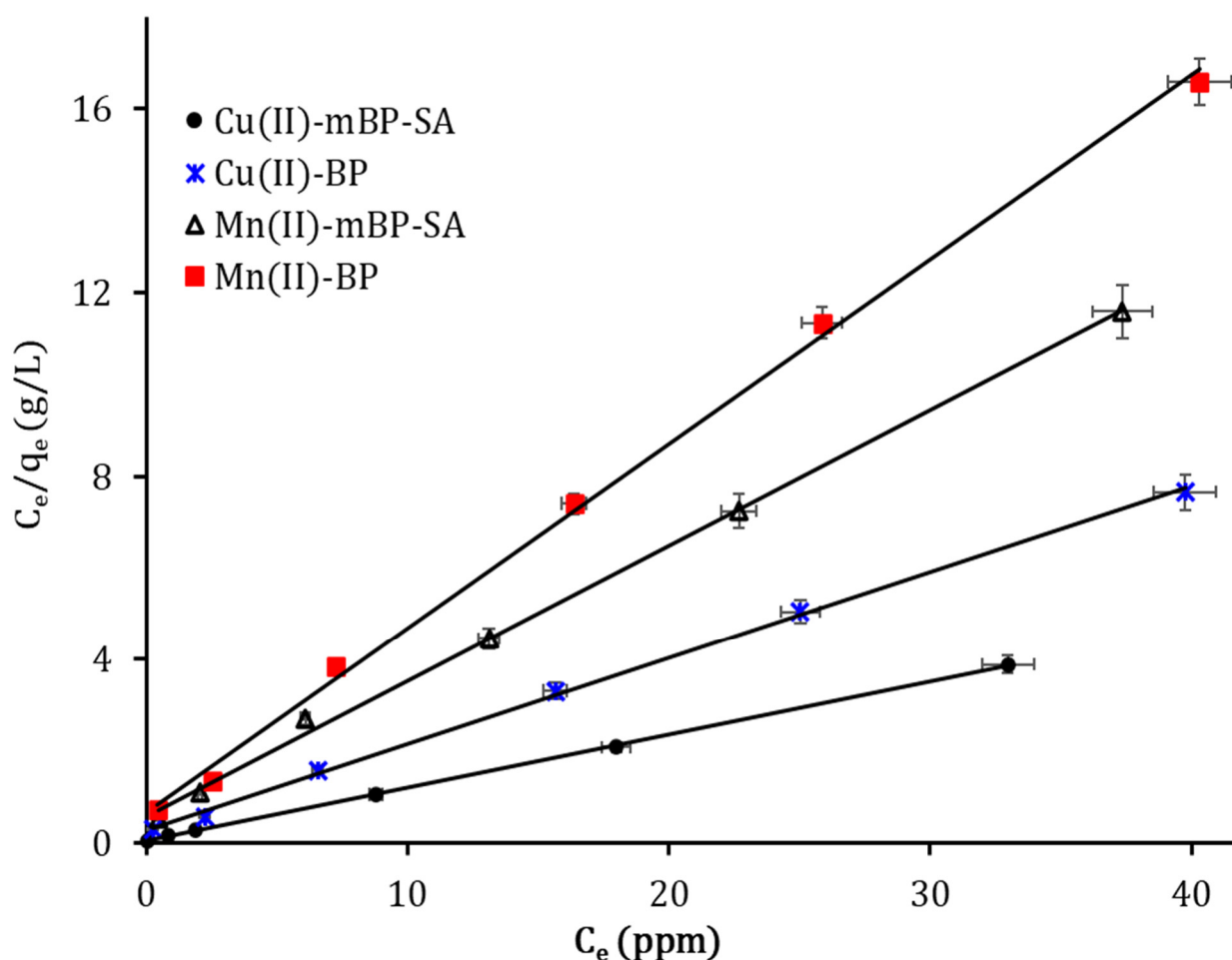


Figure 7. Langmuir model of Mn^{2+} and Cu^{2+} for BP and *mBP-SA*.

High-resolution SEM images revealed increased surface irregularities following H_2SO_4 treatment, while the significant increase in the maximum adsorption capacity (q_{max}) for both metal ions supports the conclusion that surface modification enhanced the accessibility of adsorption sites. This can be inferred from the significant increase in q_{max} for Cu^{2+} (from 5.29 to 8.70 mg/g) and Mn^{2+} (from 1.86 to 3.38 mg/g), which serves as quantitative evidence of increased active surface sites. Previous studies have suggested that heavy metal adsorption by lignocellulosic biosorbents may involve multiple mechanisms, including surface complexation, ion exchange, electrostatic interactions, simple diffusion, intra-particle diffusion, hydrogen bonding, redox interactions, and precipitation, depending on the surface chemistry and experimental conditions [37,61,74]. Acid treatment is expected to modify the biomass surface and expose additional functional groups and accessible adsorption sites, thereby improving metal uptake [37,61,75]. This interpretation is consistent with the morphological changes observed in the SEM analysis and supports the comparative evaluation of pristine and modified banana peel, which represents the primary objective of the present study. The higher affinity observed for Cu^{2+} compared to Mn^{2+} can be attributed to its smaller hydrated radius and stronger complexation tendency with existing surface functional groups.

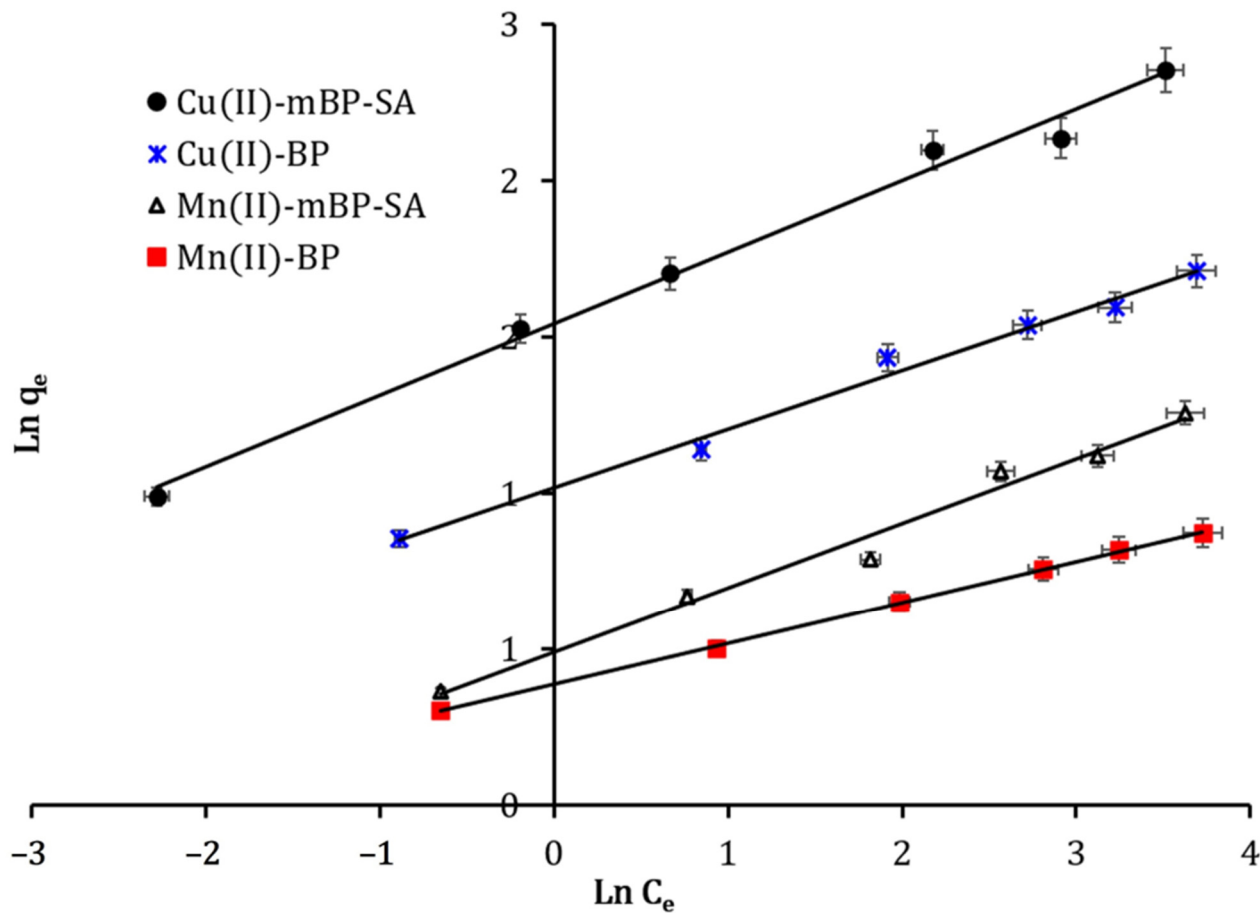


Figure 8. Freundlich model of Mn^{2+} and Cu^{2+} for BP and *m*BP-SA.

3.4. Adsorption Kinetics

This work examined and described the adsorption kinetics of Mn^{2+} and Cu^{2+} using the pseudo 1st order, pseudo 2nd order, and intra-particle diffusion rate kinetic models [76–78]. The pseudo 1st order equation representing the adsorption of a solute from a liquid solution was shown in Equation (5). A pseudo 2nd order equation based on the adsorption equilibrium capacity could be expressed in Equation (6), while the intra-particle diffusion model represented by Equation (7).

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

$$q_t = k_p * t^{\frac{1}{2}} + C \quad (7)$$

where q_e is the adsorbed ammonium ion mass at equilibrium (mg/g), q_t is the adsorbed ammonium ions mass at time t (mg/g), K_1 is the pseudo 1st order reaction rate constant (l/min), and K_2 is a constant that represents the pseudo 2nd order reaction rate equilibrium (g/mg min), K_p is the rate constant of intra-particle diffusion (mg/g.min^{1/2}) and C (mg/g) is the intercept, which is identified with the thickness of the boundary layer, and $t^{1/2}$ (min) represents the square root of time.

The adsorption kinetic behavior of Cu^{2+} and Mn^{2+} ions was investigated using the pseudo 1st order, pseudo 2nd order, and Weber–Morris intraparticle diffusion models (Figure 9a–c). The kinetic parameters derived from these models are listed in Table 3. Among the evaluated kinetic models, the pseudo 2nd order model (Figure 9b) provided

the best description of the experimental data. The corresponding correlation coefficients ($R^2 = 0.993\text{--}0.997$) were consistently higher than those obtained for the pseudo 1st order model ($R^2 = 0.560\text{--}0.888$), indicating that the adsorption rate is more accurately represented by the pseudo 2nd order expression. In contrast, the pseudo 1st order model (Figure 9a) underestimated the adsorption behavior, as reflected by its relatively poor correlation coefficients and the noticeable discrepancy between the calculated and experimental equilibrium adsorption capacities. Nevertheless, it is important to recognize that a good fit to the pseudo 2nd order model alone does not conclusively establish a chemisorption mechanism. Instead, the results demonstrate that the adsorption kinetics are primarily governed by the availability of active adsorption sites and the interaction between the adsorbate species and the adsorbent surface.

Comparison of the pseudo 2nd order rate constants (K_2) revealed differences in adsorption rates among the investigated systems. Cu^{2+} adsorption on BP exhibited the highest rate constant ($0.09 \text{ g mg}^{-1} \text{ min}^{-1}$), indicating rapid uptake during the initial stage of adsorption, whereas Mn^{2+} -BP showed a lower adsorption rate ($0.04 \text{ g mg}^{-1} \text{ min}^{-1}$). These differences can be attributed to variations in ionic properties, including hydrated ionic radius and affinity toward the oxygen-containing functional groups present on the adsorbent surface. Surface modification also influenced adsorption performance by increasing the accessibility of active binding sites, thereby improving the overall adsorption efficiency.

To further clarify the adsorption mechanism, the experimental data were analyzed using the Weber–Morris intraparticle diffusion model. As shown in Figure 9c, the adsorption curves consist of three distinct linear regions, confirming that adsorption proceeds through multiple sequential stages rather than a single diffusion-controlled process [79].

The initial linear region (Step I) corresponds to the rapid migration of metal ions from the bulk solution to the external surface of the adsorbent. The relatively large diffusion rate constants (k_1) obtained during this stage indicate that external mass transfer dominates the early adsorption period. Subsequently, the adsorption enters a second stage (Step II), where the diffusion of metal ions into the internal pore structure becomes the principal transport process. The reduced slopes observed in this region suggest that intraparticle diffusion is slower than external diffusion because of increased resistance within the porous network. Finally, the third stage (Step III) represents the approach to equilibrium, during which the adsorption rate decreases markedly as the remaining active sites become progressively occupied and the concentration gradient between the solution and the adsorbent diminishes [80].

Although intraparticle diffusion contributes significantly to the adsorption process, none of the linear segments pass through the origin. The positive intercept values obtained for all adsorption systems indicate that intraparticle diffusion is not the sole rate-limiting step. Instead, adsorption is controlled by the combined influence of external film diffusion, pore diffusion, and surface adsorption. Furthermore, the larger intercept values observed for Cu^{2+} -mBP-SA suggest a greater boundary-layer contribution and stronger initial interaction between Cu^{2+} ions and the modified adsorbent surface.

From all above, the kinetic results demonstrate that adsorption of Cu^{2+} and Mn^{2+} onto BP and mBP-SA is governed by a multistep mechanism involving rapid external diffusion, gradual intraparticle diffusion, and equilibrium adsorption. The superior performance of the modified adsorbent can be attributed to its enhanced surface characteristics and increased density of accessible functional groups, which facilitate efficient metal-ion uptake while reducing diffusion resistance.

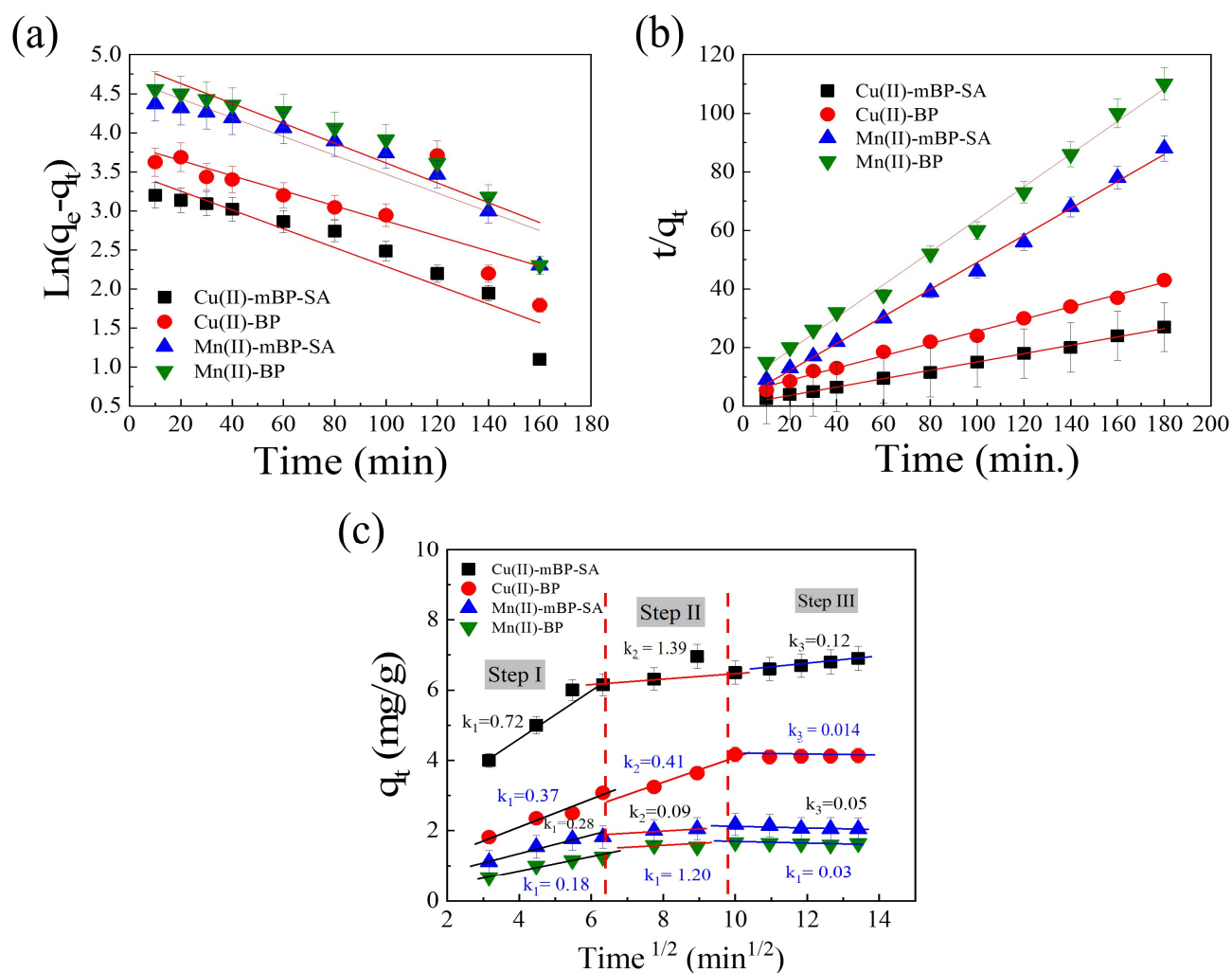


Figure 9. (a) Pseudo 1st order, and (b) pseudo 2nd order, and (c) intraparticle diffusion models for adsorption of Mn²⁺ and Cu²⁺ ions onto BP and mBP-SA.

Table 3. Kinetic parameters of the metal ions onto BP and mBP-SA (Kinetic parameters were calculated from experimental data expressed as mean $\pm$ SD ($n = 3$)).

Adsorbents		Parameters			
Pseudo 1st Order					
	q _e (mg/g)	K ₁ (min ⁻¹)	R ²		
Cu ²⁺ -mBP-SA	32.88	-0.012	0.888		
Cu ²⁺ -BP	46.43	-0.009	0.560		
Mn ²⁺ -mBP-SA	107.23	-0.012	0.883		
Mn ²⁺ -BP	131.6	-0.013	0.857		
Pseudo 2nd Order					
	q _e (mg/g)	K ₂ (min ⁻¹)	R ²		
Cu ²⁺ -mBP-SA	7.02	0.02	0.997		
Cu ²⁺ -BP	4.79	0.09	0.993		
Mn ²⁺ -mBP-SA	2.17	0.07	0.996		
Mn ²⁺ -BP	1.69	0.04	0.995		
Intra-particle diffusion					
Step I		Step II		Step III	
C	k ₁	r ₁ ²	k ₂	r ₂ ²	k ₃
(mg/g)					r ₃ ²

		(mg/g min ^{1/2})		(mg/g min ^{1/2})		(mg/g. min ^{1/2})	
Cu ²⁺ -mBP-SA	1.79	0.72	0.96	1.39	0.99	0.12	0.99
Cu ²⁺ -BP	0.64	0.37	0.95	0.41	0.99	0.014	0.98
Mn ²⁺ -mBP-SA	0.22	0.28	0.99	0.09	0.97	0.05	0.88
Mn ²⁺ -BP	0.12	0.18	0.97	1.20	0.99	0.03	0.99

All adsorption experiments were conducted in triplicate ($n = 3$), and the results are expressed as mean $\pm$ (SD). Statistical analysis was performed using one-way analysis of variance (ANOVA) to evaluate the effects of pH, contact time, adsorbent dose, and initial metal ion concentration on the adsorption efficiency of Mn²⁺ and Cu²⁺ ions, while Student's *t*-test was applied to compare the adsorption performance of BP and mBP-SA adsorbents. The obtained results demonstrated statistically significant differences among the experimental conditions investigated ($p < 0.05$), confirming the important roles of these parameters in controlling adsorption behavior. In addition, the relatively small SD values and corresponding error bars indicated low experimental variability and high reproducibility of the adsorption measurements. Regression analysis of the adsorption isotherm and kinetic data revealed high R^2 values, particularly for the Langmuir isotherm and pseudo 2nd order kinetic models, indicating satisfactory fitting and reliable interpretation of the adsorption process. More statistical analyses, including one-way and two-way ANOVA results with F-statistics, degrees of freedom, and exact *p*-values, are provided in Supplementary (Tables S1 and S2). When considered together with the pseudo 2nd order kinetic behavior and the presence of oxygen-containing functional groups identified by FTIR analysis, the results indicate that the uptake of Cu²⁺ and Mn²⁺ likely involves interactions between the metal ions and the biosorbent surface through mechanisms such as surface complexation and ion exchange. These complementary findings are consistent with the enhanced adsorption performance of the mBP-SA and provide supportive although not conclusive, evidence regarding the adsorption mechanism.

As we mentioned before, all adsorption experiments in this study were performed using single-metal solutions to evaluate the intrinsic adsorption behavior of BP and mBP-SA toward Cu²⁺ and Mn²⁺ ions. We confirm that competitive adsorption studies are important for practical wastewater applications and consider this aspect a valuable direction for future investigations involving multicomponent wastewater to further assess the applicability of the proposed biosorbents under realistic operating conditions.

Information on adsorption performance towards Mn²⁺ and Cu²⁺ that was achieved in the current investigation is compared with previously used adsorbents as illustrated in Tables 4 and 5, respectively.

Table 4. Comparison of adsorption capacity between BP and mBP-SA with other adsorbents for Mn²⁺ ion.

Adsorbent	$q_{\max}$ (mg/g)	Conditions			Ref.
		pH	Temp. (°C)	Dose (g/L)	
BP *	1.86	6.50	Amb. Temp.	4.0	This work
mBP-SA *	3.38	6.50	Amb. Temp.	4.0	This work
Staphylococcus aureus	1.31	---	---	---	[4]
SB *	1.01	6.00	Amb. Temp.	8.0	[13]
mSB-SA *	1.62	6.00	Amb. Temp.	8.0	[13]
TW *	0.16	---	---	20.0	[14]
Kaolinite	0.45	---	25.0	10.0	[15]
	0.46	---	40.0	10.0	
SDT *	1.01	5.21	Amb. Temp.	20.0	[16]

IOS *	0.71	5.51	25.0	20.0	[17]
DMP–SC20 *	0.45	6.90	---	5.0	[18]
DM–SC20 *	0.89	5.20	---	5.0	[18]
CC and SPSP *	0.98	5.01	40.0	8.0	[19]

* BP: Banana Peel; *m*BP–SA: Banana Peel modified with H₂SO₄; SB: Sugarcane Bagasse; *m*SB–SA: Sugarcane Bagasse modified with H₂SO₄; TW: Tea waste; SDT: Sawdust of deciduous trees; IOS: Iron–ore–sludge; DM–SC20: Demineralized crab–shell chitin; DMP–SC20: demineralized/deproteinized crab–shell chitin; CC: Corn Cob; SPSP: Strychnospotatorum seed powder.

Table 5. Comparison of sorption capacity between BP and *m*BP–SA with other adsorbents for Cu²⁺ ion.

Adsorbent	q _{max} (mg/g)	Conditions			Ref.
		pH	Temp. (°C)	Dose (g/L)	
BP *	5.29	5.51	Amb. Temp	2.0	This work
<i>m</i> BP–SA *	8.70	5.50	Amb. Temp	2.0	This work
Sawdust	5.75	6.82	25.0	0.4	[7]
SB *	2.88	5.51	Amb. Temp.	4.0	[13]
<i>m</i> SB–SA *	4.15	5.50	Amb. Temp.	4.0	[13]
CC and SPSP *	1.01	5.00	40.0	8.0	[19]
Wheat Straw	4.30	6.73	Amb. Temp.	20.0	[20]
<i>m</i> SB–CA *	6.87	5.01	---	10.0	[21]
Bagasse fly ash	2.36	4.01	50.0	10.0	[22]
LS *	9.59	5.03	60.0	20.0	[23]
WS *	17.42	6.05	60.0	20.0	[23]
RS *	2.95	5.98	60.0	20.0	[23]
CSAC *	5.92	---	25.0	10.0	[24]
CCAC *	4.42	---	25.0	10.0	[24]
Biochar powder *	4.14	5.01	30.0	5.0	[25]
EC *	2.06	6.02	Amb. Temp.	12.0	[26]
Fe ₂ O ₃ –EC *	3.53	6.02	Amb. Temp.	12.0	[26]
BOP *	28.06	5.01	Amb. Temp.	1.0	[27]
GNSCP *	4.82	5.00	40.0	0.75	[28]
SSCP *	4.24	5.00	40.0	1.0	[28]
CCP *	4.32	5.00	40.0	1.0	[28]

* BP: Banana Peel; *m*BP–SA: Banana Peel modified with H₂SO₄; SB: Sugarcane Bagasse; *m*SB–SA: Sugarcane Bagasse modified with H₂SO₄; CC: Corn Cob; SPSP: Strychnospotatorum seed powder; *m*SB–CA: Sugarcane bagasse modified with Citric Acid; LS: Shells of lentil; WS: Shells of wheat; RS: Shells of rice; CSAC: Coconut Shell Activated Carbon; CCAC: Corncob Activated Carbon; EC: Biochar derived from water hyacinth; Fe₂O₃–EC: Magnetic Biochar derived from water hyacinth; BOP: Biochar derived from Orange peels; GNSCP: Ground Nut Seed Cake Powder; SSCP: Sesame Seed Cake Powder; CCP: Coconut Cake Powder.

Although the adsorption capacities of both BP and *m*BP–SA are generally comparable to those reported for other BP-derived biosorbents, H₂SO₄ modification produced a marked improvement in adsorption performance. Specifically, the maximum adsorption capacities increased by approximately 64% for Cu²⁺ and 82% for Mn²⁺ following H₂SO₄ treatment. Considering that the modification involves a simple and low-cost procedure using readily available reagents and does not require sophisticated equipment, the observed enhancement in adsorption efficiency justifies the additional processing step. These findings demonstrate that H₂SO₄ modification represents a practical strategy for

improving the performance of BP biosorbents while maintaining their economic and environmental advantages.

3.5. Greenness Assessment

In recent years, increasing attention has been directed toward the development of sustainable and environmentally friendly approaches for wastewater treatment, particularly for the removal of hazardous heavy metal ions from contaminated aqueous systems. Consequently, evaluating the environmental impact and greenness of proposed treatment methodologies has become an essential aspect of modern environmental chemistry. Greenness assessment tools provide an efficient contemporary approach for determining the sustainability, safety, energy efficiency, and environmental compatibility of proposed analytical and remediation procedures through the evaluation of reagent toxicity, waste generation, energy consumption, and operational simplicity [81,82]. In the present study, the proposed adsorption procedure based on banana peel (BP) and chemically modified banana peel (mBP-SA) represents an eco-friendly and low-cost alternative for the removal of Mn^{2+} and Cu^{2+} ions due to the utilization of renewable agricultural biomass, aqueous media, simple operational conditions, and minimal chemical consumption. Therefore, to demonstrate its environmental sustainability and practical applicability for wastewater remediation, the greenness profile of the developed adsorption system was evaluated using different recognized green assessment metrics including the Analytical Eco-Scale Assessment (ESA) [52], the Green Analytical Procedure Index (GAPI) [53] and the Analytical GREENness metric (AGREE) [54]. The biosorbent represents a sustainable approach through the valorization of agricultural waste; however, its operational sustainability through repeated adsorption-desorption cycles remain to be established.

3.5.1. Analytical Eco-Scale Assessment (ESA)

In the Analytical Eco-Scale Assessment (ESA) system, the ideal green procedure is assigned a score of 100, whereas any deviation from this ideal procedure is represented by penalty points related to factors such as reagent hazards, energy consumption, waste generation, and occupational risks. These penalty points are subsequently subtracted from the perfect score of 100 to obtain the final Eco-Scale score of the proposed method. The greenness of the proposed adsorption procedure was evaluated using the Analytical Eco-Scale Assessment (ESA) approach, in which penalty points are assigned according to several determinants, including the type and quantity of used chemicals, energy consumption by the utilized instruments, waste generation and its treatment, instrumentation requirements, and occupational hazards associated with the analytical procedure [52]. The ESA does not rely on graphical representation; instead, it is evaluated using a numerical scoring system with a maximum value of 100. If the acquired score occurred in the range starting from 75 up to 100, it indicates excellent green performance of the proposed method, while scores between 50 and 74 reflect acceptable green performance. In contrast, scores below 50 indicate inadequate green performance. According to data illustrated in Table 6, the calculated ESA score was 75, indicating that the proposed method can be classified as an excellent green analytical procedure. This favorable environmental profile is mainly attributed to the utilization of renewable banana peel biomass, aqueous media, simple instrumentation, moderate operating temperature (70 °C), and relatively low chemical and energy consumption.

Table 6. Calculated PPs and the resulting ESA score for the proposed adsorption procedure utilized BP and mBP-SA for the removal of Mn^{2+} and Cu^{2+} ions.

Item	Calculated Penalty Points (PPs)
Chemicals	
Banana peel ((BP/mBP-SA)	0
Water	0
Sulfuric acid (H_2SO_4) (modification step)	4
Metal ion solutions (Cu^{2+} , Mn^{2+})	6
Sodium hydroxide (NaOH) (pH adjustment)	2
Instrument energy	
FTIR, SEM, shaker, balance, drying oven, and pH meter	2
Moderate heating at 70 °C with mechanical shaking	2
Occupational hazard	
Acid handling	2
Heavy metal solutions	2
Waste	
Metal-containing aqueous waste	4
Biomass solid waste	1
Total	Σ25
ESA score	75

3.5.2. Green Analytical Procedure Index (GAPI)

The Green Analytical Procedure Index (GAPI) is an assessment tool used to evaluate the environmental impact of a proposed method throughout all stages of the procedure, from sample collection to final analysis. The outcomes of this assessment tool are represented using a pictographic symbol composed of five pentagrams divided into 15 sections, each corresponding to a specific aspect of the process, including sample preparation, the quantity and toxicity of chemicals used, and the characteristics and energy requirements of the instrumentation employed. The sections are color-coded as green, yellow, and red to indicate low, moderate, and high environmental impact, respectively [53]. Greenness assessment of the proposed potentiometric method using GAPI is depicted in Figure 10A. The obtained GAPI profile exhibited predominantly yellow and green with limited red regions, indicating acceptable environmental compatibility of the developed adsorption system. The green areas (4 segments) were mainly attributed to the utilization of renewable BP biomass, simple adsorption methodology, absence of sample preservation requirements, and feasible waste treatment. Meanwhile, yellow zones (7 segments) were associated with off-line analysis, moderate reagent consumption, instrumentation requirements, and the use of H_2SO_4 and heavy metal ion solutions. The limited red zones (4 segments) were primarily related to macro-scale adsorption experiments and aqueous waste generation during the adsorption process.

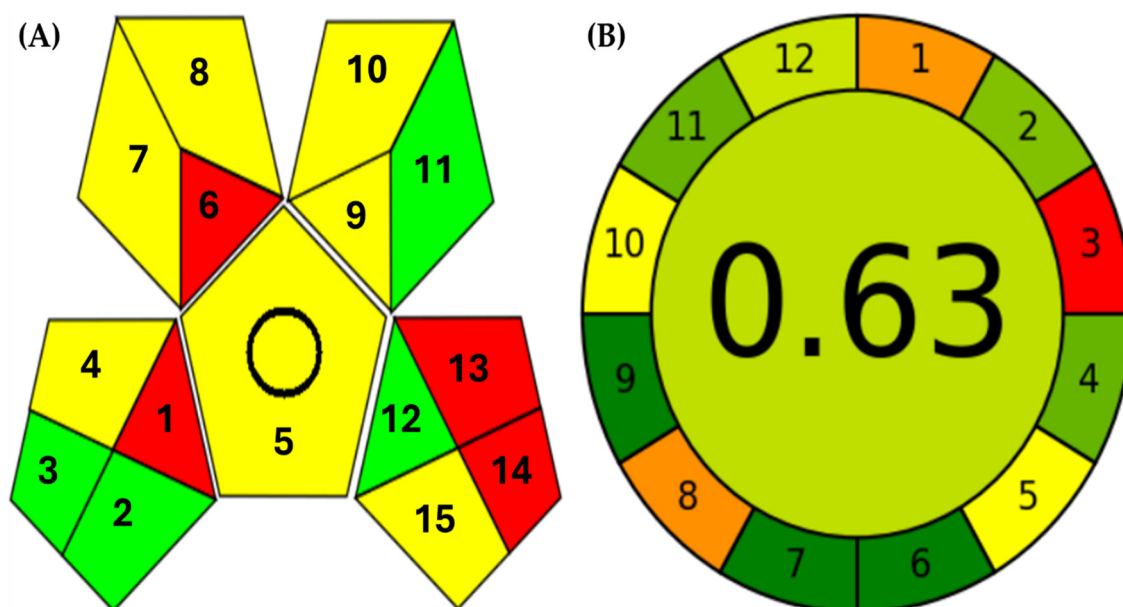


Figure 10. Pictogram of (A) GAPI and (B) AGREE greenness assessment methods for the proposed adsorption procedure.

3.5.3. Analytical GREENness Metric (AGREE)

The greenness of the proposed adsorption procedure was further evaluated using the Analytical GREENness metric (AGREE) approach based on the 12 principles of Green Analytical Chemistry. AGREE is a comprehensive metric system used to assess the environmental sustainability of analytical procedures by simultaneously considering all principles of green analytical chemistry. The final AGREE score is presented at the center of a 12-segmented pictogram, in which each segment is assigned a specific color and weight according to the greenness performance of the evaluated procedure. A final score approaching 1, accompanied by a darker green color in the pictogram center, indicates that the proposed procedure is more environmentally friendly and sustainable [54]. The calculated AGREE score was approximately 0.61, indicating good green performance of the developed adsorption system (Figure 10B). The favorable score was mainly attributed to the utilization of renewable banana peel biomass, aqueous media, low waste generation, and moderate energy consumption. Nevertheless, slight reductions in the AGREE score were associated with the off-line batch adsorption procedure, manual operation, and the use of H_2SO_4 acid and heavy metal ion solutions during the adsorption process.

The greenness assessment outcomes obtained using the three complementary metrics; ESA, GAPI, and AGREE, collectively demonstrate that the proposed adsorption procedures employing either BP or mBP-SA represent environmentally friendly and sustainable approaches for the removal of Mn^{2+} and Cu^{2+} ions from aqueous media. Although each assessment tool provides valuable insight into the environmental performance of the proposed procedures, each also possesses inherent limitations. ESA primarily emphasizes reagent hazards, energy consumption, and waste generation without comprehensively evaluating the entire analytical workflow. GAPI provides a holistic qualitative assessment of all analytical steps; however, its color-based pictogram may not adequately distinguish subtle quantitative differences between closely related methods. AGREE integrates the twelve principles of Green Analytical Chemistry into a single numerical score, although the overall score may be influenced by the relative weighting assigned to individual criteria. Therefore, the combined application of ESA, GAPI, and AGREE provides a more balanced, comprehensive, and reliable evaluation of the environmental sustainability of the proposed adsorption procedures than any individual metric alone.

4. Conclusions

In the present work, banana peels, an inexpensive agricultural waste material, either in pristine form (BP) or sulfuric acid-modified (mBP-SA), were investigated as biosorbents toward Mn^{2+} and Cu^{2+} uptake from aqueous solutions. Surface morphology characterization was performed, as well as key operational parameters, like the studied system pH or that related to the adsorbent (its exposure time and dosage) and the adsorbate initial concentration, were investigated. The proposed chemical modification improved the adsorption performance of BP toward Mn^{2+} and Cu^{2+} , likely through acid-induced structural and chemical changes that enhanced the accessibility of adsorption sites and promoted metal–surface interactions. The Langmuir and Freundlich isotherm models were investigated for the adsorption process using BP and mBP-SA, and the Langmuir model was proved to be the superior one suited for interpreting the observed adsorption performance. Observed outcomes demonstrated that pseudo 2nd order model provided an outstanding depiction. FTIR characterization showed that modified biosorbent (mBP-SA) contains active functional groups conducive its adsorption efficiency toward the removal of Mn^{2+} and Cu^{2+} . The improved adsorption performance is associated with acid-induced structural and chemical modification of the biomass matrix. The findings highlight that despite moderate adsorption capacities, the simplicity, low cost, and effectiveness of the modified banana peel make it a promising candidate for sustainable wastewater treatment, particularly in developing regions where access to advanced materials is limited. Although the present study demonstrates the environmental sustainability of the biosorbent through the utilization of abundant agricultural waste and a simple chemical modification strategy, regeneration and adsorption–desorption cycle experiments were beyond the scope of this work. Therefore, future investigations should evaluate the reusability and long-term stability of the modified biosorbent through multiple regeneration cycles to further establish its practical sustainability for wastewater treatment applications.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/su18147109/s1>, Table S1. Descriptive statistics and one-way ANOVA of the experimental replicates; Table S2. Two-way ANOVA results for Figure 6.

Author Contributions: Conceptualization, B.S.A.-F., A.H.N. and O.A.F.; methodology, S.K.A., A.Y.A., A.H.N., A.S.A.A. and A.F.; validation, S.K.A., A.F. and A.Y.A.; formal analysis, A.A.G. and A.H.A.; writing—original draft preparation, B.S.A.-F., A.H.N. and O.A.F.; writing—review and editing, A.H.N., O.A.F., A.S.A.A., A.A.G. and A.H.A. All authors have read and agreed to the published version of the manuscript.

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