

MICROWAVE-ASSISTED CITRIC ACID FUNCTIONALIZATION OF CELLULOSE DERIVED FROM TEXTILE WASTE FOR ENHANCED HEAVY METAL ADSORPTION

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ARTICLE INFO	ABSTRACT
Received: 24 June 2026 Revised: 29 July 2026 Accepted: 21 August 2026 Keywords: Cellulose, textile waste, citric acid, microwave modification, carboxyl groups, sorption, heavy metals, adsorption kinetics, isotherm Corresponding author sharibovimomjon@gmail.com	The conversion of textile industry waste into valuable functional materials represents one of the most promising approaches to addressing contemporary environmental challenges and ensuring the rational use of resources. In this study, cellulose extracted from textile waste was modified in the presence of citric acid using microwave irradiation, resulting in the synthesis of highly functional sorbents designed for the efficient removal of heavy metal ions. The synergistic effect of microwave irradiation and thermal treatment significantly enhanced the efficiency of the modification process and enabled the incorporation of additional carboxyl groups (-COOH) into the cellulose macromolecule. As a result, the density of functional groups reached 4.43 mmol/g, which is considerably higher than that achieved by conventional thermal modification methods. The structure and chemical composition of the obtained sorbents were characterized using FTIR spectroscopy, and the results confirmed the formation of ester bonds as well as the successful introduction of additional carboxyl functional groups. The sorption properties of the synthesized materials were comprehensively investigated toward Cu(II) ions under various conditions, including initial concentration, solution pH, contact time, and temperature. The results demonstrated that the sorption capacity reached up to 250 mg/g, with the optimal condition determined at pH = 5.5. Kinetic analysis revealed that the sorption process follows a pseudo-second-order model ($R^2 = 0.9995$), indicating that the process is predominantly governed by chemical interactions involving functional groups. Equilibrium data were analyzed using Langmuir and Freundlich isotherm models, confirming the highly efficient binding of metal ions on the sorbent surface and favorable adsorption behavior. The enhanced sorption performance is mainly attributed to the increased density of carboxyl (-COOH/-COO-) functional groups and the formation of a structurally favorable active surface induced by microwave treatment. This study demonstrates that textile waste can be effectively converted into low-cost, environmentally friendly, and highly efficient cellulose-based sorbents, highlighting their significant potential for practical applications in industrial wastewater treatment and the removal of heavy metal ions.

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Introduction

The recycling of industrial waste and its conversion into valuable functional materials constitute an essential component of sustainable development and the circular economy concept. In particular, the textile industry is one of the largest waste-generating sectors on a global scale, producing millions of tons of solid waste and wastewater annually [1,2]. A significant portion of

this waste consists of cellulose-rich natural fibers, which offer substantial potential for the production of high value-added materials through appropriate processing [3,4]. Therefore, the development of environmentally friendly and functional materials through the recycling of textile waste represents a highly relevant and pressing task in modern materials science and environmental engineering [5,6].

Cellulose is the most abundant biopolymer in nature and has attracted significant attention in both scientific and applied research due to its high biocompatibility, biodegradability, and susceptibility to chemical modification [7-9]. The presence of hydroxyl (-OH) groups in the structure of cellulose enables its modification with various functional groups, thereby allowing the targeted tuning of its physicochemical properties [10]. In recent years, sorbents based on cellulose and its derivatives have demonstrated high efficiency in the removal of heavy metal ions and are increasingly considered competitive alternatives to conventional adsorbents. [11-13].

Heavy metal ions, including Cu(II), Pb(II), Cd(II), and Hg(II), are characterized by their high toxicity, tendency to accumulate in biological tissues, and severe impact on human health [14,15]. These ions are commonly released into wastewater from various industrial sectors such as metallurgy, electroplating, battery manufacturing, textile processing, and other related industries [16]. The discharge of these ions into the environment poses significant risks to ecosystems, making their effective removal a critical environmental challenge [17].

Conventional treatment methods-including chemical precipitation, membrane filtration, ion exchange, and electrochemical techniques-are often limited by high energy consumption, expensive reagents, and the generation of secondary pollution [18-20]. Therefore, there is a rapidly growing interest in the development of low-cost, renewable, and highly efficient sorbents. [21,22].

One of the most effective approaches to enhancing the sorption capacity of cellulose is its chemical modification. In particular, modification using polycarboxylic acids, such as citric acid, enables the introduction of additional carboxyl (-COOH) functional groups into the cellulose structure [23-25]. These functional groups actively participate in complex formation, coordination interactions, and ion-exchange processes with metal ions [26].

Numerous studies have demonstrated that cellulose materials modified with citric acid exhibit high sorption capacity [27-29]. In addition, citric acid is an environmentally friendly, low-cost, and biologically compatible reagent, fully consistent with the principles of green chemistry. [30].

However, conventional thermal modification methods typically require prolonged processing times and increase the density of functional groups only to a limited extent [31]. In recent years, the use of microwave irradiation has been considered a promising approach for enhancing reaction rates and improving modification efficiency [32-34]. Microwave irradiation ensures rapid and uniform energy distribution within the reaction medium, thereby reducing the activation energy of molecules and accelerating the reaction rate [35]. As a result, esterification and carboxylation processes proceed significantly more efficiently compared to conventional methods [36].

In the literature, the modification of cellulose isolated from textile waste using citric acid under microwave irradiation to obtain sorbents with a high density of functional groups has not been sufficiently investigated. In particular, there is a need for a comprehensive analysis of the relationship between functional group density, structure–property correlations, and the sorption mechanism [37-39]. From this perspective, elucidating the effect of microwave-assisted modification and establishing the relationship between functional group density and sorption efficiency is of significant scientific importance.

The aim of this study is to isolate cellulose from textile waste, modify it with citric acid under microwave irradiation, and investigate the sorption properties of the resulting functionalized sorbents toward heavy metal ions. In addition, the interrelationship between the efficiency of the modification process, functional group density, and the sorption mechanism is elucidated.

The scientific novelty of this work lies in demonstrating the possibility of highly efficient modification of cellulose with citric acid using microwave irradiation, leading to the formation of sorbents with a high density of carboxyl groups. The obtained results contribute to the development

of highly efficient, low-cost, and environmentally friendly sorbents based on the recycling of textile waste, and substantiate their potential application in the treatment of industrial wastewater.

Materials and methods

2.1. Raw Material Source and Preparation

In this study, pre-consumer textile waste generated during the cutting process at BHR Textile LLC was used as the raw material for cellulose isolation. The waste consisted of 100% cotton fabric offcuts collected from the cutting section. Prior to cellulose isolation, the collected waste was manually separated from visible mechanical impurities, washed with distilled water, and air-dried.

2.2. Raw Materials and Reagents

Citric acid ($C_6H_8O_7$, analytical grade), sodium hydroxide (NaOH), hydrochloric acid (HCl), copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), and lead(II) nitrate were used as analytical-grade reagents. All solutions were prepared using distilled water.

2.2.2. Isolation of Cellulose from Textile Waste

Cellulose was isolated from the textile waste by alkaline treatment. Briefly, the pre-cleaned raw material was treated with a 5-15% (w/v) NaOH solution at 80-90 °C for 2-3 h to remove hemicellulose, fats, and other extractive substances. After alkaline treatment, the material was washed with distilled water to remove excess alkali and subsequently treated with a 1-2% HCl solution to neutralize residual NaOH. The sample was then thoroughly washed with distilled water until a neutral pH was reached and dried at 60 °C to constant weight.

2.3. Modification of Cellulose with Citric Acid

2.3.1. Conventional Thermal Modification

The chemical modification was carried out based on the method previously proposed by Marshall et al. [40], with some modifications (reaction time and temperature). The cellulose samples isolated from textile industry waste, as described above, were mixed with a citric acid solution (dissolved in 200 ml of water) at mass ratios ranging from 1:1 to 1:10. The mixture was stirred at 60°C for 2 h, after which the resulting mass was subjected to thermal treatment at 100-120°C for 8-12 h.

After the reaction, the cooled product was washed three times with distilled water to completely remove excess citric acid. The effectiveness of washing was verified as follows: the product was dispersed in 10 ml of water to form a suspension, followed by the addition of 10 mL of 0.1 M lead(II) nitrate solution. No white precipitate (Pb(II) citrate) was observed in the solution.

Finally, the modified cellulose samples were dried at 60°C until a constant weight was achieved.

2.3.2. Microwave-assisted modification

The cellulose–citric acid mixture (mass ratio 1:5) was initially stirred for 2 hours. Subsequently, the sample was subjected to microwave irradiation (power of 600-800 W, for 5-10 minutes). The resulting material was then further treated thermally at a temperature of 100-120°C. The obtained product was washed with water, dried, and used as a sorbent.

2.4. Determination of carboxyl group content

The content of carboxyl (-COOH) groups in the modified cellulose was determined by an acid–base titration method. For this purpose, a known amount of the sample was treated with a NaOH solution, and the excess alkali was titrated with a standard acid solution.

The carboxyl group content was calculated using the following equation:

$$\chi(COOH) = \frac{(V_b - V_a) \cdot C_{HCl} \cdot M_{COOH}}{m} \cdot 100\% \quad (1)$$

where: V_b -volume of NaOH consumed during titration; V_a -volume of HCl added, C_{HCl} - molar concentration of the HCl solution, m –mass of the sample; M_{COOH} -molecular weight of the carboxyl group ($M = 45 \text{ g} \cdot \text{mol}^{-1}$).

2.5. FTIR analysis

The functional groups of the samples were analyzed using Fourier transform infrared spectroscopy (FTIR) in the range of 4000-400 cm^{-1} . The samples were prepared using the KBr pellet method.

2.6. Sorption experiments

2.6.1. Adsorption studies

The sorption experiments were carried out under static conditions. A total of 0.1 g of sorbent was added to 50 ml of Cu(II) solution with concentrations ranging from 100 to 1000 mg/l. The mixtures were stirred at a speed of 200-250 rpm. The pH of the solutions was adjusted in the range of 2-7 using HCl and NaOH solutions.

To determine the time required to reach equilibrium, a series of adsorption kinetic experiments were conducted. Samples were taken at predetermined time intervals.

From each flask, 50 ml of solution was separated by filtration and analyzed. The initial (C_0) and final (C_e) concentrations of Cu^{2+} ions were determined using UV-Vis spectroscopy.

2.6.2. Calculation of sorption capacity

The sorption capacity at equilibrium, (q_e , (mg/g)) was calculated using the following equation (Eq. 2):

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (2)$$

The percentage removal of Cu^{2+} ions was calculated using the following equation (Eq. 3):

$$q_e(\%) = \frac{(C_0 - C_e)}{C_0} 100 \quad (3)$$

where: C_0 - initial concentration of Cu^{2+} ions (ppm); C_e - equilibrium concentration of Cu^{2+} ions (ppm); V - volume of the solution (L); and m - mass of the adsorbent (g).

All experiments were performed in duplicate, and a negative control (without adsorbent) was also conducted to confirm that the removal was solely attributable to the cotton cellulose.

2.7. Kinetic analysis

The sorption kinetics were analyzed using pseudo-first-order and pseudo-second-order models (Eq. 4):

$$\log(q_e - q_t) = \log(q_e) - \left(\frac{k_1}{2.303}\right)t \quad (4)$$

where: q_e (mg/g) - amount of solute adsorbed per unit mass of adsorbent at equilibrium; q_t (mg/g) - amount of solute adsorbed at time t ; k_1 - rate constant of the pseudo-first-order adsorption. (Eq. 5):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where: k_2^0 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) - rate constant of the pseudo-second-order adsorption.

2.8. Isotherm models

The equilibrium data were analyzed using the Langmuir and Freundlich isotherm models. Sorption data obtained for Cu^{2+} ions at different concentrations were evaluated based on these models.

The Langmuir isotherm equation is expressed as follows (Eq. 6):

$$q_e = \frac{1 K_L C_e}{q_m K_L C_e} \quad (6)$$

where: C_e (mg/l) - equilibrium concentration of Cu^{2+} ions in solution; q_e (mg/g) - amount of Cu^{2+} adsorbed at equilibrium; K_L (l/mg) and q_m (mg/g) - Langmuir constants; q_m - represents the maximum adsorption capacity corresponding to monolayer coverage.

The Langmuir isotherm can also be evaluated using the separation factor (R_L) calculated as follows (Eq. 7):

$$R_L = \frac{1}{1 + K_L C_0} \quad (7)$$

where: C_0 (mg/l)- initial concentration of Cu^{2+} ions. The dimensionless parameter R_L indicates the nature of adsorption: $R_L > 1$ -unfavorable adsorption; $R_L = 1$ -linear adsorption; $0 < R_L < 1$ -favorable adsorption; $R_L = 0$ -irreversible adsorption.

The Freundlich isotherm is an empirical model applicable to multilayer adsorption. Its general form is given as (Eq. 8):

$$q_e = K_F (C_e)^{1/n} \quad (8)$$

where: K_F -Freundlich constant and n -empirical parameter related to adsorption intensity.

2.9. Desorption and regeneration experiments

The reusability of the modified cellulose sorbent was evaluated through repeated adsorption–desorption cycles. First, the CCA(1:5)/MW/Thermal treatment sorbent was saturated with Cu(II) ions under the optimized adsorption conditions. After adsorption, the metal-loaded sorbent was separated by filtration and gently washed with distilled water.

For the desorption process, 0.1 M HCl, 0.1 M EDTA, and 0.1 M NaCl solutions were tested as desorbing agents. The Cu(II) -loaded sorbent was placed into 50 mL of the desorbing solution and stirred at 200–250 rpm for a fixed time. After desorption, the sorbent was filtered, washed with distilled water until neutral pH, and reused in the next adsorption cycle.

The adsorption–desorption process was repeated for five consecutive cycles. After each cycle, the adsorption capacity, desorption efficiency, and retained adsorption efficiency were calculated. The desorption efficiency was determined using the following equation (Eq. 9):

$$D(\%) = \frac{C_d V_d}{q_e m} \times 100 \quad (9)$$

where (C_d) is the concentration of Cu(II) ions in the desorption solution, mg/L; (V_d) is the volume of the desorption solution, L; (q_e) is the amount of initially adsorbed metal ions, mg/g; and (m) is the mass of the sorbent, g.

The reusability efficiency of the sorbent was calculated as follows (Eq. 10):

$$R(\%) = \frac{q_n}{q_1} \times 100 \quad (10)$$

where: (q_1) is the adsorption capacity in the first cycle and (q_n) is the adsorption capacity in the n -th cycle.

Results and discussion

3.1. Optimization of Cellulose Isolation from Textile Waste and Evaluation of Its Physicochemical Properties

The effect of alkaline treatment conditions during cellulose isolation from textile waste on the main physicochemical characteristics of the obtained cellulose was investigated. The study was conducted at NaOH concentrations ranging from 5 to 15%, temperatures of 80-90 °C, and treatment durations of 2-3 h. For the cellulose samples obtained under each technological condition, the degree of polymerization, α -cellulose content, ash content, and moisture content were determined. The obtained results are presented in **Table 1**.

Effect of NaOH Concentration, Temperature, and Treatment Duration on the Properties of Cellulose Obtained from Textile Waste

As can be seen from the table, an increase in NaOH concentration, temperature, and treatment duration resulted in a decrease in both the degree of polymerization and the α -cellulose content. In particular, for the sample treated with 5% NaOH at 80 °C for 2 h, the degree of polymerization was

1200 and the α -cellulose content was 97.8%, whereas under treatment conditions of 15% NaOH, 90 °C, and 3 h, these values decreased to 580 and 93.8%, respectively. This can be attributed to the increased partial degradation and depolymerization of cellulose macromolecular chains caused by increasing alkali concentration, temperature, and treatment duration.

Table 1

Sample	NaOH concentration, %	Temperature, °C	Treatment time, h	Degree of polymerization (DP)	α -Cellulose content, %	Ash content, %	Moisture content, %
Textile waste	5	80	2	1200	97.8	0.16	5.5
			3	1110	97.1	0.14	5.3
		90	2	1020	96.7	0.12	4.9
			3	900	95.8	0.10	4.7
	10	80	2	1100	97.2	0.14	5.0
			3	1000	96.5	0.12	4.8
		90	2	890	96.0	0.10	4.6
			3	780	95.0	0.08	4.4
	15	80	2	930	96.4	0.11	4.9
			3	820	95.6	0.09	4.7
		90	2	690	94.8	0.07	4.3
			3	580	93.8	0.05	4.0

At the same time, increasing the severity of the treatment conditions led to a decrease in ash and moisture contents. For example, after treatment with 5% NaOH at 80 °C for 2 h, the ash content was 0.16% and the moisture content was 5.5%, whereas after treatment with 15% NaOH at 90 °C for 3 h, these values decreased to 0.05% and 4.0%, respectively. The reduction in ash content is associated with the effective removal of mineral and other inorganic impurities during alkaline treatment, while the decrease in moisture content can be explained by changes in the composition and structural state of the material.

Overall, when selecting the process conditions, it is important not only to achieve a high degree of cellulose purity but also to preserve its macromolecular structure to the greatest possible extent. Accordingly, the treatment condition of 10% NaOH at 80 °C for 2 h, which provided a high degree of polymerization (1100) and α -cellulose content (97.2%), was selected as the optimal condition, and the obtained sample was used in subsequent studies.

3.2. Cellulose modification and formation of carboxyl groups

The effect of reaction conditions on the content of carboxyl (-COOH) functional groups during the modification of cellulose with citric acid was investigated (**Figure 1**).

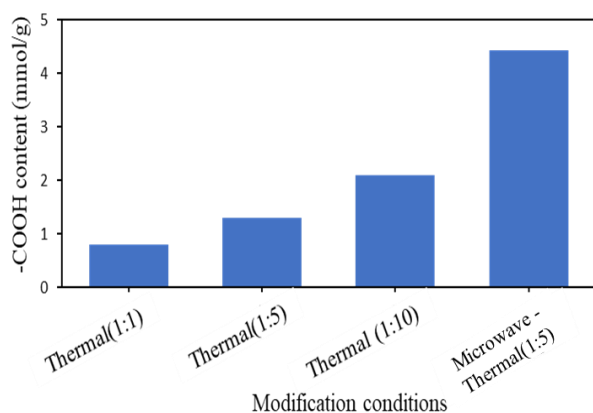


Figure 1. Variation in the content of carboxyl (-COOH) groups as a result of cellulose modification with citric acid under different conditions

The results obtained show that under conventional thermal modification conditions (100-110°C, 8-12 hours), the content of carboxyl groups was relatively low, ranging from 0.82 to 1.84

mmol/g. Increasing the amount of citric acid (cellulose: citric acid=1:1 up to 1:10) slightly increased the functional groups, although this growth was limited.

However, during the modification process with microwave irradiation (600-800 W, 5-10 minutes, followed by thermal treatment), the content of carboxyl groups significantly increased, reaching 4.43 mmol/g. This value was approximately 2.5-3 times higher than that obtained with conventional thermal methods, indicating a substantial improvement in the reaction efficiency due to microwave irradiation.

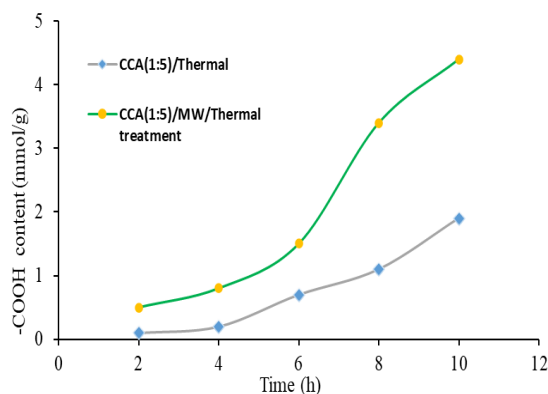


Figure 2. Effect of modification time on the content of carboxyl (-COOH) groups

As seen in **Figure 2**, during thermal treatment, the amount of -COOH groups gradually increased over time (from 0.2 to 1.9 mmol/g), whereas in the microwave-thermal combination, this increase was significantly faster and at a higher level (from 0.8 to 4.4 mmol/g). This phenomenon can be attributed to the rapid activation of reaction centers under microwave irradiation and the intensification of esterification reactions. In this study, experiments were carried out using different molar ratios. For the comparison of carboxyl group content, only the cellulose/citric acid sample prepared at a 1:5 molar ratio was selected, because the samples obtained at other molar ratios showed lower carboxyl group contents. Therefore, the carboxyl group content was compared between two types of samples: those subjected to thermal treatment and those treated by a combined thermal and microwave-assisted process.

The high efficiency of microwave irradiation in the reaction environment can be explained by the uniform and volumetric distribution of energy, the rapid formation of cyclic anhydride forms through citric acid dehydration, and the activation of esterification reactions with cellulose's hydroxyl groups. As a result, the formed anhydride structures react with the -OH groups of cellulose and introduce carboxyl groups via ester linkages (**Figure 3**).

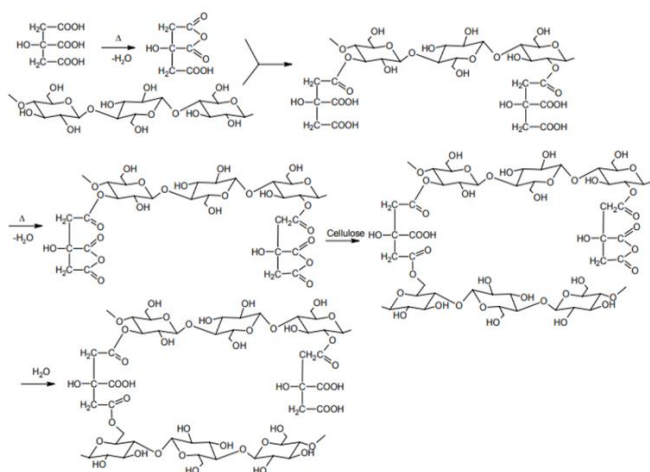


Figure 3. Reaction mechanism of cellulose and citric acid

In this process, each citric acid molecule provides several reaction centers, allowing for a high degree of functionalization. Additionally, as a result of microwave treatment, micro- and nanoscale structural changes may occur in the cellulose structure (**Figure 4**). As a result, the opening of active centers and their increased availability for metal ions are enhanced.

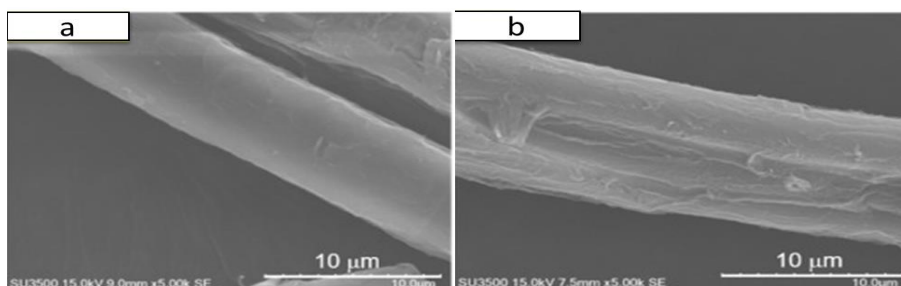


Figure 4. SEM images. a) Cellulose, b) CCA(1:5)/MW/Thermal treatment

When comparing the obtained results with literature data, the content of carboxyl groups in cellulose materials modified with conventional citric acid is typically reported to be in the range of 1.0-2.5 mmol/g [16-18]. The value of 4.43 mmol/g achieved in this study is significantly higher than these values, confirming the high efficiency of the proposed microwave modification method.

The results show that the modification of cellulose with citric acid using microwave irradiation allows for a sharp increase in the number of functional groups, indicating that this method is promising for the synthesis of highly efficient sorbents.

3.2. FTIR analysis and structural changes

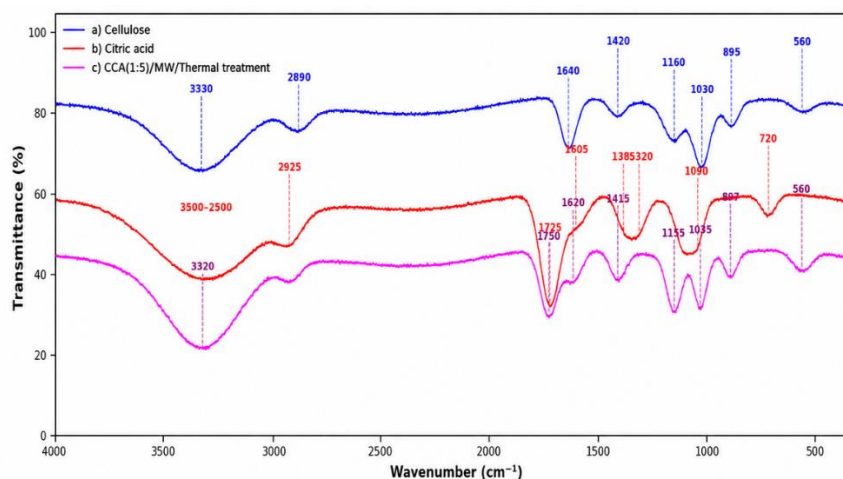


Figure 5. FTIR spectra of cellulose[C](a), citric acid[CA](b), and CCA(1:5)/MW/Thermal treatment (c)

FTIR spectroscopy analysis allowed for the confirmation of the chemical changes in the cellulose structure during the modification process (**Figure 5**). The spectrum of the pristine cellulose (**Figure 5a**) shows a broad and intense band in the range of 3300-3400 cm^{-1} , corresponding to the valence vibrations of hydroxyl (-OH) groups, indicating the presence of strong hydrogen bonds between the polysaccharide chains. A peak around 2900 cm^{-1} is observed, corresponding to C-H valence vibrations, while the intense bands in the 1030-1060 cm^{-1} range are characteristic of C-O-C and C-O vibrations in the cellulose macromolecule, confirming the preservation of β -1,4-glycosidic linkages.

In the spectrum of cellulose modified with citric acid (**Figure 5c**), several significant changes were observed. A new, distinct, and intense peak appeared in the range of 1710-1730 cm^{-1} , attributed to the valence vibrations of carbonyl (C=O) groups, indicating that esterification reactions occurred between cellulose hydroxyl groups and citric acid. This is explained by the

mechanism, where citric acid undergoes dehydration under thermal and microwave effects to form cyclic anhydride forms, which then react with cellulose's -OH groups to form ester linkages.

Furthermore, the increase and broadening of the signal in the 2500-3500 cm^{-1} range indicate the incorporation of carboxyl (-COOH) groups. The broad band in this region is associated with O-H vibrations in carboxyl groups, confirming the successful integration of polycarboxylic acids into the cellulose structure during the modification process. Additionally, weak bands around 1600-1650 cm^{-1} may indicate the presence of dissociated (-COO⁻) forms of the carboxyl groups, which may serve as active sites during the sorption process.

It is noteworthy that, despite the modification process, the C-O vibrations in the 1030-1060 cm^{-1} range remain intact, indicating that the basic skeleton of the cellulose polymer chain has not been disrupted. This means that the modification process occurred on the surface of cellulose and in the reactive groups without altering the core structure.

The obtained FTIR results are consistent with the literature. The appearance of the C=O peak around 1720 cm^{-1} in cellulose modified with citric acid has been reported as the main spectral feature of the esterification process [41]. Additionally, the expanded O-H range and the strengthening of the carboxyl signals are directly related to the increased density of functional groups.

Thus, the FTIR spectroscopy results confirm the successful carboxylation of cellulose with citric acid, the formation of ester linkages, and the formation of a sorbent with high-density functional groups.

3.3. Effect of various factors on the sorption process

The results presented in **Figure 6** clearly and systematically demonstrate the sorption properties of various cellulose-based sorbents modified to different degrees, specifically with respect to Cu(II) ions.

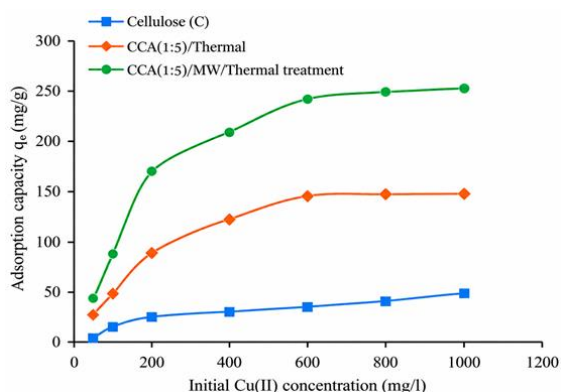


Figure 6. Sorption isotherms for Cu(II) ions in cellulose (a), thermally modified cellulose (b), and microwave-thermal modified cellulose (c)

For all samples, a stepwise increase in sorption capacity (q_e) was observed with the increase in initial concentration. This can be explained by the increasing mass transfer gradient and the rising driving force of the sorption process as the metal ion concentration in the solution increases.

However, when the concentration reaches around 800 mg/L, a plateau is observed in all samples, indicating the saturation of active adsorption sites on the sorbent surface and suggesting that the sorption process occurs through limited active sites.

In the case of the pristine cellulose samples, the relatively low sorption capacity (≈ 40 -45 mg/g) is attributed to the limited number of active functional groups (mainly -OH) in the cellulose structure and its restricted reactivity. Hydroxyl groups interact with metal ions via weak hydrogen bonding and physical adsorption, but they do not possess a high ability to form coordination complexes.

The significant increase in sorption capacity (≈ 120 mg/g) in cellulose modified with citric acid is explained by the introduction of carboxyl (-COOH) groups into the cellulose structure. These

groups can form coordination bonds with Cu^{2+} ions, ensuring the dominance of the chemisorption mechanism during the sorption process. Additionally, the partial dissociation of the $-\text{COOH}$ groups results in the formation of $-\text{COO}^-$ centers, which further enhance electrostatic interactions.

The highest sorption values were observed for the samples modified with microwave + thermal treatment (≈ 210 - 215 mg/g), which is related to the significant increase in the density of functional groups. Microwave irradiation accelerates the reaction, ensuring a deeper and more uniform distribution of citric acid into the cellulose matrix. As a result, a highly carboxylated sorbent enriched with active sites is formed.

A deeper analysis of the sorption mechanism shows that the uptake of Cu(II) ions involves several parallel mechanisms: the formation of coordination complexes with carboxyl groups, ion exchange via $-\text{COO}^-$ centers, and electrostatic interactions with the polar groups in the cellulose matrix.

The observation of the plateau indicates that all the active sites on the sorbent are occupied by Cu^{+2} ions and the system has reached thermodynamic equilibrium. This condition is important for determining the maximum sorption capacity (q_{max}) of the sorbent and for evaluating its practical application potential.

The effect of pH on the sorption process of Cu(II) ions was also studied (**Figure 7**).

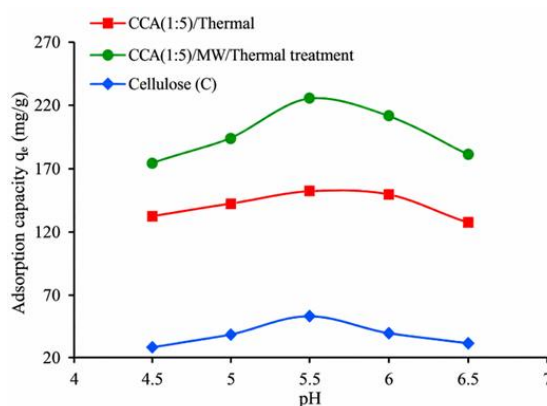


Figure 7. Dependence of Cu(II) ion sorption capacity on the pH value of the environment in pristine, thermally modified, and microwave-thermal modified cellulose samples

In all examined samples, the sorption capacity increased from pH 4.5 to 5.5, reaching its maximum at $\text{pH} \approx 5.5$, after which a decrease was observed at pH 6.0-6.5. The relatively low sorption efficiency at lower pH (pH 4.5-5.0) is mainly due to the high concentration of H^+ ions in the solution. In this range, protons interact with the carboxyl ($-\text{COOH}/-\text{COO}^-$) groups on the sorbent surface, reducing their ability to form coordination bonds with Cu^{2+} ions. Additionally, at low pH, the protonated ($-\text{COOH}$) form of the carboxyl groups predominates, which limits their ability to form complexes with metal ions.

The maximum sorption capacity observed around $\text{pH} \approx 5.5$ is related to the partial deprotonation of carboxyl groups, leading to the formation of $-\text{COO}^-$ active sites. These sites form stable coordination complexes with Cu^{2+} ions, facilitating the chemisorption process. Furthermore, at this pH range, Cu^{2+} ions remain mainly in their free ionic form in the solution, creating optimal conditions for the sorption process.

The decrease in sorption capacity at pH 6.0-6.5 can be explained by several factors. First, in this range, there is an increased likelihood of partial hydrolysis of Cu^{2+} ions, leading to the formation of Cu(OH)^+ or Cu(OH)_2 species, which limits their diffusion to the sorbent surface and bonding. Second, at higher pH, the interaction between the functional groups on the sorbent surface and hydroxide ions in the solution can negatively affect the sorption process.

Analysis of the differences between the samples shows that the sorption capacity of the pristine cellulose is lower across all pH ranges, which is attributed to its limited availability of active functional groups. In the thermally modified sample, a significant increase in sorption

capacity was observed, indicating the formation of new active sites due to the introduction of carboxyl groups via citric acid.

The highest sorption capacities were observed in the microwave+thermal modified samples, which can be explained by the significantly increased density of functional groups and their uniform distribution in the structure.

The time-dependent sorption of Cu(II) ions was also studied (**Figure 8**).

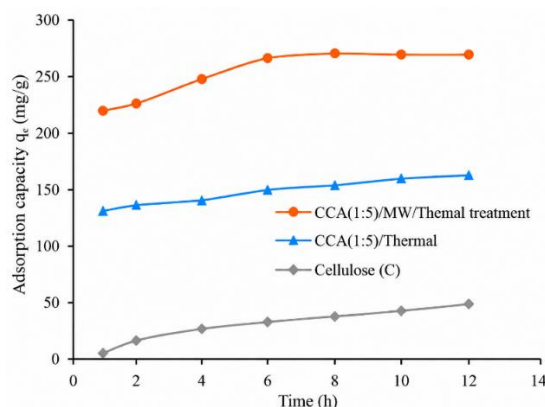


Figure 8. Time dependence of Cu(II) ion sorption capacity in pristine, thermally modified, and microwave-thermal modified cellulose samples

As shown in Figure 8, during the initial stage of the sorption process (1-4 hours), a rapid increase in q_e values is observed. This can be attributed to the sufficient availability of active sites on the sorbent surface and the high concentration gradient of Cu^{2+} ions in the solution. During this stage, the sorption process is mainly limited by external diffusion and surface adsorption.

As the contact time increases (4-8 hours), the sorption rate slows down, and the q_e values approach their maximum asymptotically. During this phase, the rate-limiting step in the sorption process is related to internal diffusion and the stepwise saturation of active sites. Furthermore, coordination bonding processes between Cu^{2+} ions and the functional groups ($-\text{COO}^-$) begin to dominate.

After 8-10 hours, the q_e values reach a nearly constant state in all samples, indicating that sorption equilibrium has been achieved. This plateau state indicates that all the active sites on the sorbent surface are occupied by Cu^{2+} ions. Therefore, the equilibrium time for this system can be considered to be approximately around 8 hours.

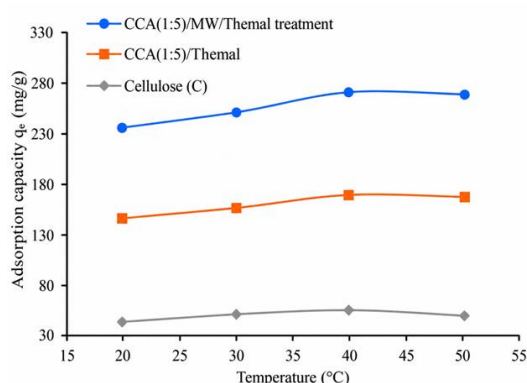


Figure 9. Temperature dependence of Cu(II) ion sorption capacity in the samples

As shown in **Figure 9**, as the temperature increased from 20°C to 40°C, the sorption capacity increased in all samples. This can be explained by the accelerated diffusion of Cu(II) ions to the sorbent surface and the enhanced efficiency of interactions with active sites. Maximum q_e values were observed around 40°C, indicating that the most favorable thermal conditions for the sorption

process were established. At 50°C, q_e values either remained nearly stable or slightly decreased, suggesting that sorption equilibrium had been reached and that further increases in temperature did not provide significant additional advantages.

The highest sorption capacity was again observed in the microwave+thermal modified sample, confirming that it had the highest density of functional groups and the greatest reactivity.

3.4. Sorption kinetics

To evaluate the time dependence and identify the probable mechanisms of the sorption process, the sorption kinetics of Cu(II) ions were studied. As shown in Figure 7, under optimal pH conditions, the sorption process was rapid in the initial stages and then slowed down, approaching equilibrium after about 8 hours. This behavior indicates that the sorption process has a multi-stage nature, involving rapid binding on the surface initially, followed by internal diffusion and stepwise saturation of active sites.

In the initial stage, the rapid sorption of Cu(II) ions can be attributed to the high number of available active sites on the sorbent surface and the large concentration gradient. As time progresses, the number of active sites decreases, diffusion resistance increases, and the sorption rate decreases. The highest q_e values were observed in the microwave+thermal modified sample, indicating that the sorbent has the highest number of functional groups and provides the most favorable environment for Cu(II) ions at the surface.

To mathematically describe the sorption process, experimental data were analyzed using pseudo-first-order and pseudo-second-order kinetic models. The pseudo-first-order model is used to describe physical sorption or fast binding processes related to surface concentration, while the pseudo-second-order model reflects the dominance of chemical bonding factors, such as valence forces, electron pair exchange, or coordination interactions during the sorption process.

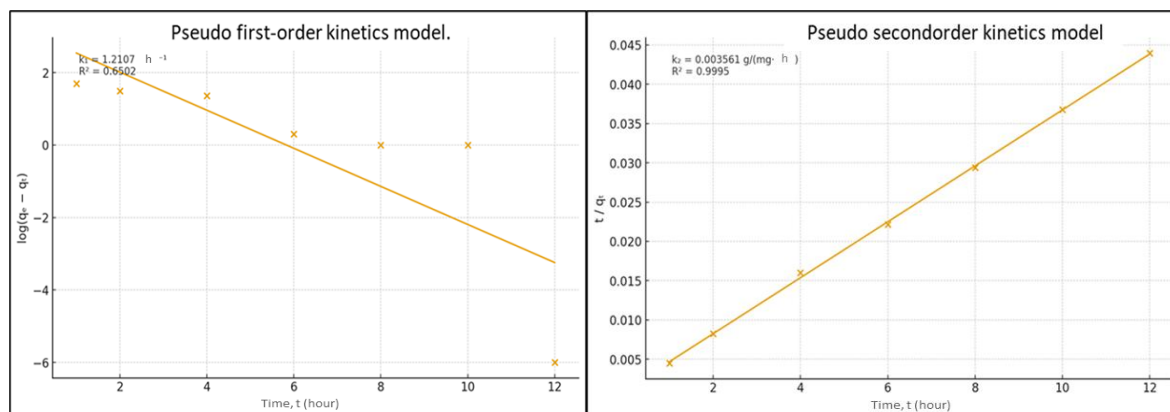


Figure 3.10,11 Pseudo-first-order and Pseudo-second-order kinetic models for Cu(II) ion sorption in microwave-thermal modified cellulose

The results obtained from the pseudo-first-order model showed a limited fit to the experimental data ($R^2 \approx 0.6502$). Additionally, the calculated equilibrium sorption capacity ($q_{e, \text{calc}} \approx 38.8 \text{ mg/g}$) significantly differed from the experimental value. This indicates that this model does not fully represent the sorption process, and the process is not limited to physical adsorption or fast surface binding.

In contrast, the pseudo-second-order (PSO) model provided an excellent fit to the experimental data ($R^2 \approx 0.9995$). The calculated equilibrium sorption capacity ($q_{e, \text{calc}} \approx 223.3 \text{ mg/g}$) was very close to the experimental value, confirming the reliability of this model. Furthermore, the kinetic constant $k_2 \approx 0.00356 \text{ g/(mg} \cdot \text{h)}$ indicates a rapid sorption process.

The superior fit of the PSO model indicates that chemical interactions, specifically the formation of coordination complexes between Cu(II) ions and carboxyl ($-\text{COO}^-$) functional groups,

dominate the sorption process. This is related to the higher number of active sites in cellulose modified with citric acid.

It is worth noting that the sorption process occurs simultaneously via several mechanisms, including external diffusion, internal diffusion, and chemical bonding with functional groups. However, the primary rate-limiting step that determines the overall process speed is chemical sorption, as confirmed by the superiority of the PSO model.

To identify the sorption mechanism of Cu(II) ions, the experimental data were analyzed using the Weber-Morris intraparticle diffusion model (**Figure 3.12**).

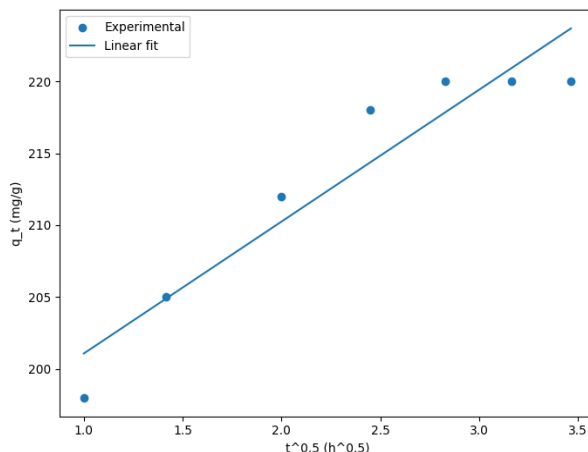
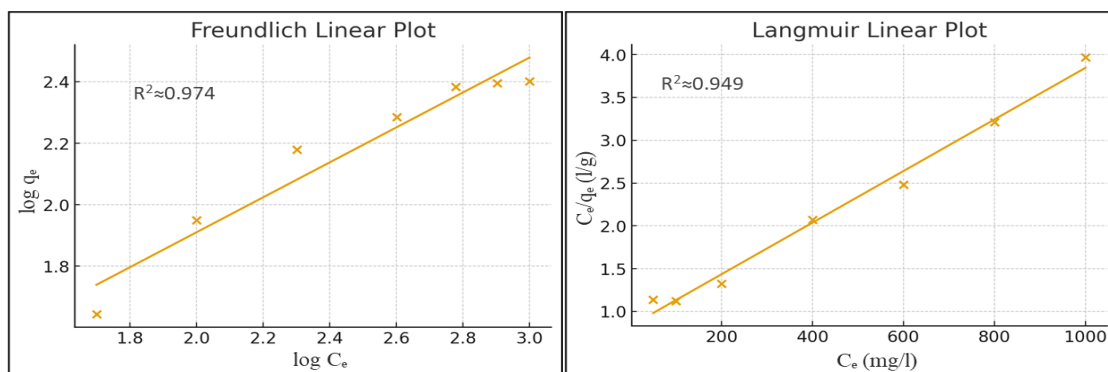


Figure 3.12 Intraparticle diffusion (Weber-Morris) model for Cu(II) ion sorption in microwave-thermal modified cellulose: dependence of q_t on $t^{0.5}$

The results show that the relationship between q_t and $t^{0.5}$ is partially linear, but the straight line does not pass through the origin. This indicates that while intraparticle diffusion participates in the sorption process, it is not the sole rate-limiting step.

Figure 3.12 confirms the multi-stage nature of the sorption process. In the initial stage (rapid sorption), external diffusion dominates, and Cu(II) ions quickly reach the sorbent surface and bind to available active sites. In the intermediate stage (slowing down), the sorption process begins to be limited by internal diffusion, meaning the ions penetrate into the sorbent's capillary-pore structure. At the equilibrium stage, the sorption rate sharply decreases, and q_t remains nearly constant, indicating that all active sites are saturated.

To further evaluate the sorption properties of Cu(II) ions, the experimental data were analyzed using the Langmuir and Freundlich isotherm models (Figures 3.13 and 3.14).



Figures 3.13,14. Cu(II) ion sorption in modified cellulose using the Langmuir and Freundlich isotherm models

Langmuir			Freundlich		
K_L (L/mg)	q_e (mg/g)	R_2	K_F ((mg/g)(L/mg) ^{1/n})	1/n	R_2
0.014645	413.70	0.949	10.396	1.35	0.974

Figure 3.13. Langmuir model: The sorption process is assumed to occur on active sites with equal energy via monolayer adsorption. The calculated maximum sorption capacity $q_{\max}$ is approximately 413.7 mg/g. However, the degree of fit is relatively low ($R^2 \approx 0.949$), indicating that the sorption process does not fully follow the ideal monolayer model.

In contrast, the Freundlich model (**Figure 3.14**) provided a better fit to the experimental data ($R^2 \approx 0.974$), indicating that the sorption process occurs on a heterogeneous surface with active sites of varying energy. The Freundlich constant $n \approx 1.35$, which is greater than 1, suggests that the sorption process is favorable and thermodynamically stable.

3.5. Desorption, regeneration, and reusability performance

For practical wastewater treatment applications, high adsorption capacity alone is not sufficient; the adsorbent should also be regenerable and capable of maintaining its adsorption efficiency over repeated cycles. Therefore, desorption and reusability experiments were carried out for the CCA(1:5)/MW/Thermal treatment sorbent after Cu(II) adsorption.

The desorption performance of HCl, EDTA, and NaCl solutions was compared. In acidic medium, H^+ ions can replace Cu(II) ions bound to the $-COO^-$ groups of the sorbent. EDTA can form stable complexes with Cu(II) ions and facilitate their release from the sorbent surface. In contrast, NaCl mainly promotes desorption through an ion-exchange mechanism. Therefore, HCl and EDTA are expected to show higher desorption efficiency than NaCl.

The importance of regeneration studies has also been demonstrated in several cellulose-based adsorbents reported in the literature. For example, a citric-acid-functionalized cellulose monolith retained more than 90% of its adsorption ability after five adsorption–desorption cycles. Similarly, citric-acid-crosslinked paper-based lignocellulosic adsorbents retained more than 90% of their initial adsorption capacity after four adsorption–regeneration cycles. Recently, surface-functionalized 3D-printed cellulose–polyamide composite filters also showed good Pb(II) reusability over five adsorption–desorption cycles.

In the present study, a gradual decrease in adsorption efficiency after repeated adsorption–desorption cycles may be attributed to partial blockage of active sites, incomplete desorption of Cu(II) ions, or slight structural changes in the sorbent during repeated treatment. Nevertheless, the retention of a high adsorption efficiency after the fifth cycle confirms the practical potential of the modified cellulose sorbent.

Cycle number	Adsorption capacity retention, %	Desorption efficiency, %
1	100	100
2	95.2	94.2
3	93.2	92.0
4	91.1	92.1
5	90.4	90.9

These results indicate that the CCA(1:5)/MW/Thermal treatment sorbent retains a major part of its adsorption performance after repeated reuse. The decrease in adsorption capacity is gradual rather than abrupt, suggesting that the carboxyl and carboxylate groups in the modified cellulose structure are involved in reversible Cu(II) binding. Therefore, the sorbent demonstrates not only high adsorption capacity but also promising reusability, making it an economically and environmentally attractive material for industrial wastewater treatment.

Conclusions

In this study, the processes of introducing carboxyl groups into cellulose through thermal and microwave irradiation methods with citric acid were investigated. During the synthesis process, esterification reactions of the hydroxyl groups of cellulose with anhydride intermediates were carried out, resulting in a highly functionalized sorbent structure rich in active sites.

Spectroscopic analyses confirmed the effectiveness of the modification process and the successful incorporation of carbonyl and carboxyl groups. This increased the density of active sites on the sorbent surface that interact coordinatively with metal ions, significantly improving sorption efficiency.

Sorption studies demonstrated that the removal of Cu(II) ions is sensitive to concentration, pH, time, and temperature, confirming that the process achieves high sorption capacity under optimal conditions. Isotherm analysis showed a good fit to the Freundlich model, indicating the heterogeneous nature of the sorption process and the involvement of active sites with different energies.

Kinetic modeling results showed the superiority of the pseudo-second-order model, confirming that chemisorption mechanisms, particularly coordination interactions between carboxyl groups and Cu(II) ions, play a major role in the sorption process. Intraparticle diffusion analysis revealed the multi-stage nature of the process.

Thus, cellulose modified with citric acid through microwave-thermal methods demonstrates high functionality, heterogeneity, and superior sorption efficiency, making it a promising material for the effective removal of heavy metal ions, particularly Cu(II), from wastewater.

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Declaration of generative AI in scientific writing

During the preparation of this research, the author partially used ChatGPT for editing and improving the language of the manuscript. After using this tool, the author reviewed and made necessary changes to the content and takes full responsibility for the content of the published article.

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