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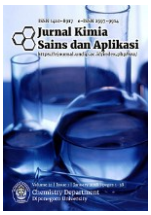

The Potential of Sonication Residue of *Hydrilla verticillata* Modified with Citric Acid as a Biosorbent for Cadmium Metal

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Abstract

The increase in the number of industries in this era has an impact on water-related environmental problems, particularly heavy-metal waste, including cadmium. This study aims to determine the ability and optimal conditions of the sonication residue biosorbent *Hydrilla verticillata*. Biosorbents were obtained from sonication residues, then demineralized with 0.4 M HNO_3 and modified with 1 M citric acid. Pure and modified biosorbents were subjected to adsorption tests at varying pH levels (5-9), contact times of 15, 30, 45, 60, 75, 90, 105, and 120 minutes, and initial concentrations of 5, 10, 15, 20, and 25 ppm. All adsorption experiments were conducted in triplicate, and the results are presented as mean values. This approach ensures the reliability of the adsorption performance evaluation. The resulting solution was then digested, analyzed using the AAS instrument, and characterized using the FTIR instrument. The results of the research were the successful modification of the biosorbent, marked by a change in color from brownish green to brown and a rough texture, and the detection of the IR spectrum of the C=O group at 1728.21 cm^{-1}. The optimum conditions were obtained with the modified biosorbent: pH 7 (93.6%), contact time 105 minutes (98.3%), and initial concentration 10 ppm (98.7%).

1. Introduction

Hydrilla verticillata is the most troublesome aquatic weed found in many waters. The rapid growth and spread of *Hydrilla verticillata* can threaten ecosystems [1]. *Hydrilla verticillata* is often used for the extraction of phytochemical compounds via the ultrasonic-assisted extraction (UAE) method, as it contains secondary metabolites such as alkaloids, flavonoids, tannins, saponins, triterpenoids, and steroids [2]. However, extracting phytochemicals from *Hydrilla verticillata* using UAE yields substantial solid residues. Petpheng *et al.* [3] stated that the cellulose, hemicellulose, and lignin content in the sonication residue of *Hydrilla verticillata* were 29%, 63.5%, and 7.5%.

The discovery of cellulose in the sonication residue of *Hydrilla verticillata* suggests its potential as a biosorbent for heavy-metal adsorption. The hydroxyl groups in cellulose can bind heavy metals through interactions with positively charged metal ions. One toxic heavy metal that can disrupt aquatic life is cadmium (Cd^{2+}), which has a maximum limit of 0.01 ppm according to PP RI No. 22 of 2021 [4]. Adsorption performance can be improved by citric acid modification, which forms mono-, di-, and triesters with the hydroxyl groups of Hydrilla [5] and introduces at least two carboxylate groups on the biosorbent surface [6]. This modification occurs through an esterification mechanism in which citric acid reacts with the hydroxyl groups of cellulose, forming ester linkages and introducing additional carboxyl functional groups that enhance metal-binding capacity [7].

One of the factors that affects the adsorption of cadmium by the sonication-residue biomass of *Hydrilla verticillata* is pH, contact time, and initial concentration. The effect of pH on adsorption capacity is caused by the exchange of metal ions and cations on the surface of the adsorbent. Contact time can affect adsorption capacity due to diffusion and attachment of the adsorbate to the

adsorbent, along with the longer contact time. Meanwhile, the initial concentration can affect adsorption because it determines the amount of adsorbate available to bind to the biosorbent surface [8]. Therefore, a test will be conducted to determine the optimal pH, contact time, and initial concentration for the Cd^{2+} adsorption process using the sonicated residue of *Hydrilla verticillata*.

2. Experimental

2.1. Materials

Hydrilla verticillata biomass, 96% food-grade ethanol (One Med), distilled water, aquademine (OneMed), $Cd(NO_3)$ (Loba Chemi), citric acid (Merck), Na_2HPO_4 (Smartlab), H_3BO_3 (Smartlab), NaOH 0.2 M (Smartlab), HNO_3 (Smartlab), H_2O_2 (Smartlab), filter paper, plastic wrap, pH meter, and universal pH indicator paper.

2.2. Sample Preparation

Hydrilla verticillata samples obtained from Lake Ranu Grati Pasuruan were then washed clean, dried, and ground. The *Hydrilla verticillata* biomass powder was then sieved through a 60-mesh sieve.

2.3. Extraction of *Hydrilla verticillata*

The extraction method used in this study was sonication. *Hydrilla verticillata* powder (up to 25 g) was added to 250 mL of 96% ethanol (1:10) in an Erlenmeyer flask, then covered with plastic wrap. Furthermore, extracted using a water bath sonicator at 42 kHz for 30 minutes. The extraction results were filtered using a Buchner funnel, then dried in an oven at 95°C for 2 hours. The dried sonication residue was then air-dried at room temperature and stored for further treatment.

2.4. Biosorbent Demineralization

Demineralization of the biosorbent was carried out using 0.4 M HNO_3. A total of 10 g of *Hydrilla verticillata* sonication residue powder was soaked in 100 mL of 0.4 M HNO_3 (solid-to-liquid ratio of 1:10, w/v) in an Erlenmeyer flask and stirred for 2 hours. The mixture was subsequently filtered using a Büchner funnel and washed with distilled water until the pH reached approximately 7. The demineralized residue was then dried in an oven at 95°C for 4 hours, cooled to room temperature, and stored for further use.

2.5. Biosorbent Modification

Biosorbent modification was performed using 1 M citric acid. A total of 10 g of demineralized *Hydrilla verticillata* was mixed with 100 mL of 1 M citric acid (solid-to-liquid ratio of 1:10, w/v) in an Erlenmeyer flask. The mixture was stirred at 250 rpm for 2 hours at 60°C. Afterward, the solution was allowed to cool to room temperature. The modified biomass was then separated and washed with distilled water until the filtrate reached neutral pH. Finally, the sample was dried in an oven at 50°C for 24 hours.

2.6. Adsorbent Test

2.6.1. Adsorbent Test with pH Variations

Adsorption experiments at varying pH were conducted by contacting 75 mg of pure and modified *Hydrilla verticillata* with 20 mL of a 20 ppm Cd^{2+} solution adjusted to the desired pH using a buffer. The mixture was shaken at 150 rpm for 60 minutes, then filtered using fine filter paper. The filtrate was digested with an HNO_3–H_2O_2 mixture (10:3, v/v; 5 mL HNO_3 and 1.5 mL H_2O_2) at 105°C for 2 hours until a clear solution was obtained, ensuring complete dissolution of Cd species and removal of potential organic interferences prior to analysis. The Cd^{2+} concentration was determined using Atomic Absorption Spectroscopy (AAS) at 228.8 nm.

2.6.2. Adsorbent Test with Contact Time Variations

The optimum contact time for biosorption was determined at the previously established optimum pH. A total of 75 mg of pure and modified *Hydrilla verticillata* sonication residue was added to 20 mL of a 20 ppm Cd^{2+} solution. The mixtures were agitated at 150 rpm for contact times of 15, 30, 45, 60, 75, 90, 105, and 120 minutes. After each contact time, the suspensions were filtered, and the filtrates were digested and analyzed following the same HNO_3–H_2O_2 digestion and AAS procedure described in the pH variation experiment. The Cd^{2+} concentration was determined using AAS at 228.8 nm.

2.6.3. Adsorbent Test with Initial Concentration Variations

Adsorption experiments were conducted to evaluate the effect of initial Cd^{2+} concentration at the previously determined optimum pH and contact time. A total of 75 mg of pure and modified *Hydrilla verticillata* sonication residue was added to 20 mL of Cd^{2+} solutions with initial concentrations of 5, 10, 15, 20, and 25 ppm. The mixtures were agitated at 150 rpm under the established optimum conditions. After equilibrium was reached, the suspensions were filtered, and the filtrates were digested and analyzed following the same HNO_3–H_2O_2 digestion and AAS procedure described in the pH variation experiment. The Cd^{2+} concentration was determined using AAS at 228.8 nm.

The adsorption capacity at equilibrium (Q_e) was calculated to evaluate the amount of Cd^{2+} adsorbed per unit mass of biosorbent, as presented in Equation (1).

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Where, C_0 is the initial concentration of Cd(II) (mg/L), C_e is the equilibrium concentration after adsorption (mg/L), V is the volume of the solution (L), and m is the mass of the biosorbent used (g). This parameter provides a more comprehensive comparison of adsorption performance between pure and modified biosorbents.

3. Results and Discussion

3.1. Sample Preparation

The *Hydrilla verticillata* used in this study was collected from Lake Ranu Grati, Pasuruan. Drying significantly reduced the sample weight, yielding 0.36 kg of dry biomass from 3.48 kg of wet material, corresponding to a yield of 10.34% and a final moisture content of 5.3%. According to Masaenah *et al.* [9], a moisture content below 10% is considered suitable and safe for the long-term storage of simplicial, as it helps prevent microbial growth.

Drying also affected the color of *Hydrilla verticillata*. Fresh samples were dark green, whereas the dried samples became brownish green. This discoloration is associated with moisture-dependent enzymatic reactions occurring in the leaves. Prolonged drying allows water to remain in the simplicia for a longer period, thereby increasing the degradation of chlorophyll into pheophytin, which contributes to the brownish coloration [10].

3.2. Extraction of *Hydrilla verticillata* as Biosorbent

During the extraction process, secondary metabolites present in *Hydrilla verticillata* were solubilized in the ethanol solvent. This was indicated by the reduction in biomass weight from 25 g before sonication to a lower mass after treatment (Table 1). The average yield of the residue was 86.30 ± 1.99% (n = 3), which is slightly lower than the value reported by Petpheng *et al.* [3] (89.75%). This difference may be attributed to variations in biomass origin, which can influence its chemical composition.

The residue obtained after sonication exhibited a brownish-green color, in contrast to the original green color of the raw material. This change suggests partial removal of chlorophyll, which is known to dissolve in ethanol due to its semi-polar characteristics. Following the principle of "like dissolves like," ethanol is capable of extracting compounds with similar polarity, including chlorophyll [11]. A previous study [6] has shown that ethanol extracts of *Hydrilla verticillata* contain various secondary metabolites, including alkaloids, flavonoids, phenols, terpenoids, and saponins, while tannins, glycosides, and proteins were not detected.

3.3. Demineralization of *Hydrilla verticillata* Biosorbent Sonication Residue

Biosorbents naturally contain various mineral components, including Mg, Ca, Al, K, Fe, P, and Na, with concentrations depending on the biomass source [12]. During demineralization, these metal ions bound to the functional groups of the biosorbent are replaced by protons (H^+) from nitric acid, thereby increasing the availability of active sites and promoting pore development. This process was reflected in the decrease in biomass weight after treatment, with an average yield of 58.62% relative to the initial mass, indicating the removal of mineral constituents.

As shown in Table 2, the biosorbent color changed from brownish green to dark greenish brown after demineralization. This change is associated with chlorophyll transformation under acidic conditions. Chlorophyll contains a porphyrin ring with a central Mg ion; in the presence of nitric acid, Mg is replaced by H^+, forming pheophytin, which imparts a brownish coloration [13].

In addition to color changes, the texture of the biosorbent became coarser and slightly aggregated after demineralization. This observation is consistent with previous findings by Anggraini *et al.* [14], who reported that demineralized biosorbents exhibit cleaner surfaces and more open, uniform pore structures compared to untreated materials. The removal of mineral impurities enhances surface roughness and porosity, thereby improving adsorption performance by facilitating greater interaction with metal ions.

3.4. Modification of Biosorbent from Sonicated *Hydrilla verticillata* Residue

The modification process aimed to alter the surface chemistry of the biosorbent by introducing additional functional groups. Citric acid treatment is expected to enhance adsorption capacity by increasing the number of carboxyl (–COOH) groups on the biosorbent surface. Under heating conditions, citric acid undergoes dehydration to form reactive anhydride intermediates, which subsequently react with the hydroxyl (–OH) groups of cellulose via esterification, forming ester linkages. This modification increases the availability of active binding sites for metal-ion adsorption.

A decrease in biosorbent mass was observed after modification, with a yield of 73.26%. This reduction may be attributed to the removal of loosely bound components and partial loss of volatile substances during heating at 60°C. Additionally, minor structural changes in biomass constituents, such as hemicellulose and lignin, may contribute to the observed weight loss [15]. The color difference from dark greenish brown to grayish brown can be caused by the pheophytinization reaction, which is the formation of pheophytin compounds from chlorophyll compounds. The observation results of the modified biosorbent, including final weight, yield percentage, and color changes, are presented in Table 3.

Table 1. Results of the extraction yield

Repetition	Weight (g)	Yield (%)	Color
1	21.021	84.08	Coarse
2	21.730	86.92	Coarse
3	21.978	87.91	Coarse

Table 2. Results of observation of biosorbents after demineralization

Final weight (g)	Yield (%)	Color	Texture
5.922	59.22	Greenish dark brown	Coarse
5.805	58.06	Greenish dark brown	Coarse
5.859	58.59	Greenish dark brown	Coarse

Table 3. Results of observation of biosorbents after modification

Final weight (g)	Yield (%)	Color
7.326	73.26	Greyish brown

3.5. Biosorbent Test

3.5.1. Biosorbent Test with pH Variation

All adsorption experiments were conducted in triplicate (n = 3), and the results are presented as mean values with standard deviation. Figure 1 shows the effect of pH on Cd^{2+} adsorption using both pure and modified biosorbents. For the pure biosorbent, adsorption decreased to 29.7% at pH 6, then increased at higher pH values to 41.4% (pH 7) and 79.7% (pH 8), before dropping sharply to 28.1% at pH 9. The highest adsorption efficiency was therefore observed at pH 8.

This is in accordance with Anggraini *et al.* [14], who also reported optimum Cd^{2+} adsorption under slightly alkaline conditions. At lower pH, the high concentration of H^+ ions competes with Cd^{2+} for active binding sites on the biosorbent surface, reducing adsorption efficiency. As the pH increases, this competition decreases, allowing more Cd^{2+} ions to bind. However, at higher pH values (e.g., pH 9), the decrease in adsorption may be attributed to the onset of $Cd(OH)_2$ precipitation, which reduces the availability of free Cd^{2+} ions in solution rather than reflecting true adsorption performance.

However, a different trend was observed for the modified biosorbent, where adsorption increased with increasing pH and reached an optimum at pH 7 (93.9%). This result is consistent with the findings of Darjito *et al.* [16], who reported optimum Cd^{2+} adsorption using chitosan at neutral pH. At low pH, excess H^+ ions compete with Cd^{2+} for binding sites, particularly the introduced carboxyl (−COOH) groups, which remain protonated and less available for metal binding. As the pH approaches neutral conditions, these functional groups become deprotonated ($-COO^-$), enhancing electrostatic attraction and complexation with Cd^{2+} ions. Consequently, adsorption efficiency increases. At higher pH values, a decline in adsorption may occur due to the formation of $Cd(OH)_2$ precipitates, which reduces the concentration of free Cd^{2+} ions available for adsorption.

At pH 5–6, both biosorbents exhibited low adsorption efficiency due to protonation of surface functional groups. Under acidic conditions, excess H^+ ions compete with Cd^{2+} for binding sites, particularly hydroxyl (−OH) and carboxyl (−COOH) groups, which remain protonated and less available for coordination. This results in electrostatic repulsion between the positively charged surface and Cd^{2+} ions, thereby reducing the adsorption capacity [17].

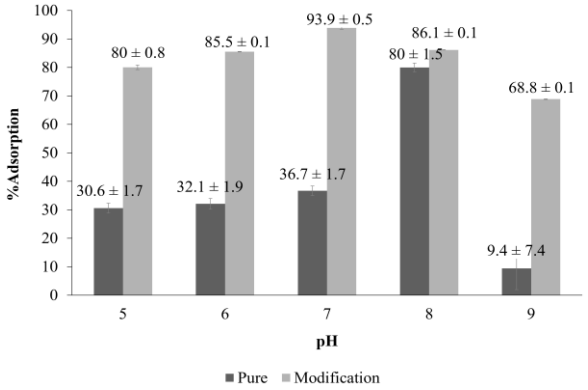

Figure 1. Graph of the relationship between pH variation and percent adsorption

As pH increases, deprotonation of functional groups increases the availability of negatively charged sites, thereby improving Cd^{2+} binding. However, a decline in adsorption was observed at pH > 7 for the modified biosorbent and pH > 8 for the pure biosorbent. This behavior is attributed to the formation of cadmium hydroxide precipitates at higher pH values. Increasing OH^- concentration promotes the reaction (2). The formation of $Cd(OH)_2$ reduces the concentration of free Cd^{2+} ions in solution, leading to an apparent decrease in adsorption efficiency [18].

$$Cd^{2+}{}_{(aq)} + NaOH_{(aq)} \rightarrow Cd(OH)_{2\,(s)} + 2Na^+{}_{(aq)} \qquad (2)$$

The difference in optimum pH between the two biosorbents, pH 8 for the pure biosorbent and pH 7 for the modified biosorbent, can be explained by their surface chemistry. The pure biosorbent predominantly contains hydroxyl groups, which require slightly alkaline conditions for effective deprotonation and interaction with Cd^{2+} ions. In contrast, the modified biosorbent contains additional carboxyl groups (−COOH) introduced through citric acid treatment. These groups deprotonate at lower pH to form carboxylate ions ($-COO^-$), enabling effective Cd^{2+} binding under near-neutral conditions. This contributes to the higher adsorption efficiency observed for the modified biosorbent.

However, both biosorbents showed a significant decrease in absorption percentage at pH > 8. Susanto [19] said that $Cd(OH)_2$ deposits begin to form when pH 8.5 is reached. Based on this explanation, the decrease in percent absorption at pH 9 can be attributed to the formation of $Cd(OH)_2$ deposits, which prevent the detection of Cd metal when analyzed using the AAS instrument.

3.5.2. Adsorbent Test with Contact Time Variation

The results of the adsorption experiments with varying contact times are presented in Figure 2. In general, adsorption increased with increasing contact time until equilibrium was reached, after which no significant increase in Cd^{2+} uptake was observed. This indicates that the available active sites on the biosorbent surface had become saturated.

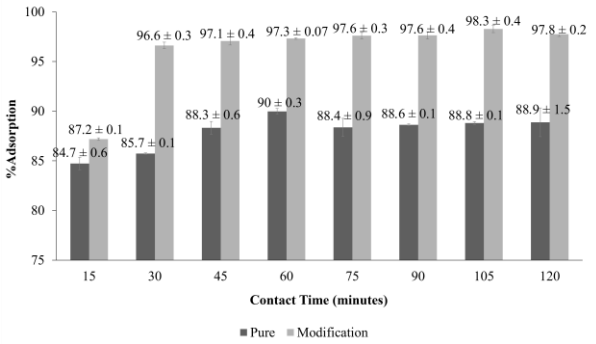

Figure 2. Effect of contact time on Cd^{2+} adsorption efficiency

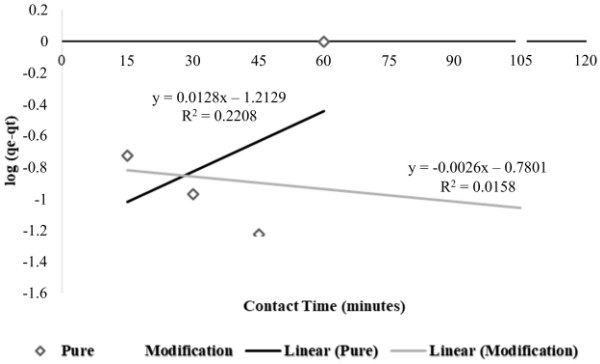

Figure 3. Kinetic plot pseudo-first order (PFO)

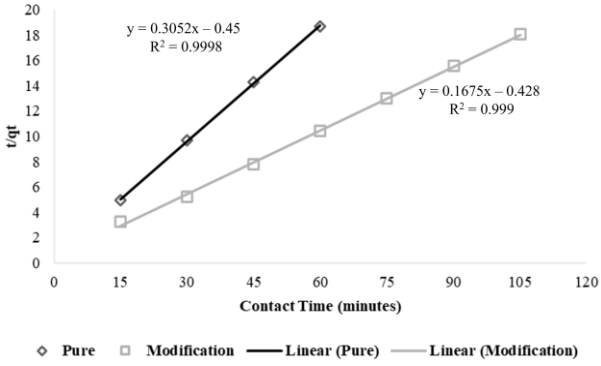

Figure 4. Kinetic plot pseudo-second order (PSO)

For the pure biosorbent, adsorption increased rapidly from 15 to 60 minutes before approaching equilibrium. In contrast, the modified biosorbent required a longer contact time, with adsorption continuing to increase up to 105–120 minutes before stabilizing. The difference in equilibrium time suggests variations in surface characteristics and binding mechanisms between the two biosorbents. The equilibrium adsorption efficiencies were 89.98% for the pure biosorbent and 98.3% for the modified biosorbent. The higher performance of the modified biosorbent is attributed to the introduction of additional functional groups, particularly carboxyl ($-COO^-$) groups, which enhance Cd^{2+} binding through electrostatic interactions and complexation.

The results obtained are consistent with Fatmawati *et al.* [20], showing that different biosorbent treatments affect adsorption capacity, optimum contact time, and overall efficiency. The modified biosorbent showed higher adsorption performance and a longer equilibrium time than the pure biosorbent. This behavior is attributed to the greater number of active sites, which require more time to become fully occupied. As contact time increases, more interactions occur between Cd^{2+} ions and the biosorbent surface until equilibrium is reached. Beyond the optimum contact time, adsorption slightly decreases, possibly due to surface saturation and desorption. Similar behavior has been reported for H_2O_2-modified biosorbents, where equilibrium was reached at approximately 120 minutes [21].

The contact time data were further analyzed using adsorption kinetics models to describe the rate and mechanism of Cd^{2+} uptake [22]. Based on Figures 3 and 4, both pure and modified biosorbents follow the PSO kinetic model, with high coefficients of determination (R^2 = 0.9998 and 0.9990, respectively). This indicates that the adsorption process is primarily governed by chemisorption, involving electron sharing or exchange between Cd^{2+} ions and functional groups on the biosorbent surface.

This interpretation is supported by FTIR analysis, which shows shifts and changes in the intensity of –OH and C=O absorption bands after adsorption, indicating their involvement in Cd^{2+} binding. These oxygen-containing functional groups act as electron donors, facilitating the formation of coordination bonds or surface complexes with Cd^{2+} ions. Therefore, the rate-limiting step is likely related to surface complex formation. These findings are consistent with previous studies. Lach and Okoniewska [23] reported that Cd^{2+} adsorption using activated carbon followed the PSO model, with a higher R^2 (0.996) than the PFO and Elovich models. Similarly, Deri *et al.* [24] observed PSO-dominated kinetics in Cd^{2+} adsorption using an areca nut biosorbent, with an R^2 value of 0.9999, which was significantly higher than that of the PFO model.

3.5.3. Adsorbent Test with Initial Concentration Variation

The significant difference in adsorption percentage between the pure and modified biosorbents is also evident from their highest values. The modified biosorbent achieved a maximum adsorption of 98.3%, while the pure biosorbent reached only 91.6%. This indicates that modifying the biosorbent surface with citric acid increases the number of active functional groups (such as –COOH and –OH), so that the biosorbent's ability to bind metal ions becomes greater and more stable. As shown in Figure 5, the modified biosorbent consistently exhibited higher adsorption percentages than the pure biosorbent at all initial concentration variations.

Table 4. Adsorption capacity of Cd(II) using pure and modified biosorbents

Initial concentration (ppm)	Q_e (mg/g)	
	Pure	Modified
5	1.257	1.418
10	3.079	3.340
15	4.199	4.583
20	5.834	6.197
25	6.697	7.118

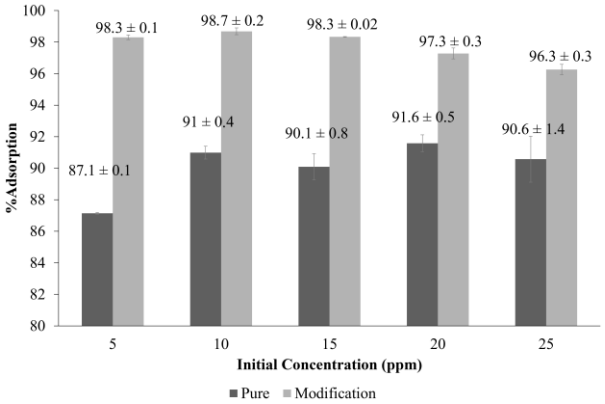

Figure 5. Graph of the relationship between initial concentration and percent of adsorption

The effect of the initial concentration on the adsorption capacity (Q_e) of the pure and modified biosorbents is presented in Table 4. The results indicate that the adsorption capacity increases with increasing initial concentration from 5 to 25 ppm for both biosorbents. For the pure biosorbent, the Q_e value increases from 1.257 mg/g at an initial concentration of 5 ppm to 6.697 mg/g at 25 ppm. A similar trend is observed for the modified biosorbent, where the adsorption capacity increases from 1.418 mg/g to 7.118 mg/g within the same concentration range. This increase in adsorption capacity with higher initial concentration can be attributed to the greater availability of adsorbate molecules in the solution, which enhances the interaction between the adsorbate and the active sites on the surface of the biosorbent. Moreover, an increase in the initial concentration provides a higher mass transfer driving force, facilitating the diffusion of adsorbate molecules from the bulk solution to the biosorbent surface. Overall, these results indicate that at various initial Cd solution concentrations, the modified biosorbent exhibits higher adsorption percentages than the pure biosorbent.

3.6. Biosorbent Test

Fourier Transform Infra-Red (FTIR) spectral analysis was performed in this study to identify the functional groups present in all biosorbent variations and investigate the possibility of interaction between the functional group and the Cd(II) metal after the adsorption process. The results of the FTIR spectrum are shown in Figure 6 with a spectrum range of 450–4000 cm^{-1}.

Based on Figure 6, it is evident that most biosorbent variations exhibit similar group characteristics, but with different wave numbers and intensities. The first wide band is related to the O-H vibration in cellulose at BMU pH, BMU-WK, BMO PH, and BMO-WK. This shift in the number of waves indicates a change in the energy and bonding patterns of the functional groups [24]. In addition, compared to the BMU biosorbent condition, the peak intensity of the demineralized and modified biosorbent spectrum has increased, whereas that of biosorbents after excavation has decreased. This shows that the demineralization of biosorbents can remove surface-bound metals, allowing oxygen to bind to hydrogen from HNO_3, and that modified biosorbents can increase the number of functional groups; therefore, the IR spectrum shows strong hydrogen bonds from the hydroxyl group in BD as well as the carboxyl group in BMO.

The C=O vibration associated with the formation of carbonyl groups in carboxylic acids and esters was detected at wave number 1728.21 cm^{-1} for BMO, BMO pH, and BMO-WK. This shows that the modification process has been successful, as evidenced by the formation of carboxylate and ester groups within the biosorbent structure. The FTIR spectra of the biosorbents after Cd^{2+} adsorption (BMO-pH and BMO-WK) show noticeable changes in several characteristic absorption bands associated with oxygen-containing functional groups. In particular, slight shifts and changes in the intensity of the –OH stretching band and the C=O stretching band were observed after Cd^{2+} adsorption. A more detailed discussion of the FTIR spectral changes after Cd^{2+} adsorption has been added to the FTIR analysis section to clarify the involvement of –OH and –COOH functional groups in the biosorption mechanism.

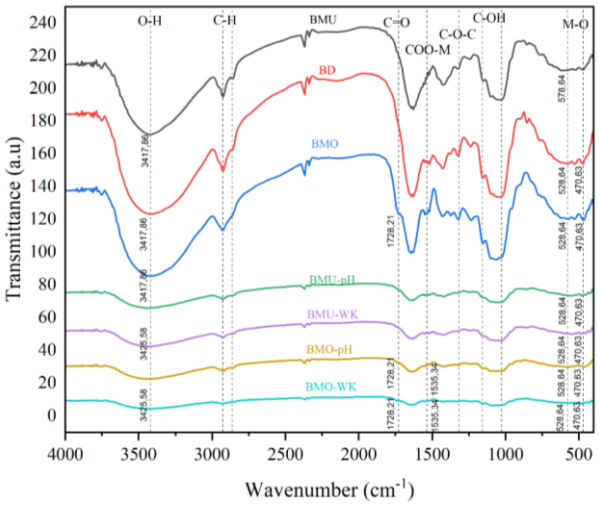

Figure 6. IR spectrum characterization. Interpretation of the functional group of pure sonication residue (BMU), demineralization (BD), modification (BMO), pure pH variation (BMU-pH), pure contact time variation (BMU-WK), pH variation modification (BMO-pH), and contact time variation modification (BMO-WK)

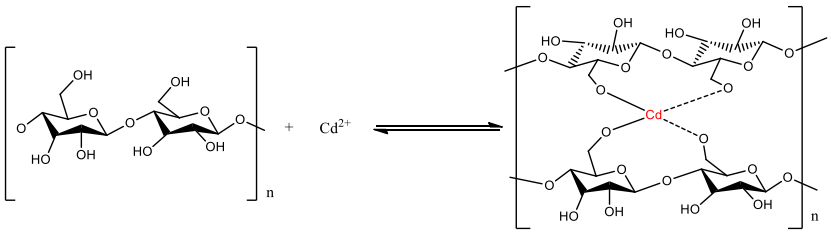

Figure 7. Cellulose complex with metal Cd [25]

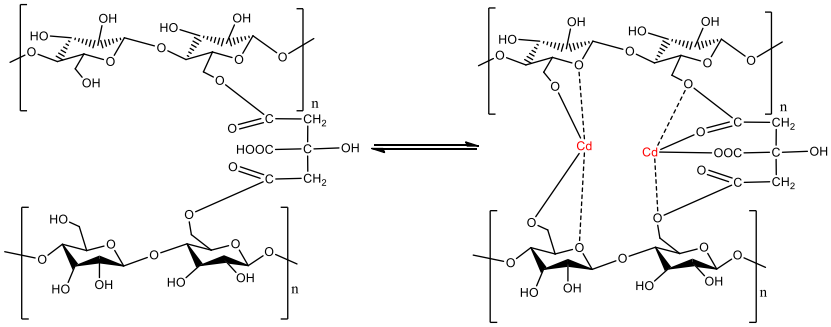

Figure 8. Complexation of cellulose citrate with metal Cd [25]

The FTIR characterization results of BMO-pH and BMO-WK indicate the presence of COO−M vibrations along with slight shifts in the O−H and C=O stretching bands after Cd adsorption. The appearance of the COO−M vibration suggests the formation of metal−carboxylate complexes on the biosorbent surface. This phenomenon is associated with the presence of carboxyl groups in the biosorbent structure, which can be protonated by H^+ and subsequently interact with Cd^{2+} ions. These shifts in the O−H and C=O stretching bands were observed in the FTIR spectra, indicating the interaction between Cd^{2+} ions and the functional groups present on the biosorbent surface. In particular, the shift in the C=O stretching band suggests the involvement of carboxyl groups in coordinating Cd^{2+} ions. These spectral changes provide evidence for the occurrence of metal−ligand complexation between Cd^{2+} ions and the functional groups of the modified biosorbent.

The mechanism of cadmium binding by biosorbents is suspected to be chemical, based on adsorption kinetic calculations that indicate a pseudo-second-order model. Based on this, it can be suspected that the binding of the Cd^{2+} metal by the biosorbent can be through the formation of complex compounds where the O atom of the -OH group in the biosorbent acts as a ligand that contributes a free electron pair in the s orbital owned by the Cd^{2+} atom the electron pair occupies an empty orbital so as to form a hybridization of sp^3 with a tetrahedral form. The interaction that occurs between anions that are strongly alkaline (-OH) will occur very strongly through the mechanism of formation of a coordination complex [26]. With the citric acid modification, a new group, C=O, will appear, which can act as a ligand and strengthen binding.

4. Conclusion

This study demonstrates that Cd removal by the *Hydrilla verticillata* sonication residue biosorbent is governed by pH-dependent electrostatic interactions and surface complexation mechanisms. At low pH, Cd adsorption is inhibited by competition with H^+ ions, whereas near neutral pH, negatively charged functional groups on the biosorbent surface enhance electrostatic attraction toward Cd^{2+} ions. Citric acid modification significantly improves adsorption performance by introducing additional carboxyl groups, which increase the number of active binding sites and strengthen electrostatic interactions and metal−ligand complexation with Cd^{2+} ions. Consequently, the increased functional group density and altered surface charge collectively contribute to the enhanced adsorption efficiency of the modified *Hydrilla verticillata* biosorbent.

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