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Removal of Divalent Copper Ions from Aqueous Solution Using *Sorghum bicolor* L. Stem Waste as an Effective Adsorbent

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ABSTRACT

Sorghum stem (*Sorghum bicolor* L.) is a plant that has not been maximally utilized. But sorghum stems contain high cellulose. The hydroxyl (OH-) and carboxyl (-COOH) groups on cellulose can bind heavy metals; therefore, sorghum stems have the opportunity to be used as an adsorbent to absorb heavy metals, especially Cu(II) metal, which can pollute the environment. Therefore, this research was conducted to determine the optimum pH, contact time, and the adsorption capacity of Cu(II) using HNO_3 modified sorghum stem adsorbent. The stages of the research included the preparation of sorghum stem adsorbent, modification of adsorbent with HNO_3, determination of optimum pH, optimum contact time and adsorption capacity of Cu(II) metal. Furthermore, the functional groups of the adsorbent before and after modification were determined by FTIR. SEM-EDS to assess the morphological structure and chemical components contained in the adsorbent. After the research, the optimum pH of Cu(II) metal adsorption was pH 6, and the adsorption power was 99.88%. The optimum contact time is 10 minutes. The percent removal of Cu(II) metal with concentrations of 10, 30, 50, and 100 ppm were 79.96; 79.90; 56.40 and 54.04%, respectively. Adsorption of Cu(II) metal using HNO_3 modified sorghum stem adsorbent followed the Freundlich isotherm pattern compared to Langmuir with $R^2 = 0.9039$. It is concluded that activated sorghum stem can be used as Cu(II) metal adsorbent.

Keywords: adsorbent, removal, sorghum stem, copper ion, pollution.

INTRODUCTION

The burgeoning global population has significantly escalated the generation of wastewater effluents, thereby heightening the peril of water pollution and its detrimental environmental consequences [1, 2, 3, 4]. Heavy metals, such as mercury (Hg), cadmium (Cd), lead (Pb), chromium (Cr), and arsenic (As), pose a substantial threat to living organisms due to their inherently toxic nature, even at low concentrations [5, 6]. Industrial activities, including production processes that release harmful chemicals, solvents, and various organic and inorganic substances, contribute to water pollution if not adequately treated before discharge into aquatic ecosystems [7, 8]. Moreover, human practices like metal mining, smelting, and foundries are primary sources of environmental pollution, releasing metals directly into water bodies [9]. Copper (Cu) [10, 11] and lead (Pb) [12] stand out among the harmful metals. Various technologies exist to effectively reduce and separate heavy metals from water, with adsorption emerging as a viable, eco-friendly option that employs relatively simple equipment [13] While the overarching goal is to enhance water quality by efficiently removing pollutants from wastewater, conventional adsorbents have limitations, underscoring the need to develop simple, low-cost, high-performance alternatives. Bio-sorbents derived from diverse biomass resources such as agricultural, forestry, and food waste have surfaced as promising solutions. These bio-sorbents are produced through pyrolysis and chemical or thermal activation in the absence of oxygen [14], and their utilization in water treatment is gaining traction due to their natural origin, biodegradability, modifiability, and renewability [15]. Biomass, particularly agricultural waste, emerges as an abundant, eco-friendly, cost-effective adsorbent for heavy metal ions, offering a viable alternative to synthetic materials commonly used in heavy metal removal processes. Sorghum, an alternative crop with considerable potential in Indonesia [16], generates agricultural waste in the form of sorghum stems after harvest, both economically valueless and abundantly available [17]. Despite numerous studies exploring the potential of sorghum as a starting material for producing adsorbents capable of effectively removing both organic and inorganic pollutants, a critical gap exists in the literature regarding a comprehensive study on the production of adsorbents from sorghum waste. This gap includes their modification with HNO_3 and subsequent testing with actual laboratory waste, representing the uncharted territory in the quest for sustainable and efficient wastewater treatment. Therefore, the primary objective of this study is to investigate the effectiveness of biosorbents produced from HNO_3-modified sorghum wastes in removing heavy metal ions, specifically Cu(II). These heavy metal ions were chosen for their well-documented adverse effects on human health and other living organisms, leading to severe damage to vital organs such as the brain, kidneys, and liver. By filling this research gap, we aim to contribute valuable insights to sustainable wastewater treatment, paving the way for adopting sorghum-based biosorbents to address the global challenge of heavy metal pollution in laboratory waste.

MATERIAL AND METHODS

Sodium hydroxide (NaOH), nitric acid (HNO_3), copper (II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), and hydrochloric acid (HCl). The Cu(II) (1000 mg/L) stock solution was prepared by dissolving $CuSO_4 \cdot 5H_2O$ in demineralized water. The solutions of the desired concentrations were created by diluting the solution above accordingly. The solutions were pH-adjusted using either HCl or NaOH (0.1 M).

Preparation of adsorbents

The sorghum stem used in this study was obtained from Pangkajene Islands Regency, Indonesia. The stem was manually ground into a fine powder to create the biosorbents and sifted through a 60-mesh sieve. The biomass underwent numerous washes, followed by drying at a temperature of 60 °C for 24 hours, before being utilized for future procedures.

Modification of sorghum stem with nitric acid (HNO_3)

The sorghum stem powder was immersed in a solution of 1 M nitric acid, with a ratio of 1:10 (sorghum stem: nitric acid), and maintained at a temperature of 25 °C for 2 hours. Subsequently, the concoction underwent filtration and repeated washing until reaching a pH level of neutrality. Later, the altered unmodified sorghum stem was subjected to a drying process at a temperature of 60 °C for 24 hours. It was then stored in a plastic bag and is now prepared for utilization as an adsorbent.

Characterization unmodified and modified sorghum stem

The unmodified and modified adsorbents were analyzed utilizing Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy with energy dispersive X-ray Spectroscopy (SEM-EDS). The FTIR spectrometer was employed to examine alterations in vibrational frequencies of functional groups and surface functional groups of biosorbents. To examine the surface morphology of the biosorbent, we acquired SEM pictures using the Hitachi Flexsem 1000. The elemental composition of biosorbents was investigated using EDS spectroscopy. The residual concentration of metal ions under investigation was determined using the ZA3000 Model Atomic Absorption Spectrophotometer. The agitation of aqueous solutions was performed using the Barnstead MaxQ 2000 digital shaker.

Adsorption experiments

An adsorbent quantity of 50 milligrams was subjected to interaction with Cu(II) solutions of several pH values (4–9) in a volume of 50 mL for 60 minutes. The isotherm experiments involved contacting the adsorbent with Cu(II) at different concentrations. An adsorbent quantity of 50 milligrams was subjected to interaction with Cu(II) solutions of several concentrations (10, 30, 50, and 100 mg/L) in a volume of 50 mL, at the pH that yielded the best results. After being agitated for 10 minutes at a speed of 150 rpm, the mixture was filtered. The resultant liquid was then analyzed using Flame-AAS. The contact periods varied between 10, 30, 50, 60, 90, and 120 minutes. Following agitation at 150 revolutions per minute for a specified duration, the mixture underwent filtration, and the concentration of Cu(II) in the resulting liquid was measured using Flame atomic absorption spectroscopy (Flame-AAS).

RESULTS AND DISCUSSION

Characterization of adsorbent

In the analysis of Fourier transform infrared spectroscopy (FTIR), it was observed that there was a typical vibration peak at 3412 cm^{-1}. This peak is attributed to the O-H [18]. Additionally, the bands at 2920 cm^{-1} and 2852 cm^{-1} exhibited adjacent absorbance peaks, which indicated the presence of C-H (alkane) stretching vibrations with high intensity [19, 20]. The band of about 1734 cm^{-1} was a hallmark of the C=O group present in the carboxylic acid [21]. The band at 1246 cm^{-1} represents the C–O group [22]. Furthermore, the wide and high bending vibration absorption of CH_2 (1429 cm^{-1}) revealed that a substitution reaction had primarily taken place in the C-6 hydroxyl from the structure of cellulose [23, 24]. As depicted in Figure 1b, the spectra of the sorghum stem that has been treated with HNO_3 exhibit particular shifted peaks at 3415 cm^{-1}, 2918 cm^{-1}, 2852 cm^{-1}, and 1635 cm^{-1}. These shifted peaks may indicate the alteration of carboxylate and hydroxylate anions. Figure 2 shows some differences compared with the morphological image of the adsorbent without modification. The obvious difference that the eye can immediately capture is the appearance of small holes or dots along the solid particle (compact) structure. In addition, the surface looks smoother and less messy. Adding HNO_3 to This adsorbent shows changes in the surface structure when HNO_3 modifies the sorghum stem [25]. The presence of small holes or pores that are formed due to the addition of HNO_3 gives a large surface area [26]. Adding HNO_3 provides a surface area more easily accessible by cellulase. The nitric acid treatment enhanced the presence of polar oxygen-containing functional groups like hydroxyl, carbonyl, and carboxyl groups on the adsorbent's surface [26].

Effect of pH

The initial solution The pH level plays a vital role in biosorption investigations [27] as it directly impacts the sorption capacity, the speciation

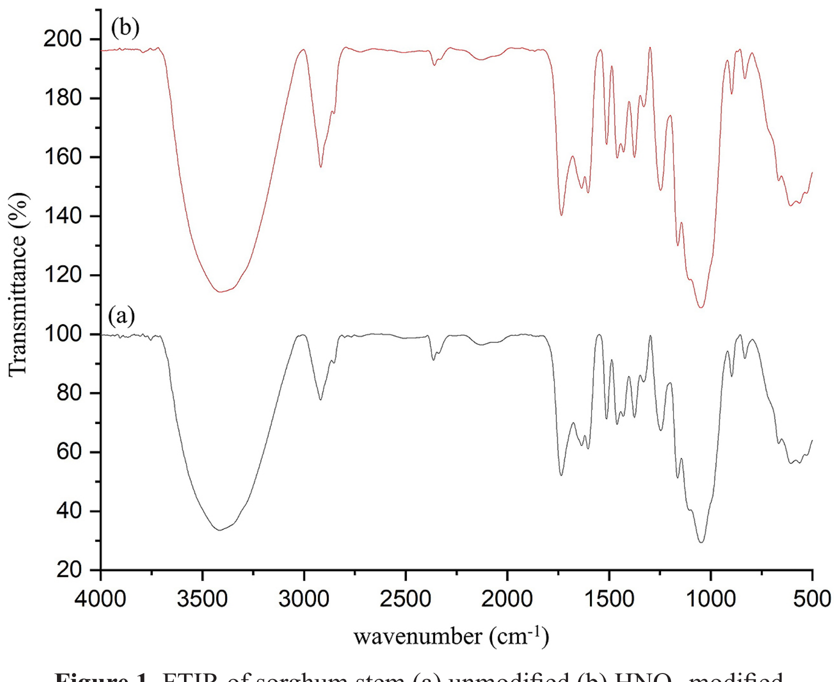

Figure 1. FTIR of sorghum stem (a) unmodified (b) HNO_3-modified

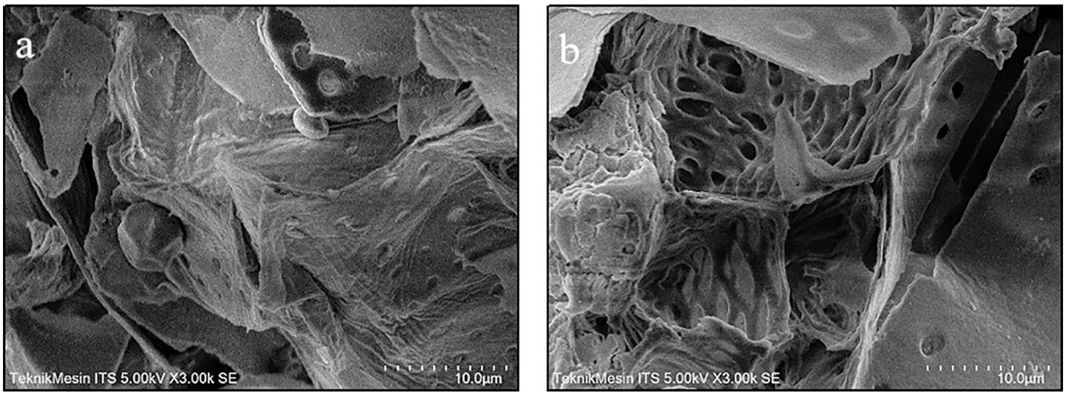

Figure 2. SEM analysis at 3000× magnification of sorghum stem (a) and HNO_3-modified sorghum stem (b)

of metal ions, and the process occurring at the interface between the solid and solution [28, 29, 30]. The pH is a critical determinant that can control and influence the adsorption process [31]. Examining the effect of pH on the adsorption of copper ions is essential as it can affect the surface charge of both the substance being adsorbed and the substance doing the adsorbing. This study examined the influence of pH levels ranging from 4.0 to 9.0 on the adsorption of copper and lead ions. Please refer to Figure 3 for further details.

At pH levels lower than 5, the ability of the modified adsorbent to remove heavy metal ions was reduced as hydrogen ions can compete and coordinate better on the available adsorption sites on the adsorbent [32]. Additionally, the decrease in removal of metal ions at low pH levels may be attributed to the protonation of functional groups [33]. The highest ability of the modified adsorbent to remove copper ions was observed at pH 6 [34, 35, 36, 37], respectively. As the pH value increases, the concentration of hydrogen ions decreases, leading to stronger electrostatic interactions between metal ions Cu(II) and active sorption sites of the modified adsorbent [38, 39]. Therefore, the optimal pH value of 6 was chosen for copper ions removal experiments throughout this study.

Effect of contact time

The adsorption equilibrium time of Cu(II) on the modified adsorbent was determined within 2, 6, 10, 30, 60, 90, 120, 150 and 180 minutes. The experiment was conducted under constant conditions, including a 0.5 gram dose of adsorbent, an initial metal concentration of 10 parts per million (ppm), a pH level of 6, and a solution temperature of 328 Kelvin. Overall, the improved adsorbent consistently demonstrates effective Cu(II) removal at various contact durations (Figure 4). The investigation of contact time patterns typically demonstrates the initial enhancement in removing heavy metals during the process. This

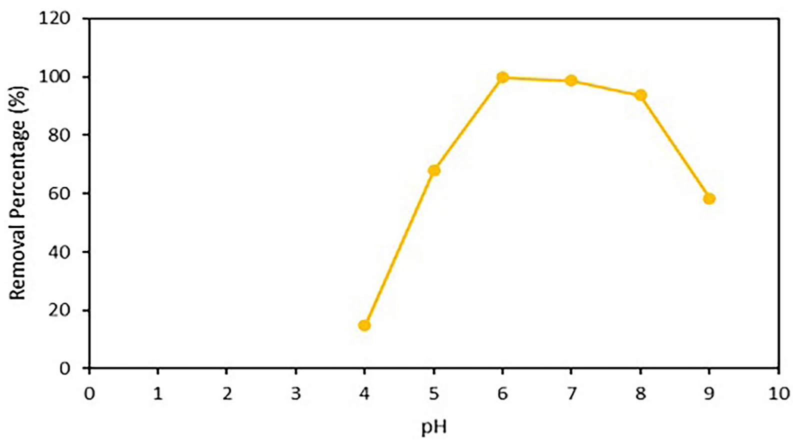

Figure 3. Effect of pH on Cu(II) removal

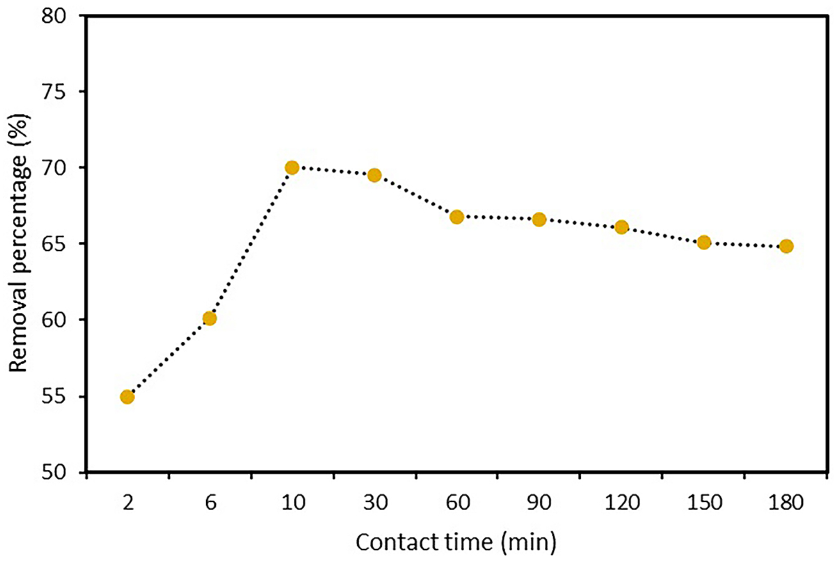

Figure 4. Effect of contact time on Cu(II) removal

phenomenon results from physical adsorption or ion exchange on the surface of the solid adsorbent. During the initial phases, there is a limited number of spaces for attaching metal ions on the surface. In contrast, there are more unoccupied binding sites that gradually decrease and become stagnant [40]. The saturation curves of this investigation were achieved promptly after the initial stage (10 minutes), indicating a restricted number of active sites on the biomass surface for metal binding. The investigation determined that the most effective duration for applying the modified adsorbent to remove Cu(II) from an aqueous solution was 10 minutes of contact time. To get the highest level of contaminant removal, surpassing the recommended contact duration is necessary. However, this will result in a gradual decline in removal efficiency [41]. After 10 minutes, the highest amount of Cu(II) removed was around 70,04%. Following that time frame, the rate of elimination reduced to 69,55%, 66,78%, 66.62%, 66.09%, 65.08% and 64.83% correspondingly, as shown in Figure 6. Due to the maximum removal percentage seen at the equilibrium time of 10 minutes, it was selected for further adsorption investigations.

Adsorption isotherm models

The impact of the initial metal concentration (ranging from 10 to 100 mg/L) on the effectiveness of biosorption was investigated using a modified adsorbent. This study was conducted under optimum conditions of pH and contact time. Figure 5 displays the results. The biosorption efficiency exhibited a negative correlation with the rising starting concentrations of metal solutions. The results indicate that the modified adsorbent had the highest capacity for removing metal ions when they were present at lower starting concentrations. Nevertheless, an inverse correlation was seen between the baseline metal ion concentrations and the removal percentage of metal ions. These patterns may be attributed to the higher proportion of active sites on the sorbent surface relative to the total concentration of metal ions at lower initial levels. As a result, the likelihood of interaction between metal ions and the sorbent is increased, leading to greater adsorption. This results in enhanced sorbent removal [41]

When the concentration of metal ions is low initially, there is a high possibility for remediation [42]. Conversely, when the concentration of metal ions is high, the sorbent's binding sites quickly become saturated due to the constant quantity of biosorbent [43]. The maximum adsorption capacity is a crucial factor in assessing the effectiveness of an adsorbent [44] since it determines the greatest amount of adsorbate that the adsorbent can absorb [45]. The adsorption isotherm was analyzed to determine the adsorption capacity of the modified adsorbent in achieving adsorption equilibrium. Adsorption isotherms are used to study the adsorption process that occurs. These isotherms explain the interaction between adsorbate and adsorbent and the maximum use of adsorbent [46], [47]. Langmuir and Freundlich are two isotherm

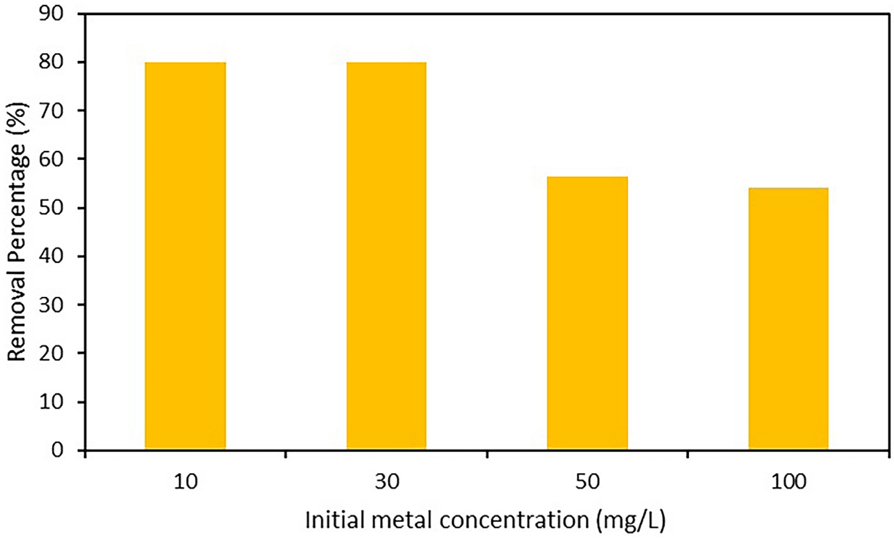

Figure 5. Effect of initial metal concentration on Cu(II) removal

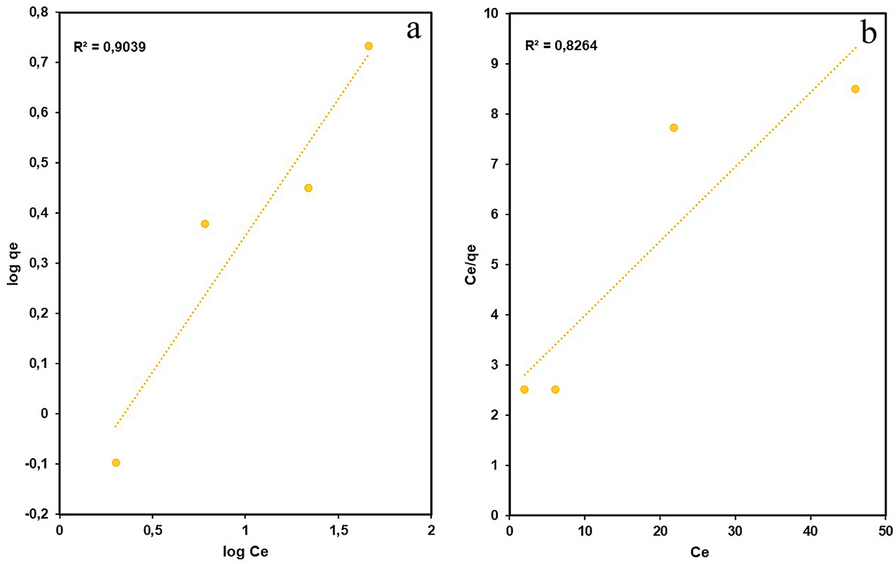

Figure 6. The Freundlich and (a) Langmuir (b) isotherm models of Cu(II) adsorption

models that are often used to predict the adsorption capacity of an adsorbent [48]. The underlying principles are predicated on several assumptions: the adsorbent possesses a homogeneous structure, the adsorbed molecules or atoms are restricted to particular locations, each location can accommodate only one molecule or atom, the adsorption energy remains consistent across all locations, and there is no interaction between adjacent adsorbates [49]. On the other hand, the Freundlich model characterizes systems with different components and reversible adsorption without imposing limitations on the adsorption of a single layer [50]. Figures 6 and Table 1 display the linear representations of experimental data using the Langmuir and Freundlich models, respectively. The Freundlich model exhibits a superior match with a regression coefficient of R^2 = 0.9039, in contrast to R^2 = 0.8264 for the Langmuir model.

Table 1. Adsorption isotherm model

Isotherm model	Parameters	Values
Langmuir	q_{max} (mg/g)	6,7431
	K_L	0,0592
	R^2	0,8264
Freundlich	K_F	0,6469
	n	1,8376
	R^2	0,9039

Table 2. Comparison of the maximum adsorption capacity (q_{max}) values of Cu(II) ion by agricultural wastes as adsorbents

Adsorbent	q_{max} (mg/g)	References
Corncob	4.96	[51]
Sugarcane bagasse	3.65	[52]
Groundnut, sesame and coconut seed cake powder	4.24	[53]
Coconut tree sawdust	3.89	[52]
Raw almond shell	2.41	[54]
Pine cone shell	6.52	[55]
HNO_3-modified sorghum stem	6.74	This study

The adsorption capacity of HNO_3-modified sorghum stem was compared with some sorbents prepared from agricultural waste in Table 2. HNO_3-modified sorghum stem had a higher adsorption capacity for Cu(II) than some adsorption materials. The results showed that HNO_3 modified sorghum stem have significant potential as heavy metal adsorbents. Data obtained from experiments showed that HNO_3 modified sorghum stem were able to effectively reduce the copper ions in solution. Further analysis showed that modification with HNO_3 resulted in an increase in the surface area and number of functional groups on the sorghum stems. The interaction between heavy metals and functional groups on the surface of sorghum stem is likely to be the main mechanism in heavy metal sorption. In addition, the morphological properties and chemical composition of modified sorghum stem also contribute to their ability as effective heavy metal adsorbents.

The implications of these findings suggest that HNO_3 modified sorghum stem have significant potential in applications as heavy metal adsorbents. The use of easy-to-find and inexpensive raw materials and the relatively simple modification process make it an attractive alternative in the remediation of heavy metal pollution in the environment. In addition, the regeneration ability of this adsorbent can also improve the sustainability of the heavy metal removal process on an industrial scale. Overall, this study shows that HNO_3 modified sorghum stem have great potential as heavy metal adsorbents and make an important contribution to environmental pollution management efforts. By continuing this research, it is hoped that more effective and sustainable solutions can be achieved in addressing heavy metal pollution problems in the future.

CONCLUSIONS

An investigation was conducted to study the effect of chemical modification using HNO_3 pretreatments on sorghum stem to decrease the concentration of copper ions. The characterization data validate that the surface of the modified adsorbent underwent a smoother transformation, resulting in an augmentation of both porosity and pore size. Analyzed and acquired were the working parameters, such as the initial metal ions concentration, pH, and contact time, which were found to impact the sorption effectiveness of the modified adsorbent. The adsorption process is primarily driven by physical adsorption, substantiated by the Freundlich model. The altered sorghum stem showed excellent potential as an adsorbent, exhibiting high effectiveness in adsorbing copper ions from aqueous solutions. Its utilization is straightforward, and it offers a cheap method for removing copper ions.

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