ISSN: 2754-4915

Journal of Material Sciences & Manufacturing Research

SCIENTIFIC Research and Community

Research Article

Open Access

Application of Biochar for the Removal of Cadmium from Industrial Waste

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ABSTRACT
The growing levels of cadmium (Cd) in environmental contexts substantially threaten public health and ecosystems. This research explores the effectiveness of biochar produced from agricultural waste as a sustainable material for capturing cadmium ions from industrial wastewater by employing batch adsorption experiments conducted under controlled laboratory conditions. The experimental factors considered were contact time, initial cadmium concentration, pH, and biochar dosage were meticulously analyzed. The findings revealed a swift adsorption process, achieving over 85% cadmium removal in just 65 minutes. The optimized pH for optimal cadmium adsorption was determined to be 7.0, which minimized competitive ion interactions. The adsorption equilibrium was described by both Freundlich and Langmuir isotherm models, with Langmuir demonstrating a more accurate fit (R^2 = 0.9569), suggesting the presence of monolayer adsorption on a surface with a limited number of identical sites. Kinetic studies indicated that the adsorption followed a pseudo-second order model, highlighting the significance of chemisorption due to the high equilibrium adsorption capacity values (qe) ranging from 3.709 to 7.880 for pseudo-second order compared to 6.720 for pseudo-first order. Conclusively, this shows that biochar is a viable and sustainable substrate that can be efficiently utilized for combating cadmium contamination in industrial waste streams. Thus, enhances environmental conservation and resource recovery initiatives.

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Received: July 14, 2025; **Accepted:** July 17, 2025; **Published:** July 28, 2025

Keywords: Cadmium, Biochar, Adsorption

Introduction
As industrialization progresses and the variety and volume of agricultural chemicals increase, pollution from heavy metals in natural water bodies and soils—stemming from industrial waste, pesticides, and fertilizers—has escalated. Heavy metal contamination poses a serious risk to environmental ecosystems and human health due to its persistent and elusive nature. Consequently, effectively removing heavy metals from water and soil has been a critical public concern for many years. Given that heavy metals resist biodegradation or transformation, recent years have seen researchers focusing on adsorption and immobilization as promising treatment strategies in environmental remediation. Amid the dual pressures of economic development and environmental sustainability, biochar has gained considerable attention for its applications in environmental pollution control as well as its ecological and economic advantages.

Biochar is a carbon-rich by product formed through the pyrolysis of biomass, including plant debris, industrial by-products, and agricultural residues, in an anoxic or anaerobic environment at temperatures below 1000 °C. It is regarded as an environmentally friendly and cost-effective material capable of adsorbing and fixing organic contaminants and heavy metals from water and soil. Biochar contains stable carbon and abundant nutrients, making it useful for enhancing soil properties and aiding carbon sequestration due to its extensive micropore structures and rich functional groups. As an adsorbent, biochar effectively removes heavy metals from water and immobilizes them in soils, fostering a sustainable approach to biomass waste utilization while achieving environmental remediation. However, its efficiency in water and soil heavy metal removal remains limited, creating a need for biochar modification to enhance its effectiveness. A search in the Web of Science (SCIE) from 2008 for topics related to "modified biochar" returned a total of 3,310 publications as of April 22, 2022. After analysing the publication timeline, it became evident that research in this area has consistently increased since 2009, particularly in the last five years. Furthermore, keyword co-occurrence analysis using Citespace from January 2009 to April 2022 indicated a strong relation between modified biochar research and the treatment of heavy metal pollution in environmental media, with mechanisms of sorption and removal being key focal areas.

Cadmium is recognised by the World Health Organization (WHO) as a toxic heavy metal which is a significant contaminant of concern in the environment. It notably has a strong association with water and soil; thus, it poses high health risks relative to kidney and lung damage in addition to being detrimental to the environment. It is a non-essential, toxic trace element with application span around industries such as metallurgy, and electronics. Its mode of entry into soil is via emission, wastewater and industrial by-products.

The persistent characteristic of cadmium and its high potential to cause serious health damage underscores the need for continuous research. This research aims to assess biochar's effectiveness in remediating cadmium presence in wastewater. Furthermore, to determine the optimal conditions, the adsorption mechanisms and the effect of its surface properties on cadmium adsorption.

Biochar

Biochars, produced from biomass pyrolysis in low-oxygen settings, offer promising applications for carbon sequestration, improving soil fertility, and adsorbing heavy metals and organic compounds from water. However, their benefits are tempered by high production costs, necessitating the development of cost-effective biochar production from readily available waste materials. Despite biochar's potential as a pollutant adsorbent, concerns about environmental consequences due to possible high heavy metal concentrations in the raw feedstocks must be addressed to ensure safe industrial waste management and removal.

Methods for Preparing Biochar

Biochar can be produced through various techniques, with pyrolysis being the most prominent. This process involves the thermal decomposition of organic material at high temperatures in an oxygen-free environment. Pyrolysis can be categorized into three types: slow, rapid, and "flash," depending on the temperature and duration of the process [1, 2]. Slow pyrolysis typically yields around 35% solid product, making it the primary method for biochar production among the pyrolysis techniques [3]. Another significant method is hydrothermal carbonization (HTC), which produces biochar that is particularly effective at adsorbing contaminants in water without generating harmful byproducts. Nevertheless, HTC has limitations, such as requiring high pressure and temperature, along with potentially high reactor costs, which may hinder its practical use [4]. Recent research suggests that treating sewage sludge and digestate with HTC can address its energy demands more efficiently than other thermochemical methods, producing more stable hydrochar that can enhance biogas production and soil health (Parmar and Ross 2019). Further research is needed to explore the integration of HTC with anaerobic digestion for large-scale applications. Besides, slow pyrolysis and HTC, other methods like rapid pyrolysis, "flash" pyrolysis, gasification, and drying are also used, but these often generate lower yields of solid products and are typically aimed at producing bio-oil or gas instead [5]. For instance, gasification yields approximately 85% gas.

Biochar Characteristics

The physical and chemical properties of biochar are significantly influenced by the type of biomass used and the conditions under which it is prepared. Almost any biomass can theoretically be transformed into biochar. Common feedstocks include agricultural, aquatic, and forestry products, as well as various biowastes like husks, sawdust, and even municipal solid wastes and sewage sludge [6]. Factors affecting biochar properties include the type of raw material, particle size, pyrolysis type (slow, rapid, or flash), temperature, heating rate, and duration of pyrolysis, all of which can significantly alter the quality of the final product [1, 7, 8]. Biochar is characterized by a high number of surface functional groups, such as hydroxyl, methyl, carbonyl, and carboxyl groups [9]. Its structure marked by high carbon content, oxygen-containing aromatic groups, and porosity enhances its ability to adsorb pollutants [10].

Factors Influencing Biochar Activity

Biochar's effectiveness is dependent on several factors including pyrolysis temperature, residence time, feedstock composition, and the thermal conversion technology used. These elements significantly influence the biochar's capability to remove various contaminants [11]. For example, research demonstrated that as the temperature of biochar produced from pine needles increased from 100 to 700 °C, its pore size and surface area also increased [12]. Similarly, it was noted that higher temperatures correlate with a greater presence of carbonized matter and an increase in adsorption capacity for organic contaminants such as naphthalene [13,14]. The increased carbonized matter promotes the removal of organic contaminants containing oxygen and hydrogen functional groups [13]. Additionally, optimizing pyrolysis temperatures can improve the adsorption of toxic metals onto biochar. For instance, investigation shows the influence of pyrolysis temperatures exceeding 500 °C on biochar, focusing on its pH and surface area relative to cadmium adsorption [15]. Interestingly, it was found that higher pyrolysis temperatures could reduce the efficiency of chromium (VI) removal from aqueous solutions, indicating a decrease in oxygen-containing functional groups that are crucial for adsorbing toxic metals [16].

Research has shown that as pyrolysis temperatures rise, the biochar's surface area increases, while the quantity of oxygen-containing functional groups declines, potentially reducing the adsorption capacity for toxic metals [17]. Inyang et al. observed that lead adsorption from biochar decreased as the pyrolysis temperature escalated from 250 to 600 °C due to fewer oxygen-containing groups at higher temperatures. Another notable factor affecting biochar's adsorption properties is the feedstock's composition. The presence or absence of minerals such as CO32− and PO43− can significantly enhance the biochar's adsorption capacity by creating additional active sorption sites for potentially toxic metals from wastewater [18]. In contrast, biochar produced via hydrothermal carbonization tends to have more oxygen-containing functional groups, which can enhance its adsorption capacity [19]. This is supported by another study focused on copper removal from wastewater using biochar generated through HTC and pyrolysis [20].

Theory of Adsorption

Adsorption is the phenomenon where gas or liquid molecules interact with and cling to a solid surface and it occurs at the interfaces between various phases, including liquid-liquid, gas-liquid, gas-solid, and liquid-solid, with the focus in water and wastewater treatment being on the liquid-solid interface. The process of adsorption for different substances onto solids arises from the increased free surface energy of solids relative to their large surface areas. According to the second law of thermodynamics, this energy must be minimized, which is accomplished by decreasing surface tension through the accumulation of external substances from both solid and liquid surfaces and the internal surfaces of porous materials. Adsorption is a prevalent method for purifying drinking water and treating wastewater, notably for removing heavy metals. The classification of adsorption is based on the type of bonding involved and can be categorized into:

- **Physisorption:** This form of physical adsorption results from energy differences and weak attractive forces like Van der Waals forces. Here, liquid contaminants (adsorbates) attach physically to the solid surfaces (adsorbents). The reversibility of physisorption relies on the strength of these attractive forces; weaker forces permit easier desorption.
- **Chemisorption:** In contrast, chemisorption involves a chemical reaction that forms new compounds between the

adsorbent and the adsorbate. This process is typically single-layer and irreversible because it releases energy during the formation of chemical bonds, and reversing it would require additional energy.
- Both physisorption and chemisorption occur as molecules in the liquid phase adhere to the solid surface, driven by attractive forces that overpower the adsorbate's kinetic energy. The substance being removed is termed the adsorbate, while the solid, liquid, or gas phase onto which this substance accumulates is referred to as the adsorbent.

Factors Influencing Adsorption
- Properties of the adsorbate, including molecular size, polarity, concentration in solution, and chemical composition.
- Characteristics of the adsorbent, such as pore size, surface area, and chemical makeup.
- Parameters of the liquid phase, namely pH and temperature.
- The retention time within the system.

Mechanisms of Adsorption
The mechanisms involved in the removal of toxic metals include surface sorption, ion exchange, electrostatic interactions, precipitation, and complexation.
- **Surface Sorption:** This physical process forms chemical bonds as metal ions diffuse into the pores of the adsorbent. The amount of surface area and pore volume in biochar, for example, is influenced by the carbonization temperature. Studies have shown that higher carbonization enhances the adsorption capacity of metals like uranium.
- **Electrostatic Interaction:** This mechanism relies on the electrostatic forces between charged biochar and metal ions, facilitating the immobilization of toxic metals. Increased pyrolysis temperatures can enhance this interaction, thus improving adsorption efficacy.
- **Cation/Ion Exchange Capacity:** This principle involves the exchange of protons and ions on the biochar surface. Better adsorption of heavy metals correlates with higher cation exchange capacities, though this may decrease at higher pyrolysis temperatures.
- **Precipitation:** In this method, mineral precipitates form either within the solution or on the adsorbent surface. The effectiveness of precipitation depends on the production conditions of the biochar, with higher pyrolysis temperatures suitable for alkaline properties that enhance metal removal.
- **Complexation:** This occurs when multi-atom complexes are formed via interactions with specific metal ligands. Biochar produced at lower temperatures is particularly adept at binding metals due to its oxygen-rich functional groups.

The physical and chemical characteristics of biochar significantly influence its effectiveness in adsorbing pollutants. These traits affect adsorption kinetics and mechanisms through chemical bonding and mass transport. Research indicates that understanding the adsorbent's surface area, diffusion mechanisms, and chemical reactions during adsorption is crucial for applying biochar effectively on a large scale. Kinetic studies often confirm that many pollutant removals via biochar conform to a pseudo-second-order kinetic model, underscoring the importance of chemical sorption as a rate-limiting step.

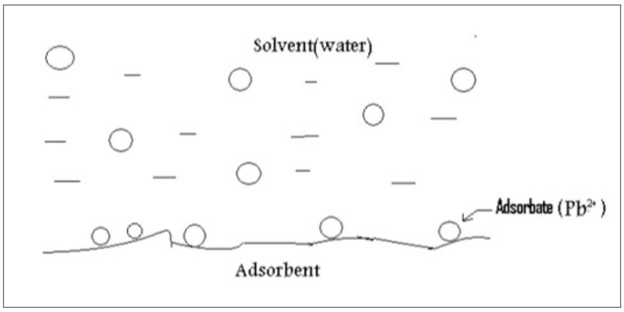

Figure 1: Mechanism of Adsorption

Adsorption Isotherm Models
Adsorption isotherm models are commonly employed to describe the equilibrium relationship between metal ions in solution and those adsorbed on the surface. These studies inform about the adsorbent's ability to sequester a specific quantity of metal ions under defined conditions. The dynamic equilibrium is reached when a certain amount of metal species is balanced with the remaining dissolved metal in solution. The most widely used isotherm models include the Langmuir and Freundlich isotherms. The Freundlich model is empirical and applies to heterogeneous surfaces with varying affinities, while the Langmuir model suggests a monolayer adsorption onto a surface with a limited number of uniform adsorption sites. The Langmuir adsorption isotherm, in its non-linear form, includes fundamental assumptions about surface homogeneity, localized adsorption, and single accommodation for each site. It has been effectively used to characterize the uptake of heavy metals, aiding in the evaluation of microorganisms' adsorption capacities and providing insights into conditions conducive to effective metal removal systems.

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

Where;
q_{max} = is the monolayer adsorption capacity of the adsorbent (mg/g) is the (maximum Amount adsorbed)

K l= is the Langmuir adsorption constant (L/mg)
C_e = the equilibrium metal ion concentration in the solution (mg/L),
q_e= is the equilibrium metal ion concentration on the adsorbent (mg/g)
The solid phase equilibrium metal concentration which is the amount of metal adsorbed
On the biomass surface in a batch system was calculated using the following mass

Balance equation:

$$q = v\,\frac{(C_o - C_t)}{W}$$

Were
q = is the metal uptake (mg metal/g biomass),
c_o = initial metal concentrations in the solution (mg metal/l fluid)
c_t = final metal concentrations in the solution (mg metal/l fluid),
V = the volume of solution,
W = is the dry weight of the added sorbent (g)

The Freundlich model is the most popular adsorption model for a single solute system. The model has found broad acceptance because of its accuracy and broad applicability. The Freundlich model assumes a heterogeneous adsorption surface and dynamic sites with different energy. The Freundlich model (Freundlich equation) is

$$\text{In } q_{e=} \text{ In}^{k}{}_{f+\frac{1}{n}} \text{ In } c_e$$

Were

q_e = amount of the adsorbate per unit weight of adsorbent (mg/g).

k_f = is a constant relating to the adsorption capacity (Freundlich constants)

$\frac{1}{n}$ = is an empirical parameter relating to the adsorption intensity

(which varies with the heterogeneity of the material).

Materials and Method

Method/Procedure

Apparatus: pH meter, electronic balance, mechanical stirrer, measuring cylinder, conical flask (250 ml), spatula, filter papers, test tubes, centrifuge, drying oven, beakers, volumetric flask (500ml), muffle furnace, crucibles, masking tape, mechanical agitator, UV spectrophotometer.

Reagents: Ethanol (300 ml), HCl (300 ml), NaCl (100 g), NaOH (100 g), Cadmium, Biochar.

Adsorption Studies

1.0g of adsorbent was added into 100 ml of solution containing 0.95 g of cadmium with a concentration of 200 mg/L in a 250 ml conical flask and agitated at a speed of 150 rpm for 24 hours. Afterwards, it was allowed to settle for 20 minutes and a 15 ml aliquot was taken from the solution and placed in a special container. The experiment continued for another 20 minutes until we arrived at 120 minutes while pH 7 was maintained. Finally, the 5 samples were subjected to AAS analysis to determine the amount of dye absorbed at equilibrium qe and the removal efficiency of Cadmium. The amount of cadmium absorbed at equilibrium q_e and removal efficiency of Cadmium was calculated using the Equations below:

$$q_e = (c_i - c_e)\frac{v}{w}$$

$$\% \text{ Removal} = \left(\frac{(c_i - c_e)}{c_i}\right) \times 100$$

C_i: initial cadmium solution concentration (mgL^{-1})

C_e: final cadmium solution concentration (mgL^{-1})

V: volume of cadmium solution (L)

W: mass of biochar (g)

Adsorbate Preparation

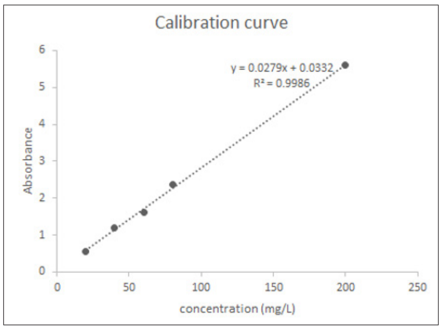

Figure 2: Calibration Curve

0.25 g Cadmium was dissolved in a 500 cm^3 volumetric flask making 500 mg/L stock solution. 10 cm3 of the stock solution was taken and diluted in 100 cm^3 of distilled water making a 100 mg/L stock solution. The experiment proceeded by preparing a serial dilution solution of different concentrations (2, 4, 6, 8, and 20 cm^3) and the absorbance of each solution was measured. The calibration curve shown in Figure 2 was plotted to obtain the absorbance-concentration profile and used to determine unknown cadmium concentration.

Results and Discussions

Effects of Different Experimental Conditions on Cadmium Removal

Effect of Temperature

2 g of biochar was measured and added into 80 ml of 0.1 M of sodium chloride in a beaker, and 0.19 g of cadmium was added to three different beakers containing 2 g of biochar. The temperature varies at 25, 35 and 50°C. Finally, agitated for two hours and the absorbance was taken for each sample. The results obtained are shown in the table below. The concentration of Cadmium was found to decrease with an increase in temperature. It further showed that the efficiency in the removal of cadmium using biochar was low at moderate temperatures and optimum at high temperatures.

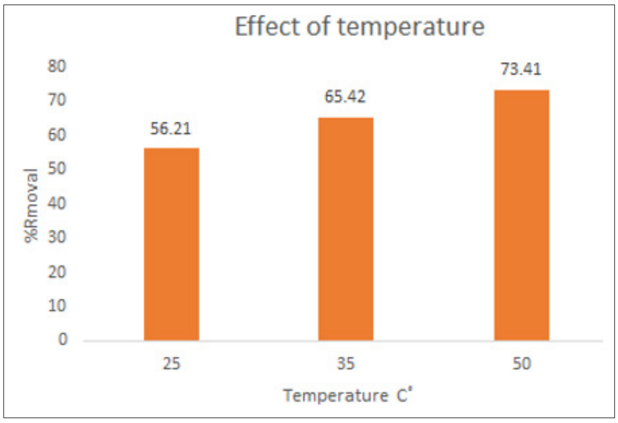

Figure 3: Effect of Temperature Graph

Effect of Contact Time

The adsorption study was done by varying the time from 20 to 100 minutes to study the adsorption capacity of biochar. From the figure below, the concentration of cadmium with biochar decreased with the increase in time which started from 20mins and decreased with time until it reached 100mins. Therefore, the longer the time it takes within the process, the higher the removal of cadmium at equilibrium.

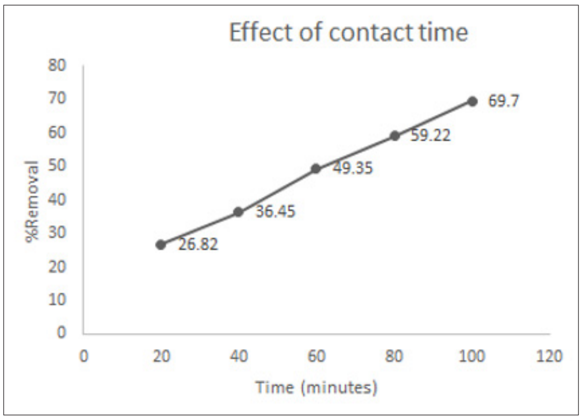

Figure 4: Effect of Contact Time

Effect of Concentration
The influence of initial cadmium concentration on the adsorption capacity of biochar can be seen in Figure 5. The initial concentration of adsorbent for this study was varied from 20 to 100 mg/L. The Figure reveals that the amount of cadmium adsorbed per unit mass of biochar increases as the initial dye concentration in solution increases. This implies that the adsorbent becomes saturated as the concentration of cadmium increases from 20 mg/L to 200 mg/L.

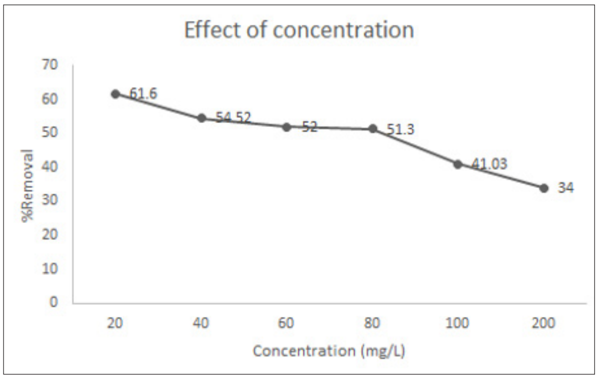

Figure 5: Effect of Concentration Graph

Adsorption Isotherm Models
As seen from the table below, the R^2 value obtained from the Langmuir was higher when compared to that of the Freundlich model hence, our adsorption process obeys the Langmuir isotherm model which shows monolayer adsorption. In addition, the values of RL ranging from 0.017-0.066 and 1/n of 0.210 obtained from both isotherms showed the favourable adsorption of cadmium.

Table 1: Adsorption Isotherm Data.

Isotherm	Parameter				
Langmuir	T(K)	qm (mgg^{-1})	KL (Lmg^{-1})	RL	R^2
	298	6.89	0.611	0.017-0.066	0.9569
Freundlich	T(K)	Kf(mg/l)($L/mg^{1/n}$)	1/n	R^2	
	298	2.5	0.210	0.9116	

Adsorption Kinetic Models
The kinetic models that were applied on this work are pseudo first and pseudo second order and via result obtained showed that the mechanism of the adsorption, highest level of adsorption and adsorption efficiency of erythrosine dye followed pseudo second order due to highest value of correlative coefficient R^2 which was 0.9980. Also adsorption capacity of the dye at equilibrium qe was high with the value of 3.709 to 7.880 in pseudo second order compared to pseudo first order with 6.720.

Table 2: Kinetic Data

Model	Parameter				
Pseudo first order	T(K)	qe,cal (mg/g)	qe,exp(mg/g)	K1(1/min)	R^2
	298	0.0211	6.720	0.033	0.9367
Pseudo second order	T(K)	qe,cal (mg/g)	qe,exp(mg/g)	1/n	R^2
	298	3.709	7.880	0.022	0.9980

Conclusion
This paper investigates the potential of biochar as an effective method for extracting cadmium from industrial waste. Cadmium contamination represents a serious threat to the environment, and biochar may provide a viable remediation solution. Produced via biomass pyrolysis, biochar possesses distinct characteristics that enhance its ability to adsorb cadmium. The study analyses the mechanisms involved in cadmium adsorption on biochar surfaces and the factors that influence this process. It also reviews recent progress in biochar applications for cadmium removal, while noting ongoing challenges such as optimizing biochar properties and ensuring its long-term effectiveness. Collaborative efforts among researchers, engineers, policymakers, and stakeholders are vital for advancing the development and application of biochar-based cadmium remediation techniques. In summary, biochar offers a sustainable and efficient means of combating cadmium pollution in industrial waste streams, which supports both environmental conservation and resource recovery initiatives [21-57].

Utilising biochar for cadmium removal from industrial waste demonstrates significant potential as a sustainable and effective remediation strategy. Its unique physicochemical characteristics and extensive surface area make it competent in cadmium adsorption and immobilization. The mechanisms of cadmium adsorption onto biochar have been clarified, emphasizing the influence of biochar properties, solution chemistry, and operational conditions. Recent improvements in biochar production and modification techniques have enhanced its effectiveness for cadmium removal across various waste streams. Nonetheless, challenges such as optimizing biochar characteristics, scaling production, and ensuring long-term stability in complex settings must be addressed to unlock its full capabilities. Advancing interdisciplinary research is crucial for deepening our understanding of biochar in cadmium remediation and applying this knowledge effectively. Collaboration among scientists, engineers, policymakers, and stakeholders will be key to devising customized solutions for different industrial waste scenarios, thereby ensuring environmental safety and sustainable resource management. Ultimately, biochar presents a promising option for reducing cadmium contamination in industrial waste, fostering a cleaner and healthier environment for both current and future generations. Ongoing research and innovation in this area are essential for maximizing the versatility of biochar as a tool in sustainable waste management. As per recommendation, the proposition of using biochar is optimistic due to its excellent adsorption capabilities, including high particle porosity, large surface area, efficiency, and cost-effectiveness in removing contaminants from the environment.

Conflicts of Interest

The authors declare no conflicts of interest.

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