Research Article

Synthesis of Iron-Modified Biochar Derived from Rice Straw and Its Application to Arsenic Removal

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A novel iron-modified biochar (FMBC) derived from rice straw was synthesized using FeCl_3 modification for efficient As(V) removal from aqueous solution. FTIR and SEM-EDX analyses were carried out to determine the mechanism involved in the removal process and also demonstrated that Fe had loaded successfully on the surface of modified biochar. The iron-modified biochar showed higher arsenic removal ability than the raw biochar. The iron-modified biochar showed a maximum adsorption with an initial solution pH of 5.0. Moreover, for the tested biochar, the As(V) removal kinetics data were well fitted by the pseudo-second-order model. Furthermore, the As(V) removal data upon being well fitted by the Langmuir model showed the maximal removal capacity of 28.49 mg/g. The simple preparation process and high adsorption performance suggest that the iron-modified biochar derived from rice straw could be served as an effective, inexpensive, and environmentally sustainable adsorbent to replace typical granular activated carbon (AC) for As(III) removal from aqueous solution.

1. Introduction

Arsenic is one of the most abundant elements in the biosphere and in the Earth's crust. Arsenic occurs in most natural waters as As(V), As(III), As (0), and As(−III) oxidation states. As-contaminated water affects a large group of population worldwide, particularly in Vietnam, China, and India. Chronic exposure to inorganic arsenic may lead to cancer or noncancer health effects [1]. Arsenic has been classified as a Class A carcinogen by the United States Environmental Protection Agency (USEPA). According to the World Health Organization (WHO) and USEPA, the limitations for As concentration are 10 $\mu\text{g/L}$

and 0.2 mg/L in safe drinking water and discharge wastewater, respectively [2]. Ingestion of arsenic, even at low concentration, has resulted in various detrimental health issues such as pulmonary disease, cardiovascular disease, nervous system dysfunction, and also cancer of the lung kidney and skin [3].

Coagulation/precipitation, ion exchange, reverse osmosis, and adsorption processes were utilized for arsenic-contaminated water remediation [4–6]. Among the various techniques, adsorption has been considered the most common and effective technology for removing contaminants from groundwater or wastewater [7]. Adsorption is often utilized at the end of a treatment plan for removal of

contaminants because of its low cost, and it does not generate any secondary waste that needs further treatment.

Biochar (BC), a carbon material produced mainly from the pyrolysis process of low-cost biomass residuals such as rice straw, has received much recent attention because of its many potential environmental abilities such as carbon sequestration, soil improvement, water treatment, and environmental remediation [8, 9]. BC can be utilized as an adsorbent because of its porosity, large surface area, and negative surface charge that can be useful for decontaminating water (organic and inorganic pollutants) [10]. Some BCs can be utilized for removal of heavy metal ions or organic polluted compounds in the aqueous solution. However, the lack of adsorption sites and functional group limits its application to As removal [11, 12]. Many researchers have modified BCs to improve their properties such as enhance the surface functional groups for effective adsorption [13, 14]. Several studies have utilized metal oxyhydroxide surfaces and clay minerals containing Fe, Mn, Al, Cu, and Co to remove As in the aqueous solution [15]. Hematite, an abundant and natural Fe mineral, was a good adsorbent for As removal from groundwater [16]. The hematite mineral was activated by the thermal method to enhance its ability to remove aqueous As [17].

Vietnam is the world's fifth largest rice producer all over the world. The total amount of rice straw generated was approximately 67 million dry ton in 2013. In order to reduce the environmental problem from rice straw burning, it is necessary to find a suitable method to remove the excess rice straw. Therefore, biochar derived from rice straw can be an effective, inexpensive, and environmentally sustainable adsorbent for environmental treatment and can reduce atmospheric pollution from rice straw burning.

In the present study, dried rice straw was used for the preparation of biochar by slow pyrolysis and then modified with the mixture of FeCl_3 and FeSO_4 before being applied for the removal of As(V) in aqueous solution.

2. Materials and Methods

2.1. Biochar Production. In this study, the rice straw biomass was collected from a rice farm in the city of Hanoi, Vietnam. It was pyrolyzed at a temperature of 500°C for 1 h using a tube-type electrical furnace under N_2 gas. The biochar was collected from the reactor after being cooled till a room temperature of $25\text{--}30^\circ\text{C}$ inside the muffle furnace. The iron-modified biochar was synthesized by the following procedure. 10 g of the obtained BC was mixed with 500 ml of 7.3 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 7.23 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in a glass tube. This mixture was heated at 50°C to form a stable suspension. The pH was raised to 11 by adding 0.05 M NaOH solution, dropwise. After mixing for 60 min, the organic residues were removed by washing with distilled water (H_2O) until the pH of the washing solution reached 7.0. The fine powdered modified biochar (FMBC) was vacuum-filtered and then dried overnight at 50°C in a hot air oven [18].

2.2. Characterization of Biochar (BC). The surface architecture of the synthesized BC (FMBC) was examined using a JED-2300 Analysis Station Plus (JEOL) scanning electron microscope (SEM). Energy-dispersive X-ray (EDX) spectroscopy analyses were carried out using a Quantax instrument (Bruker, USA). The infrared (IR) spectra of synthesized materials (as KBr pellets) were analyzed. The surface functional groups of FMBC were analyzed by using an IR spectrophotometer (PerkinElmer FTIR, USA) with an attenuated total reflectance attachment within the wavelength of $400\text{--}4,000\text{ cm}^{-1}$.

The point of zero charge (PZC) of FMBC was determined by using the pH drift method of 0.01 M NaCl pH interval of 2 and in the range of pH 2 to 12 [19]. The pH values of solutions were adjusted between 2 and 12 by using 0.1 M HCl or 0.1 M NaOH solution. The initial pH values of solutions were measured. A 0.2 g of biochar was added into a beaker with 20 mL of NaCl solution and left undisturbed for 24 h under N_2 bubbles to prevent CO_2 dissolution until the pH value became stable, and then final pH of the solutions was measured. The final pH was measured, and pH_{PZC} was determined as the value at which $\text{pH}_{\text{final}} = \text{pH}_{\text{initial}}$.

2.3. Batch Sorption of Arsenic. Adsorption experiments were conducted to determine the isotherms of arsenic sorption onto the FMBC sample. About 0.2 g of the FMBC was mixed with 100 mL of As(V) solution for each experiment. The mixture was then shaken in a mechanical shaker (120 rpm) at room temperature ($22 \pm 2^\circ\text{C}$). At the end of each experiment, the remaining As concentrations were determined by using inductively coupled plasma mass spectrometry (ICP-MS) after vacuum-filtered. Duplicate sets of samples were taken for the analysis of residual concentration of As, and the difference of two measurements should be smaller than 10%. All chemical reagents used in the experiments were of high purity grade from Sigma-Aldrich.

The amount of As(V) adsorbed onto the FMBC (adsorbent) was calculated by the concentration difference between the initial and final concentrations of the solution by using the following equation:

$$q_e (\text{mg} \cdot \text{g}^{-1}) = [C_o - C_e (\text{mg L}^{-1})] \times V (\text{L}) / W (\text{g}). \quad (1)$$

Hence, q_e is the equilibrium amount of the As(V) adsorbed ($\text{mg} \cdot \text{g}^{-1}$) on the FMBC, C_o and C_e are the initial and equilibrium concentration of As(V) (mg/L), V is the solution volume of the test sample (L), and M is the total mass of Fe-modified BC added (g).

2.4. Adsorption Isotherms and Kinetic Models. The equilibrium adsorption isotherms were utilized to determine the adsorption mechanism. In this study, Langmuir isotherm and Freundlich isotherm models were utilized to analyze the adsorption process of biochar. Langmuir isotherm is valid for monolayer sorption and expressed in the following equation:

$$\frac{c_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{c_e}{q_{\max}}, \quad (2)$$

where $q_{\max}$ ($\text{mg}\cdot\text{g}^{-1}$) indicates the monolayer adsorption capacity and K_L ($\text{L}\cdot\text{mg}^{-1}$) is the heat of adsorption. The favorability or unfavorability of Langmuir adsorption can be expressed by

$$R_L = \frac{1}{1 + K_L C_0}, \quad (3)$$

where R_L indicates favorable adsorption and has the range between 0 and 1.

A Freundlich isotherm describes the heterogeneous surface energies by multilayer adsorption and is expressed in the following equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e, \quad (4)$$

where K_F expresses the adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$) and n is an empirical parameter related to the adsorption intensity, which varies with the heterogeneity of the adsorbent. The increase in $1/n$ enhanced the adsorption favorability.

The adsorption kinetic is an important characteristic influencing the adsorption efficiency. The pseudo-first-order and pseudo-second-order kinetic models express the adsorption process as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \quad (\text{pseudo - first - order model}),$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t, \quad (\text{pseudo - second - order model}), \quad (5)$$

where q_e and q_t ($\text{mg}\cdot\text{g}^{-1}$) are concentrations adsorbed at equilibrium and at different time t and the parameters k_1 (min^{-1}) and k_2 ($\text{g}\cdot\text{mg}^{-1}\text{min}^{-1}$) are the equilibrium rate constants of pseudo-first-order and pseudo-second-order kinetic models, respectively.

3. Results and Discussion

3.1. Characteristics of BCs. The SEM analysis was investigated for the determination of shape, size, and surface morphological structure of the raw biochar (RB) and FMBC. Figure 1 reveals the surface morphologies of the two samples are distinctly different. The Fe-modified biochar showed more heterogeneous structure than the raw biochar after modification process that can contribute to enhance the sorption of As(V) in the aqueous solution [20].

The FTIR spectrum of RB and FMBC is shown in Figure 2, representing the functional groups on the RB and FMBC material introduced by the chemical modification process. The peaks found in the spectrum of the RB and FMBC show almost similar wavenumbers. Several peaks obtained around wavenumbers 1,605 and 1,379 cm^{-1} , which were assigned to C=O and C-O peaks that were attributed to carboxyl and lactone functional groups, respectively [21]. The peaks at 3,409 and 1094 cm^{-1} correspond to vibration of O-H of the adsorbent [22]. Vibration of the Fe-O peak was

observed on the FMBC at 780 cm^{-1} . These FTIR results indicated that the chemical modification plays an important role in the changing properties of biochar. The modification process enhanced the functional group intensity on the surface of the biochar; thus, these functional groups can be new active sites for the adsorption improvement on the biochar. The EDX spectra of the RB and FMBC (Figure 3) further indicated the increasing Fe content on the biochar surface after modification. It revealed that magnetite was added to the biochar surface after the modification process.

The point of zero charge (PZC) of a biochar determines the pH at which the surface of the biochar has positive or negative charge [23]. In this work, the points of zero charge of RB and FMBC were 5.44 and 6.88, respectively (Figure 4). The acidic value of the FMBC indicated that arsenic removal is feasible below this pH because the net positively charged surfaces are favorable to attract the anions.

3.2. Effect of Initial Solution pH. A pH solution is an important adsorption parameter for the adsorption study because the pH solution demonstrates the H^+ ions of specific functional groups on the biochar surface and varies the form of As in the solution. pH_{PZC} also plays an important role in the adsorption process. At $\text{pHs} < \text{pH}_{\text{PZC}}$, the surface of the FMBC is positively charged and gives a strong electrostatic attraction between surface groups and anion species in the solution that could enhance the adsorption process. The decrease in the adsorption amount observed at pH higher than pH_{PZC} (when the surface of the adsorbent is negatively charged) could lead to increased competition between OH^- and anion species for the adsorption sites [24]. The effect of solution pH on the adsorbent's arsenic sorption (removal) was identified by varying the initial solution pH while keeping other sorption parameter constants. The pH effect on adsorption was determined by mixing 1.0 g of modified BC with 100 ml of a 10 mg/l As(V) solution at various pH values ranging from 2.0 to 8.0 for 120 min.

The pH effect ranging from 2.0 to 8.0, on the adsorption of As(V) on biochar, is shown in Figure 5. The removal of As(V) ions was relatively low in the alkaline solution ($\text{pH} > 6.8$) compared with that at lower pH values, ranging from pH 2.0 to 6.8 (pH_{PZC}), because the OH^- ions at alkaline conditions can compete with As(V) anion for active sites under strong alkaline conditions, resulting in the blocking of As(V) adsorption on the surface of the modified BC. This is because As(V) existed in the aqueous solutions in the form of H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} , AsO_4^{3-} , and especially H_2AsO_4^- at the pH range of 2.0–6.0 [25]. Therefore, increasing the initial concentration of proton in aqueous solutions increased the level of As(V) removal under acid conditions, ranging from pH 2.0 to 6.8. The highest removal efficiency was 86.3 and 62.3% for FMBC at the condition of $\text{pH} < 6.0$ and $\text{pH} > 6.0$, respectively. The RB showed lower removal efficiency even under the condition of $\text{pH} < 5.0$. This demonstrates the feasibility of the FMBC for As(V) removal from wastewater with pH values in the range of 4–7.

FIGURE 1: SEM images of raw biochar (RB) and iron-modified BC (FMBC).

FIGURE 2: FTIR spectra of RB and FMBC.

3.3. Effect of Initial Concentration. Figure 6 shows the effect of initial concentration of As(V) ion solution for removal at a pH of 5.0 and a constant agitation speed of 150 rpm for 120 min. The amount of As(V) adsorbed increased with increasing initial concentration up to 30 mg/l, indicating that As(V) removal is highly concentration dependent. At lower concentrations, the amount of ions available for adsorption by a given amount of BC is less than the available sites on the adsorbent. However, at higher concentrations, the number of available sites for adsorption decreases. These results indicate that the adsorption removal of the As(V) ions depends on the initial concentration. Figure 3 shows the removal efficiency of FMBC decreased from 91.5 to 63.5% when the concentration increased from 4 to 30 mg/L.

3.4. Effect of Phase Reaction Time. The As(V) removal was also controlled by the reaction time. The rapid interaction of the As(V) ions to be removed by BC is desirable and beneficial for practical removal of arsenic anions from aqueous solutions or wastewater. Figure 7 shows the effects of reaction time for arsenic ion removal by the FMBC. For a given concentration of As(V), the amount of adsorbed As(V) ions was almost proportional to the increasing reaction time up to 45 min. The adsorption equilibrium was obtained at a reaction time of 90 min, with an adsorption capacity of 23.57 mg/g. The adsorption rate was relatively fast at the initial adsorption stage but then slowed down gradually after more sites were occupied by the adsorbed As(V) ions. The slower adsorption was due to the gradual decrease in the number of available adsorption sites.

3.5. Adsorption Isotherm. The adsorption isotherm data of FMBC were fitted to the Langmuir and Freundlich isotherms were fitted to the Langmuir adsorption isotherm ($R^2 = 0.9955$) ($p < 0.01$) than the Freundlich isotherm ($R^2 = 0.9360$) (Table 1). The results showed a monolayer As(V) adsorption onto the adsorption sites of the iron-modified biochar. The maximum adsorption capacities ($q_{\max}$) of As(V) decreased in the order of FMBC ($28.49 \text{ mg} \cdot \text{g}^{-1}$) > RB ($10.3 \text{ mg} \cdot \text{g}^{-1}$). The controls showed that the As(V) adsorption capacity of FMBC was higher than that of RB. The adsorption capacity of FMBC may relate to the increasing number of surface functional groups of the modified material. The maximum adsorption capacity of the FMBC for As(V) ions, based on the Langmuir isotherm, was 28.49 mg/g. Table 2 compares this study's result for the As(V) adsorption capacity of FMBC with values reported from other similar studies. The adsorption capacity of FMBC was much higher than that of other commercial material, and the FMBC can be utilized as a green adsorbent for the removal of As(V) in groundwater.

FIGURE 3: EDX spectra of RB (a) and FMBC (b).

FIGURE 4: pH_{pzc} of RB and FMBC.

FIGURE 6: Effect of initial concentration for the As(V) removal on FMBC.

FIGURE 5: Effect of pH for the As(V) removal on RB and FMBC.

FIGURE 7: Effect of reaction time for the As(V) removal on FMBC.

TABLE 1: Adsorption isotherm of Fe-modified BC.

	Langmuir isotherm			Freundlich isotherm		
	$q_{\max}$ (mg/g)	K_L	R^2	$\ln K_F$	$1/n$	R^2
Fe1-BC	28.49	0.563	0.9955	2.2118	0.5128	0.9360

TABLE 2: Adsorption comparison with other studies.

Material	Adsorption capacity (mg/g)	Reference
TiO ₂ -CNTs	1.8	[26]
Biochar	7.21	[27]
Supported nanoscale zero-valent iron on activated carbon	12.0	[28]
Ascorbic acid-coated Fe ₃ O ₄ nanoparticles	16.56	[29]
Activated carbon	25	[30]
FMBC	28.49	This study
Activated carbon	34.46	[30]
Al ₂ O ₃ /Fe(OH) ₃	36.63	[31]

FIGURE 8: Groundwater sample before and after treatment.

The FMBC was applied for the removal of As(V) in the groundwater sample which had the concentration of As(V) 91 $\mu\text{g/L}$. Figure 8 shows the groundwater sample before and after treatment. The testing experiments showed that 1 kg of the Fe-modified BC can treat 278 and 141 m³ of contaminated groundwater to clean water of 50 $\mu\text{g/L}$ and 10 $\mu\text{g/L}$ As(V) based on the regulation of Vietnam for water supply and drinking water, respectively.

3.6. Adsorption Kinetics. Pseudo-first- and pseudo-second-order models were utilized to determine the kinetics of As(V) removal. The kinetic model of FMBC for As(V) in the aqueous solutions is shown in Table 3. The adsorption experimental data were best described by the pseudo-second-order kinetics that was proved by the obtained values of correlation coefficient ($R^2 = 0.988$) to describe the adsorption behavior of As(V) onto the modified BC. The experimentally obtained adsorption capacity ($q_{e(\text{exp})}$) values were close to the calculated data from the pseudo-second-order model, which also showed good evidence to support the

pseudo-second-order model and chemisorption [32]. For the pseudo-first-order kinetic model, the calculated adsorption capacity ($q_{e(\text{cal})}$) was much lower than the experimental value ($q_{e(\text{exp})}$) and the determination coefficient (R^2) was low ($R^2 = 0.844$).

Figure 9 presents the intraparticle diffusion model for sorption by the FMBC. The adsorption processes of As(V) are related by two steps—the first step depicting macropore diffusion and the second micropore diffusion [33]. In the first stage, the sharper portion may be considered as an external surface adsorption or faster adsorption stage. The second phase describes the gradual adsorption stage, where intraparticle diffusion is rate-controlled. These results of As(V) adsorption showed only the pore diffusion adsorption. The rate of uptake might be limited by the size of the adsorbate molecule, the concentration of the adsorbate and its affinity to the adsorbent, the diffusion coefficient of the adsorbate in the bulk phase, the pore-size distribution of the adsorbent, and the degree of mixing [34]. The first and second phases can be attributed to the external mass transfer and intraparticle diffusion mechanisms, respectively [35–

TABLE 3: Kinetic adsorption models.

$q_{e(\text{exp})}$ (mg/g)	Pseudo-first-order model			Pseudo-second-order model		
	$q_{e(\text{cal})}$ (mg/g)	K_1 (g/mg/min)	R^2	$q_{e(\text{cal})}$ (mg/g)	K_2 (g/mg/min)	R^2
28.49	3.238	0.0051	0.844	30.53	0.0892	0.988

FIGURE 9: Intraparticle diffusion model for As(V) removal by the FMBC.

37]. Furthermore, the regression did not pass through the origin, showing that the intraparticle diffusion is not the only rate-controlling step in the sorption process. Thus, it can be inferred that external mass transfer and intraparticle diffusion occurred simultaneously during the As(V) sorption onto the Fe-modified BC.

The pseudo-second-order model and Langmuir isotherm usually assume that chemisorption of As(V) on FMBC is the rate-limiting step; it is inferred that As(V) was likely adsorbed on the surface of FMBC via chemical interaction. The proposed mechanisms of the removal of As(V) onto the FMBC through the complexation with iron are shown in the following equations:

4. Conclusion

This study investigated the removal of As(V) from aqueous solution using iron-modified biochar (FMBC) produced from the slow pyrolysis of rice straw. The FMBC afforded maximum adsorption at a pH of 5.0. The adsorption data were strongly correlated with the Langmuir adsorption isotherm, indicating surface homogeneity and unilayer adsorption. The equilibrium sorption capacity of 28.49 mg·g⁻¹ for As(V), as determined from the Langmuir isotherm, was very high compared to that of previously reported adsorbents. The As(V) adsorption was well fitted with the pseudo-second-order kinetic model ($R^2 = 0.988$)

which showed good evidence to support the chemisorptions of As(V) onto Fe-modified BC. The arsenic removal capacity of the FMBC is comparable to that of many commercial water treatment agents, including AC. Because the FMBC can be produced from rice straw relatively inexpensively, this simple activation method can also be applied to other thermally produced BCs to create an alternative and value-added sorbent for arsenic removal in groundwater.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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