ADSORPTION OF ARSENATE IN WATER BY MAGNETIC $ZnFe_2O_4$/α-Fe_2O_3/BIOCHAR NANOCOMPOSITES: ISOTHERM AND KINETIC STUDIES

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ABSTRACT

The adsorption of arsenate into the water by magnetic $ZnFe_2O_4$/α-Fe_2O_3/biochar nanocomposite (MBC) were investigated in this article. Batch mode adsorption studies were carried out by varying pH, shaking temperature, and initial As^{5+} concentration. The adsorption of As^{5+} was pH dependent and showed maximum removal efficiency of As^{5+} at pH 8.0. Adsorption studies of 5–35 mg/L initial As^{5+} concentration were carried out at pH 8.0 and temperature of 303 K, 313 K, and 323 K. Langmuir and Freundlich, Temkin isotherm adsorption models were used to analyze the experimental data. The kinetic adsorption was studied using pseudo-first-order, pseudo-second-order, and Elovich models. The pseudo-second-order and Langmuir models fitted the adsorption of As^{5+} onto MBC. The adsorption of arsenate onto MBC was mainly controlled by the chemisorption and physisorption adsorption mechanisms. MBC could be easily recovered and reused using an external magnetic field. MBC had the potential to be high adsorption efficiency.

HẤP PHỤ ARSENATE TRONG NƯỚC BẰNG VẬT LIỆU TỔ HỢP NANO TỪ TÍNH $ZnFe_2O_4$/α-Fe_2O_3/THAN SINH HỌC: NGHIÊN CỨU NHIỆT, ĐỘNG HỌC

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TỪ KHÓA

Hấp phụ
Anion Arsen
Than sinh học
Từ tính $ZnFe_2O_4$/α-Fe_2O_3
Mô hình nhiệt học
Mô hình động học

TÓM TẮT

Sự hấp phụ arsenate trong nước bằng vật liệu tổ hợp nano từ tính $ZnFe_2O_4$/α-Fe_2O_3/than sinh học (MBC) đã được nghiên cứu trong bài báo này. Các nghiên cứu thực nghiệm hấp phụ được thực hiện bằng cách thay đổi độ pH, nhiệt độ rung lắc và nồng độ As^{5+} ban đầu. Khả năng hấp phụ As^{5+} phụ thuộc vào pH và cho thấy hiệu quả loại bỏ As^{5+} tối đa ở pH 8.0. Nghiên cứu sự hấp phụ asen ở nồng độ ban đầu là 5–35 mg/L được thực hiện ở pH 8.0 và nhiệt độ 303 K, 313 K và 323 K. Mô hình hấp phụ đẳng nhiệt Langmuir, Freundlich và Temkin được sử dụng để phân tích số liệu thực nghiệm. Động học hấp phụ được nghiên cứu bằng mô hình giả bậc nhất, giả bậc hai và mô hình Elovich. Các mô hình giả bậc hai và mô hình Langmuir được làm khớp phù hợp với sự hấp phụ As^{5+} trên MBC. Sự hấp phụ arsenate bằng vật liệu MBC chủ yếu được kiểm soát bởi cơ chế hấp phụ hóa học và vật lý. MBC có thể dễ dàng được thu hồi và tái sử dụng bằng cách sử dụng từ trường bên ngoài. MBC có tiềm năng đạt được hiệu suất hấp phụ cao.

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1. Introduction

Water, which is required for the survival of all living things on Earth, is facing a major global challenge as a result of environmental pollution. Arsenic (As) is one of the most well-studied heavy metals found in water. In recent years, magnetic biochar nanocomposite materials with numerous functional groups and excellent chemical stability have been developed for water treatment. These materials showed excellent ability to remove arsenic from water and have the potential for practical applications [1] – [3]. Arsenic is typically removed through methods such as oxidation, co-precipitation, membrane filtration, ion exchange, and adsorption [4]. Adsorption has recently been identified as an effective method for arsenic removal due to its high efficiency, low cost, and ease of use [2] – [8]. Among porous materials, magnetic nanoparticle-based biochar has received significant attentions [1], [2], [9]. The porous structure and magnetism of the materials allow contaminants to be transported and captured quickly. Several studies have demonstrated their excellent adsorption performance and potential practical use in arsenic removal. Zhang et al. synthesize γ-Fe_2O_3-based biochar material composite through pyrolysis method, and used it to adsorb As^{5+} from water with maximum adsorption amount of 3.147 $mg \cdot g^{-1}$. Wen et al. investigated the excellent adsorbent of arsenic from water on biochar supported $MnFe_2O_4$ magnetic nanocomposite [1].

Novel ternary magnetic $ZnFe_2O_4$/α-Fe_2O_3/biochar nanocomposite materials have high adsorption capacities and remarkable stability for removing pollutants in water [2]. Our previous study found that the $ZnFe_2O_4$/α-Fe_2O_3/biochar nanocomposite was successfully fabricated by one-step pyrolysis in oxygen-limited environment and used as an excellent adsorbent for simultaneous removal of direct red 79 species from water environment. This study investigates the effect of various experimental conditions, such as initial pH, initial arsenic concentration, shaking temperature, and contact time, as well as thermodynamics models on the ability to remove arsenic from water. Finally, the regeneration, and reusability studies of $ZnFe_2O_4$/α-Fe_2O_3/biochar nanocomposites were explored with the goal of evaluation the practical application.

2. Materials and methods

2.1. Materials

Peanut shells were collected from the local market in the Vietnamese province of Thai Nguyen and used as precursor materials for biochar production. Zinc Chloride Hexahydrate ($ZnCl_2.6H_2O \geq 98\%$) and Iron (II) Chloride Tetrahydrate ($FeCl_2.4H_2O \geq 98\%$) were acquired from Sigma Aldrich. Silver Nitrate ($AgNO_3$, 98%) was acquired from Xilong, China. Disodium arsenate (Na_2HAsO_4) were guaranteed reagent (purity > 99.5%). All of the water used in the experiments was distilled water.

2.2. Methods

2.2.1. Preparation of MBC

MBC adsorbent material was synthesized via direct pyrolysis in oxygen-limited conditions with the mass ratio of $ZnCl_2.6H_2O$ and $FeCl_2.4H_2O$ was set to 1 and activation temperature was set at 700^o C. The process of preparing MBC and properties are presented in detail in a previous study [2].

2.2.2. Adsorption experiment

The adsorption process of As^{5+} on MBC was studied through studying the effects of pH, adsorption time, temperature and initial concentration of As^{5+}. Adsorption experiments were performed on a model MAXQ 4000 Thermo Scientific with a shaking speed of 200 rpm. Typically, 25 mL of As^{5+} solution with a certain concentration and 25 mg of MBC were added into 50 mL glass flasks and shaken for a certain time. The effect of pH on the adsorption properties of MBC toward As^{5+} was studied using an As^{5+} solution with an initial concentration of 20 mg L^{-1}, and then adjusting the pH of the solution in the range of 2 to 9 using NaOH or HCl solution (0.1 mol L^{-1}). The kinetic experiments were carried out with As^{5+} initial concentrations of 20 mg/L at a pH of 8 at different temperatures (303 K, 313 K, and 323 K) and various time intervals (30 min to 20 h). The adsorption isotherm experiments were carried out by mixing 25 mL of As^{5+} solutions with various initial As^{5+} concentrations ranging from 5 mg L^{-1} to 35 mg L^{-1} at a pH of 8 for 360 min. The As^{5+} concentrations in the liquid phase samples were determined by using inductively coupled plasma-atomic emission spectrometry (ICPAES). As^{5+} concentrations on the solid phase were calculated based on the initial and final aqueous concentrations.

The removal efficiency (%) and the adsorption capacity of samples (mg/g) were calculated using the following equations, respectively:

$$H = \frac{C_0 - C_e}{C_0} 100 \quad (1)$$

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

3. Results and discussion

3.1. Effect of pH

The surface of MBC could be positively charged or negatively charged. Absorbent pore walls had several surface functional groups. The pH dependence of As^{5+} adsorption is mostly determined by the kind and ionic state of these functional groups, as well as the chemistry of the adsorbate in solution. The solution pH is a crucial parameter for heavy metal removal from aqueous solution because it affects adsorbate solubility, counter ion concentration on adsorbent functional groups, and the degree of ionization of the adsorbate during reaction [7]. As^{5+} removal was investigated as a function of pH over a pH range of 2-9 on MBC at the initial concentration of 20 mg/L as shown in Figure 1.

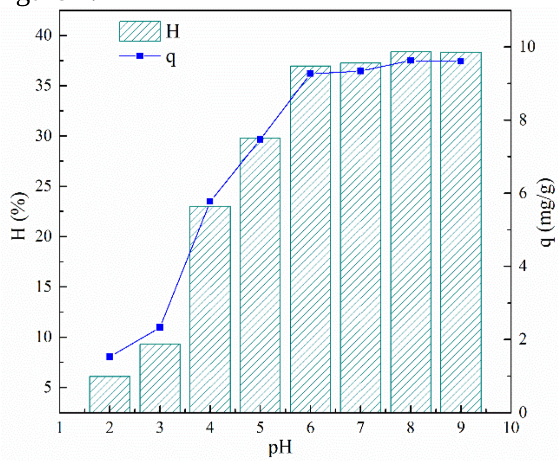

Figure 1. *Effect of pH on As^{5+} adsorption on $ZnFe_2O_4/\alpha\text{-}Fe_2O_3$/biochar*

As seen in Figure 1, metal ion adsorption is minimal at pH 3 and increases with increasing pH, and reaches its highest value at pH 8. Compared to acidic media, alkali solutions had overall heavy metal removal values that were significantly greater. Anionic arsenic adsorption is thought to decrease at lower solution pH, where the magnetic material behaves like a weak acid and can be destroyed by forming a negative surface [6], [8]. The increase in adsorption with increasing pH may be caused by the dominance of electrostatic attraction. Hence, pH 8.0 was taken as the optimal values for further studies of As^{5+} adsorption on MBC.

3.2. Effect of contact time

The amount of As^{5+} adsorbed on MBC was studied as a function of shaking time at initial concentrations 20 mg/L of As^{5+} at different temperature 303 K, 313 K, 323 K, 0.025 g of adsorbent and pH 8.0. The results are given in Figure 2(a). General, the removal and amount of As^{5+} adsorbed was found to be increased with increase in temperature. In the first 360 minutes of contact, MBC removes a greater quantity of As^{5+}, and the equilibrium is reached in 600 minutes. The fact that the As^{5+} ion reaches its maximal removal in 360 minutes and then stops adsorbing further indicates that the adsorption is very rapid. At an early stage of adsorption for the As^{5+}, a substantial number of empty sites with active functional groups were available on MBC. When the temperature rose from 303 to 323 K, the equilibrium adsorption of As^{5+} increased from 9.23 to 9.82 mg/g and the removal efficiency of As^{5+} increased from 36.80 to 39.15%, respectively.

3.3. Kinetics of adsorption

The adsorption of As^{5+} on the MBC was fast and reached equilibrium within 10 h (Figure 2a). The relatively fast kinetics suggests that biochar might play an import role in the dispersion of $ZnFe_2O_4/\alpha\text{-}Fe_2O_3$ nanoparticles which efficiently increased the surface area of the particles and active sites of metal oxides by separation [9]. The adsorption kinetics of the As^{5+} were investigated using the pseudo-first-order rate equation, the pseudo-second-order rate equation, and the Elovich model rate equation. The three sorption kinetic equations are expressed as follows in eqn (3)-(5):

The pseudo-first-order equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

The pseudo-second-order equation:

$$\frac{t}{q_t} = \frac{1}{k_2.q_e^2} + \frac{1}{q_e}t \tag{4}$$

Elovich equation:

$$q_t = \frac{1}{\alpha}\ln(\alpha\beta) + \frac{1}{\alpha}\ln(t) \tag{5}$$

where k_1 is the rate constant of the pseudo-first-order equation (min^{-1}), and k_2 is the rate constant of the pseudo-second-order equation (g mg^{-1} min), α (mg/g. min) is the initial adsorption rate, β (g/mg) is desorption constant during each experiment, q_e is the adsorption capacity at equilibrium (mg g^{-1}), and q_t is the adsorption capacity at any time t (mg g^{-1}).

Table 1. *The adsorption kinetics parameters of As^{5+} on $ZnFe_2O_4/\alpha\text{-}Fe_2O_3$/biochar*

		Pseudo-first-order			Pseudo-second-order			Elovich model		
T(K)	**$q_{e,exp}$ (mg/g)**	**k_1x10^{-3} (min^{-1})**	**$q_{e,cal}$ (mg/g)**	**R^2**	**k_2x10^{-3} (g mg^{-1} min)**	**$q_{e,cal}$ (mg/g)**	**R^2**	**α (mg/g. phút)**	**β (g/mg)**	**R^2**
303	9.12	0.00	2.387	0.61	3.20	9.528	0.999	0.672	0.553	0.851
313	9.46	0.00	2.773	0.76	3.08	9.604	0.999	0.688	1.596	0.886
323	9.69	0.00	2.664	0.67	2.86	9.771	0.999	0.706	2.398	0.873

The kinetics of adsorption As^{5+} by MBC were analyzed at different temperatures. Figure 2 (a,b,c) presents the results of fitting experimental data to the first-order, the pseudo-second-order, and the Elovich models, respectively. Best-fit parameters of the models are listed in Table 1. As shown in Table 1, the value of q_e calculated using the first-order kinetic model was much smaller than the value of the equilibrium adsorption capacity ($q_{e,exp}$) obtained from the experiment. In contrast, the value of q_e calculated using the second order kinetic model was similar to $q_{e,exp}$. This means that the first order kinetic model did not fit the absorption process of As^{5+} on the MBC compared to the second order kinetic model. Moreover, the correlation coefficient (R^2) of the second order kinetics model was almost 0.999 and was greater than that of the first order kinetics model. This result indicates that the second order model is the most suitable in describing the adsorption kinetics of As^{5+} on MBC, and this process is primarily controlled by chemical adsorption [2].

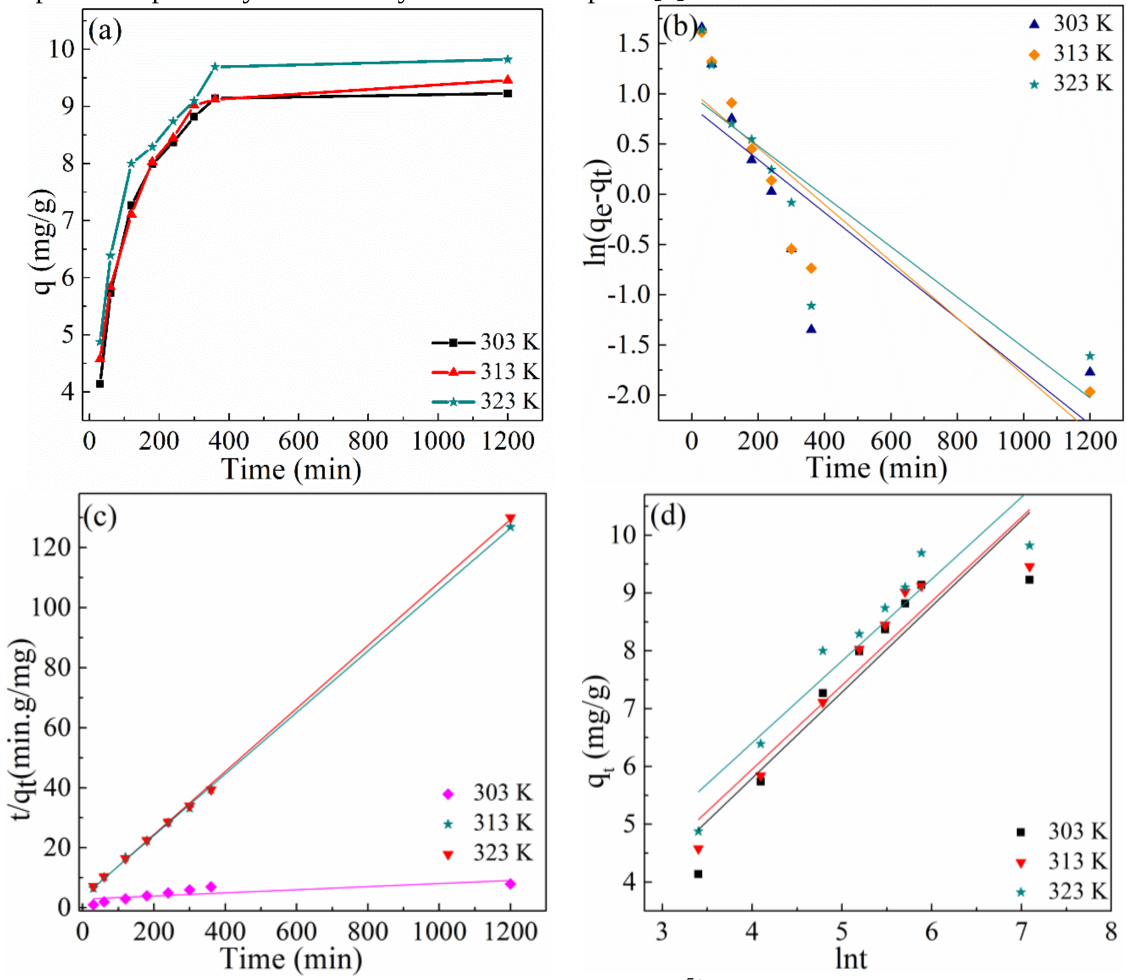

Figure 2. *(a) Effect of contact time on adsorption of As^{5+} by $ZnFe_2O_4/\alpha\text{-}Fe_2O_3$/biochar; (b) pseudo-first-order kinetic model; (c) pseudo-second-order kinetic model; and (d) Elovich model for the adsorption of As^{5+} by $ZnFe_2O_4/\alpha\text{-}Fe_2O_3$/biochar*

3.4. Adsorption isotherms

The adsorption isotherm is one of the important factors in designing an adsorption system. In fact, the adsorption isotherm describes the interaction between the adsorbent surface and the adsorbent. In this study, the adsorption isotherm experiments were carried out by mixing 25 mL of As^{5+} solutions with various initial As^{5+} concentrations (5, 10, 15, 20, 25, 30, 35 mg/L), 25 mg of the $ZnFe_2O_4/\alpha\text{-}Fe_2O_3$/biochar at temperatures 303K, for 360 min. To investigate the isotherm behaviors of As^{5+} adsorption onto the $ZnFe_2O_4/\alpha\text{-}Fe_2O_3$/biochar, the theories of Langmuir [10], Freundlich [11], and Temkin [12], were employed. The equations of the theories are as follows:

Langmuir isotherm:

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

Freundlich isotherm:

$$q_e = K_F.C_e^{1/n_F} \quad (7)$$

Temkin isotherm:

$$q_e = B_T.\ln A_T + B_T \ln C_e \quad (8)$$

where C_e is the As^{5+} concentration at equilibrium (mg/L), q_e is the adsorption capacity at equilibrium (mg/g), q_{max} is the maximum adsorption capacity (mg/g); K_L is the Langmuir constant related to the adsorption rate (L/mg), K_F is the Freundlich constant representing the adsorption capacity [(mg/g) $(L/mg)^{1/n}$], n_F is the heterogeneity factor, A_T is the Temkin equilibrium binding constant (L/mol), B_T is the Temkin constant; B_s (L.mg). The Langmuir model assumes monolayer adsorption onto a homogeneous surface with no interactions between the adsorbed molecules. The Freundlich model is an empirical equation, which is often used to describe chemisorption on heterogeneous surface. Temkin isotherm model incorporates the effects of adsorbate–adsorbate interactions on the adsorption process.

Table 2. *The adsorption isotherm parameters of As^{5+} on $ZnFe_2O_4$/α-Fe_2O_3/biochar*

Models	Isotherm parameters	
Langmuir model	q_{max} (mg/g)	31.48
	K_L (L/mg)	0.046
	R^2	0.992
Freundlich model	n_F	1.757
	K_F	2.666
	R^2	0.943
Temkin model	A_T (L/mol)	0.385
	B_T(J/mol)	7.506
	R^2	0.978

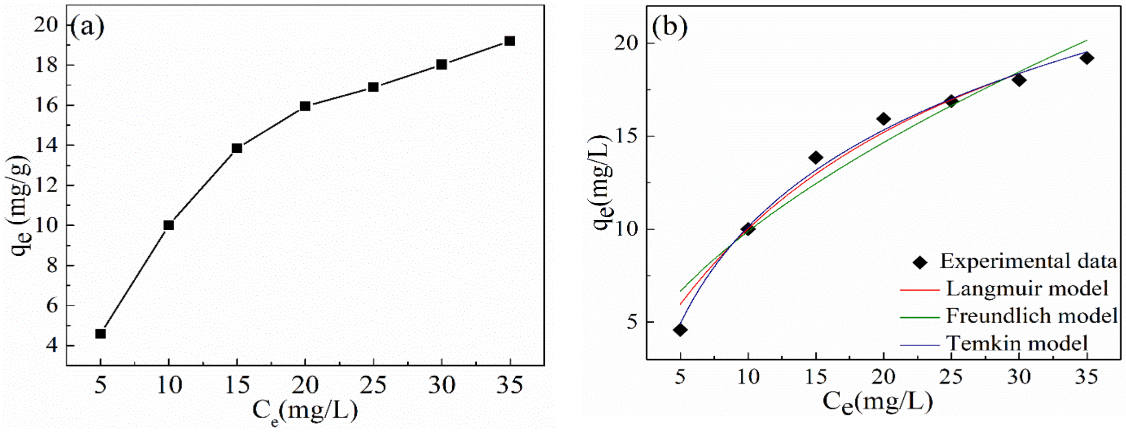

Figure 3. *Adsorption isotherm for As^{5+} on $ZnFe_2O_4$/α-Fe_2O_3/biochar*

All the models reproduced the isotherm data fairly well with correlation coefficients (R^2) above 0.90 (Figure 3b). The best-fit model parameters are also listed in Table 2. As shown in the table, R^2 value of the Langmuir model is higher than that of the Freundlich and Temkin models, suggesting the adsorption of As^{5+} onto the MBC was mainly controlled by the Langmuir surface adsorption mechanisms. This result is consistent with the reported adsorption mechanisms of As^{5+} removal by monolayer adsorption on biochar/γ-Fe_2O_3 composite surface [9]. Previous studies have indicated that the adsorption of As^{5+} to metal oxide surfaces is mainly via surface complexation reactions, which are characterized by the one and two site models [9], [13]. The monodentate and bidentate As^{5+} adsorption reactions can be written as follows:

$$SOH + H_3AsO_4 \leftrightarrow SH_mAsO_4^{m-2} + (2\text{-}m)\ H^+ + H_2O, \text{ Monodentate} \quad (9)$$

$$S(OH)_2 + H_3AsO_4 \leftrightarrow SH_nAsO_4^{1-2} + (2\text{-}n)\ H^+ + H_2O, \text{ Bidentate} \quad (10)$$

where S denotes metal oxide (e.g., γ-Fe_2O_3) surface, and m (0, 1, or 2) and n (0 or 1) are integers. These adsorption reactions are monolayer and site-limited and thus can be described with Langmuir adsorption theory well. The Langmuir maximum adsorption capacity of the $ZnFe_2O_4$/α-

Fe_2O_3/biochar to As^{5+} is 31.48 mg/g, which is comparable to or that of many adsorbents (Table 3). When considering the contribution from magnetic nanoparticles or magnetic/biochar nanocomposites, the $ZnFe_2O_4/\alpha\text{-}Fe_2O_3$/biochar has a maximum arsenic adsorption capacity of 31.48 mg/g, which is higher than that of biochar/$\gamma\text{-}Fe_2O_3$ (3,147 mg/g) [9]. These findings also suggest that arsenic can be effectively removed from aqueous solutions in water treatment processes by using the $ZnFe_2O_4/\alpha\text{-}Fe_2O_3$/biochar composite as a high efficiency adsorbent.

Table 3. *Summary of As^{5+} adsorption capacity of various adsorbents*

Adsorbents	As^{5+} adsorption capacity (mg/g)	Reference
$\gamma\text{-}Fe_2O_3$	50	[5]
$MnFe_2O_4$ nanoparticles	68.25	[9]
Biochar supported $MnFe_2O_4$ magnetic nanocomposite	90	[1]
Iron modified activated carbon	6.57	[14]
Biochar/$\gamma\text{-}Fe_2O_3$	3.147	[9]
MIL-88A(Fe) decorated on cotton fibers	164	[15]
Fe-based Metal-Organic Framework material	281	[3]
$ZnFe_2O_4/\alpha\text{-}Fe_2O_3$/biochar	31.48	This work

3.5. Chemical composition of $ZnFe_2O_4/\alpha\text{-}Fe_2O_3$/biochar composite before and after adsorption

The chemical composition of MBC before and after adsorption was analyzed Fourier transform infrared (FTIR) spectroscopy. The FTIR spectra (Figure 4a) demonstrated the surface of MBC contains some oxygen-containing functional groups, as evidenced by the presence of the characteristic absorption peaks at 3360 cm^{-1} (-OH), 1573 cm^{-1} (C=C), 1236 cm^{-1}, (C–O), 874 cm^{-1} (C-H), and magnetic materials with absorption peaks at 459 and 523 cm^{-1} ($ZnFe_2O_4/\alpha\text{-}Fe_2O_3$). In the curve obtained after the adsorption of As^{5+}, about 1382 cm^{-1} absorption peaks appeared. It's likely that is the impact of O-H on arsenic [16]. It shows that the physisorption and co-precipitation exist in the process of removing As^{5+} from MBC.

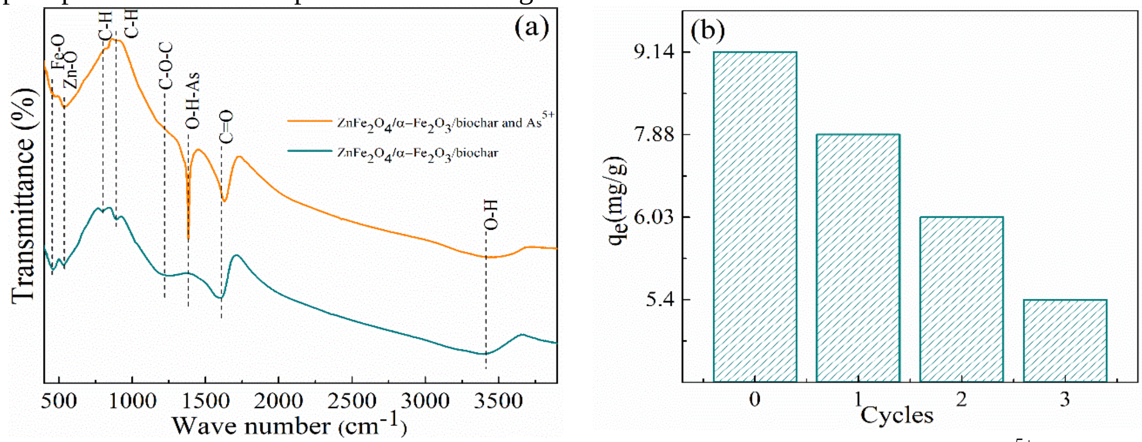

Figure 4. *(a) IR spectra of $ZnFe_2O_4/\alpha\text{-}Fe_2O_3$/biochar before and after adsorption As^{5+}; (b) As^{5+} adsorption capacity after 3 reuses of $ZnFe_2O_4/\alpha\text{-}Fe_2O_3$/biochar*

Reusing the adsorption process

Figure 4b illustrates the ability to reuse MBC adsorbent material, demonstrating that even after desorption, the material can still remove As^{5+} from water. The As^{5+} adsorption capacity of MBC decreases gradually with each regeneration. Specifically, after three reuses, the As^{5+} adsorption capacity decreased to 86%, 66%, and 59% of the initial capacity (cycle 0). This result could attributed to the decrease in adsorption sites on the MBC adsorbent following each regeneration. The higher the number of regenerations, the fewer the adsorption sites, and thus the adsorption capacity decreases.

4. Conclusion

$ZnFe_2O_4/\alpha\text{-}Fe_2O_3$/biochar nanocomposite material has the ability to remove As^{5+} from water environment by adsorption method at pH 8, with an equilibrium time of 600 minutes. The adsorption process involved chemisorption, which was followed by a pseudo-second-order model. The Langmuir isotherm model provided the best fit for the equilibrium study. The maximum adsorption capacity was 31.48 mg/g at 303 K. MBC materials can be easily recovered with an external magnetic field. After three reuses, the As^{5+} adsorption capacity reached 59% that of the original material. MBC could be used as a potential adsorbent for the treatment of organic pollutant wastewater.

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