Specifically Designed Magnetic Biochar From Waste Wood for Arsenic Removal

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Specifically designed magnetic biochar from waste wood for arsenic removal

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ABSTRACT

Arsenic is a kind of metal elements, widely distributed in nature. Many technologies, including adsorption, ion exchange, membrane separation and extraction, have been developed to treat arsenic-containing wastewater due to a series of drinking water safety problems caused by arsenic pollution. Biochar has some advantages of big surface area, low cost and so on. Therefore, waste wood was used as biochar, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and KMnO_4 were also used to promote the performance of arsenic removal. The results of XRD, BET, EA and VSM analysis show that modified biochar has major elements of Fe, Mn with KMnO_4 . The modified biochar ($\text{Fe}_1\text{Mn}_1\text{C}_1$) has higher magnetism of 40 emu g^{-1} . Through adsorption performance assessment, the best ratio of Fe/C is 1:1 and the adsorption efficiency and capacity of Fe_1C_1 is 61.6% and 0.681 mg g^{-1} , respectively. Then, the best ratio of Mn, Fe and C is 4:1:1 with highest adsorption efficiency of 80.8% and capacity of 0.724 mg g^{-1} . The best dosage of Fe_1C_1 and $\text{Fe}_1\text{Mn}_2\text{C}_1$ is the same as 1 g L^{-1} . It shows better adsorption capacity under higher pH with pristine biochar (PB) and Fe_1C_1 while under lower pH with $\text{Fe}_1\text{Mn}_2\text{C}_1$. The adsorption patterns of PB and $\text{Fe}_1\text{Mn}_2\text{C}_1$ fit Langmuir well. In contrast, adsorption pattern of Fe_1C_1 fits Freundlich well. In addition, three types of biochars all fit the pseudo second order adsorption kinetics.

Keywords: Magnetic biochar, FeMnC, FeC, modification, arsenic

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1. Introduction

Arsenic removal technologies mainly include ion exchange, coagulation-precipitation, membrane separation, biological treatment, oxidation and adsorption. Ion exchange was often used to remove arsenic from water. It used ions or functional groups inside to combine with target arsenic in order to separate arsenic ions from water [1]. This method to remove arsenate in water was much better than arsenite because arsenate existed in the form of ions while arsenite existed mostly in the form of molecules [2]. Anirudhan et al. (2007) used a novel anion exchange resin named CP-AE to remove arsenic with the initial arsenic concentration of 1 mg L^{-1} and the removal efficiency reached 99.2% [3]. Coagulation-sedimentation method was a traditional method of arsenic removal, with the advantages of easy operation and low cost. This method was to add coagulants in arsenic containing water. Therefore, the stability of colloid was destroyed by the chemical or physical reactions with arsenic. Floccules particles were produced and then came into larger precipitation particles because of cluster phenomenon. The purpose of separating arsenic pollutants and water was achieved through filtration [4]. Karn et al. (2017) used FeCl_3 as flocculants to remove arsenite and the efficiency reached 77%. The removal efficiency did not increase obviously, when the dosage of FeCl_3 continued to increase [5]. Membrane separation technology was divided into two types of high pressure membrane technology, including reverse osmosis and nano-filtration, and low pressure membrane technology, including ultra-filtration and microfiltration. The removal of arsenic from surface water by nano-filtration membrane was studied in the research of Waypa et al. (1997) and the removal efficiency reached 99% [6]. Kang et al. (2000) studied the influence of pH on arsenic removal performance of reverse osmosis membrane. The results showed that the removal efficiency of arsenate was higher than that of arsenite when the pH value was between 3 and 10. In addition, arsenite removal was greatly affected by pH through changing its state in water [7]. Wang et al. (2009) used ultra-filtration membrane to treat arsenate. It was found that the method could remove at least 90% arsenate within 40 minutes [8]. Biological method was a promising alternative to traditional arsenic removal techniques. The method was to reduce toxicity by enriching arsenic in water by itself or its metabolites or transferring arsenite into arsenate [9]. Kao et al. (2013) found the bacteria named As-7325 in Taiwan which can oxidize arsenite into arsenate within three days. After that, arsenate was released by the metabolic products of bacteria through the process of adsorption or co-precipitation [10]. Oxidation methods commonly include chemical oxidation and photo-catalytic oxidation. O_3 , H_2O_2 , Cl_2 and others belong to chemical oxidants. In study of Pincus et al. (2020),

oxidation of As(III) to As(V) by Cu(II) in the presence of dissolved oxygen is examined to elucidate the ability and mechanism of Cu(II) and Cu(II)-n-TiO₂ participation in Fenton-like reactions. The results showed that the amount of As(III) oxidized to As(V) is strongly controlled by the loading of Cu(II), with a higher loading of Cu(II) leading to more As(III) oxidized and bound on the surface of the adsorbent as As(V) [11]. The photochemical oxidation of As(III) to the less toxic As(V) using peroxydisulfate ions as the oxidizing agent under UV light irradiation was investigated in study of Neppolian et al. (2008). This simple technique was, thus, considered a cost-effective and safe method for the oxidation of As(III) to As(V) [12]. The adsorption method to treat arsenic-containing wastewater mainly uses physical, chemical or ion exchange processes to fix arsenic on the adsorbent surface. Therefore, it can be separated from water together with adsorbents. The types of adsorbents mainly contained activated carbon, modified biochar, metal hydroxide, inorganic nano-metal oxides and their composites. The adsorbents need to take advantages of large specific surface area, abundant porous structure and strong function groups [13].

Biochar has been identified as an effective adsorbent that can be used to remove various heavy metals dissolved in water, because the specific surface area and micro-porous structures of biochar are high. It hosts several surface functional groups, such as carboxyl (-COOH), hydroxyl (-OH) and amino (-NH₂), for adsorbing heavy metal effectively [14-15]. These groups can work through electron donation, cation exchange, electrostatic attraction, or surface complexation to effectively remove heavy metals [16]. Recent studies have focused on the use of potential adsorbents, the utilization of hard wood [17], peanut hull [18], natural lignocellulose materials [19-21], cottonwood [22], animal waste [23], agriculture and industrial waste [24-25], corn straw [26], coconut shell [27], walnut shells [28], hazelnut [29], cotton stems [30-32] and sawdust or rice straw [33] as cheap and environment friendly materials has attracted increasing attention. Therefore, in this research, a novel adsorbent with a high sorption capacity for arsenic was prepared from wood chips. The objectives of this work are to (a) preparation of biochar and modified biochar; (b) to study the characteristics analysis of material; (c) to study the effect of pH, initial concentration and dosage; (d) to study the adsorption isotherm and adsorption kinetics; and (e) to study the mechanism analysis of arsenic removal.

2. Materials and Methods

2.1. Preparation of pristine biochar

The pristine biochar (PB) was prepared by pyrolysis method from wood biomass obtained in the wood processing factory. Firstly, the biomass was washed three times using the tap water to remove the dirt, such as soil, plastics and dust and washed continually using the deionized water to eliminate the influence of other metal ions. Afterwards, it was dried in the oven at the temperature of 333 K for the duration of 48 hours. Next, it was kept into the muffle furnace at the heat-up speed of 300 K min⁻¹ and pyrolysis temperature of 873 K for 1 hour. Rehman et al. (2018) subjected the biomass to be heated in a muffle furnace for pyrolysis with heating rate of 283 K min⁻¹ to achieve the temperature of 1073 K for the duration of 1 hour [34]. Then, it was taken out from the muffle furnace when it became cooled and washed using the deionized water twice to remove the floating objects. After filtering and drying, the PB was obtained finally.

2.2. Preparation of biochar modified with both iron and manganese ions

To enhance the efficiency of magnetism and adsorption, the Mn was also added. The prepared steps for Mn contained magnetic biochar before getting pre-treated biomass are also same with the PB. Four different concentrations of KMnO₄, including 25, 50, 100 and 200 g L⁻¹, were prepared. Then, 10 g of pre-treated biomass and 10 g of FeCl₃·6H₂O were put into the different solutions and stirred for 2 hours. After that, the mixture was heated in water bath and dried in the oven. Further, it was put in the muffle furnace for the pyrolysis at the same condition as of PB. At last, the modified biochar was collected after washing and dried. The finally obtained biochar modified with both Fe and Mn is represented as Mn_yFe₁C₁. Lin et al. (2019) also used the same method to prepare Mn modified biochar [35]. The value of ‘y’ depends on the weight ratio of KMnO₄ and Fe₁C₁, prepared from FeCl₃·6H₂O and biomass. For example, Mn_{0.5}Fe₁C₁, Mn₁Fe₁C₁, Mn₂Fe₁C₁ and Mn₄Fe₁C₁ stands for the weight ratio with KMnO₄ of 5, 10, 20 and 40 g, separately, when the weight of pre-treated biomass is 10 g and FeCl₃·6H₂O is 10 g.

2.3. Characterization

The pore volume, pore size distribution and specific surface area were determined by performing N₂ adsorption-desorption measurements with an ASAP 2020 apparatus by using Barrett-Joyner-Halenda (BJH) and Brunauer-Emmett-Teller (BET) calculation methods. The morphology of the material was measured through a SEM with EDS analysis. The crystal phase of the material was determined by an XRD with employing Cu K α radiation wavelength of 0.15405 nm, accelerating

voltage of 40 kV and current of 30 mA over the 2θ range of 20-80°. A TGA instrument with a heating rate of 20 °C min⁻¹ has studied the thermal properties of carbonized and material.

2.4. Adsorption performance assessment

Adsorption performance assessment was carried out in 100 mL adsorption system. The porous adsorbents were mixed with 80 mL of the appropriate arsenic solution under 25 °C for 24 hr. The solution was filtered with using a membrane filter (pore size 0.45 µm). In addition, the residual As in the aqueous solutions was determined with using an inductively coupled plasma atomic emission spectroscopy (ICP-AES). The limit for arsenic detection is 10 ppb. The test results were regularly tested with standard solution to get the accurate data. To obtain the accurate results, this experiment was repeated for three times, and the standard deviation was just 20 ppb.

The capacity adsorption of As was calculated by mass balance as follows:

$$q_e = [(C_o - C_e)/W] \times V \quad (2-1)$$

Where q_e (mg g⁻¹) is the equilibrium adsorption capacity, C_o (mg L⁻¹) is the initial concentration of As, C_e (mg L⁻¹) stands for the equilibrium concentration measured after adsorption, W (mg) is the amount of adsorbent used in the experiments and V (mL) is the volume of As solution.

2.5. The methods of kinetics models analysis

2.5.1. Pseudo-first-order

The pseudo-first-order equation is given as Equation (2-2) [36].

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2-2)$$

Where, q_t is adsorption capacity at the time of “t” (mg g⁻¹); q_e is adsorption capacity at balance (mg g⁻¹); k_1 is rate coefficient of the first-order adsorption mode (min⁻¹); and t is time (min).

After the Equation (2-2) is integrated, the function formula can be obtained as Equation (2-3).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2-3)$$

2.5.2. Pseudo-second-order

The pseudo-second-order model is represented as Equation (2-4) [37-38].

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2-4)$$

Where, k_2 is rate coefficient of the second-order adsorption mode ($\text{mg g}^{-1} \text{ min}^{-1}$).

After arranging the above equation, the Equation (2-5) can be obtained as shown followed.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2-5)$$

2.6. Isothermal adsorption models analysis

2.6.1. Langmuir model

Based on the above assumptions, Langmuir adsorption Equation (2-6) is derived as follows [39].

$$Q = \left(\frac{ab \times C_0}{1 + aC_0} \right) \quad (2-6)$$

After taking the inverse of the above equation, Equation (2-7) can be obtained

$$\frac{1}{Q} = \frac{1}{b} + \frac{1}{ab \times C_0} \quad (2-7)$$

Where, C_0 is the equilibrium initial concentration dye in the solution and Q is the amount of dye adsorbed by the additive. a and b are Langmuir constants related to adsorption capacity and adsorption energy, respectively. Plotting Q^{-1} versus C_0^{-1} , and again measuring the slope and intercept of the plot, a and b can be directly interpreted.

2.6.2. Freundlich model

The empirical formula of constant temperature adsorption is proposed, as shown below [40].

$$Q = K C_0^{1/n} \quad (2-8)$$

Taking the natural logarithm of both sides gives:

$$\ln Q = \ln K + \frac{1}{n} (\ln C_o) \quad (2-9)$$

Where, C_o is the equilibrium initial concentration dye in the solution and Q is the amount of dye adsorbed by the additive. If experiment absorption matches the above empirical model, then by plotting $\ln Q$ versus $\ln C_o$ the values of the Freundlich constants of K and n can be directly interpreted from the plot as the intercept and slope.

2.6.3. Temkin model

Temkin isotherm model takes adsorbate–adsorbent interactions into account. It is assumed that the relationship between adsorption capacity and pollutant concentration at equilibrium state is linear rather than logarithmic which is different from Freundlich equation. Besides, the adsorption heat decreases linearly rather than exponentially as all adsorbents gradually cover the adsorbent is also assumed [41].

The Equation (2-10) for the linear form of Temkin model can be shown as follows:

$$Q = B(\ln K_T + \ln C_o) \quad (2-10)$$

Here, B is Temkin constant related to heat of adsorption (J mol^{-1}); and K_T is Equilibrium binding energy constant (J g^{-1}).

3. Results and Discussion

3.1. Characteristics analysis

3.1.1. XRD analysis

The XRD analysis of different Fe content modified biochar and PB is shown in [Figure 1](#). The PB does not have any obvious and regular diffraction peaks, so PB is amorphous indeed. After the modifications with Fe, the materials appear obvious characteristics peaks, which is in accordance with the crystalline Fe species of hematite (Fe_2O_3) and magnetite (Fe_3O_4). This can identify that the Fe is successfully loaded into the biochar. The characteristics peaks intensity of Mn modified

biochar, $\text{Mn}_y\text{Fe}_1\text{C}_1$, are changed a little from Fe_xC_1 biochar with increasing Mn content in $\text{Mn}_y\text{Fe}_1\text{C}_1$ biochar. Therefore, it shows that Mn is successfully added into biochar after Mn modification.

3.1.2. SEM and EDS analysis

To get the typical surface morphologies and element message, the SEM and EDS analysis have been done. As shown in Figure 2 (a), the surface of PB is smooth and the abundant pores are arranged regularly. The formation of pore is generated by the decomposing of lignocelluloses and lignin under high temperature [42]. The EDS results in Figure 2 (b) reveal that the elemental composition includes C and O and is consistent with the results of EA. There are many small particles in the surface uniformly blocking the pores in Figure 2 (c), corresponding to Fe particles. Along with the EDS results in Figure.2 (d), it is evident that the particles are Fe. In Figure 2 (e), a layer of dense particles emerges in the surface decreasing the pore amounts and causing the roughness. The EDS results in Figure 2 (f) reveal that the covering particles are Fe and Mn, which is in accordance with the former analysis results of XRD.

3.1.3. The hysteresis regression analysis

Considering the recycling of biochar after adsorption through magnetic field, the magnetization strength is tested. From the results in Figure 3(a), PB almost does not have any magnetism. But, the modification of Fe increases the magnetism of materials in contrast to pristine due to the formation of Fe_3O_4 . Especially, the $\text{Fe}_{0.5}\text{C}_1$ can reach the largest magnetism as 5.3 emu g^{-1} . However, it is not enough to recycle the biochar. Hence, the Mn is used to enhance the materials magnetism ability. It can be seen in Figure 3(b), the Mn modified biochar shows much higher magnetism due to the interaction with Fe and Mn, which is good for enhancing the recycling ability. The highest obtained magnetization strength is 43 emu g^{-1} . In the research of Son et al. (2018), the saturation magnetization values of iron modified biochar is 8.64 emu g^{-1} [43]. It is enough ferromagnetic to recollect the used biochar from suspended solution by means of the external magnetic field. In comparison, the $\text{Mn}_1\text{Fe}_1\text{C}_1$ and $\text{Mn}_2\text{Fe}_1\text{C}_1$ in this study can be readily obtained by the external magnetic field with the saturation magnetization value of 43 emu g^{-1} and 21 emu g^{-1} .

3.1.4. Nitrogen absorption and desorption analysis

To get the pore size distribution and surface area of different biochars, nitrogen absorption and desorption analyzer was used before and after modification. From [Table I](#), it shows the specific surface area of PB, Fe₁C₁ and Mn₂Fe₁C₁ is 524, 181 and 135 m² g⁻¹, respectively. The specific surface area decreases after modification due to the Fe and Mn blocking. The results also show that it is in good agreement with the SEM analysis. The mean pore size of PB, Fe₁C₁ and Mn₂Fe₁C₁ is 20.9, 21.7 and 46.3 Å, respectively. They belong to mesoporous materials on the basis of its own pore size between 2 nm and 50 nm, while the pore size of Mn₂Fe₁C₁ is bigger than that of PB and Fe₁C₁ since many original small pores of PB are missing owing to its heavier blocking with metals and metal contents of biochar.

3.2. Performance test analysis

3.2.1. The influence of modification for biochar

[Figure 4 \(a\)](#) shows that the Fe modified biochar improved the removal efficiency of As, comparing to the PB. The obtained results are in accordance with the experimental results of Kim et al. (2019) [44]. The highest removal efficiency with Fe modified biochar can reach 61.6%, almost 5 times with PB, owing to the formation of R-FeH₂AsO₃, R-FeHAsO₃⁻, R-FeAsO₃²⁻, R-Fe₂HAsO₃ and R-Fe₂AsO₃⁻ species, which R means function group of biochar. The ligand exchange between arsenite anion and hydroxyl functional group of Fe oxide in the Fe-modified adsorbents can increase the interaction of As and biochar. With the increasing Fe, the efficiency first increases, but decreases thereafter. The reason of decreasing might be Fe blocking of pore structure, which can directly decrease the specific surface area. From [Figure 4 \(b\)](#), it can be clearly deduced that the Mn modification has a significant effect on the removal ability. The highest efficiency is 80.8% with Mn₂Fe₁C₁, which is seven times higher than that with PB. This may be due to the reduction of arsenite to arsenate with adding Mn. It is well known that the trivalent As is more difficult to remove. Moreover, similar observations of the redox potential of Mn have been recently found by Lin et al. (2019) [35]. Apart from this, the reduction products Mn²⁺ can play the role like Fe ions as aforementioned.

3.2.2. The influence of pH

The pH of solutions is a very important variable affecting metal adsorption in solution. The influence of pH to remove As was studied by varying the pH values over the range of 3.0-11.0. To

study the electrostatic force between As and adsorbents, the zeta potential experiment of three types biochar was studied and the results is shown in Figure 5. The pH at zeta potential is 4.2, 6.1 and 2.1 of PB, Fe₁C₁ and Mn₂Fe₁C₁, respectively. It can help to judge the surface charge of adsorbents. When the solution pH is below the zeta potential pH, the surface is positively charged, and vice-versa. As shown in Figure 5 (b), pH shows different influence on the removal efficiency of the three types of biochar, which may relate to the reaction mechanism. PB shows negligible influence. In contrast, the efficiency with Fe₁C₁ increases with the slightly increasing pH. The adsorption efficiency with Mn₂Fe₁C₁ decreases obviously with the increasing pH.

The rise in As (III) removal efficiency might be due to the chemi-sorption rather than the electrostatic attraction. H₃AsO₃ could connect with deprotonated Fe–O surface sites through hydrogen-bond at higher pH prior to chemi-sorptions [45]. The Mn₂Fe₁C₁ has the highest removal efficiency at the low pH around 3. Comparing to other adsorption forces, the electrostatic attraction is dominant. The zeta potential of Mn₂Fe₁C₁ is around 2.0 and the As exists as almost negative species in the experimental range. Above pH 3, the biochar surface is much more negative. Therefore, the electrostatic repulsion will reduce the As uptake heavily.

3.2.3. The influence of initial concentration

The three lines reveal that the removal capacity increases from 0.056 to 0.163, from 0.173 to 0.892 and from 0.223 to 1.090 mg g⁻¹, respectively, with the increase of As initial concentration from 0.25 to 5.0 ppm in Figure 6. Prior to the saturation of active sites present on adsorbent surface and the higher concentration of As, the more active sites can be used. Hence, the value of q_e can increase much. However, the q_e of PB stopped increasing after 2 ppm mainly due to the earlier saturation than the modified biochar. In contrast, the increasing trend of modified biochar reveals the higher removal potential than unmodified biochar.

3.2.4. The influence of dosage

As shown in Figure 7, six different dosages (0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 g L⁻¹) of PB, Fe₁C₁ and Mn₂Fe₁C₁ have been tested. The maximum removal efficiency of 72% is found at the dosage of 1.2 g L⁻¹. The more is the adsorbents and the more active sites can be supported. Therefore, much more As can be removed with increasing active sites. In addition, the removal efficiency increased in the range of 0-28.5%, 17.4-64.9% and 21.1-71.8%, respectively, under the studied dosages from 0.2

to 1.2 g L^{-1} . In contrast, the measurement of q_e shows the opposite results because of the diminution of equivalent active functional sites on the surface of adsorbents. The decrease of adsorption capacity is due to the increase in intermolecular attraction between adsorbent [46].

3.3. Adsorption isotherm models analysis

Foo and Hameed (2010) explained that the analysis of adsorption isotherms models can be used for investigating the adsorption behavior and assess the feasibility of field application [47]. To get the three types of biochar surface properties and the behaviors to adsorb As, the commonly used adsorption isotherm models, such as Langmuir, Freundlich and Temkin, have been applied to fit the experimental data in the present study. The Langmuir adsorption isotherm model is based on the assumption that the entire adsorption process is a single-molecule layer adsorption between the gas and solid phases, while the Freundlich adsorption isotherm model is an empirical equation without assumptions and without considering adsorption saturation. The multi-molecular layer adsorption process occurring on an uneven surface is simulated. The Freundlich model is based on the hypothesis that the binding sites are not equal and heterogeneous surface for adsorption [48]. The Temkin equation is used to describe the adsorption equilibrium of a single molecular layer in a non-ideal adsorption system.

The experiments are operated for the concentrations of 0.25, 0.5, 1.0, 2.0 and 5.0 ppm, respectively. Comparing to the other models, the research fits better with Langmuir model with the linear correlation coefficient 0.990, 0.992 and 0.980. This result reveals that the adsorption belongs to single molecule adsorption. In addition, the maximum adsorption capacity based on the simulation of Langmuir model is 0.184, 1.004 and 0.895 mg g^{-1} for PB, Fe_1C_1 and $\text{Mn}_2\text{Fe}_1\text{C}_1$, respectively. In terms of the constant value n for Freundlich adsorption isotherm model, the value is 3.19, 2.57 and 3.46, respectively, all in the range of 2 to 10. It is unfavorable for As adsorption with prepared biochars. According to the value B of Temkin model, the adsorption energies for typical physisorption processes are reported to be less than -40 kJ mol^{-1} . In this research, the value of B is 0.03, 0.18 and 0.16 kJ mol^{-1} , indicating that the adsorption process involves both physisorption and chemisorptions, as shown in Table II and Figure 8.

3.4. Adsorption dynamics

Adsorption of As in wastewater by adsorbent is a complicated adsorption reaction process. To explore the speed of the three different types of biochar to adsorb As, the kinetic adsorption models are tested to get the related constants. In the research, the pseudo-first-order and pseudo-second-order are mainly simulated and the relevant kinetic parameters about K_1 (rate constant of pseudo first order), K_2 (rate constant of pseudo second order), $q_{\max dy}$ (maximum adsorption capacity of dynamic simulation) and R^2 (coefficient of determination) are presented in [Table III](#) and [Figure 9](#).

The three types of biochar fit the pseudo-second-order better under the consideration of both the R^2 value and q_e value [\[49\]](#). The R^2 value of pseudo-second-order is 0.981, 0.986 and 0.991, respectively, and the value is 0.980, 0.919 and 0.938 for pseudo-first-order. It also can be seen in the [Table III](#) that modified biochar reveals much stronger adsorption ability towards As and the saturated adsorption capacity of three types of biochar is 0.137, 0.674 and 0.618 mg g^{-1} , respectively, with PB, Fe_1CB_1 and $\text{Mn}_2\text{Fe}_1\text{CB}_1$ under the simulation of pseudo-second-order at pH 7 and 298 K. This is much closer to the specific experimental data of 0.128, 0.681 and 0.616 mg g^{-1} , respectively, compared with the R^2 value 0.118, 0.500 and 0.477 mg g^{-1} obtained from pseudo-first-order.

In addition, the adsorption capacity of the three types of biochar towards As follows the ranks order as $\text{Fe}_1\text{C}_1 > \text{Mn}_2\text{Fe}_1\text{C}_1 > \text{PB}$. This simulation trend is corresponding with the actual experiment data in the given situation of pH 7 and 298 K. The results may suggest that the adsorption mechanism belongs to both the physical and chemical reaction. Furthermore, the limitation of the adsorption speed is caused by chemical reaction. Between the adsorbent and As, the bindings are established through the electron transfer and electron pair. It is in good agreement with the experimental results of Igberase et al. (2017) [\[50\]](#).

3.5. Mechanism assumption

According to the results of material property analysis and adsorption performance evaluation, possibly existence reaction models can be assumed in [Figure 10](#). The reaction to adsorb arsenic by biochar contains physical reaction and chemical reaction. Biochar can connect with arsenic through hydrogen bonding from the function group -OH in biochar and arsenic itself. Besides, they can contract each other by electron force when the biochar surface is filled with positive charge. The compounds of manganese have strong oxidizability to oxidize arsenite to arsenate. In comparison, arsenate is easier to remove. At last, the iron ion is just like the bridge to connect biochar and arsenic resulting in the formation of new complex compounds.

4. Conclusion

XRD analysis results show that Fe_2O_3 and Fe_3O_4 occur in the surface of Fe_xC_1 . SEM-EDS analysis results proves that iron and Mn ions are successfully coated because the smooth surface changes to rough surface after coating and the elements of Fe and Mn are appeared in EDS analysis. From hysteresis regression analysis shows that magnetism of Fe_xC_1 and $\text{Mn}_y\text{Fe}_1\text{C}_1$ are improved much better than that of PB. $\text{Fe}_{0.5}\text{C}_1$ adsorbents can reach the largest magnetism as 5.3 emu g^{-1} . The highest magnetization strength is 43 emu g^{-1} from $\text{Mn}_1\text{Fe}_1\text{C}_1$. From the nitrogen absorption and desorption analysis, the specific surface area of PB, Fe_1C_1 and $\text{Mn}_2\text{Fe}_1\text{C}_1$ is 524, 181 and $135 \text{ m}^2 \text{ g}^{-1}$, respectively. Besides, they all belong to mesoporous materials through their average pore size analysis. The arsenic removal efficiency with Fe_xC_1 and $\text{Mn}_y\text{Fe}_1\text{C}_1$ are much higher than that with PB at pH 7. In particular, the removal efficiency with Fe_1C_1 and $\text{Mn}_4\text{Fe}_1\text{C}_1$ can reach 61.6 and 80.8%, respectively. As pH increases, the removal efficiency with PB and Fe_1C_1 increases a little while decreases obviously with $\text{Mn}_2\text{Fe}_1\text{C}_1$. The adsorption behaviors with PB, Fe_1C_1 and $\text{Mn}_2\text{Fe}_1\text{C}_1$ all fit Langmuir isothermal adsorption model and pseudo-second-order adsorption dynamics model better. The reaction mechanisms to remove arsenic contain physical reaction and chemical reaction including electrostatic function, oxidation reaction, complexation reaction and hydrogen bonding function.

Declarations

Availability of data and materials

All data generated or analyzed during this study are examined by our group and certified for several times.

Competing interests

The authors declare they have no competing interests.

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Authors' contributions

Chih-Kuei Chen provided real test data, Jia-Jia Chen supported the test data, Nhat-Thien Nguyen wrote the paper, Thuy-Trang Le analyzed the test data, and Chang-Tang Chang organized the researched full structure. All authors read and approved the final manuscript.

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Table I. Analysis data of surface area and pore size

Materials	Surface Area ($\text{m}^2 \text{g}^{-1}$)	Pore Size ($\text{\AA}$)
PB	524	20.9
Fe_1C_1	181	21.7
$\text{Mn}_2\text{Fe}_1\text{C}_1$	135	46.3

Table II. Parameters for different isotherm of As adsorption with biochars

Model	Parameters	PB	Fe_1C_1	$\text{Mn}_2\text{Fe}_1\text{C}_1$
Langmuir	b (mg g^{-1})	0.184	1.004	0.895
	a (L mg^{-1})	2.319	2.728	12.48
	R^2	0.990	0.992	0.980
Freundlich	K_d (mg g^{-1})	0.112	0.607	1.299
	n	3.189	2.569	3.455
	R^2	0.874	0.871	0.940
Temkin	B (J mol^{-1})	0.03	0.18	0.16
	K_T (J g^{-1})	39.98	41.86	159.32
	R^2	0.953	0.955	0.975

Table III. The adsorption dynamics parameters of different models

Adsorption model		PB	Fe_1C_1	$\text{Mn}_2\text{Fe}_1\text{C}_1$
Pseudo-first-order	k_1 (min^{-1})	0.003	0.002	0.003
	q_{maxdy} (mg g^{-1})	0.118	0.500	0.477
	R^2	0.980	0.919	0.938
Pseudo-second-order	k^2 ($\text{g mg}^{-1} \text{min}^{-1}$)	0.056	0.029	0.031
	q_{maxdy} (mg g^{-1})	0.137	0.674	0.618
	R^2	0.981	0.986	0.991

Figure captions

Figure 1. The XRD analysis of (a) Fe_xC_1 and (b) $\text{Mn}_y\text{Fe}_1\text{C}_1$

Figure 2. SEM images and EDS analysis of (a, b) PB, (c, d) Fe_2C_1 and (e, f) $\text{Mn}_2\text{Fe}_1\text{C}_1$

Figure 3. Hysteresis regression analysis of (a) Fe_xC_1 and (b) $\text{Mn}_y\text{Fe}_1\text{C}_1$

Figure 4. As removal efficiency with (a) Fe_xC_1 and (b) $\text{Mn}_y\text{Fe}_1\text{C}_1$

Figure 5. (a) Zeta potentials and (b) effects of pH on the As (III) removal efficiency

Figure 6. The influence of initial concentration of As

Figure 7. The influence of adsorbents dosage

Figure 8. Adsorption isotherm analysis of (a) Langmuir; (b) Freundlich and (c) Temkin model

Figure 9. Kinetic adsorption curves of As on materials: (a) Pseudo-first-order and (b) Pseudo-second-order kinetics.

Figure 10. Schematic diagram of reaction mechanism analysis

Figure 1. Chen et al.

Figure 2. Chen et al.

Figure 3. Chen et al.

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Figure 7. Chen et al.

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Figure 9. Chen et al.

Figure 10. Chen et al.

Figures

Figure 1

The XRD analysis of (a) Fe_xC_1 and (b) $\text{Mn}_x\text{Fe}_{1-x}\text{C}_1$

Figure 2

SEM images and EDS analysis of (a, b) PB, (c, d) Fe₂C₁ and (e, f) Mn₂Fe₁C₁

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