

Effect of Fe, Al, Mn modification on the properties and arsenic adsorption capacity of biochar

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Abstract

This study aims to screen arsenic pollution remediation materials. Based on the porous material of biochar (BC), iron chloride, aluminum chloride and potassium permanganate are used to modify the porous material to prepare iron modified porous material (Fe-BC), aluminum-modified porous material (Al-BC), manganese-modified porous material (Mn-BC), iron-aluminum composite modified porous material (Fe-Al-BC), iron-manganese composite porous material (Fe-Mn-BC), aluminum-manganese composite porous material (Al-Mn-BC). The basic properties and arsenic adsorption capacity of the material were analyzed. The results show that: After modification, the pH of the porous materials decreased in varying degrees, from alkaline to acidic or weak acidic. The specific surface area of Fe-BC is 2.88 times that of BC, and that of Mn-BC is 2.85 times that of BC. Adsorption capacity for arsenic in solution: Fe-Al-BC > Mn-BC > Al-BC > Fe-Mn-BC > Al-Mn-BC > Al-Mn-BC > Al-Mn-BC > Fe-Mn-BC > Fe-BC > BC..

Keywords

Porous material, biochar, modify, arsenic.

1. Introduction

Arsenic is a toxic element to human body and listed as high carcinogenic risk by the World Health Organization. Arsenic is ubiquitous in nature. The content of arsenic in the crust is about $1.5 \text{ mg}\cdot\text{kg}^{-1}$, and that in soil is about $5\text{-}10 \text{ mg}\cdot\text{kg}^{-1}$. Generally, arsenic is fixed in the form of stable minerals, which is difficult to release into the surrounding environment. Only in a few areas, arsenic in minerals enters the food chain through water source under weathering, which is toxic to human body. However, with the progress of science and technology, arsenic is gradually applied to pesticide manufacturing, alloy smelting and other fields. During the mining, transportation, smelting of arsenic bearing minerals and the manufacturing and utilization of arsenic bearing products, some arsenic will inevitably enter the soil, air and water, causing arsenic pollution. It is reported that tens of thousands of arsenic contaminated areas are distributed all over the world, with the highest arsenic content of $26.50 \text{ g}\cdot\text{kg}^{-1}$ in the soil [1]. The arsenic content of the copper mine soil in the northern Andes of Peru is $1.43 \text{ g}\cdot\text{kg}^{-1}$. The arsenic content of the soil in Lagunera, Mexico is $2.66 \text{ g}\cdot\text{kg}^{-1}$ [2], and that of the gold mine soil in Silesia, Poland is $18.10 \text{ g}\cdot\text{kg}^{-1}$. There are more than 10000 soil arsenic contaminated sites in Australia, and several of them have soil arsenic concentrations exceeding $9.90 \text{ g}\cdot\text{kg}^{-1}$ [3], of which the highest is $14.80 \text{ g}\cdot\text{kg}^{-1}$. In tin and antimony mines in Hunan, China, the soil arsenic content is $14.95\text{-}363.19 \text{ mg}\cdot\text{kg}^{-1}$, that in Guizhou is $38.57\text{-}91.31 \text{ mg}\cdot\text{kg}^{-1}$, and that in Yunnan is $493.39\text{-}2290.51 \text{ mg}\cdot\text{kg}^{-1}$. Porous material prepared from straw is a kind of high quality arsenic pollution remediation materials. Its complex pore structure, large specific surface area and rich functional groups endow it with strong adsorption performance. The adsorption of arsenic is

mainly completed through electrostatic attraction, physical adsorption, surface complexation and other processes. The results showed that the adsorption capacity of porous materials prepared from cow dung, pine needles and straw in arsenic containing solution with a concentration of $10 \text{ mg}\cdot\text{L}^{-1}$ was $16.9 \text{ mg}\cdot\text{kg}^{-1}$, $23.4 \text{ mg}\cdot\text{kg}^{-1}$ and $41.7 \text{ mg}\cdot\text{kg}^{-1}$, respectively. The adsorption capacity of porous materials for arsenic can be improved by modifying porous materials with metals, minerals or organic matter. The specific surface area of porous materials was increased from $2.85 \text{ m}^2\cdot\text{g}^{-1}$ to $33.11 \text{ m}^2\cdot\text{g}^{-1}$ by the modification of ferric chloride. When porous materials was added to arsenic contaminated soil (3% of soil mass), the stability rates of water-soluble As (III) and As (V) in contaminated soil with arsenic concentration of $150 \text{ mg}\cdot\text{kg}^{-1}$ were 39.56% and 53.67%, respectively.

Although the adsorption capacity of porous materials modified by a single substance has been improved to a certain extent, its adsorption capacity has not been fully developed. The composite modification of the two substances can further improve the adsorption efficiency of porous materials. In this study, ferric chloride, aluminum chloride and potassium permanganate were used as modified materials to construct composite modified porous materials. Through experiments, the adsorption properties of modified porous materials were quantified, and modified porous materials with strong adsorption capacity for arsenic are selected, which is of great significance for improving the utilization efficiency of materials and treating arsenic pollution with high efficiency and low cost.

2. Research Methods

2.1. Preparation of porous materials

2.1.1. Preparation of BC

Corn straw was washed with ionized water and dried, then was cut into to a particle size less than 1mm, and fill it in a ceramic crucible with a lid. The crucible was placed in the muffle furnace. The temperature was raised at $20 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ to $350 \text{ }^\circ\text{C}$ and was kept for 4 h. The pyrolyzed porous material was cooled to room temperature, and then grinded through a 1mm sieve.

2.1.2. Preparation of Fe-BC

The biochar (BC) was mixed with $0.3 \text{ mol}\cdot\text{L}^{-1}$ FeCl_3 solution in a ratio of 1:10(g: mL) and kept under magnetic stirring for 2 hours. And then left for 48 hours at $25 \text{ }^\circ\text{C}$, after which the solid was separated from the solution by centrifugation at $3,880 \times \text{g}$ in a centrifuge. The modified porous material was washed once with deionized water and then washed with ethanol to chloride-free ions (tested with $0.1 \text{ mol}\cdot\text{L}^{-1}$ AgNO_3). The modified porous material is dried and ground to pass through a 1mm sieve for use.

2.1.3. Preparation of Al-BC

The biochar (BC) was mixed with $0.3 \text{ mol}\cdot\text{L}^{-1}$ AlCl_3 solution in a ratio of 1:10(g: mL) and kept under magnetic stirring for 2 hours. And then left for 48 hours at $25 \text{ }^\circ\text{C}$, after which the solid was separated from the solution by centrifugation at $3,880 \times \text{g}$ in a centrifuge. The modified porous material was washed once with deionized water and then washed with ethanol to chloride-free ions (tested with $0.1 \text{ mol}\cdot\text{L}^{-1}$ AgNO_3). The modified porous material is dried and ground to pass through a 1mm sieve for use.

2.1.4. Preparation of Mn-BC

The biochar (BC) was mixed with $0.3 \text{ mol}\cdot\text{L}^{-1}$ KMnO_4 solution in a ratio of 1:10(g: mL) and kept under magnetic stirring for 2 hours. And then left for 48 hours at $25 \text{ }^\circ\text{C}$, after which the solid was separated from the solution by centrifugation at $3,880 \times \text{g}$ in a centrifuge. The modified porous material was washed once with deionized water and then washed with ethanol until

colorless.. The modified porous material is dried and ground to pass through a 1mm sieve for use.

2.1.5. Preparation of Fe-Al-BC

The biochar (BC) was mixed with $0.3 \text{ mol}\cdot\text{L}^{-1}$ FeCl_3 and $0.3 \text{ mol}\cdot\text{L}^{-1}$ AlCl_3 solution in a ratio of 1:10(g: mL) and kept under magnetic stirring for 2 hours. And then left for 48 hours at 25°C , after which the solid was separated from the solution by centrifugation at $3,880 \times g$ in a centrifuge. The modified porous material was washed once with deionized water and then washed with ethanol to chloride-free ions (tested with $0.1 \text{ mol}\cdot\text{L}^{-1}$ AgNO_3). The modified porous material is dried and ground to pass through a 1mm sieve for use.

2.1.6. Preparation of Fe-Mn-BC

The biochar (BC) was mixed with $0.3 \text{ mol}\cdot\text{L}^{-1}$ FeCl_3 and $0.3 \text{ mol}\cdot\text{L}^{-1}$ KMnO_4 solution in a ratio of 1:10(g: mL) and kept under magnetic stirring for 2 hours. And then left for 48 hours at 25°C , after which the solid was separated from the solution by centrifugation at $3,880 \times g$ in a centrifuge. The modified porous material was washed once with deionized water and then washed with ethanol to chloride-free ions (tested with $0.1 \text{ mol}\cdot\text{L}^{-1}$ AgNO_3) and colorless. The modified porous material is dried and ground to pass through a 1mm sieve for use.

2.1.7. Preparation of Al-Mn-BC

The biochar (BC) was mixed with $0.3 \text{ mol}\cdot\text{L}^{-1}$ AlCl_3 and $0.3 \text{ mol}\cdot\text{L}^{-1}$ KMnO_4 solution in a ratio of 1:10(g: mL) and kept under magnetic stirring for 2 hours. And then left for 48 hours at 25°C , after which the solid was separated from the solution by centrifugation at $3,880 \times g$ in a centrifuge. The modified porous material was washed once with deionized water and then washed with ethanol to chloride-free ions (tested with $0.1 \text{ mol}\cdot\text{L}^{-1}$ AgNO_3) and colorless. The modified porous material is dried and ground to pass through a 1mm sieve for use.

2.2. Study on arsenic adsorption kinetics of different porous materials

0.5 g of porous materials (BC, Fe-BC, Al-BC, Mn-BC, Fe-Al-BC, Fe-Mn-BC, Al-Mn-BC) and 25 mL of $25 \text{ mg}\cdot\text{L}^{-1}$ arsenic solution was added into a 50 mL centrifuge tube (24 per porous material) respectively. The centrifuge tube was put in a thermostatic oscillator and were oscillated under $200 \text{ r}\cdot\text{min}^{-1}$, 25°C . Three centrifuge tubes of every kind of porous materials were taken out after oscillating for 0.25h, 0.5h, 1h, 1.5h, 3h, 12h, 24h and 72h. The tubes were centrifuged for 20 min in a centrifuge with a rotating speed of $3500 \text{ r}\cdot\text{min}^{-1}$. The supernatant were taken to determine the arsenic content and the adsorption kinetics curve of every porous materials were drew based on the arsenic content data.

2.3. Data statistics and analysis

Data were summarized through Excel 2007.

3. Result Analysis

3.1. Basic physical and chemical properties of porous materials

The pH of porous material BC is 10.6, which is alkaline. After modification with FeCl_3 , the pH of material Fe-BC decreased to 3.27, 69.15% lower than that of material BC. After modification with AlCl_3 , the pH of material Al-BC decreased to 6.75, showing weak acidity, which was 36.32% lower than that of material BC. After being modified with KMnO_4 , the pH of material Mn-BC was reduced to 6.79, which was weak acid, and was 35.94% lower than that of the material BC. After the composite modification with FeCl_3 and AlCl_3 , the pH of material Fe-Al-BC decreased to 4.42, which was acidic and 58.30% lower than that of material BC. After the composite modification with FeCl_3 and KMnO_4 , the pH of material Fe-Mn-BC decreased to 3.81, which was acidic and 64.06% lower than that of material BC. After the composite modification with KMnO_4 and AlCl_3 , the pH of material Al-Mn-BC decreased to 6.47, showing weak acidity, which was 38.96% lower

than that of material BC. The pH of the modified porous material is mainly affected by the pH of the modified substance solution. The Zeta potential of porous material BC is -26.56 mV. After modification with FeCl_3 , the Zeta potential becomes positive (30.62 mV), and the stability becomes slightly worse. After modification with AlCl_3 , Zeta potential slightly increases to -21.84 mV, and its stability becomes slightly stronger. After modification with KMnO_4 , Zeta potential changed to 33.41 mV, and the stability becomes slightly worse. After composite modification with FeCl_3 and AlCl_3 , Zeta potential changed to 13.06 mV, and the colloid tends to be stable. After composite modification with FeCl_3 and KMnO_4 , Zeta potential changed to 13.08 mV, and the colloid tends to be stable. After composite modification with KMnO_4 and AlCl_3 , Zeta potential decreased and colloid tended to disperse. After modification, the specific surface area of porous materials increased by 1.36-2.88 times. The order of specific surface area of materials is $\text{Fe-BC} > \text{Mn-BC} > \text{Fe-Al-BC} > \text{Fe-Mn-BC} > \text{Al-Mn-BC} > \text{Al-BC} > \text{BC}$. The total organic carbon content of the material is consistent, which is determined by the nature of the base material. The Fe, Al and Mn content of porous material was determined by the solution of the modified substance.

Table 1: Basic physical and chemical properties of porous materials

Number	Porous Material	pH	Zeta Potential (mV)	Specific Surface Area ($\text{m}^2 \cdot \text{g}^{-1}$)	Total Organic Carbon ($\text{g} \cdot \text{kg}^{-1}$)	Fe (%)	Al (%)	Mn (%)
1	BC	10.6	-26.56	4.32	453.2	/	/	/
2	Fe-BC	3.27	30.62	12.46	453.2	3.21	/	/
3	Al-BC	6.75	-21.84	5.86	453.2	/	2.37	/
4	Mn-BC	6.79	33.41	12.32	453.2	/	/	4.57
5	Fe-Al-BC	4.42	13.06	10.86	453.2	2.34	1.27	/
6	Fe-Mn-BC	3.81	13.08	10.43	453.2	1.73	/	2.14
7	Al-Mn-BC	6.47	-29.19	6.32	453.2	/	2.32	1.69

3.2. Arsenic adsorption capacity of different porous materials

From the adsorption kinetics curve, it can be seen that the absorption of arsenic in solution by porous materials increases gradually, and the absorption of unmodified porous materials (BC) in solution containing arsenic increases gradually within 3 hours after being immersed in the solution containing arsenic, after 3 hours, the adsorption amount of As increased gradually, and reached the maximum value of $1.12 \text{ mg} \cdot \text{g}^{-1}$ at about 24 hours. The adsorption of As on Fe-modified porous materials was similar to that on BC. The difference was that the adsorption capacity of As on Fe-modified porous materials was about $1.71 \text{ mg} \cdot \text{g}^{-1}$ after 24 hours, which was 53% higher than that on BC, the adsorption of arsenic tended to be the same, the adsorption amount increased rapidly within 3 hours, and slowly between 3 and 12 hours. The adsorption amount increased rapidly between 12 and 24 hours, and tended to be gentle after 24 hours. Among all the materials, the adsorption time of Fe-Al modified porous materials was the earliest, and the concentration of arsenic in solution could be significantly decreased at 15 min. The amount of arsenic adsorption was $0.06 \text{ mg} \cdot \text{g}^{-1}$, the adsorption of As on Al, Mn, Fe-Mn and Al-Mn composite porous materials was less than that on Al, Mn, Fe-Mn and Al-Mn composite porous materials. In all materials, the adsorption capacity of arsenic in solution was modified by $\text{Fe-Al-BC} > \text{Mn-BC} > \text{Al-BC} > \text{Fe-Mn-BC} > \text{Al-Mn-BC} > \text{Fe-BC} > \text{Fe-BC} > \text{BC}$. The adsorption capacity of Fe-Al-BC for arsenic is about 5 times that of BC, the adsorption capacity of Mn-BC for arsenic is about 4.4 times that of BC, and the adsorption capacity of Al-BC for arsenic is about 4.2 times that of BC, the adsorption capacity of Fe-Mn-BC for arsenic is about 3.7 times of that

of BC, the adsorption capacity of Al-Mn-BC for arsenic is about 2.7 times of that of BC, and the adsorption capacity of Fe-BC for arsenic is about 1.6 times of that of BC.

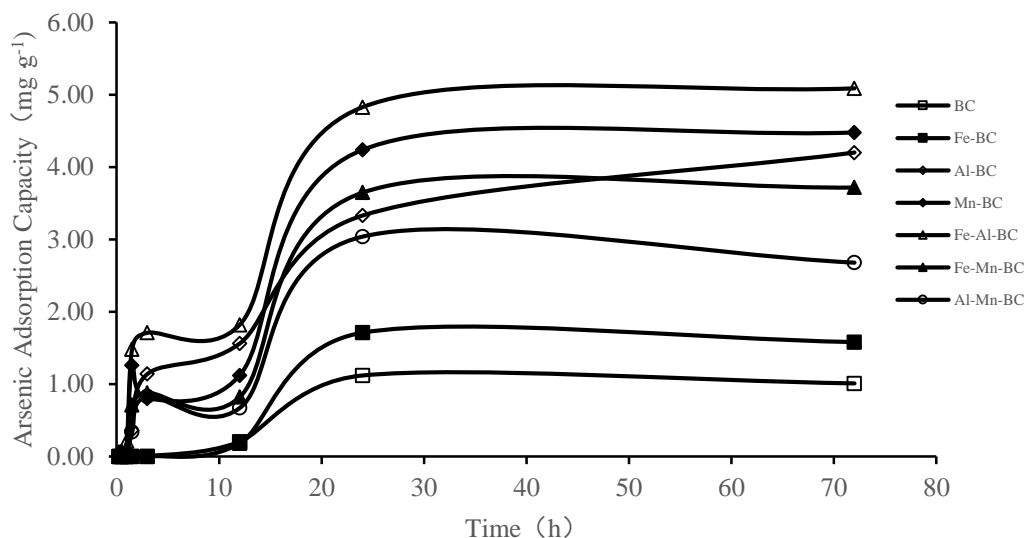


Figure 1: Arsenic adsorption kinetics of different porous materials

4. Conclusion

After modification, the pH of the porous materials decreased in varying degrees, from alkaline to acidic or weak acidic. The specific surface area of Fe-BC is 2.88 times that of BC, and that of Mn-BC is 2.85 times that of BC. Adsorption capacity for arsenic in solution: Fe-Al-BC > Mn-BC > Al-BC > Fe-Mn-BC > Al-Mn-BC > Al-Mn-BC > Al-Mn-BC > Fe-Mn-BC > Fe-BC > BC. The arsenic adsorption capacity of Fe-Al-BC is about 5 times that of BC, and the arsenic adsorption capacity of Mn-BC is about 4.4 times. On the one hand, the enhancement of arsenic adsorption capacity of Fe-Al-BC and Mn-BC is due to the increase of specific surface area of porous materials after the composite modification with ferric chloride and aluminum chloride or the modification with potassium permanganate. On the other hand, the compound of iron, aluminum and manganese on the surface of the porous material promotes the absorption of arsenic. The study showed that, after manganese modification, the acidic groups on the surface of porous materials increase, significantly improve the surface hydrophilicity of porous materials, reduce the zero point charge of porous materials, and significantly improve the arsenic adsorption capacity [4]. Manganese oxides can form ligands or coprecipitate with As to enhance the fixation ability of Mn-BC on As [5-7].

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