Packed bed column investigation on As(V) adsorption using magnetic iron oxide/bagasse biomass carbon composite adsorbent

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Abstract. In this study, the magnetic iron oxide/bagasse biomass carbon composite adsorbent (M-Fe₃O₄-BC) was achieved by the microwave precipitation one-step carbonization heating chemical modification method with bagasse as the main raw material. The effects of initial As(V) concentration, solution pH, solution flow rate and bed height on the breakthrough curve of M-Fe₃O₄-BC adsorption As(V) were studied. The results shown that the penetration time was shortened with growing initial As(V) concentration, solution pH and solution flow rate, and it lengthened with growing bed height. The exhaustion time was prolonged with increasing initial As(V) concentration and height of bed, and the influence of solution pH on the exhaustion time was not significant. When the solution flow rate is lower than 1.5 ml/min, the exhaustion point was not reached within 2000 min, and the exhaustion time was 720 min when the solution flow rate was 2.0 ml/min. The regenerated adsorbent still maintained a high adsorption capacity for As(V).

1. Introduction
Arsenic concentrations have been discovered in ground water and potable water resources around the world, Making a Threat more than 0.2 billion people in developing and developed countries [1]. The World Health Organization believe that drinking water of 10 ug/L of As is at risk, and more than 0.1 billion people around the world are at risk. Moreover, more than 4.5 billion of them may be at risk of
being exposed to more than 50 μg/L of As, such as Bangladesh delta [3] and Xinjiang of China in Asia, et al [4, 5]. Currently, treatment processes for metal-contaminated wastewater contain ion exchange technique, Membrane separation, chemical precipitation, adsorption and co-precipitation/adsorption [6]. Because of the advantages of cost-effectiveness, high efficiency and easy operation, Adsorption has become one of the most promising water purification methods [7, 8]. Magnetic nano-iron oxide particles have a bulky adsorption capacities for As (V) and As (III), and it is a exceedingly effective material for arsenic adsorbents [9].

Biochar is difficult to be separated from aqueous solution [10], but it is quite easily detach from water solution by magnetic modification [11, 12]. Magnetic carbon nanometer composite materials are highly efficiently magnetically recoverable catalysts [13] that possess immobilization capabilities to combine with a variety of active ingredients and complex structural material [14]. Xuan li et al. [15] have studied the dynamic adsorption and regeneration adsorption of As(III) in water by Mn-Fe binary oxides. Jos Ignacio z. Montero et al [16] have studied the static adsorption and intermittent desorption of As(III) removal from Waste water by Fe(III) modified bagasse and corn cob biochar. The results indicated that [15] high concentration of silicate and phosphate will have powerful competition for arsenic by Fe-Mn modified biochar. Javier A et al. [17] studied the iron modified activated carbon and found that the existence of iron was crucial to improve the adsorption capacity of arsenic, the linear coefficient is $R^2=0.4$, and the amount of As(V) adsorbed is the largest when the iron content is about one percent of activated carbon. The results shown that iron content has significant effects on the experiment result of dynamic adsorption.

The breakthrough curve is the main expression in the dynamic adsorption process [18]. It expresses the change rule of effluent concentration with contact time, which is a kind of ideal and intuitive figure, and it can provide important theoretical basis for the design and manufacture of dynamic adsorption device. In this paper [19], the dynamic adsorption of As(V) by M-Fe$_3$O$_4$-BC was studied, and the influence of initial As(V) concentration, pH value of As(V) solution, continuous flow rate of fixed bed and the height of adsorbent bed on column breakthrough and exhaustion time are studied [20].

2. Experimental

2.1 Materials

2.1.1 Bagasse. Sugarcane bagasse was taken from a sugar plant in Guigang, Guangxi Province, China. It was cleaned by distilled deionized water, and dried in drying oven at 85°C, then broken and sieved to desired 20 mesh size (0.84 mm) and stored in desiccators for use.

2.1.2 Main reagents and instruments
Reagents: FeSO$_4$, NaOH, HNO$_3$, NH$_3$H$_2$O, Na$_3$AsO$_4$·12H$_2$O, Na$_2$S$_2$O$_3$, Anhydrous ethanol, etc. The chemicals used in the experiment were analytically pure grade and the experimental water was ultrapure water. The 1 mg/mL standard solution of As was bought from National Iron and Steel Materials Testing Center Iron and Steel Research Institute and the medium of standard solution was 10% HCl, it was diluted with ultrapure water in steps when use it.

Instruments: FS-80 atomic fluorescence spectrometer (Beijing jitian instrument Co. Ltd., China), medium pressure water-cooled jacketed chromatographic column (Shanghai xiamei biochemical technology Co. Ltd.).

2.2 Methods

2.2.1 Adsorbent preparation. The M-Fe$_3$O$_4$-BC used in this study was prepared as follows [21]. 1000 mL 0.15 mol/L FeSO$_4$ solution and 50 g of dried bagasse were added to a 2L wide-mouthed reagent bottle with a sanding port then sealed cap. The mixture solution was constantly stirred and shaken by ultrasound for 30 min, aged at indoor temperature for 36 h. Afterwards, the mixed sample was well-adjusted to pH=8.5 with 1% or 10%(v/v) ammonia solution by using automatic titration apparatus.
Under the circumstance, a bagasse/Fe(OH)$_2$/Fe(OH)$_3$ compound was formed in the liquid mixture. Then target solution was placed in a microwave oven to heated to 85 °C. The suspended solid was filtered and washed by ultrapure water until it was neutral. The bagasse/Fe(OH)$_2$/Fe(OH)$_3$ solid was mixture with 200 mL absolute ethanol and shaken for 30 min in a sonicator, then filtered again. Later, the bagasse/Fe(OH)$_2$/Fe(OH)$_3$ solid was desiccated in dryer at 105-110°C for 16-24 h. In the end, the bagasse/Fe(OH)$_2$/Fe(OH)$_3$ material was carbonized at 500 °C, cooled, ground, and passed through a <100 mesh sieve to obtain the M-Fe$_3$O$_4$-BC composite adsorbent.

### 2.2.2 Dynamic adsorption method

The dynamic adsorption column was a medium pressure water-cooled jacketed chromatography column, which was a plexiglass material. The inner diameter and length of column were 10 mm 150 mm, respectively. The experimental device refers to the RSSCT small column rapid adsorption model, and schematic diagram of experimental set up was express in Figure. 1.

![Figure 1. Schematic diagram of experimental set up.](image)

1. Solution pool, 2. Peristaltic pump, 3. Burette stand, 4. Medium pressure water-cooled chromatographic column, 5. Adsorbent layer, 6. Measuring cylinder, 7. The silicone tube

A certain amount of M-Fe$_3$O$_4$-BC (120–96 um) was placed in the column, which was installed by dry method. According to the mass of the M-Fe$_3$O$_4$-BC to fix the height of the bed by adjusting the movable nut at both ends column. For purpose of reduce the effect of eddy current on dynamic adsorption, deionized water was used to flush and drive gas before adsorption experiment. The As(V) solution was passed through the column from top to bottom by using a peristaltic pump. The peristaltic pump inlet flow rate of was adjusted to the set value of the experiment. Receiving the same volume effluent solution with a covered polyethylene plastic bottle within the same set time interval. The concentration of As(V) in the effluent solution was measured by atomic fluorescence spectrometry. According to the experiment, the concentration of As(V) in effluent solution was five percent of the initial As(V) concentration (C$_t$/C$_0$=5%), and the time consumed was the breakthrough time, Marked as T$_b$. When the strength of solution of As(V) in the effluent solution was ninety-five percent of initial As(V) concentration (C$_t$/C$_0$=95%). The corresponding time was the exhaustion time, Marked as T$_e$.

### 3. Results and discussion

#### 3.1 Factors affecting adsorption

##### 3.1.1 Effect of initial concentration

The effect of original As(V) concentrations on the breakthrough curve of M-Fe$_3$O$_4$-BC dynamic adsorption As(V) is shown in Figure. 2. Figure 2 showed that with the growing of initial As(V) concentration, the adsorption rate of M-Fe$_3$O$_4$-BC on As(V) and the slope of the outflow curve increased, and both the breakthrough point and the exhaustion time were shortened.
When the initial As(V) concentration was 1.0, 2.0 and 5.0 mg/L, $T_b$ were 246, 103 and 65 min, respectively. The possible reason was that the mass transfer driving force increased with increasing As(V) mass concentration under the same flow rate [22]. The more As(V) adsorbed by M-Fe$_3$O$_4$-BC in the same time the shorter both the breakthrough time and the saturation time with growing initial As(V) mass concentration.

![Figure 2](image_url) Effect of initial concentration on arsenic adsorption breakthrough curve onto M-Fe$_3$O$_4$-BC ($T=25^\circ$C, $V=2.0$ ml/min, pH=6.8, H=6.8 cm).

![Figure 3](image_url) Effect of pH on arsenic adsorption breakthrough curve onto M-Fe$_3$O$_4$-BC ($T=25^\circ$C, $V=2.0$ ml/min, $C_{As}=2$ mg/L, $H=6.8$ cm).

### 3.1.2 Effect of solution pH

Figure 3 showed that with the growing of pH value of the solution, the adsorption rate of M-Fe$_3$O$_4$-BC on As(V) decreased, and the slope of the outflow curve decreased. When the pH value of the solution was 4.8, 6.8 and 8.8, $T_b$ was 92, 103 and 140 min, and $T_e$ was 720 min, respectively. The main reason for the same exhaustion point was that the pH value of the solution plays a rather significance role in the adsorption process, which not only affects the chemical morphology of arsenic in the solution [23], but also influence the surface charge of the adsorbent [24]. The anion formed after arsenic dissociation in the solution was absorbed into the adsorbent surface tissue. The arsenic was mainly controlled by the adsorbent surface charge and affected by the pH value of the solution [24], and arsenic adsorption depends on pH [25]. The point of zero charge value (pH$_{ZC}$) of M-Fe$_3$O$_4$-BC was 6.2. While the pH of the mixture solution was less than 6.2, the surface of M-Fe$_3$O$_4$-BC was positively charged. It was speculated that surface charge would induce M-Fe$_3$O$_4$-BC to generate electrostatic attraction between charged anions in the surrounding water phase, which was conducive to adsorption. Because the pH of the solution affects the adsorption mechanism of the adsorbent from the solution to the surface of the solid adsorbent [26], when the adsorption pH values was less than pH$_{ZC}$, the adsorption mechanism may be the same.

### 3.1.3 Effect of solution flow rate

Figure 4 showed that with the growing of solution flow, the adsorption rate of M-Fe$_3$O$_4$-BC on As(V) increased, the slope of the outflow curve increased, and the time to reach the breakthrough point and the exhaustion point decreased. When the solution flow was 1.0, 1.5 and 2.0 mL/min, $T_b$ was 385, 233 and 103 min, respectively. When the solution flow was 1.0 and 1.5 mL/min, the exhaustion point was not reached during the experimental time. When the solution flow was 2.0 mL/min, $T_e$ was 720 min. The reason was that M-Fe$_3$O$_4$-BC adsorption As(V) needs to go through liquid membrane diffusion and internal diffusion of adsorbent. However, the flux of solution has a great impact on liquid film diffusion and the inside of the adsorbent diffusion. Therefore, With the solution flow increasing, liquid film diffusion and internal diffusion of adsorbent were not fully sufficient [27].

### 3.1.4 Effect of bed height

Figure 5 showed that with the height of the bed increasing, the adsorption rate of M-Fe$_3$O$_4$-BC on As(V) decreased, the slope of the outflow curve decreased, reaching the breakthrough point and the exhaustion time increased. When bed height was 4.4, 6.6 and 8.8 cm, $T_b$ was...
95, 103 and 190 min, respectively. T_e was 363, 720 and 1680 min, respectively. The possible reason was that when the thickness of the filter layer was low, the contact time between the filtrate and the filter layer was short and the adsorption cannot be conducted. With the height of the bed increasing, the adsorption site and residence time of As(V) ions in the adsorption column were extended, which increases the distance of the transfer belt, making the As(V) ions have sufficient contact with M-Fe_3O_4-BC, and the adsorption process was more sufficient[22].

**Figure 4.** Effect of inlet flow rate on arsenic adsorption breakthrough curve onto M-Fe_3O_4-BC (T=25ºC, V=2.0 ml/min, pH=6.8, H=6.8 cm).

**Figure 5.** Effect of bed height on arsenic adsorption breakthrough curve onto M-Fe_3O_4-BC (T=25ºC, V=2.0 ml/min, CAs=2 mg/L, pH=6.8).

### 3.2 Adsorbent regeneration and reuse

The As(V) concentration of the solution was 1 mg/L, pH=6.8, and the flow rate of the solution was 2.0 ml/min. The M-Fe_3O_4-BC dynamic adsorption As(V) device (Figure. 1). After M-Fe_3O_4-BC adsorbed As(V) saturated, 1 mol/L of EDTA solution was used to regenerate M-Fe_3O_4-BC, with a flow rate of 2.0 ml/min. The inlet direction of the solution was the same As that of dynamic adsorption. As shown in Figure. 6, after 200 min regeneration, the concentration of As(V) in the regenerated liquid was less than 50 g/L, and the desorption rate of As(V) was 31.81%. At the same solution flow, the volume of the desorption solution was approximately 25.0% of the volume of the adsorbed As(V) solution. The saturated adsorption capacity of the regenerated M-Fe_3O_4-BC adsorption column for the second adsorption of As(V) was 0.38 mg/g.

**Figure 6.** Regeneration out fall As(V) concentration as function of time.
4. Conclusions

(1) The breakthrough time was shortened with the increasing of initial As(V) concentration, solution pH and solution flow rate, yet the breakthrough time was lengthened with the increasing of bed height.

(2) The exhaustion time was prolonged with the growing of initial As(V) concentration and height of bed, while the influence of solution pH on the exhaustion time was not significant. When the solution flow rate was no more than 1.5 ml/min, the exhaustion point was not reached within 2000 min, and the exhaustion time was 720 min when the solution flow rate was 2.0 ml/min.

(3) Selection of lower flow rate, higher As(V) concentration and higher height of bed can promote the dynamic adsorption process of M-Fe$_3$O$_4$-BC on As(V), and the regenerated adsorbent still maintained a high adsorption capacity for As(V).

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