Dynamic adsorption of As(V) by hydroxyapatite/bagasse biomass carbon composite adsorbent

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Abstract. Hydroxyapatite/bagasse biomass carbon composite adsorbent (HAP-BC) was prepared by hydrothermal precipitation one-step carbonization heating chemical modification method with sugarcane bagasse as main raw material. The effects of initial As(V) concentration, solution pH, bed height and influent flow rate on the penetration curve of HAP-BC adsorption As(V) were discussed. The influence on regeneration and recycling of HAP-BC were analyzed in this paper. The results shown that with increasing initial As(V) concentration, pH and influent flow rate, the break through time and exhaustion time were shorten, but the break through time and the exhaustion time would be prolonged with increasing bed height. Moreover The regenerated adsorbent still maintained a high adsorption capacity for As(V).

1. Introduction
Arsenic is a naturally semimetal, more than 245 minerals contain arsenic [1]. Arsenic contaminated waters are dangerous to human health [2, 3, 4]. The latest conclusion from WHO is that lung cancer, kidney cancer, bladder cancer and skin cancer are directly related to excess arsenic in edible water, and skin cancer is an initial symptom that can be directly observed [5, 6, 7]. At present, the removal of As technology in water bodies mainly includes: anion-cation exchange, precipitation, membrane filtration, solidification, osmotic reaction, phytoremediation, ion exchange with microbial/biological treatment et al [8]. However, traditional As remediation technologies has high cost, it is a development trend to search for low-cost, effective technologies.

Compared to these physicochemical methods, adsorption energy have shown more selective and efficient in removing heavy metal in water. In recent years, research on the removal of heavy metals by low-cost modified biosorbents has been increasing [9]. Most studies on the adsorption of arsenic in aqueous solutions are carried out in batches in the laboratory. The experiment was used to determine the adsorption effect of the adsorbent. It can be used for the treatment of small amounts of polluted water, but it is not suitable for systems with a large amount of sewage treatment [10, 11].
the dynamic system is easy to extend, low cost, few operating steps and suitable for applications[12]. Homero et al [13] studied the experiment of removing As(V) under dynamic conditions of concrete/magnetic nanocomposites. Borano et al [14] researched the dynamic adsorption of As(V) in water by Iron-Mixed Mesoporous Pellet. Oke et al [15] studied the removal of arsenic from aqueous solution in untreated powdered eggshell under dynamic adsorption conditions. Dousova et al [16] studied the dynamic adsorption of As(V) by Fe/Mn modified raw clay. The results show that the difference of iron content has obvious influence on the results of dynamic adsorption experiments. In this study, the effect of HAP-BC adsorption As(V) breakthrough curve are studied from initial As(V) concentration, pH, influent flow rate and bed height. In order to further improve the theoretical knowledge of dynamic adsorption, more theoretical and experimental studies are needed.

2. Materials and methods

2.1. Materials

2.1.1 Sugar cane residue. Sugarcane bagasse that was not removed marrow was taken from a sugar factory in Guigang, Guangxi Province, China. After the bagasse was washed with distilled water, the bagasse was dried in an oven at 80 ºC. Bagasse samples were sieved through a 20 mesh (0.84 mm), all samples were placed in a desiccator for use.

2.1.2 Main reagents and instruments. Reagents: FeCl₃·6H₂O, NaOH, HNO₃, NH₃·H₂O, Na₃AsO₄·12H₂O, C₁₉H₄₂BrN and Absolute ethanol. Analytically pure chemicals were used in the experiments. The experimental water was ultrapure water. The standard solution of As was bought from National Iron and Steel Materials Testing Center Iron and Steel Research Institute, the medium of standard solution was 10% HCl at a concentration of 1 mg/ml and is diluted stepwise with ultrapure water.

Instrument: FS-80 atomic fluorescence spectrometer (Beijing Jitian Instrument Co., Ltd., China), medium pressure water-cooled jacketed chromatography column (Shanghai Ximei Biochemical Technology Co., Ltd., China).

2.2 Methods

2.2.1 Preparation. Method for preparing HAP-BC according to reference [17]. In a 2 L beaker, 250 ml of a 0.2 mol / L calcium acetate solution was added, followed by 250 ml of a 4.4 mol / L ammonium acetate buffer solution. After mixing evenly, 50 g of dried bagasse was added to the beaker. Solution and bagasse in the beaker were stirred with electric waves, and shook for 30 minutes, and let immersed for 24 h. Then, 500 ml of 0.06 mol/L ammonium dihydrogen phosphate solution was added to the mixture solution and bagasse under rapid stirring was adjusted to pH=7.5 with 10% aqueous ammonia under slowly stirring and continue to stir for 10 min. The beaker was covered with a glass watch and placed in a constant temperature water bath reacted for 48 hours at 100 ºC. Under this condition, a bagasse/Ca₅(PO₄)₃OH mixture was formed in the suspended solution. The beaker was taken out from the water bath, naturally cooled, the suspended solid was filtered and solid phase precipitate was repeatedly washed twice with ultrapure water, and then washed once with absolute ethanol. The solid phase was dried at 70 ºC for 16 h in oven. Finally, the bagasse/Ca₅(PO₄)₃OH solid was carbonized at 500 ºC for 4 h in a muffle furnace to get HAP-BC. Then HAP-BC was ground and passed through a 100 mesh screen.
2.2.2 Dynamic adsorption. The particle size of HAP-BC adsorbent was 120–160 mesh (120–96 μm), and the mass of activated carbon was 1.000–2.000 g. The effects of initial As(V) concentration, pH, influent flow rate and bed height on the breakthrough curve of HAP-BC adsorption As(V) were studied. The dynamic adsorption column is a medium-pressure water-cooled jacketed chromatography column, which is plexiglass material. The inner diameter of column is 10 mm and the length of it is 150 mm. The experimental device draws on the RSSCT small column rapid adsorption model. Figure 1 shows the schematic diagram of experimental setup.

A certain amount of HAP-BC adsorbent was placed in the chromatography column, and the column was packed by dry method. According to the quality of the adsorbent to fix the height of the bed by adjusting the movable nut at both ends column. To reduce the effect of solution vortex on dynamic adsorption, the deionized water was used to flush the purge before the adsorption experiment. The As(V) solution flow through the column from top to bottom by a peristaltic pump. The peristaltic pump inlet flow rate was adjusted to the experimental set value, and receiving the same volume effluent solution with a covered polyethylene plastic bottle at the same set time interval. The concentration of As(V) in the effluent solution were determined by atomic fluorescence spectrometry. The experiment stipulates that the concentration of As(V) in the effluent solution was five percent \((C_t/C_0=5\%)\) of the As(V) concentration in the influent solution, which is the breakthrough time, expressed by \(T_b\); When the concentration of As(V) in the effluent solution was ninety-five percent \((C_t/C_0 = 95\%)\) of the As(V) concentration in the influent solution, which is the exhaustion time, expressed by \(T_e\).

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

1. Solution pool 2. Peristaltic pump 3. Burette tube rack 4. Medium pressure water cooled chromatography column 5. Adsorbent layer 6. Measuring cylinder 7. Silicone tube

3. Results and discussion

3.1 The factor of adsorption

3.1.1 Initial concentration. The effect of initial As(V) concentrations on the penetration curve of HAP-BC dynamic adsorption As(V) is shown in Fig. 2. Fig. 2 shown that the adsorption rate of As(V) by HAP-BC and the slope of the outflow curve grow with increase of initial As(V) concentration. the time to reach the breakthrough point and exhaustion point became shorter with increase of initial As(V) concentration.. At high initial concentrations, Shortening of breakthrough time and exhaustion time may be due to the rapid exhaustion of the sorption sites [18]. When the initial As(V) concentrations were 1 mg/L, 2 mg/L and 5 mg/L, \(T_b\) were 310 min, 231 min and 63 min, respectively, and \(T_e\) were 1850 min, 790 min and 713 min, respectively.

3.1.2 pH. The effect of pH on the breakthrough curve of HAP-BC dynamic adsorption As (V) is shown in Fig. 3. Fig. 3 shown that when the pH values of the solutions were 4.8, 6.8, and 8.8, \(T_b\) were 246 min, 230 min, and 178 min, \(T_e\) were 960 min, 790 min, and 720 min, respectively. The variation of
adsorption breakthrough time with pH was: $T_b(pH=4.8)>T_b(pH=6.8)>T_b(pH=8.8)$, It indicated that the change of adsorption breakthrough time and adsorption exhaustion time under different pH conditions is different. The main reason for the different saturation time points is the pH of the solution, which not only affects the chemical form of arsenic in the solution, but also influences the surface charge of adsorbent. After the arsenic dissociation in the solution, anions were formed, the arsenic adsorbed to the surface of the adsorbent was mainly controlled by the surface charge, and was affected by the pH of the solution [19].

3.1.3 Inlet flow rate. The effect of solution flow on the breakthrough curve of HAP-BC dynamic adsorption As (V) is shown in Fig. 4. Fig. 4 showed that as the increasing inlet flow rate, the adsorption rate of HAP-BC to As(V) grow, the slope of the outflow curve became larger, It had a shorter time to reach the breakthrough point and exhaustion point. When the inlet flow rates were 1.0 ml/min, 1.5 ml/min, and 2.0 ml/min, $T_b$ were 218 min, 231 min and 243 min respectively. When the inlet flow rate was 1.0 ml/min, exhaustion time was not reached within 2000 min. When the inlet flow rates were 1.5 ml/min and 2.0 ml/min, the exhaustion times were 1112 min and 790 min, respectively. This was reason that the adsorption of arsenate ions by HAP-BC required diffusion through the liquid membrane and internal diffusion of the adsorbent. The inlet flow rate not only affects the diffusion of the liquid film, but also has a large effect on the internal diffusion of the adsorbent [20].

3.1.4 Bed height. The effect of bed height on the penetration curve of HAP-BC dynamic adsorption As(V) is shown in Fig. 5. Fig. 5 showed that as the increasing of bed, the adsorption rate of As(V) by HAP-BC decreased, the slope of the outflow curve cut down, and the time to reach the breakthrough point and the exhaustion point was prolonged. When the bed heights were 4.0 cm, 6.0 cm and 8.0 cm, $T_b$ were 231 min, 250 min and 260 min, $T_e$ were 790 min, 1500 min and 2100 min, respectively. The change was consistent with experimental results of the references [21]. The possible reason was that the increase of the aspect ratio of the bed increased the specific surface area of adsorbent, and also increased the tortuosity of the fluid channel in the fixed bed, provided more active sites for the adsorption process [22].

**Figure 2.** Effect of initial concentration on arsenic adsorption breakthrough curve onto HAP-BC($T=25^\circ C$, $V=2.0$ ml/min, $pH=6.8$, $H=4.0$ cm).

**Figure 3.** Effect of pH on arsenic adsorption breakthrough curve onto HAP-BC($T=25^\circ C$, $V=2.0$ ml/min, $C_{As}=2$ mg/L, $H=4.0$ cm).
3.2 Regeneration of adsorbent materials

A device for dynamic adsorption of As(V) by HAP-BC with initial As(V) concentration of 1 mg/L, pH of 6, and inlet flow rate of 2.0 ml/min (Fig. 1). After As(V) was absorbed, the regeneration experiment was carried out with a 1 mol/L hydrochloric acid solution. The flow rate of the hydrochloric acid solution was 1.75 ml/min. The inlet water had the same direction with the dynamic adsorption inlet water, experimental results are shown in Fig. 6. Fig. 5 shown that after 164 minutes of regeneration, the As(V) concentration was less than 50 μg/L in the regenerant, and the desorption rate was 37.41%. At the same inlet flow rate, the time to reach exhaustion adsorption was 1850 min, so the volume of desorbed solution was about 8.9% of the volume of the adsorbed As(V) solution, and the desorption effect was good. This may be because the pH of the 1 mol/L hydrochloric acid solution is less than 1, As (V) is mainly in the form of neutral H$_3$AsO$_4$ in the solution, and As(V) is easily eluted from the adsorbent. After regeneration, the saturated adsorption capacity and desorption rate of As(V) adsorbed on the HAP-BC adsorption column were 1.74 mg/g and 28.67%, respectively. The reason for the decrease in the adsorption amount and desorption rate of As(V) may be that the hydrochloric acid solution was used as the regeneration solution, and the acidity was strong, so that the surface charge of HAP-BC was changed, and the adsorbed arsenate was easily eluted under acidic conditions.

![Figure 4](image1.png)

Figure 4. Effect of inlet flow rate on arsenic adsorption breakthrough curve onto HAP-BC(T=25°C, pH=6.8, $C_A$s=2 mg/L, H=4.0 cm).

![Figure 5](image2.png)

Figure 5. Effect of bed height on arsenic adsorption breakthrough curve onto HAP-BC(T=25°C, pH=6.8, $C_A$s=2 mg/L, V=1 mg/L).

![Figure 6](image3.png)

Figure 6. Regeneration out fall As(V) concentration as a function of time.
4. Conclusion
(1) With increasing initial As(V) concentration, pH and influent flow rate, the adsorption breakthrough time and adsorption exhaustion time were shortened; The adsorption breakthrough time and the adsorption saturation time were prolonged as the bed height increases.
(2) Through selecting a low flow rate, a high solution concentration and a high filler layer height can promote the dynamic adsorption process of As(V) by HAP-BC, Moreover the regenerated adsorbent still maintained a high adsorption capacity for As(V).

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