An Investigation of Fluoride Adsorption and Removal by Iron Salt and Aluminum Salt Composite Modified Bone Biochar

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Abstract: The F⁻ adsorption capacity of cattle bone biochar (CBB) modified with by $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, and $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ composite was investigated. Results showed that the adsorption capacity of CBB modified with $Fe_2(SO_4)_3$ and $Al_2(SO_4)_3$ composite (Fe-Al-CBB) reached 45.45 mg/g, which was 8.5 times the adsorption capacity of unmodified CBB (5.34 mg/g). The adsorption data were well fitted to the pseudo-second-order kinetic model for raw and modified CBB. The adsorption isotherm is more consistent with the Langmuir isotherm adsorption equation. The order of point of zero charge found is that of Al-Fe-CBB > Al-CBB > Fe-CBB > CBB, which was 7.47, 7.20, 6.62 and 6.19, respectively. The highest removal efficiency of F⁻ of Fe-Al-CBB, Al-CBB, Fe-CBB and CBB was 98.56%, 74.77%, 20.95%, and 11.57%, respectively. The higher removal efficiency of F- of Fe-Al-CBB was related to its higher zero charge point. Results suggest that the $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ composite modified CBB is a promising absorbent for removal of F⁻ from water.

Keywords: Aluminum salt; iron salt; modification; cattle bone biochar; adsorption; fluoride

1. Introduction

Fluoride (F⁻) found in the environment mainly comes from anthropogenic activity, including coal combustion, improper discharge of waste products by various industries, such as nickel, steel, copper and aluminum smelting; and the industrial manufacture of masonry, ceramics, semiconductors, phosphate fertilizers and glass[1]. Over exposure to fluoride can result in health problems particularly if higher concentrations of fluoride from drinking water are ingested over time. For example, exposure to drinking water with high fluoride concentration (> 1.0 mg/L), may result in effects on the immune and human reproductive systems, children's neurodevelopment, kidney and gastrointestinal tract health[2]. In addition, Susan *et al.*[3] found that F- can form strong bonds with other toxic metals such as aluminum and lead, altering the toxicity of the substance when digested. The WHO guideline F-concentration range in drinking water is 0.5–1.5 mg/L[4]. About 260 million people in the world are drinking water with F- >1.5 mg/L[5]. Therefore, it is currently an important water quality and public health issue.

Much research effort has focused on developing technologies or methods for removal of F- from water to reduce its concentrations to levels below 1.5 mg/L. Adsorption is a promising method for the removal of fluoride from water and has the advantages of low cost, high removal efficiency, and ease of management. Many materials including activated carbon, zeolites, aluminum, nanomaterials, biochars and bone char[6,7] could be used as an absorbent. Therefore, it is very important to choose suitable absorbent materials to removal F- from water.

Meat industries worldwide produce millions of tonnes of bone waste annually. Bone waste could be made into bone biochar, which has been used as an absorbent for decolorization in the sugar industry[8]. The principal constituents of bone biochar are 70–76% hydroxyapatite (HAP), 7–9% calcium carbonate and 9–11% amorphous carbon[9], which is known to have a high pollutant removal efficiency. Methods to enhance the removal efficiency of F- through modification of bone biochar have been investigated. Zhu *et al.*[10], for example, reported that the maximum removal F- by $AlCl_3$ modified bone biochar was 97% at pH 7. Similarly, Nigri *et al.*[11] demonstrated that the maximum adsorption F⁻ capacity from water by bone biochar modified with $AlCl_3.6H_2O$ was 6.8 mg/g.

Bone biochar has gained considerable attention owing to its low cost, ease of preparation and

biocompatibility[12]. As noted, there is much research on bone biochar modified with aluminum salts or iron salts. However, there is little information on bone biochar doped modified with both composite aluminum salt and iron salt. Therefore, in this study, the capacity of adsorption F⁻ of modification by composite aluminum salt and iron salt bone biochar was researched. In addition, the effect of pH, co-existing anion and addition absorbent on capacity of adsorption F⁻ was also discussed. Results could inform the development of the novel absorbents with high capacity to remove F⁻ from water.

2. Material and methods

2.1 Preparation of bone biochar

Cattle bone collected from a hotel in Nanjing was washed with distilled water, and then air-dried. The materials were put in a ceramic pot in a muffle furnace for heating at 450 °C for 2 h to produce biochar. The biochar produced was termed as cattle bone biochar (CBB), and this CBB was ground and then passed through a sieve to obtain CBB with particle size 0.2 -2 mm.

2.2 Cattle bone biochar modification

CBB and 8% $Al_2(SO_4)_3$ solution were added to a beaker with a ratio 1:5 of solid to liquid . After stirring for 1 h, the CBB was taken out, and washed to neutral with deionized water. The washed CBB was dried at 100°C to obtain $Al_2(SO_4)_3$ modified CBB, which is termed as Al-CBB. Similarly, CBB was mixed in a beaker with 4% $Fe_2(SO_4)_3$ solution at a ratio of 1:5. After stirring for 0.5 h, the CBB was taken out, and washed to neutral with deionized water. The washed CBB was dried at 100°C to obtain $Fe_2(SO_4)_3$ modified CBB, which is termed as Fe-CBB. The Fe-CBB was then mixed in a beaker with 8% $Al_2(SO_4)_3$ solution at a ratio of 1:5. After stirring for 1 h, the cattle bone biochar was taken out, and washed to neutral with deionized water. The washed cattle bone biochar was dried at 100°C to obtain $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ composite modified cattle bone biochar, which was labeled as Fe-Al-CBB.

2.3 Adsorption kinetics experiments

The adsorption experiments using the batch method were conducted at room temperature (25 °C). Solutions were prepared for each bone biochar (CBB, Fe-CBB, Al-CBB and Fe-Al-CBB). 1g of the biochar was added to a 100ml solution containing F⁻ at a concentration of 200 mg/L. The pH of the solution was adjusted to 7 by adding 1 M HCl or 1 M NaOH. The solutions were shaken at 180 rpm in a mechanical shaker at 25 °C. Subsamples were taken after 1, 3, 5, 8, 10, 12, 24 and 36 h. The F⁻ concentrations in the supernatants were determined using the F- ion selective electrode (PXSJ-216). The Felectrode was calibrated for concentrations 1, 10, 100 mg/L F- solutions using the total ionic strength adjustment buffer (TISAB). The calibrated electrode was used for measuring F⁻ concentrations of all experimental water samples.

The amount of F⁻ adsorbed by the studied bone biochars was calculated by the following equation (Eq. (1)).

$$q_t = \frac{(C_0 - C_t) \times V}{W} \tag{1}$$

Where q_t (mg/g) is the amount of F⁻ adsorbed by the studied bone biochar at the given time; C_0 and C_t (mg/L) are the F⁻ concentration before and after adsorption at time t, respectively; V (L) is the volume of adsorption solution; and W (g) is the weight of the studied bone biochar.

The experimental data were fitted to three typical kinetic models (Pseduo-first-order Eq. (2)), Pseduo-second-order Eq. (3) and Intraparticle diffusion Eq. (4)).

$$\ln(q_e - q_t) = \ln q_e - K_1 t \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} = \frac{1}{h} + \frac{t}{q_e} \tag{3}$$

$$q_t = K_3 t^{0.5} + C \tag{4}$$

Where q_e (mg/g) is the amounts of F⁻ adsorbed by the studied bone biochar at the equilibrium time;

K_1(1/h), K_2 (g/mg/h), and K_3 (mg/g/h$^{0.5}$) are the rate constants of the corresponding model; and C (mg/g) is a constant.

2.4 Adsorption isotherm experiment

Sorption isotherms of F$^-$ were measured using a series of batch experiments in centrifugal tubes containing different concentrations of F$^-$. 0.5 g of biochar absorbent (CBB, Fe-CBB, Al-CBB and Fe-Al- CBB) was respectively added to 40 mL of F$^-$ solution ranging from 0 to 640 mg/L (10, 20, 40, 80, 160, 320 and 640 mg/L). Sorption isotherm condition was the same as above. After being shaken for 24 h, the suspensions were centrifuged and filtered to obtain the supernatant solution for determination of F$^-$ concentration. The amount of adsorption F$^-$ was calculated according to Eq. (5).

$$q = \frac{(C_0 - C_e) \times V}{W} \tag{5}$$

where q(mg/g) is the adsorbed amount of F$^-$ per unit weight of the studied bone biochar at an equilibrium concentration; V(L) is the volume of F$^-$ solution; W(g) is the weight of the studied bone biochar; C_0 (mg/L) and C_e (mg/L) is the initial and equilibrium F$^-$ concentration, respectively.

Experiment data were fitted to the Langmuir (Eq. (6)) and Freundlich (Eq. (7)) equations to quantify the adsorption capacities of the studied bone biochars.

$$q = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{6}$$

$$q = K_F C_e^{\frac{1}{n}} \tag{7}$$

where q (mg/g) and C_e (mg/L) are the same as above; 1/n is the intensity of adsorption or affinity; q_{max} (mg/g) is the maximum sorption capacity; K_F (mg/g) and K_L (L/mg) are Freundlich adsorption constant and Langmuir constant, respectively.

2.5 Effect of quantity of bone on removal efficiency of F-

The bone biochars (CBB, Fe-CBB, Al-CBB and Fe-Al-CBB) with 0.1, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.5, 2 and 3 g were respectively added to 100 mL F$^-$ solution with concentration of 200 mg/L. After being shaken for 24 h, the suspensions were centrifuged and filtered to obtain the supernatant solution for determination of F- concentration. The amount of F$^-$ adsorbed by the bone biochars was calculated by the equation (Eq. (1)). Removal efficiency of F$^-$ was calculated according to Eq.(8).

$$\eta = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{8}$$

Where η (%) is the removal efficiency of F-; C_0 and C_t (mg/L) are the F$^-$ concentration before and after adsorption at time t, respectively.

2.6 Effect of pH on adsorption F- capacity of bone biochar

0.5 g absorbent (CBB, Fe-CBB, Al-CBB and Fe-Al-CBB) was added to 100 mL of F- solution of known initial F$^-$ concentration of 200 mg/L with different pH (4, 5, 6, 7, 8, 9 and 10), respectively. After 24h at shaken at 180 rpm in a mechanical shaker at room temperature (25 °C), the suspensions were centrifuged and filtered to obtain the supernatant solution for determining F- concentration. The amount of F$^-$ adsorbed by the bone biochar was calculated according to equation.

2.7 Point of zero charge analysis

0.5 g absorbent (CBB, Fe-CBB, Al-CBB and Fe-Al-CBB) was respectively added to 40 mL of concentration of 200 mg/L F$^-$ solution with different range of pH (2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12). The F- solutions were shaken at 180 rpm in a mechanical shaker at room temperature (25 ºC). After 24 h, the suspensions were centrifuged and filtered to obtain the supernatant solution for determining Zeta potential. The Zeta potential was measured using a zeta potential analyzer (Zetasizer Nano ZS90). The pH at point zero charge (pH$_{pzc}$) of absorbent occur when Zeta potential is zero.

2.8 Statistical analysis

All experiments were conducted in triplicate. The Origin Pro 8.0 was used to fit the kinetics and isotherms sorption, and R^2 values were calculated to evaluate the performance of different models.

3. Results and discussion

3.1 Adsorption kinetics of bone biochar

It can be seen from Fig. 1, reaction of adsorption of F^- on CBB is fast up to 5 h owing to the availability of large numbers of active sites on the surface. Then, adsorption rate slows down gradually until the equilibrium is reached after 8 h for CBB and Fe-CBB. However, the adsorption of F^- reached equilibrium after 24 h for Al-CBB and Al-Fe-CBB. A rapid increase in the F- adsorption rate is observed from 0- 5 h for both raw CBB and modified CBB; the rate decreased after 10 h for CBB and after 24 h for Fe-Al-CBB (Fig. 1). This pattern is likely related to the availability of more active sites on the surface of the CBB resulting in the initial increase of adsorption F^- ion, while with the increase in the time of contact with F^-, the availability of active sites on the surface of the cattle bone biochar decreased resulting in the decrease in the rate of adsorption.
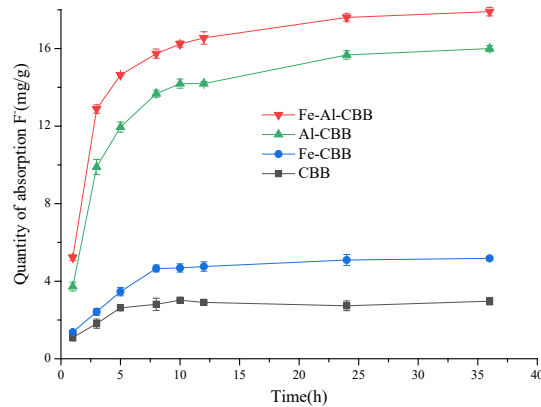

Fig. 1 F- adsorption on the studied biochars over time. CBB represented cattle bone biochar. Fe-CBB, Al-CBB and Fe-Al-CBB is modified by $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, and $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ composite modified cattle bone biochar.

The kinetic parameters of F- sorption on the tested CBB and modified CBB are shown in Table 1. The sorption data were well fitted to the pseudo-second-order kinetic model for the CBB and modified CBB with a higher R^2 in a range of 0.994-0.998. However, the adsorption data did not fit the intra-particle diffusion well with a low R^2 between 0.917-0.980 (Table 1), indicating that intrapore diffusion was not the dominant process of F- sorption.

Table 1 Kinetic parameters of F- sorption on the biochars for different models.

Biochar	Pseudo-first-order kinetics model		Pseudo-second-order kinetics model		Intra-particle diffusion model	
	K_1(min)	R^2	K_2(g/(mg·min)	R^2	K_p/(mg/(g·min)	R^2
CBB	0.341	0.961	0.289	0.994	0.902	0.951
CBB	0.341	0.961	0.063	0.996	1.648	0.980
Fe-CBB	0.269	0.947	0.023	0.998	4.704	0.917
Al-CBB	0.249	0.971	0.031	0.998	2.077	0.963

CBB represented cattle bone biochar. Fe-CBB, Al-CBB and Fe-Al-CBB is modified by $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, and $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ composite modified cattle bone biochar, respectively.

3.2 Adsorption isotherm of cattle bone biochar

F- adsorption of CBB, Fe-CBB, Al-CBB and Fe-Al-CBB increased with increased initial F-concentration (Fig.2). The amount of adsorption F- of Fe-Al-CBB was the highest, but that of CBB was lowest.

The sorption equilibrium data fitted well to both Freundlich (R^2 in a range of 0.961-0.975) and

Langmuir (R^2 in a range of 0.958-0.983) isotherm models (Table 2). The maximum adsorption capacity observed was 5.336-45.455 mg/g for Langmuir. Fe-Al-CBB showed better adsorption capacity as compared to other bone biochar. Fe-Al-CBB could remove F- from aqueous solution in a promising and cost-effective way indicating that it might be an excellent choice for the removal of F- from contaminated groundwater. Saikia et al.[13] reported that maximum F^- removal capacity of *Sacchrum ravannae* biochar was 12.5 mg/g. In the present study the maximum adsorption capacity of Fe-Al-CBB observed was 45.455 mg/g, which is higher than *Sacchrum ravannae* biochar.

In this study, the maximum adsorption capacity of F- for CBB was 5.34 mg/g, but the maximum adsorption capacity of F^- for aluminum sulfate modified bone biochar was 34.48 mg/g. Therefore, the adsorption capacity of F- was significantly improved by modifying bone biochar with aluminum sulfate.
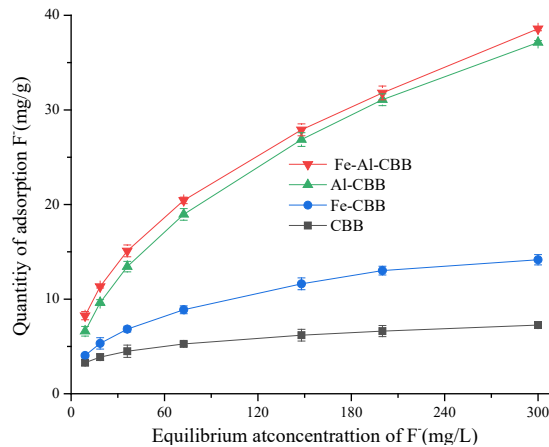

Fig. 2 Sorption isotherm of F- on the studied biochars. CBB represented cattle bone biochar. Fe-CBB, Al-CBB and Fe-Al-CBB is modified by Fe2(SO4)3, Al2(SO4)3, and Al2(SO4)3 and Fe2(SO4)3 composite modified cattle bone biochar, respectively.

Table 2 Sorption parameters of F^- on the biochars obtained from the Langmuir and Freundlich isotherm model

Biochar	Langmuir			Freundlich		
	Q_m (mg/g)	K_L(L/mg)	R^2	K_f(L/mg)	n	R^2
CBB	5.34	0.482	0.958	1.996	4.417	0.975
Fe-CBB	13.33	0.170	0.963	1.769	2.655	0.973
Al-CBB	34.48	0.052	0.983	3.175	2.300	0.975
Al-Fe-CBB	45.46	0.025	0.978	2.633	2.124	0.961

CBB represented cattle bone biochar. Fe-CBB, Al-CBB and Fe-Al-CBB is modified by $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, and $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ composite modified cattle bone biochar, respectively.

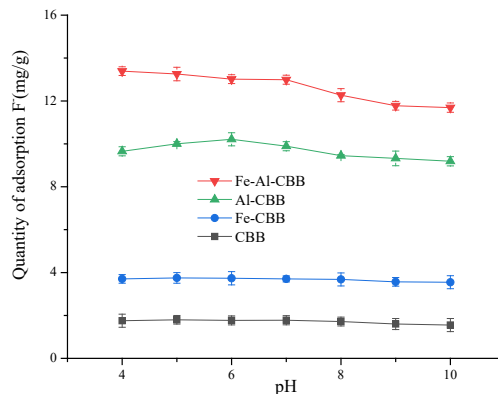### 3.3 Effect of pH on adsorption fluoride capacity

Fig. 3 Effect of pH on capacity adsorption F^- on the studied biochars. CBB represented cattle bone biochar. Fe-CBB, Al-CBB and Fe-Al-CBB is modified by $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, and $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ composite modified cattle bone biochar, respectively.

In the range of pH 4.0–10.0, CBB and Fe-CBB maintain a relatively stable adsorption capacity of F⁻ (Fig.3). At pH greater than 8, the F⁻ adsorption capacity by Al-CBB and Al-Fe-CBB decreased slightly. Fluoride is generally difficult to remove at higher pH conditions, with better removal efficiency observed at low pH[14]. In the present study, efficient F⁻ removal with high uptake capacity has been obtained at the range of pH 4.0–10.0. Thus, the comparison of adsorption capacities and pH revealed that the Al-Fe-CBB is an efficient absorbent for the removal of F⁻ from aqueous solution.

3.4 Zero charge point of modification bone biochar

Zeta potential of before and after adsorption of F- by different bone biochar were shown in Fig.4. The curves were drawn by the pH values and the Zeta potential, and the pH corresponding to the intersection of the curves was zero charge point (pH$_{zpc}$). A higher zeta potential after F⁻ adsorption than before F⁻ adsorption was found. According to the zeta potential data, the pH value of the zero charge point (pH$_{ZCP}$) was determined. Before adsorption F-, Zero charge point of CBB, Fe-CBB, Al-CBB and Al-Fe-CBB occur at pH 6.19, 6.62, 7.20 and 7.47, respectively.
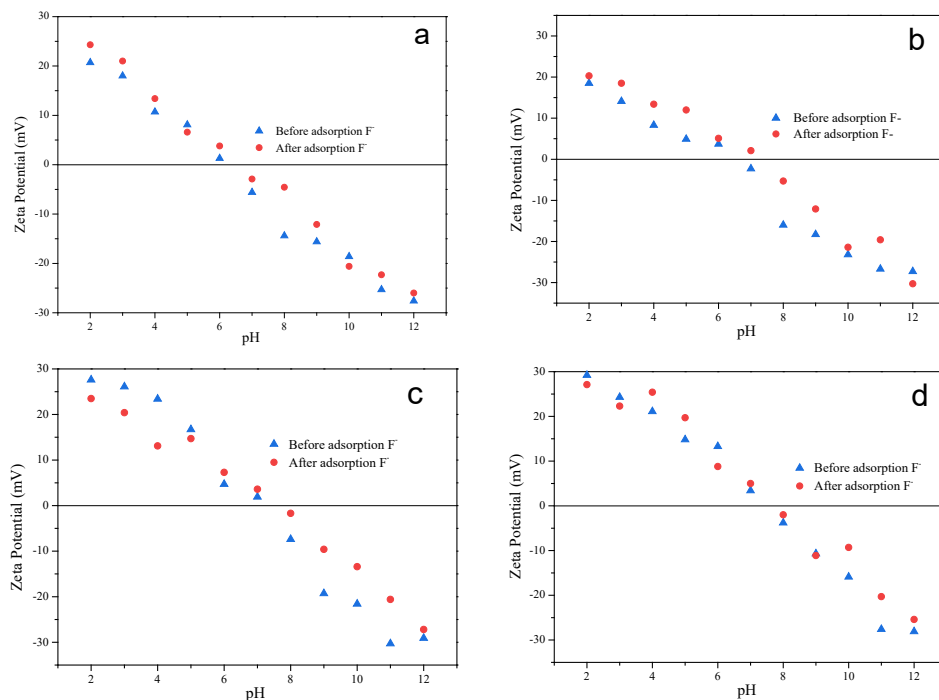

Fig. 4 Zeta potential of before and after adsorption F- of CBB (a), Fe-CBB (b), Al-CBB (c) and Fe-Al-CBB (d) under different pH. CBB represented cattle bone biochar. Fe-CBB, Al-CBB and Fe-Al-CBB is modified by $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, and $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ composite modified cattle bone biochar, respectively.

According to Fig.4 a, zero charge point for CBB occurs at pH=6.19 before adsorption and at pH=6.57 after adsorption of F⁻. The zero charge point of Fe-CBB occurs at pH=6.62 before, and 7.28 after adsorption F^{-1}. Positive charged sites on Fe-CBB exist when pH<6.62 (Fig.4a).According to Fig.4c, the zero charge point of Al-CBB occurs at pH=7.2 before, and 7.57 after adsorption F^{-1}. There were positive charged sites on Al-CBB when pH<7.2. From Fig.4d, the zero charge point of Al-Fe-CBB occurs at pH=7.47 and 7.71 before and after F^{-1} adsorption. There were positive charged sites on Fe-CBB when pH<7.47. As shown in table 3, the order of point of zero charge is that of Al-Fe-CBB > Al-CBB > Fe-CBB > CBB. At pH levels below the point of zero charge, the surface of absorbent is positively charged, and this will increase the affinity of the negatively charged F⁻ ions to adsorb onto the biochar. The electrostatic interaction between the bone biochar surface and the F⁻ plays an important role in the removal process. This mechanism is affected by the changes in the pH of the solution, in that it controls the isoelectric point of the bone biochar surface and hence affects its electrical attraction to entities in proximity to it. For example, in weakly acidic and neutral conditions, the surfaces of CBB and Fe-CBB would be negatively charged, and there would be no electrostatic attraction between the CBB or Fe-CBB and F-. However, the surface of Al-CBB and Al-Fe-CBB would be positively charged (Fig.4), and there would be electrostatic attraction between the Al-CBB or

Al-Fe-CBB and F⁻.

CBB have negative charge under neutral (Fig.4a), but CBB have capacity to adsorp F- (Fig.3) contribution to ion exchange occur on bone biochar. Herath *et al.*[15] demonstrated that the formation of F- precipitants on the surface of the bone biochar takes place with high F^- concentrations, or in the case of metal coated bone biochar, with cations such as Al^{3+}, Fe^{3+} etc. Therefore, the higher F- adsorption capacity of aluminum and iron salt composite modified bone biochar also contributed to precipitants such as CaF_2, AlF_3 or FeF_3. These results suggest that the mechanism of F- by removal Fe-Al-CBB could include the following processes: electrostatic interaction, ion exchange, and precipitation or a combination of these mechanisms.

Table 3 pH_{zcp} value before and after adsorption fluoride for different bone biochar

biochar	before adsorption fluoride	After adsorption fluoride
BBC	6.19	6.57
Fe-BBC	6.62	7.28
Al-BBC	7.20	7.57
Al-Fe-BBC	7.47	7.71

CBB represented cattle bone biochar. Fe-CBB, Al-CBB and Fe-Al-CBB is modified by $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, and $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ composite modified cattle bone biochar, respectively.

3.5 Removal efficiency of F- changed with quantity of addition of bone biochar
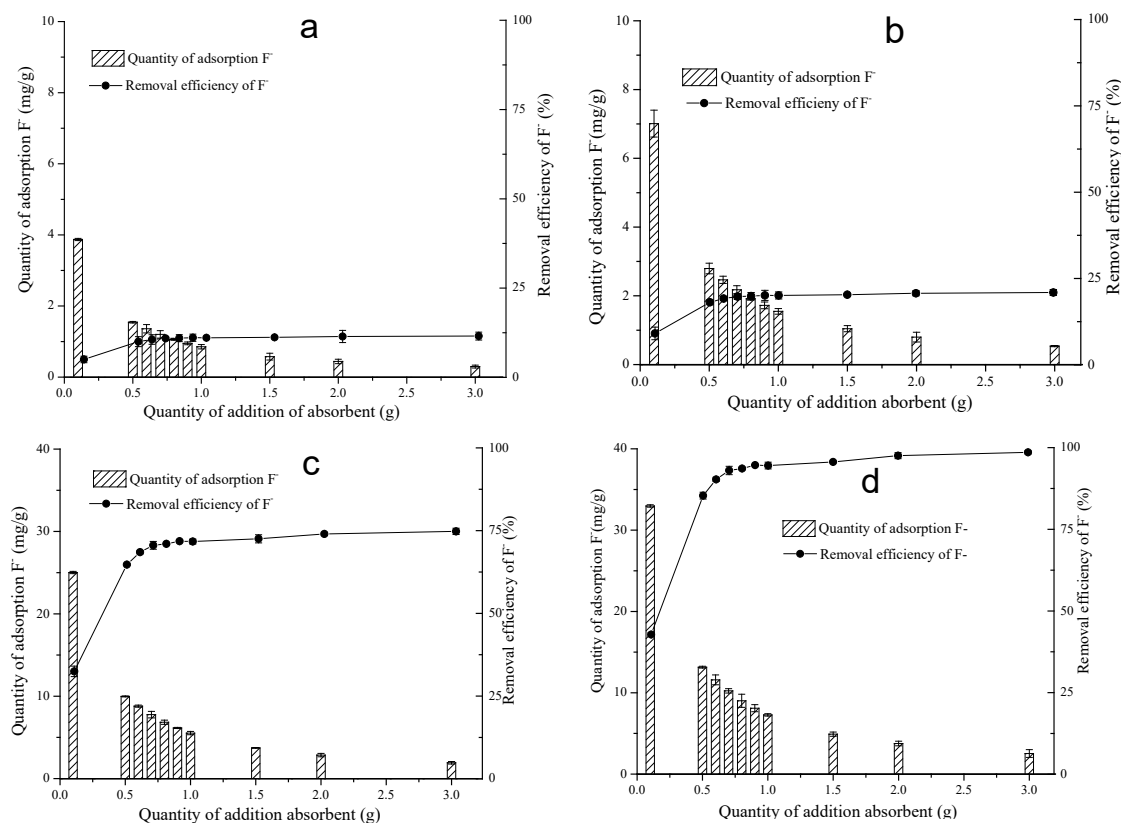

Fig.5 Removal efficiency of F- for CBB (a), Fe-CBB (b), Al-CBB (c) and Fe-Al-CBB (d). CBB represented cattle bone biochar. Fe-CBB, Al-CBB and Fe-Al-CBB is modified by $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, and $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ composite modified cattle bone biochar, respectively.

F- adsorption decreased with increasing quantity of absorbent (Fig. 5). For example, the amount of adsorption F- decreased from 3.87 mg/g to 0.30 mg/g when quantity of CBB increased from 0.1 to 3 g (Fig. 5a). However, removal efficiency of F- increased with increasing quantity of bone biochar. When increasing CBB, Fe-CBB, Al-CBB and Fe-Al-CBB from 0.1 to 3 g, removal efficiency of F- was respectively 5.02%-11.57% (Fig.5a), 9.10%-20.95% (Fig.5b), 32.46%-74.77% (Fig.5c) and 42.79%-98.56% (Fig. 5d). Therefore, removal efficiency of F- of different bone biochar followed the order of Fe-Al-CBB > Al-CBB > Fe-CBB > CBB. Multivalent metal ions (such as aluminum, iron, etc.)

have the small size and high electronegativity, resulted in their highly capacity attracted to F^-[16]. This is the main reason that the removal efficiency of F^- was higher for Fe-CBB and Al-CBB than CBB. In this study, the removal efficiency of $Al_2(SO_4)_3$ modification bone biochar (Al-CBB) was obviously higher than that of $Fe_2(SO_4)_3$ modification bone biochar (Fe-CBB).

Results showed that the F^- removal efficiency of Fe-Al-CBB was obviously higher than that of CBB. Based on Fig.5d, removal efficiency of F- was 93.61% when 0.8 g Fe-Al-CBB was added into F-solution with concentration of 200mg/L. When further increasing the quantity of Fe-Al-CBB, the removal efficiency of F- was increased. These results suggest that the suitable quantity for removal of F- from a 200 mg/L F- solution is 8 g/L for Fe-Al-CBB.

4. Conclusions

The adsorption capacity of the composite aluminum salt and iron salt modified cattle bone biochar (Fe-Al-CBB) reached 45.45 mg/g, which was 8.5 times greater than the adsorption capacity of 5.34 mg/g of cattle bone biochar (CBB). The adsorption capacity of cattle bone biochar was significantly improved by composite aluminum salt and iron salt. When pH of solution at 7, Al-Fe-CBB has higher capacity of adsorption F-. The zeta potential of CBB was obviously improved by composite aluminum salt and iron salt. The highest removal efficiency of F- was 98.56%, 74.77%, 20.95%, and 11.57% in initial F- solution with concentration of 200 mg/L, respectively for Fe-Al-CBB, Al-CBB, Fe-CBB and CBB. Zero charge point of Fe-Al-CBB, Al-CBB, Fe-CBB and CBBB was 7.47, 7.2, 6.62 and 6.19, respectively. The higher removal efficiency of F- of Fe-Al-CBB was related to its higher zero charge point.

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