

Research Article

Infrared Spectroscopic Study on the Modified Mechanism of Aluminum-Impregnated Bone Charcoal

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Fluoride contamination in drinking water is a prominent and widespread problem in many parts of the world. Excessive ingestion of fluoride through water can lead to the high risk of fluorosis in human body. Bone charcoal, with the principal active component of hydroxyapatite, is a frequently used adsorbent for fluoride removal. Many laboratory experiments suggest that the aluminum-impregnated bone charcoal is an effective adsorbent in defluoridation. However, the mechanisms underlying this modification process are still not well understood, which in turn greatly impedes the further studies on other different modified adsorbents. To address this issue, we used the infrared spectroscopy to examine the bone charcoal and the aluminum-impregnated bone charcoal, respectively. The comparative results show that the $-OH$ peak of infrared spectroscopy has been intensified after modification. This significant change helped speculate the modified mechanism of the aluminum-impregnated bone charcoal. In addition, it is found that the hydroxide ion dissociates from hydroxyapatite in the modification process. Such finding implies that the tetrahydroxaluminatate can be combined with the hydroxyapatite and the aluminum ion can be impregnated onto the bone charcoal surface.

1. Introduction

Fluoride is widely distributed in nature, which mainly exists in lithosphere, hydrosphere, biosphere, and atmosphere [1, 2]. Most fluorides are soluble, even the lowest solubility of calcium fluoride can reach 40 mg/L in normal condition [3]. The soluble fluorides in rocks can dissolve in water, which are the main sources of the fluorides in fresh water. Therefore, humans obtain fluorides largely from drinking water [4]. There exists about 2 to 3 g (commonly 2.6 g) fluorine in a healthy adult body, 90% of which distributes in bones and teeth [5, 6]. A trace of fluorine is useful to prevent spondylitis but excessive amount tends to be harmful [7, 8]. It is supposed to be poisonous if the intake of fluorine is higher than 4 mg/d; therefore, people are more likely to develop fluorosis of bone when the amount of fluorine in drinking water is more than 4 ppm [9].

As the fluorine-containing substances are increasingly applied in industry, the amount of the fluorine-containing

wasted water tends to become higher. Purification and defluoridation of high-fluorinated drinking water have drawn more and more attention. Conventional methods of defluoridation are precipitation and adsorption [10–13]. Adsorption method is mainly used in the deep disposal of low fluorine-containing waste water and natural water. Because the adsorption method of disposing fluorine-containing waste water has the advantages of lower cost and higher removal rate [14], the modification of traditional fluorine removal agent and the research of new fluorine removal materials are popular topic in relative area [15–17]. Traditional fluorine removal agents include alumina, natural zeolite, and rare earth while the new adsorbent with good adsorption effects is calcium aluminate slag, aluminum sulfate modified bamboo charcoal, and bone charcoal [18–23]. In the midst of these adsorbents, bone charcoal is now considered to be one of the most recommendatory adsorbents in defluoridation since World Health Organization regarded bone charcoal as

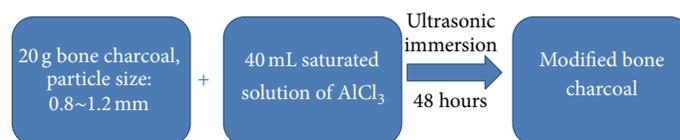
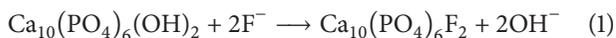


FIGURE 1: Manufacturing approach of aluminum-impregnated bone charcoal.

the high-performance adsorbent of fluorine in undeveloped regions [24]. Based on this reason, we aimed at studying the defluorination effect of bone charcoal and finding out the mechanism of the modification and adsorption.

Bone charcoal is a porous, black, granular material produced by charring animal bones [25]. It is made up of hydroxyapatite (57–80%), calcium carbonate (6–10%), and activated carbon (7–10%). In the development of purification, bone charcoal was primarily used for filtration and decolorisation, which can also adsorb a large quantity of pollutants like pigments as well as fluorine from water [26]. Based on the adsorption theory, the hydroxyapatite in bone chars can be used to remove fluoride and metal ions from water, making it useful for the treatment of drinking supplies.

Adsorption is a separation method with the equilibrium principle. The main components of bone charcoal are hydroxyapatite. The mechanism of the removal of fluorine is mainly the adsorption and ion exchange reaction, which is shown as follows:



Previous research [27] reported that, being immersed in aluminum solution for certain temporal, bone charcoal can be modified. The aluminum can impregnate onto the surface of bone charcoal, improving the effect of the defluorination, which is the main core of our work. However, although this novel modified approach to optimize the performance of aluminum-impregnated bone charcoal in defluorination has been discovered, the mechanism of the modification is still undefined. It is undoubtedly a huge impediment for us to explore the further studies of modified adsorbent. Therefore, we paid our attention to construct a probable reaction during the modified process in order to resolve this crucial problem.

Infrared spectroscopy is one of the most common analytical techniques in material characterization [28]. It is the spectroscopy that deals with the infrared region of the electromagnetic spectrum, with longer wavelength and lower frequency compared to the visible light. It covers a range of techniques, mostly based on absorption spectroscopy. As with all spectroscopic techniques, it can be used to study chemicals and relative substances [29]. In recent years, there are more and more explorations of reaction mechanism detected by spectroscopic methods [30–37]. Green and his coworkers [30] obtained the information of dual catalytic sites during oxidation of CO on Au/TiO₂ catalyst by spectroscopic observation. Roithová [31] concluded the characterization approaches of reaction intermediates by ion spectroscopy. Acik and his coworkers [32] have detected the role of oxygen during thermal reduction of graphene oxide using infrared absorption spectroscopy. Black and his coworkers [33] used spectroscopic method to screen

for superoxide reactivity in Li–O₂ batteries. Chen and his coworkers [34] used FT-IR spectroscopy as a part of the instruments to determine mechanisms in water-gas-shift reaction on Au/CeO₂. Huang and his coworkers [35] utilized surface-enhanced Raman spectroscopy to study p-aminothiophenol. Costa and his coworkers [36] used relative spectroscopic methods to determine the clues to the internal barrier layer capacitance mechanism. Xu and his coworkers [37] clarified the thermal deterioration mechanism of bio-oil pyrolyzed from rice husk using Fourier transform infrared spectroscopy. The common point of the studies listed above is that all of them utilized the relative spectroscopic approaches to determine or infer the mechanism of the chemical reaction and process, proving that the spectroscopy is an available approach to estimate the mechanism of chemical reactions. What is worth mentioning is that all of these listed researches were published in the recent three years, showing that using spectroscopic approaches to establish the conjecture of chemical reactions is becoming a popular method among relative academic fields. Since detecting the modified mechanism of aluminum-impregnated bone charcoal and calculating the main reaction process by the modeling approach are difficult, in our study, we innovatively used infrared spectroscopy to obtain the infrared spectrums of the modified bone charcoal and the unmodified one, so that the mechanism can be inferred during the change of the modification.

2. Materials and Methods

2.1. Material Source and Treatment. Raw materials of bone charcoal in our experiments were supplied by Langfang Huaya Water Treatment Ltd., Hebei Province, China. All the bone charcoals were sieved by screens, of which the granularity is approximately from 0.8 to 1.2 mm. Because of the adsorption mechanism shown in (1), alkaline environment of solution can provide a better effect of defluorination; thus to ensure the good adsorbability materials were firstly immersed in saturated solution of sodium hydrate for 12 hours and then immersed in deionized water for 12 hours. After repetitive scrubbing, these raw bone charcoals were stoved by electric thermostatic drying oven under the temperature of 120°C. Afterwards, the bone charcoals were sealed in the desiccator.

The manufacturing approach of aluminum-impregnated bone charcoal in our study met the standards of modified approaches created by previous studies. 20 g bone charcoal was immersed in 40 mL saturated solution of AlCl₃, and the modification system was immersed in the ultrasonic oscillator, so that aluminum ion can impregnate onto the bone charcoal better. The modification procedure is shown in Figure 1.

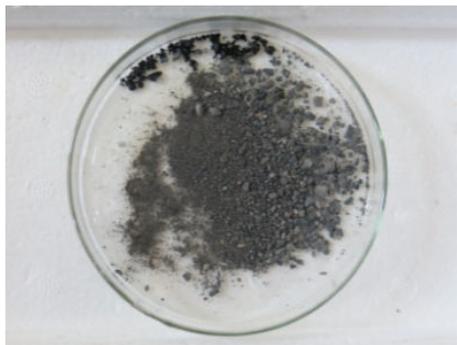


FIGURE 2: Aluminum-impregnated bone charcoal.

To guarantee the modification, we chose the saturated solution so the aluminum ion can impregnate onto the bone charcoal during the process of ultrasonic immersion. The dried aluminum-impregnated bone charcoal is shown as Figure 2.

The aluminum-impregnated bone charcoal takes on a color of silvery white and grey, while the unmodified bone charcoal is atrous. The change of macroscopic features can be observed obviously from this characteristic.

For comparison, we also designed a series of other modified bone charcoals. After the testing results, ferri-impregnated bone charcoal and magnesium-impregnated bone charcoal are also considered to be good modified adsorbents, with high removal rates of fluorinon. Therefore, we used these two modified bone charcoals together with the blank control group (those ultrasonic immersed in the saturated solution of sodium hydroxide) as the control groups in the analysis of adsorption isotherm (see Section 3.1: *Adsorption Isotherm*).

2.2. Preparation of Fluoride Solution. The sodium fluoride (NaF, AR) with deionized water configured to stock fluorinon solution of 1.0 g/L. Then it was diluted to be 5.0 mg/L, as to be used for the follow-up test. This actual initial mass concentration was determined by fluoride selective electrode.

2.3. Adsorption Isotherms. To test the rationality of choosing aluminum-impregnated bone char as the object of study, we chose ferri-impregnated bone charcoal, aluminum-impregnated bone charcoal, and magnesium-impregnated bone charcoal as the main objects of studying the adsorption isotherms. All the metal-modified bone charcoals were modified under the same conditions and procedures. In addition, those raw bone charcoals immersed in the saturated solution of sodium hydroxide ultrasonically were taken as the blank control group. In the midst of these four types of bone charcoal, each kind of bone charcoals was divided into 6 groups, respectively: 0.2, 0.4, 0.8, 1.2, 1.6, and 2.0 g. After three-hour defluoridation, adsorption isotherms were developed during sample analysis.

3. Results and Discussion

3.1. Adsorption Isotherm. Previous studies show that the adsorption process of bone charcoal is corresponded with

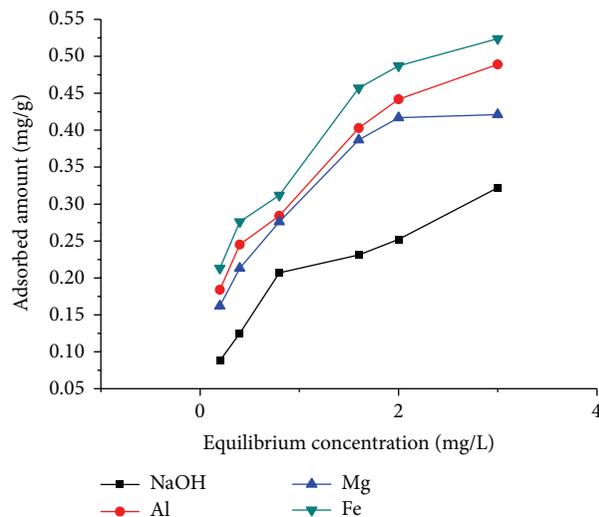


FIGURE 3: Adsorption isotherms of different modified bone charcoals in defluoridation.

Langmuir isotherm [38–41], which is an ordinary adsorption process of general adsorbents. For a better comparison, several modification experiments with different immersed ions were done and we obtained the adsorption isotherms for different ion-modified bone charcoal in defluoridation, which is shown in Figure 3 (blank control group: bone charcoal immersed in saturated solution of sodium hydrate).

Results shown in Figure 3 indicate the descending order of the corresponding defluoridation efficiency as follows: ferri-impregnated bone charcoal, aluminum-impregnated bone charcoal, magnesium-impregnated bone charcoal, and sodium hydrate immersed bone charcoal. Nevertheless, our experimental results are quite different from Shen's previous study [42]. In Shen's study, the defluoridation effect of aluminum bone charcoal is higher than those of ferri-impregnated bone charcoal. However, due to the different source of raw bone charcoals and the precise procedure of our modification experiments, we considered our results are accurate and reliable.

Although ferri-impregnated bone charcoal had the best defluoridation effect in our experiments, however, ferri ion is toxic and harmful to human body, which means that it cannot be applied to the practical applications [43]. Therefore, aluminum-impregnated bone charcoal is still the most rational option for defluoridation. Besides, results also prove that the aluminum-impregnated bone charcoal of our research is effective and can be used for further studies of the modified mechanism.

3.2. Infrared Spectroscopic Study on Aluminum-Impregnated Bone Charcoal. In order to study the modified mechanism of aluminum-impregnated bone charcoal, two samples from the same raw bone charcoal were determined by infrared spectrum. Figure 4 shows the infrared spectrum of raw bone charcoal without modification, while Figure 5 shows the infrared spectrum of aluminum-impregnated bone charcoal.

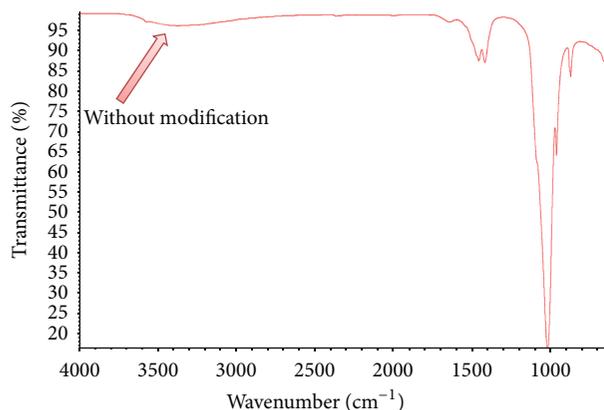


FIGURE 4: Infrared spectrum of bone charcoal without modification.

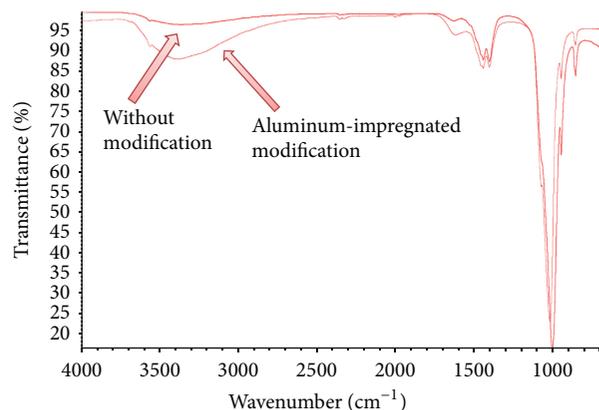


FIGURE 6: The overlapped infrared spectrum of Figures 4 and 5.

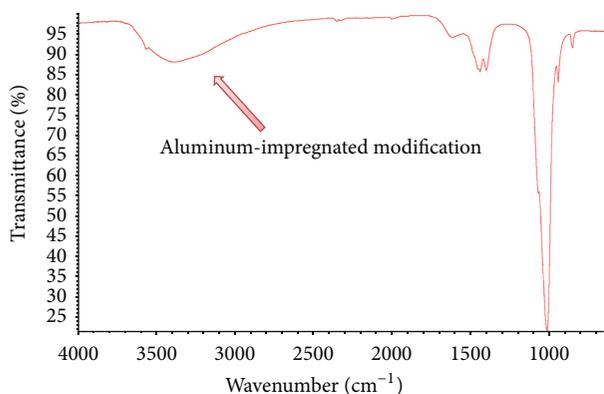


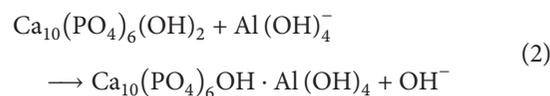
FIGURE 5: Infrared spectrum of aluminum-impregnated bone charcoal.

Figures 4 and 5 show the infrared spectrums of the two samples of bone charcoal, respectively. It is obvious that there are some differences of the peaks between the two infrared spectrums. The arrow heads in Figures 4 and 5 are the indexes of these main differences. In order to present these differences in a more evident way, Figures 4 and 5 were overlapped into the one picture, which is shown in Figure 6.

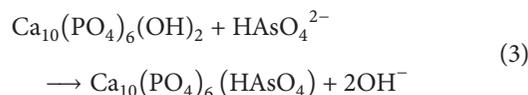
Figure 6 depicts an interesting phenomenon: after modification, in the stretching vibration area of hydrogen bond held together with $-OH$, intensity of the typical absorption band of hydroxyapatite (3400 cm^{-1} nearby) [44, 45] has risen obviously. In contrast, other peaks have tiny significant change. This strange phenomenon attracted our attention: under the theoretically dry condition, how to explain this bizarre change of the peak?

To explain the interesting phenomenon presented in Figure 6, we should consider the possible reaction between aluminum ion and bone charcoal at first. One of the most striking explanations of this phenomenon is that anion exchange has happened during the modified process. Hydroxide ion is dissociated from $Ca-OH$ during the anion exchange, elevating the PH value. Under this circumstance, aluminum ion can combine with hydroxyl ion, forming tetrahydroxoaluminate ion. Based on this conjecture, the

modified mechanism is constructed as the reaction shown as follows:

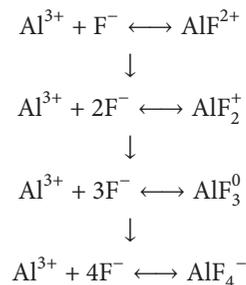


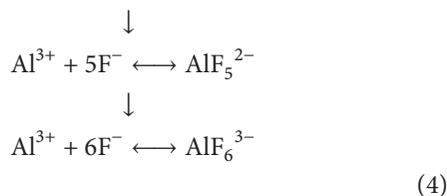
In previous study, Chen and her coworkers [46] offered an explanation for the mechanism of removal of arsenic (V) using bone charcoal as the adsorbent:



Compared to our conjecture of the modified mechanism, Chen's research indicates that bone charcoal can arise from the ion exchange reaction during the adsorption, from which we can infer that the mechanism of adsorption and modification is extremely similar. In other words, during the modification process, aluminum ion can be "adsorbed" onto the surface of bone charcoal, and we deduce that this combination is stable and thus the aluminum can impregnate firmly.

As for the adsorption mechanism of aluminum-impregnated bone charcoal, Dong [47] offered an explanation for the high performance of the modified bone charcoal. This explanation discusses that because the aluminum ion has the unoccupied orbital, there exists the complex reaction between aluminum ion and fluorine, and the maximum coordination number is considered to be six:





Dong's explanation of aluminum-impregnated bone charcoal seems reasonable. However, according to our study, some of the unoccupied orbitals of the aluminum impregnated onto the bone charcoal had actually been occupied during the modified process. Therefore, the average maximum coordination number of aluminum in the aluminum-impregnated bone charcoal may be less than six. Based on our opinion, the adsorption mechanism explained by Dong [47] is not totally perfect, which may overestimate the adsorption effects of aluminum-impregnated bone charcoal. Our research indicates that, in the process of defluoridation, aluminum-impregnated bone charcoal is undergoing two kinds of adsorption process. On the one hand, hydroxyapatite in bone charcoal is undergoing the adsorption process as (1) presents; on the other hand, aluminum which has been impregnated onto the bone charcoal's surface is undergoing the process of coordination reaction: aluminum combines with fluorine in a stable way.

According to previous studies [48–51], some similar researches on determining the mechanisms of different adsorbents were used to make comparison. Namasivayam and Kavitha [48] detected the adsorption interactions of dye, phenol, and chlorophenol onto coir pith carbon from aqueous solution using various detection techniques. Nadeem and his coworkers [49] detected the modified carbon adsorbents by SEM. In addition, Ahmad and Kumar [50] also utilize SEM to detect the adsorption information of amaranth dye onto alumina reinforced polystyrene. Gupta and his coworkers [51] detected the details about banana pseudostem fiber in the removal of harmful malachite green dye using Fourier transform infrared spectroscopy, scanning electron microscope, and X-ray diffractometer. These studies are advanced in detecting the properties of adsorbents which can seem as the excellent references. Nevertheless, these researches did not detect the adsorption processes of the modification mechanisms of the studied adsorbents by infrared spectroscopic methods. Hence, our research has successfully made up the blank of this area. According to the comparison, using infrared spectroscopy to detect and infer the modification mechanism of bone charcoal is proved to be effective and available.

4. Conclusion

Fluoride contamination is a prominent and widespread problem in many parts of the world. Such contamination in drinking water is mostly natural and unpreventable that affects the health for human beings. There is a common agreement that drinking fluoridated water can lead to a high risk of fluorosis in human body. To reduce the risk, metal-impregnated bone charcoal has been frequently used as an ideal material for fluoride removal. In this

study, the defluoridation efficiency of the bone charcoals modified by different metal ions was investigated. Their adsorption isotherms help highlighting the descending order of the corresponding defluoridation efficiency as follows: ferri-impregnated bone charcoal, aluminum-impregnated bone charcoal, magnesium-impregnated bone charcoal, and sodium hydrate immersed bone charcoal. Considering the potential toxicity of ferri-impregnated bone charcoal, the aluminum-impregnated bone charcoal was adapted as the most rational adsorbent for defluoridation in our experiments. Its modified mechanism was further successfully explored using the infrared spectroscopy. The strengthening of the hydroxyl peak intensified in infrared spectrum was examined. The results imply that the probable modified reaction is ion exchange and tetrahydroxoaluminate can combine with hydroxyapatite, which in turn suggests that aluminum ion can be impregnated onto the surface of the bone charcoal. In future study, more attention deserves to be paid to the adsorption of lead and arsenic as some advanced researches provide great inspirations on the topic [46, 52–55].

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Authors' Contribution

Hao Li and Yufan Yang contributed equally to this paper.

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