Selective Adsorption of Metal lons on Salix psammophila Fibre Activated Carbon

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As an adsorbent of metal ions, activated carbon is often used to purify sewage. However, activated carbon fibres typically show similar adsorption capacity for different metal ions. Salix psammophila fibre (Spsf) was used as raw material to prepare activated carbon fibres (SP-FAC). This was modified with nitric acid (HNO₃) to obtain HNO₃-SP-FAC (FACHNO3). At 65 wt% concentration of HNO3, the impregnation ratio was 1:35 during 12 h, at 100 °C drying temperature, and the adsorption effect of FAC_{HNO₃} on Pb(II) was the best. At C_{HNO_3} = 75 wt%, the impregnation ratio was 1:25. After an impregnation time of 36 h at the same drying temperature, the effect of FAC_{HNO3} on Mn(II) was the best. At $C_{HNO3} = 55$ wt%, the impregnation ratio was 1:35, impregnation time was 36 h at 120 °C drying temperature, and the adsorption effect of FACHNO3 on Zn(II) was the best. These results indicate the existence of a close relationship between the pore structure of activated carbon fibres and the adsorption capacity of metal ions, and that the control variables changed the pore structure of activated carbon fibres so that it can achieve a competitive adsorption effect for different ions.

DOI: 10.15376/biores.17.3.4410-4431

Keywords: Sandy shrub; Activated Carbon Fibres; Selective adsorption; HNO₃ modification; Heavy metal ions

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INTRODUCTION

Commonly used wastewater treatment methods include chemical precipitation, ion exchange, membrane filtration, and adsorption through porous material. Porous materials have the potential to provide an obvious adsorption effect, low price, and environmental protection (Chen *et al.* 2011; Fu and Wang 2011; Gupta *et al.* 2012). Activated carbon is widely used in wastewater treatment as a porous material. It is usually used to adsorb metal ions in sewage. Activated carbon can be classified into powder, granular, and fibrous forms. Powdered activated carbon can quickly remove impurities, but it often floats above the liquid level. In addition, this form of activated carbon is difficult to recover, which can lead to secondary pollution (Liu *et al.* 2011). Meanwhile, with granular activated carbon, the metal ions attach mainly to its surface, which is called monolayer adsorption, resulting in a poor adsorption effect (Hete *et al.* 2012; Loganathan *et al.* 2018; Jjagwe *et al.* 2021). Fibrous activated carbon often exhibits the best performance and fastest adsorption rate among the three forms. The impurities in the water can be easily adsorbed on the inside of

the activated carbon; thus, the fibrous activated carbon exhibits strong adsorption capacity (Phan *et al.* 2006).

However, most activated carbon materials absorb mixed ions present in sewage, and the inability to make a selection leads to a decrease in the secondary utilization of metal ions (Seco et al. 1997; Luo et al. 2015). Conventional activated carbon is unable to selectively adsorb mixed metal ions (Marzal et al. 1996; Srivastava et al. 2008; Uchimiya et al. 2010). In principle, the selective adsorption of activated carbon can be achieved in two ways. Firstly, it is necessary to use raw materials with larger specific surface area to prepare activated carbon, because this raw material can obtain activated carbon with excellent adsorption capacity and lay a foundation for the adsorption of metal ions. Among them, Salix psammophila fibre (Spsf) exhibits large specific surface area, high activity, and softness, and has more pore structure than most wood. It is a natural porous material commonly used as a base material for activated carbon (Li et al. 2014). Therefore, it is used to prepare activated carbon and used to improve the capacity of sewage treatment (Liu and Lang 2020). Secondly, by changing the adsorption capacities of adsorbents for different metal ions to achieve optimal selective adsorption effect, the sustainable development of resources is important (Kuroki et al. 2019). Wang et al. (2017) used HCl to change the pore structure of activated carbon, the results showed that in the mixed solution of Cu(II) and Cd(II), activated carbon preferentially adsorbed Cu(II), indicating that selective adsorption can be achieved by changing the pore structure of activated carbon. Changing the pore structure of activated carbon by modifying it with nitric acid can effectively adjust the adsorption capacities of metal ions (Gokce and Aktas 2014; Ge et al. 2014; Li et al. 2019).

Ghosh (2009) modified activated carbon with H₂SO₄ and HNO₃. Under the same conditions, the modification effect of HNO₃ was more evident, which yielded 10.93 mg/g maximum adsorption capacity of activated carbon to metal ions. However, the adsorption capacity needs to be further improved. Choma et al. (1999) modified activated carbon with different concentrations of hydrogen oxide, perchloric acid, and nitric acid solutions. The results showed that nitric acid changed the pore structure of activated carbon most significantly. Qu et al. (2012) modified activated carbon fibre with nitric acid and hydrogen peroxide solutions of various concentrations. The results showed that the modification by nitric acid improved the adsorption capacity of activated carbon to metal ions. A comparison of different modifiers indicated that HNO₃ exhibited the most evident change effect on the pore structure. However, the adsorption effect of activated carbon on metal ions needs to be further improved. Zhang et al. (2013) modified activated carbon by controlling the HNO₃ concentration to change its surface chemical properties, increase acidic functional groups, and enhance the adsorption capacity. Li et al. (2018b) used nitric acid to modify activated carbon fibre and found that the adsorption process of modified activated carbon is a spontaneous endothermic process with excellent adsorption capacity. Oter et al. (2021) modified activated carbon by HNO₃. The results showed that HNO₃ modification can adjust the adsorption rates of Th(IV) and U(VI) ions and yield adsorption capacities of $Q_{\rm Th} = 37.60 \text{ mg/g}$ and $Q_{\rm U} = 18.38 \text{ mg/g}$, respectively. Saputro *et al.* (2019) found that after acid modification of activated carbon, the adsorption capacity of Pb(II) was significantly increased, and the Pb(II) present in the waste was effectively removed. Ucer et al. (2006) studied the adsorption capacity of nitric acid-modified activated carbon for various metal ions and found that the adsorption capacity of Mn(II) was $Q_{Mn} = 1.11 \text{ mg/g}$. Considerable research has shown that nitric acid can increase the adsorption capacity of activated carbon. However, the adsorption capacity of mixed ions was average. Therefore,

it is necessary to study the relationship between nitric acid and pore structure to achieve the selective adsorption of mixed metal ions by activated carbon.

In this study, *Spsf* activated carbon fibres (SP-FAC) were modified with HNO₃ to selectively adsorb Pb(II), Mn(II), and Zn(II) plasma in sewage, thus facilitating the removal of useless metals and recycling of useful metals. Through controlling factors, such as $C_{\rm HNO3}$, impregnation ratio, impregnation time, and drying temperature, and adjusting the pore structure, the relationship between the adsorption capacities of different metal ions and the pore structure of activated carbon fibres was determined. In addition, the optimal process for activated carbon fibres modification was identified, and a new route for metal resource recycling was developed.

EXPERIMENTAL

Materials and Reagents

Salix psammophila (Sps) was purchased from Ordos, China. All the water used in the experiment was distilled water, which was prepared in the laboratory of Inner Mongolia Agricultural University. All reagents used were of analytical grade. The materials include: potassium pyrophosphate trihydrate from Zhengzhou Paini Chemical Reagent Factory (Henan, China), potassium bromide from Shandong Lvying Chemical Technology Co., Ltd. (Shandong, China), zinc oxide reference and anhydrous sodium acetate from Dezhou Runxin Experimental Instrument Co., Ltd. (Shandong, China), lead nitrate and hexamethylenetetramine from Hunan Hanhua Chemical Co., Ltd. (Hunan, China), manganese chloride from Shanghai Zhanyun Chemical Co., Ltd. (Shanghai, China), and hydrochloric acid, concentrated nitric acid, and concentrated sulfuric acid from Maoming Xiongda Chemical Co., Ltd. (Guangdong, China). The zirconium hydrogen phosphate, potassium periodate, glacial acetic acid, xylenol orange, sodium hydroxide, and anhydrous ethanol were purchased from Shanghai McLean Biochemical Technology Co., Ltd. (Shanghai, China) and used as received.

Methods

Preparation of SP-FAC

5g Spsf was impregnated into 35% (NH₄)₂HPO₄ solution in the 1:3.5 impregnation ratio (the ratio of *Spsf* mass to (NH₄)₂HPO₄ solution mass, W/W) within a 12 h impregnation time. The impregnated *Spsf* was placed in a muffle furnace and carbonized at 200 °C for 60 min under 0.02 MPa vacuum, followed by activation at 800 °C for 60 min. After the reaction, the fibre was cooled to room temperature. The products were gathered and soaked in 5% hydrochloric acid solution for 1.0 h to remove the ash and metal ions generated during the activation process. Then, the solution was washed with distilled water to make it neutral, and then filtered and dried to obtain SP-FAC.

Preparation of FACHNO3

Various impregnation ratios (1:25, 1:30, and 1:35), HNO₃ concentrations (55%, 65%, and 75%), impregnation times (12 h, 24 h, and 36 h), and drying temperatures (80 °C, 100 °C, and 120 °C) were set for the activated carbon fibres prepared under the process conditions, as shown in Table 1. First, 1.0 g of activated carbon fibres was added to a beaker, to which the required amount of HNO₃ was added, and the mixture was stirred using a magnetic mixer for 15 min. The sample was immersed for a fixed period and then

washed with distilled water repeatedly until the solution became neutral. The impurities were removed using a vacuum filter, dried in an oven for 6 h, and the activated carbon fibres thus obtained was stored for later use.

| | Sample | Сниоз (wt%) | Impregnation | Impregnation | Drying Temperature | | | | |
|--|-------------------------------|-------------|--------------|--------------|--------------------|--|--|--|--|
| | | | ratio | Time (h) | (°C) | | | | |
| | FAC нNO ₃ 1 | 55 | 1:25 | 12 | 80 | | | | |
| | FACHNO ₃ 2 | 55 | 1:30 | 24 | 100 | | | | |
| | FACHNO ₃ 3 | 55 | 1:35 | 36 | 120 | | | | |
| | FAC _{HNO3} 4 | 65 | 1:25 | 24 | 120 | | | | |
| | FACн _{NO3} 5 | 65 | 1:30 | 36 | 80 | | | | |
| | FAC нNO ₃ 6 | 65 | 1:35 | 12 | 100 | | | | |
| | FACн _{NO3} 7 | 75 | 1:25 | 36 | 100 | | | | |
| | FAC нNO ₃ 8 | 75 | 1:30 | 12 | 120 | | | | |
| | FACHNO ₃ 9 | 75 | 1:35 | 24 | 80 | | | | |

Table 1. Orthogonal Experimental Design Table

Testing of adsorption properties of Pb(II), Mn(II), and Zn(II) by FACHNO3

The samples were prepared with standard solutions of 50 mL Pb(II), Mn(II), and Zn(II) in various iodine bottles, and the pH value was adjusted to 4; then, 0.1 g of FAC_{HNO3} was added to the solution, which was placed in a constant-temperature water bath oscillator. The temperature was set at 40 °C and the speed was set at 120 rpm. After the reaction, the mixture was repeatedly filtered with filter paper until there was no solid residue in the filtrate, and the absorbance of the filtrate was measured.

The FAC_{HNO3} adsorption of Pb(II): To a certain amount of filtrate, hexamethylenetetramine solution and dimethyl phenol orange solution were added in a 50-mL volumetric flask. The absorbance at 575 nm after a period of color development was measured. Then, a standard curve was prepared and the adsorption capacity was calculated.

 FAC_{HNO3} adsorption of Mn(II): To a certain amount of filtrate, potassium pyrophosphate–sodium acetate solution and potassium periodate solution were added in a 50-mL volumetric flask, and the absorbance at 525 nm was measured. Then, a standard curve was drawn and the adsorption capacity was determined.

FAC_{HNO3} adsorption of Zn(II): To a certain amount of filtrate, acetic acid–sodium acetate solution and dimethyl phenol orange solution were added in a 50-mL volumetric flask and the absorbance at 570 nm was measured after a period of color development. Then, a standard curve was drawn and the adsorption capacity was calculated.

The adsorption quantity (Q) can be obtained using Eq. 1,

$$Q = \frac{c_0 - c_1}{m} \times V \tag{1}$$

where Q is the adsorption capacity (mg/g), C_0 is the initial concentration of the metal ion solution (mg/L), C_1 is its residual concentration after adsorption, m is the amount of FAC_{HNO3} added (g), and V is the volume of the solution (L).

The adsorption capacity of activated carbon fibres was tested according to the GB/T standards 12496.22 (1999) and 12496.13 (1990). The specific surface area and pore structure were tested according to the GB/T standards 7702.21 (1997b) and 7702.20 (1997a), respectively. The concentrations of metal ions before and after adsorption were evaluated according to the GB/T standard 26798 (2011), and the adsorption capacity was calculated.

Specific surface area and pore size (BET) analysis

The specific surface area and pore size were used to test the SP-FAC, FAC_{HNO3}, and the adsorbed samples. The specific surface area and pore size of samples were measured by BET (ASAP-2460, Micromeritics Instruments Corporation, Norcross, GA, USA) tests were determined on the samples treated in nitrogen and helium environments (test range 2 nm to 200 nm) to obtain pore structure data. Each sample was tested three times and the results were averaged.

Fourier transform-infrared spectroscopy (FT-IR) analysis

First, the sample was mixed with potassium bromide and ground to a uniform powder. Secondly, the KBr tablet was obtained by pressing 1.0 min on the pressure table. Finally, the FT-IR (Nicolet-6700, Thermo Fisher Scientific, Waltham, MA, USA) spectrum was recorded. The changes in the functional groups of the samples were analysed by comparing the peaks of the spectra.

X-ray diffraction (XRD) analysis

The test tray was filled with the sample and placed in an XRD analyser (X-pert Pro, Malvern Panalytical B.V., Almelo, Netherlands) for testing. The diffraction range of the XRD analyser was 5° to 90° and the scanning speed used was 2 days/min. The XRD pattern was obtained, and the crystal structure of the sample was analyzed, to follow the structural changes.

Field emission-scanning electron microscopy (SEM) and spectroscopy (EDS) analyses

The surface morphology and elemental changes of activated carbon fibers were analyzed by field emission-scanning electron microscopy (S-4800, Hitachi, Ltd., Tokyo, Japan) and energy-dispersive spectroscopy (S-4800, Hitachi, Ltd., Tokyo, Japan). Because SEM and EDS are tested on different computer terminals in the same sample table, it is necessary to observe the images of computers equipped with SEM and DES analysis software at the same time during each sample test. Among them, each sample was tested three times, and the image with the best effect was taken as the result analysis. The sample was subjected to vacuum spraying treatment with gold (99.99%, Li Jisheng New Materials Co., Ltd., Shijiazhuang, Hebei, China) (samples must be repeatedly treated), and tested after the treatment. Firstly, the morphology of activated carbon fiber was analyzed by SEM. Secondly, EDS tests were carried out on the samples collected at the same location to analyze the chemical composition of the samples.

RESULTS

Effects of Various Process Conditions on the Adsorption Capacities of Pb(II), Mn(II), and Zn(II) lons

The initial concentrations of Pb(II), Mn(II), and Zn(II) were set at 300 mg/L, and their absorbance capacities were measured by adding these solutions to activated carbon fibres for a fixed period. As shown in Fig. 1, a standard curve was obtained to calculate the adsorption capacities of heavy metal ions on activated carbon fibres according to Eq. 1. As shown in Figs. 1a and 1b, the test results conformed to a normal distribution.



Fig. 1. Effects of different processes on the adsorption capacities of Pb(II), Mn(II), and Zn(II) ions (a, c, e: standard curves of Pb(II), Mn(II), and Zn(II) ions, respectively; b, d, f: Adsorption distribution histogram of Pb(II), Mn(II), Zn(II) ions)

The adsorption capacity of FAC_{HNO3} in tests 1 to 6 for Pb(II) increased rapidly, the adsorption capacities of tests 6 to 9 for Pb(II) decreased slowly, and the adsorption capacity of FAC_{HNO3} 6 for was the highest ($Q_{Pb} = 85.46 \text{ mg/g}$). At this point, the histogram distribution frequency was 0.16, reaching the peak value, which verifies the correctness of the test results. As shown in Figs. 1c and 1d, the adsorption capacity of Mn(II) in FAC_{HNO3} tests 1 to 7 increased rapidly, and the adsorption capacity of Mn(II) on tests 7 to 9 decreased slowly. At this time, the distribution frequency of the histogram was 0.17, and it reached

the peak value, indicating that the adsorption of FAC_{HNO3} test 7 was the largest (Q_{Mn} = 92.32 mg/g). As shown in Figs. 1e and 1f, the adsorption capacity of FAC_{HNO3} tests 1 to 3 on Zn(II) increased rapidly, and that of FAC_{HNO3} tests 3 to 9 on Zn(II) decreased rapidly. At this time, the distribution frequency of the histogram was 0.17 and it reached the peak value, indicating that of FAC_{HNO3} test 3 on Zn(II) was the highest ($Q_{Zn} = 59.93 \text{ mg/g}$). There are two reasons for this phenomenon. First, the change of nitric acid concentration, impregnation ratio, impregnation time, drying temperature and other technological conditions led to the reaction between SP-FAC and HNO₃, which changes the pore structure of activated carbon fiber. The measurement of pore structure includes specific surface area, outer surface pore radius, inner pore radius, and pore volume, which all change with the change of relative pressure (P/P_0) to varying degrees, which is a manifestation of the change of pore structure. Secondly, it was concluded by adsorption tests that the pore sizes of different ions were different. The maximum pore diameters of Pb(II), Mn(II), and Zn(II) were 1.00 to 1.15 nm, 1.10 to 1.38 nm, and 0.56 to 1.00 nm, respectively, which indicated that under different technological conditions, the adsorption capacity of FAC_{HNO3} to metal ions was different. The selective adsorption was realized by changing the technological conditions, and the pore structure was closely related to the technological conditions. Therefore, it can be concluded that the technological conditions of nitric acid modified activated carbon fiber had significant influence on the adsorption of metal ions, and it is necessary to discuss the influence of four technological conditions on the pore structure of activated carbon. The detailed results are analyzed in the following section.

Through controlling the modification process using HNO₃, FAC_{HNO3} test 6 exhibited the best adsorption effect on Pb(II), FAC_{HNO3} 7 exhibited the best effect on Mn(II), and FAC_{HNO3} 3 exhibited the best adsorption effect on Zn(II) ions.

Effects of HNO₃ Concentrations on Pb(II), Mn(II), and Zn(II) lons Adsorption Capacities

Figures 2a and 2b show that the outer surface pore radius of FAC_{HNO3} decreased with increasing HNO₃ concentrations (SP-FAC were used as the blank control group). The pore radius of *Spsf* itself was larger, while the outer surface pore radius of FAC was smaller than that of Spsf because the activator corroded many small pores on its surface, and most of the large porous structure of Spsf was destroyed after high-temperature carbonization. When HNO₃ was added to FAC, HNO₃ corroded the surface of activated carbon fibres to form more micropores; when $C_{\text{HNO3}} = 55 \text{ wt\%}$ and $C_{\text{HNO3}} = 65 \text{ wt\%}$, the increase in the pore pore radius, r, was not evident. When $C_{\text{HNO3}} = 75 \text{ wt\%}$, the increase in the SP-FAC radius, R, was evident. This is because part of the HNO₃ solution entered the pore and increased its radius; the specific surface area first increased and then decreased with increasing HNO₃ concentration. At $C_{\text{HNO3}} = 0$ to 65 wt%, the exact surface area continued to increase; at $C_{\rm HNO_3} = 75$ wt%, the specific surface area decreased rapidly. This is because, with an increase in HNO₃ concentration, more micropores were formed on the FAC surface, and the specific surface area increased. Nitric acid caused the pores of the FAC surface to collapse, reducing the specific surface area; with an increase in HNO₃ concentration, the pore volume first increased and then decreased, while the pore radius first decreased and then increased. Combined with the specific surface area, the rate of change of the specific surface area was much higher than that of the pore radius; thus, the change trends of the pore volume and specific surface area were consistent. In addition, P/P_0 first decreased and then increased with an increase in HNO₃ concentration, because P/P_0 increased with the smaller pore volume, and *vice versa*.

Figure 2c shows that the adsorption capacity of FAC_{HNO3} on Pb(II) increased first and then decreased with increasing C_{HNO3} . The adsorption capacity reached the maximum when C_{HNO3} was 65 wt%, $Q_{\text{Pb}} = 85.46 \text{ mg/g}$, indicating that FAC_{HNO3} selectively adsorbed Pb(II) at this time. The adsorption capacity of FAC_{HNO3} on Mn(II) increased with the increase of C_{HNO3} , but at $C_{\text{HNO3}} = 55 \text{ wt\%}$, the adsorption capacity of FAC decreased slightly compared to that without any added HNO3. This was attributed to the fact that HNO3 destroyed the original pore structure of FAC, reducing the pore size suitable for the Mn(II) ion. At $C_{\text{HNO3}} = 75 \text{ wt\%}$, the adsorption capacity reached the highest, $Q_{\text{Mn}} = 92.32 \text{ mg/g}$, indicating that FAC_{HNO3} selectively adsorbed Mn(II). The adsorption capacity of Zn(II) first increased and then decreased with an increase in C_{HNO3} . At $C_{\text{HNO3}} = 55 \text{ wt\%}$, the adsorption capacity reached the maximum, $Q_{\text{Zn}} = 59.93 \text{ mg/g}$, indicating that FAC_{HNO3} selectively adsorbed Zn(II) at this time. The results show that selective adsorption of FAC_{HNO3} on different metals can be achieved by controlling C_{HNO3} .

In summary, when C_{HNO3} is controlled, the adsorption capacity of FAC_{HNO3} for heavy metal ions is positively correlated with the outer surface pore radius, specific surface area, pore volume, and P/P_0 , and it is negatively correlated with the inner pore radius. Thus, the selective adsorptions of Pb(II), Mn(II), and Zn(II) by FAC_{HNO3} can be realized by controlling the concentration of HNO3.



Fig. 2. Correlations among nitric acid concentration, pore structure, and adsorption capacity; a: effects of C_{HNO3} on outer surface pore radius, inner pore radius, and specific surface area; b: effects of C_{HNO3} on pore volume and P/P_0 ; and c: effects of C_{HNO3} on the adsorption capacities of Pb(II), Mn(II), and Zn(II) ions

Effect of Immersion Ratio on the Adsorption Capacities of Pb(II), Mn(II), and Zn(II) lons

As shown in Figs. 3a and 3b, the outer surface pore radius, inner pore radius, and P/P_0 of FAC_{HNO3} decreased with an increase in the HNO3 impregnation ratio. This was because the higher impregnation ratios of SP-FAC and HNO3 resulted in a better corrosion effect on the surface of activated carbon fibres and more micropores were generated. The number of micropores was much larger than the number of medium pores, making the outer surface pore radius smaller; the specific surface area and pore volume increased with the impregnation ratio, and the specific surface area and total pore volume increased with the porosity of micropores. The pore radius of SP-FAC was smaller than that of FAC_{HNO3} when the impregnation ratio was 1:25. This was because HNO3 caused the formation of many micropores on SP-FAC and increased the outer surface pore radius of FAC_{HNO3}; P/P_0 was positively correlated with the pore radius.



Fig. 3. Correlations among impregnation ratio, pore structure, and adsorption capacity (a: influence of impregnation ratio on outer surface pore radius, inner pore radius, and specific surface area; b: influence of impregnation ratio on pore volume and P/P_0 ; and c: effect of impregnation ratio on the adsorption capacities of Pb(II), Mn(II), and Zn(II) ions)

As shown in Fig. 3c, the adsorption capacities of Pb(II) and Zn(II) by FAC_{HNO3} increased with the impregnation ratio and reached the maximum at an impregnation ratio of 1:35. The adsorption capacity of Mn(II) decreased with the increase in the impregnation ratio and reached the maximum when the impregnation ratio was 1:25. The adsorption

capacity of Mn(II) by SP-FAC was higher than that by *Spsf* because more pores were formed on the surface of *Spsf* at high temperature, and the adsorption capacity of Mn(II) by FAC_{HNO3} increased by adding considerable HNO₃ to activated carbon fibres. Therefore, the best impregnation ratio of Pb(II) and Zn(II) was 1:35 and that of Mn(II) was 1:25.

In conclusion, when the impregnation ratio is controlled, the adsorption capacity of FAC_{HNO3} for heavy metal ions is positively correlated with the specific surface area and pore volume, and negatively correlated with the outer surface pore radius, inner pore radius, and P/P_0 . Thus, the selective adsorption capacities of Pb(II), Mn(II), and Zn(II) by FAC_{HNO3} can be realized by controlling the impregnation ratio.

Effect of Impregnation Time on Adsorption Capacities of Pb(II), Mn(II), and Zn(II) lons

Figures 4a and 4b show that the outer surface pore radius, intracellular radius, and P/P_0 of FAC_{HNO3} decreased with increasing HNO3 immersion time, which was the same as the effect of immersion ratio. A longer immersion time resulted in a better corrosion effect on the SP-FAC surface and more micropores formed; the specific surface area and pore volume increased with the impregnation time. The reasons for the decrease in *r* and P/P_0 of SP-FAC are in line with those shown in Figs. 3a and 3b.



Fig. 4. Relationships among impregnation time, pore structure, and adsorption capacity (a: effect of impregnation time on outer surface pore radius, inner pore radius, and specific surface area; b: effect of impregnation time on pore volume and P/P_0 ; and c: effect of impregnation time on the adsorption capacities of Pb(II), Mn(II), and Zn(II) ions)

Figure 4c shows that the adsorption capacities of Mn(II) and Zn(II) by FAC_{HNO3} increased with the immersion time and reached the maximum at the immersion time of 36 h; the adsorption capacity of Pb(II) decreased first and then increased with the increase of immersion time. The maximum was reached at 12 h. Therefore, the best impregnation time of Mn(II) and Zn(II) was 36 h and that of Pb(II) was 12 h.

In conclusion, when the impregnation time is controlled, the adsorption capacity of FAC_{HNO3} for heavy metal ions was positively correlated with the specific surface area and pore volume, and it was negatively correlated to the outer surface pore radius, inner pore radius, and P/P_0 . Thus, the selective adsorptions of Pb(II), Mn(II), and Zn(II) by FAC_{HNO3} can be realized by controlling the impregnation time.

Effect of Drying Temperature on Adsorption Capacities of Pb (II), Mn (II), and Zn (II)

Figures 5a and 5b show that the outer surface pore radius, inner pore radius, and P/P_0 of FAC_{HNO3} decreased with the increase in drying temperature. This is because the reaction rate was accelerated with the increase in temperature, and many micropores were rapidly generated within a short time. The number of micropores was much larger than the number of medium pores; thus, the outer surface pore radius was reduced. The specific surface area and pore volume increased with the drying temperature.



Fig. 5. Relationships among drying temperature, pore structure, and adsorption capacity (a: effects of drying temperature on outer surface pore radius, inner pore radius, and specific surface area; b: effects of drying temperature on pore volume and P/P₀; and c: effects of drying temperature on pore volume and P/P₀; and c: effects of drying temperature on the adsorption capacities of Pb(II), Mn(II), and Zn(II) ions)

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Figure 4a shows that the adsorption capacity of FAC_{HNO3} on Zn(II) increased with the drying temperature and reached the maximum when the drying temperature was 120 °C. As the drying temperature increased, the adsorption capacities of Pb(II) and Mn(II) ions increased first and then decreased, and reached the maximum at 100 °C. Therefore, the optimum drying temperature for Zn(II) was at 120 °C and that for Pb(II) and Mn(II) was at 100 °C.

In summary, when the drying temperature is varied, the adsorption capacity of FAC_{HNO3} for heavy metal ions was positively correlated with specific surface area and pore volume, and it was negatively correlated with the outer surface pore radius, inner pore radius, and P/P_0 ; thus, the selective adsorption capacities of Pb(II), Mn(II), and Zn (II) by FAC_{HNO3} can be achieved by regulating the drying temperature.

BET Characterization

The N₂ adsorption and desorption curves obtained from BET analysis are shown in Fig. 6. *Spsf* was found to belong to a type-III isotherm, indicating that its adsorption capacity was small and the interaction force between *Spsf* and the adsorbent was weak. The adsorption and desorption values of *Spsf* were the lowest, and the SP-FAC fibre belonged to type-I isotherm (Langmuir isotherm), which was consistent with the characteristic curve of activated carbon fibres.

The BET data calculated from Fig. 6 are shown in Table 2. The multiple BET specific surface areas of *Spsf* was $3.55 \text{ m}^2/\text{g}$, while that of SP-FAC was $129.3 \text{ m}^2/\text{g}$. This result was attributed to the increase in surface voids and specific surface area of *Spsf* during carbonization at high temperature, which belongs to physical modification. The total volume of single-point pores of *Spsf* was $0.10 \text{ cm}^3/\text{g}$, and that of FAC was $0.16 \text{ cm}^3/\text{g}$.

| | Multiple BET | Total Volume of | | | Single Point |
|-----------------------|------------------|-----------------|---------------|---------|--------------|
| Sample Name | Specific Surface | Single Point | <i>R</i> (nm) | P/P_0 | Mean Pores |
| | Area (m²/g) | Pores (cc/g) | | | Radius (nm) |
| Spsf | 3.55 | 0.09 | 110.05 | 0.99 | 55.76 |
| SP-FAC | 129.32 | 0.16 | 80.37 | 0.99 | 2.42 |
| FAC нNO₃ 1 | 654.65 | 0.41 | 103.45 | 0.99 | 1.25 |
| FAC _{HNO3} 2 | 679.75 | 0.39 | 59.33 | 0.98 | 1.35 |
| FAC _{HNO3} 3 | 1033.42 | 0.58 | 53.47 | 0.99 | 0.97 |
| FAC _{HNO3} 4 | 724.08 | 0.45 | 108.98 | 0.99 | 1.15 |
| FAC _{HNO3} 5 | 789.71 | 0.41 | 102.82 | 0.99 | 1.13 |
| FAC _{HNO3} 6 | 1024.07 | 0.60 | 70.91 | 1.01 | 1.12 |
| FAC _{HNO3} 7 | 401.14 | 0.22 | 678.01 | 1.00 | 1.24 |
| FAC _{HNO3} 8 | 610.31 | 0.32 | 117.34 | 0.99 | 1.06 |
| FAC _{HNO3} 9 | 362.87 | 0.43 | 172.20 | 1.01 | 1.16 |

Because of the increase in specific surface area that increased the total volume of FAC; the pore radius of *Spsf* was 110.0 nm, and that of SP-FAC was 80.4 nm. This indicated that during carbonization of *Salix* fibre, large pores were collapsed and many mesopores were formed. The single-point mean pore radius and SP-FAC fibre were 55.8 and 2.42 nm, respectively, which indicated that during the high-temperature carbonization process, some macropores were caved in and ash-volatilized, and more mesopores were

formed on the surface of some macropores due to the addition of the activator. The pore size distributions of the samples, shown in Fig. 6I, also confirm their highly developed micropores. The pore size distributions showed a sharp peak centered at 0.2 and 0.5 nm for all the samples, and their volumes declined with increasing HNO₃ addition.



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Fig. 6. Adsorption and desorption isotherms of *Spsf*, SP-FAC, and FAC_{HNO3} (a: adsorption and desorption isotherms of *Spsf*; b: adsorption and desorption isotherms of SP-FAC; c–k: FAC_{HNO3} 1 to FAC_{HNO3} 9; and i: pore size distributions of samples)

Compared to SP-FAC, the specific surface area and total pore volume of FAC_{HNO3} increased. The maximum specific surface area achieved was 1033 m²/g, which was 7.99 times that of SP-FAC, and the maximum total pore volume was 0.60 cm³/g, which was 3.83 times that of SP-FAC. This was because of the HNO₃ etching on the SP-FAC surface, which indicated that HNO₃-modified SP-FAC can increase the adsorption capacity of

activated carbon fibres. The single-point outer surface pore radius was mostly micropores, indicating that HNO₃ modification regulates the pore radius of SP-FAC.

FT-IR Characterisation Analysis

Figure 7 shows the FT-IR spectra of Spsf, SP-FAC, FACHNO3, FACHNO3-Pb, FAC_{HNO3}-Mn, and FAC_{HNO3}-Zn In all spectra, 3350 to 3300 cm⁻¹ corresponded to an -O-H stretching vibration peak (Zhao et al. 2016), which is characteristic of cellulose. The characteristic peak of SP-FAC decreased at 3390 to 3220 cm⁻¹, which is caused by the destruction of intermolecular hydrogen bonds after high temperature carbonization of Spsf. In addition, the following characteristic peaks were observed: 2930 to 2833 cm⁻¹ corresponded to an -C-H stretching vibration peak (El Mansouri et al. 2011), the vibrations of -C-C bonds and aliphatic -C-H, -C-O, and -C-O-C groups at 1500 to 1000 cm⁻¹; and peaks in the 900 to 615 cm⁻¹ range (indicating -C-H deformation in benzene ring) (Srisasiwimon et al. 2018). The peak values of SP-FAC decreased in all these characteristic peaks, which can be attributed to the chemical reaction between Spsf and (NH₄)₂HPO₄, which destroyed the functional groups. The characteristic peak of FAC_{HNO3} was lower than that of SP-FAC, indicating that the chemical reaction between SP-FAC and HNO3 destroyed the functional groups. However, the characteristic peaks of FAC_{HNO3}-Pb, FACHNO3-Mn and FACHNO3-Zn were similar to those of FACHNO3, indicating that the functional groups in the adsorption process did not change, which further confirmed that the adsorption process was a simple physical modification.



Fig. 7. FT-IR spectra of Spsf, SP-FAC, FACHNO3, FACHNO3-Pb, FACHNO3-Mn, and FACHNO3-Zn

XRD Characterisation

Figure 8 shows the XRD patterns of *Spsf*, SP-FAC, FAC_{HNO3}, FAC_{HNO3}-Pb, FAC_{HNO3}-Mn, and FAC_{HNO3}-Zn, where the characteristic peaks C(101) and C(002) of *Spsf* resemble those of Cellulose-I, indicating that *Spsf* belongs to type-I cellulose. The characteristic peaks of FAC at C(101) and C(002) disappeared, indicating that FAC destroyed the crystal structure during high-temperature carbonization. In contrast, the characteristic peaks of FAC_{HNO3} of C(002) reappeared, indicating that HNO3 strengthened the crystal structure of FAC. The characteristic peaks of FAC_{HNO3}-Mn, and

FAC_{HNO3}-Zn agreed with that of FAC_{HNO3}, indicating that the crystal structure of activated carbon fibres remained unchanged after the adsorption of metal ions by FAC_{HNO3}.

At $2\theta = 37.76^{\circ}$, 43° , 64.38° , and 77.46° , the refraction maxima correspond to (111), (200), (220), and (311) crystal planes and belong to the graphite plane peak (Liu and Lang 2020). All three materials showed graphite plane peaks, which are the characteristic diffraction peaks of the crystal surface structure of carbon. The peak values of FAC_{HNO3}, FAC_{HNO3}-Pb, FAC_{HNO3}-Mn, and FAC_{HNO3}-Zn decreased rapidly, while those of FAC_{HNO3}-Mn and FAC_{HNO3}-Zn increased at $2\theta = 43^{\circ}$, 64.38° , and 77.46° , indicating that the crystal structure of *Spsf* was strengthened by the carbonization process of activated carbon fibres. The results further showed that HNO₃ changed the crystal structure of SP-FAC but the metal ions did not.



Fig. 8. XRD patterns of Sps, SP-FAC, FACHNO3, FACHNO3-Pb, FACHNO3-Mn, and FACHNO3-Zn

SEM and EDS Characterizations

Figure 9a shows the SEM comprehensive and detailed diagrams of Spsf, and Fig. 9b shows the EDS scanning diagram of the corresponding sample. The surface of Spsf appeared as smooth, with a few large pores, and the morphology was irregular and evidently fibrous. The results of the EDS analysis showed that the Spsf was composed of C and O elements, which conform to the content characteristics of basic elements of cellulose. Figures 9c and 9d show the characterization of SP-FAC. The surface roughness of SP-FAC was increased, there were many neatly arranged pores, and the contents of P and N elements was also increased. This is because SP-FAC was obtained after (NH₄)₂HPO₄ solution treatment of *Spsf* during the preparation process and it formed many folds and micropores after carbonization at high temperature. Figures 9e and 9f show the characterization of FAC_{HNO3}. The surface roughness, number of micropores, and specific surface area were increased, while the contents of P and N elements remained constant. This is due to the formation of many microporous structures on the SP-FAC surface via HNO₃ corrosion. Figures 9g and 9h show the characterization peaks of Pb(II) adsorbed by FAC_{HNO3}. There are many bright spots in the figure, which are the characteristic light spots reflected by metal ions. EDS shows that the Pb element content was increased in the sample, indicating that considerable Pb(II) was attached to FAC_{HNO3}. Figures 9i and 9j show the characterization of Mn(II) adsorption by FAC_{HNO3}. The figure further highlighted metal reflection and EDS showed that Mn element was added in the sample, indicating that Mn(II) was successfully attached to FAC_{HNO3}. Figures 9k and 9l show the characterization of Zn(II) adsorption by FAC_{HNO3}. Many white reflective metal ions were formed on the FAC_{HNO3} surface. The EDS showed that the Zn element was added to the sample, indicating that many Zn(II) were attached to FAC_{HNO3}.

The results showed that the *Spsf* and FAC_{HNO3} had evident adsorption effect on Pb(II), Mn(II), and Zn(II) ions in its pore structures. Therefore, there was a correlation between the adsorption capacity of activated carbon fibres for metal ions and pore structure. The sequential adsorption of different metal ions on activated carbon fibres can be clearly understood by nitric acid modification.



Fig. 9. SEM and EDS spectra. a: SEM full view and local details of *Spsf*; b: EDS spectrum of *S. psammophila* fibre; c: SEM full view and local details of SP-FAC; d: EDS spectrum of SP-FAC; e: SEM full view and local details of FAC_{HNO3}; f: EDS spectra of FAC_{HNO3}

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Fig. 9. cont. SEM and EDS spectra. g: SEM full view and local details of FAC_{HNO3}-Pb; h: EDS spectrum of FAC_{HNO3}-Pb; i: SEM full view and local details of FAC_{HNO3}-Mn; j: EDS spectrum of FAC_{HNO3}-Mn; k: SEM full view and local details of FAC_{HNO3}-Zn; and I: EDS spectrum of FAC_{HNO3}-Zn).

CONCLUSIONS

- 1. With the increase in specific surface area of SP-FAC prepared by carbonization, the adsorption capacities of Pb(II), Mn(II), and Zn(II) increased, while the outer surface pore radius and inner pore radius were decreased. The pore structure of SP-FAC appeared more suitable for the adsorption of the three metal ions.
- 2. At $C_{\text{HNO3}} = 65$ wt%, impregnation ratio 1:35, impregnation time 12 h, and drying temperature 100 °C, the maximum adsorption capacity of Pb(II) on activated carbon fiber was 85.5 mg/g, and the pore radius of FAC_{HNO3} was 1.12 nm, which is in line with the size range of Pb(II). At $C_{\text{HNO3}} = 75$ wt%, impregnation ratio 1:25, impregnation time 36 h, and drying temperature 100, the maximum adsorption capacity of Mn(II) was 92.3 mg/g, and the pore radius of FAC_{HNO3} was 1.24 nm, which is in line with the size range of Mn(II). At $C_{\text{HNO3}} = 55$ wt%, impregnation ratio 1:35, impregnation time 36 h, and drying temperature 120, the maximum adsorption capacity of Zn(II) was 59.9 mg/g, and the pore radius of FAC_{HNO3} was 0.97 nm, which is in line with the size range of Zn(II).
- 3. There was a close correlation between the pore structure and adsorption capacity. The specific surface area and pore volume were positively correlated with adsorption capacity. The outer surface pore radius, pore radius, and P/P_0 were negatively correlated with adsorption capacity. When $C_{\rm HNO3}$ increased, the specific surface area was positively correlated with adsorption capacity, and the concentration affects the specific surface area much more than other variables.
- 4. This study shows that the activated carbon fiber was modified with HNO₃ to make it have selective adsorption capacity, which provides a new idea for the recovery and utilization of metal ions. Secondly, the technology can be applied to the medical field, using the competitive adsorption of activated carbon to different ions and balancing the content of trace metals in the blood, to achieve the purpose of treating some diseases.

ACKNOWLEDGMENTS

This research was financially supported by Natural Science Foundation of Inner Mongolia Autonomous Region (Grant No. 2017MS0358), and the Autonomous Region Undergraduate Innovation and Entrepreneurship Training Program (Grant No. 202110129007).

Author Contributions

Conceptualization, X.W.; methodology, D.W.; validation, Y.W. and X.W.; formal analysis, D.W.; investigation, Y.W.; data curation, D.W.; writing—original draft preparation, D.W.; and writing—review and editing, X.W. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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Article submitted: April 2, 2022; Peer review completed: May 14, 2022; Revised version received: May 26, 2022; Accepted: May 27, 2022; Published: June 1, 2022. DOI: 10.15376/biores.17.3.4410-4431