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Studies on modified conditions of biochar and the mechanism for fluoride removal

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ABSTRACT

The modified Mongolian scotch pine tree sawdust char (MMSC), fabricated from the natural Mongolian scotch pine tree sawdust char (MSC) using phosphoric acid-microwave method, was used as the F^- adsorbent of aqueous solution. MMSC was prepared according to the optimized method as follows. MSC and 25% (vol) phosphoric acid (v/v = 1:4) were mixed in Bunsen beaker at 25℃ for 24 h. The mixer was then radiated for 3 min (Radiation power 630 W), followed by filtration, generating the desired MMSC, which was washed with distilled water until the pH reached around 7.0, and then dried in an oven at 50℃ till constant weight for further fabrication. No obvious difference of MMSC and MSC was observed in color. The adsorption capacity of MMSC reached 885 mg kg^{-1} for F^- in high-fluoride resource water. The concentration was reduced to below the recommended value (1.5 mg L^{-1}) from the concentration of 20 mg L^{-1} when the high dosage of MMSC was used. Compared with MSC, the MMSC can be used as potential F^- adsorbent for high-fluoride resource water treatment. The analysis of removal mechanism provided a theoretical basis for further application.

Keywords: Fluoride; Adsorption; Optimal modification; Characterization

1. Introduction

Fluoride is a natural mineral which was found in food, all water and wastewater. Moderate fluoride (0.5–1.5 mg L^{-1}) in resource water is an essential micronutrient for the calcification of the dental enamel and bone formation [1]. However, the long-term intake of inappropriate fluoride not only causes dental and skeletal fluorosis, but may also lead to mutations in the users' deoxyribonucleic acid [2]. It is estimated that more than 200 million people worldwide rely on resource water with high fluoride concentration (>1.5 mg L^{-1}) [3]. For these reasons, the removal of the excess fluoride from water and wastewaters is important in terms of protection of public health and environment.

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Various techniques of defluoridation, for instance, coagulation and precipitation [4], reverse osmosis [5], nanofiltration [6,7], electrodialysis and electrolysis [8,9], membrane processes [10,11], ion exchange [12,13], Donnan dialysis [14], and adsorption, have been used to reduce the excess fluoride.

The precipitation process has been widely used because it is economical and simple, but it often results in additional difficulties in eliminating excessive chemicals. The final fluoride concentration in water depends greatly on the solubility of the precipitated fluoride and precipitation reagents. Reverse osmosis, nanofiltration, electro dialysis, etc. have disadvantages in terms of maintenance cost and economic viability, thus they have not been broadly used for fluoride removal from water solution. By contrast, adsorption is inarguably regarded as one of the most suitable techniques for the defluorination because it is economical, robust, environmentally benign, and efficient [15].

Biochar, as the pyrolytic byproduct during bio-oil production, has been used as the adsorbent for removal of heavy metals [16,17], cationic dye, and neutral red [18]. However, the biochar, e.g. the MSC, has not been reported as the adsorbent of F^- ion.

Adsorption of fluoride on MSC was investigated, showing that the MSC cannot remove the fluoride effectively from aqueous solution. However, the fluoride can be effectively removed from aqueous solution by modified Mongolian scotch pine tree sawdust char (MMSC). The main aim of this work is to study the adsorption capacity and mechanism of MMSC as well as the effect of the temperature on the adsorption capacity.

2. Materials and methods

2.1. Preparation of MMSC

MSC is commercially known as biochar and manufactured from Mongolian scotch pine tree sawdust by slow pyrolyzing in a fluidized reactor [19]. MSC was obtained from the local countryside. It was air-dried for 1 d and ground and sieved to a particle size of 2 mm before usage. The pyrolytic temperature is up to 550℃ to produce bio-oil and biogas. Yield of biochar is 30% of Mongolian scotch pine tree sawdust (MSC). MSC as a byproduct was washed with distilled water several times to remove all the dirt particles, the washed materials was dried in an oven at 100℃ for 24 h. We stored it in plastic containers for further use.

MMSC was fabricated from MSC using phosphoric acid-microwave method. The selected MSC was first soaked in phosphoric acid soak, then radiated in microwave, and filtrated. The filtrated material was washed with distilled water several times to remove the remained phosphoric acid on the surface until the pH value reached around 7.0. The washed materials was dried in an oven at 100˚for 24 h, and then ground and screened through a set of sieves to get the geometrical sizes (0.25–0.27 mm) meshes. In this process, we used phosphoric acid solution, microwave radiometer, suction flask, and drying oven. Through orthogonal experiment, we discussed the most suitable modification condition.

2.2. Preparation of F^- solution

A stock solution was prepared by dissolving 442 mg NaF in 2 L deionized water (F^- 100 mg L^{-1}). All the solutions for fluoride removal experiments and analysis were prepared by an appropriate dilution from the stock solution; the concentration gradients were set based upon the fluoride proportion settings of Chinese high-fluoride resource water.

2.3. Adsorption methods

Static adsorption studies were carried out in a rotary shaker (ZHWY-2102, Zhicheng, China) at 150 rpm for each desired initial fluoride concentration and temperature. MMSC was mixed with 100 mL fluoride solutions in 250 mL polypropylene conical flasks during the experiments.

F^- concentration was measured using an ion chromatography (ICS-90, Dionex, California, USA) with F^- solutions of known concentration for calibration. NaF was used for the preparation of standard solutions. pH values of water samples were measured by a pH meter (Mettler-Toledo 320-S, Zurich, Switzerland).

In determination of textural and physicochemical properties of MSC and MMSC, the FT-IR spectra were recorded from KBr pellets in the range of 400–4,000 cm^{-1} on a Bruker Tensor 27 spectrophotometer. Elemental analyses (C, H, and N) were carried out on a FLASH EA 1112 elemental analyzer. The mineralogy of the sample was characterized by X-ray diffraction (XRD) (Tokyo Shibaura Model ADG-01E). The Specific surface area and pore volumes of MSC and MMSC were tested using the nitrogen adsorption method with a NOVA 1000 high-speed, automated surface area, and pore size analyzer (Quan-tachrome Corporation, US), and the BET adsorption model was used in the calculation. Scanning electron microscope (SEM) was recorded by a SEM (JEOL 6335F^-SEM, Japan).

The data obtained in batch mode studies was used to calculate the F^- adsorptive quantity. It was calculated for each sample by using the following equation:

$$q_e = \frac{V(C_0 - C_e)}{m} \tag{1}$$

where q_e (mg kg^{-1}) is the equilibrium uptake value; V (L) is the sample volume; C_0 (mg L^{-1}) is the initial F$^-$ concentration; C_e (mg L^{-1}) is the equilibrium F$^-$ concentration; and m (kg) is the weight of adsorbent.

All the experiments (adsorption and desorption) were performed in a batch setup taking two replicates and average values were reported.

3. Results and discussion

3.1. Modified condition

In order to get the modified conditions, during the MSC modified process, after soaking in phosphoric acid by 1:4 (MSC: phosphoric acid, volume ratio) in Bunsen beaker at 25℃, phosphoric acid soaking time, phosphoric concentration, micro-wave radiant power, and micro-wave radiant time were adjusted.

3.1.1. Phosphoric acid soaking time

The soaking time of phosphoric acid in the range of 12–60 h was discussed initially, with 25% (vol) phosphoric acid, 630 W, and 5 min microwave radiation.

As shown in Fig. 1(A), the adsorbed capacity increased with longer soaking time. When the soaking time exceeded 24 h, the adsorption capacity had no significant increase. So MMSC was prepared by soaking MSC in Bunsen beaker with 25% (vol) phosphoric acid at 25˚for 24 h.

3.1.2. Phosphoric concentration

The most suitable modified phosphoric acid concentration was studied by setting phosphoric acid of 15–35% (vol), with the soaking time 24 h, 630 W, and 5 min microwave radiation.

As can be seen from Fig. 1(B), the adsorbed capacity of MMSC for F$^-$ increased with the increase of phosphoric acid soaking concentration. In order to economize the raw materials, we prepared MMSC by soaking MSC with 25% (vol) phosphoric acid.

3.1.3. Micro-wave radiant power

In order to investigate the best micro-wave radiant power, micro-wave radiation power was set among 0–810 W and radiation 5 min, on the condition that MSC was mixing with 25% (vol) phosphoric acid for 24 h.

As illustrated in Fig. 1(C), the adsorbed capacity increased with the increasing of microwave power, but decreased sharply when the power was 810 W. So we set the micro-wave power at 630 W during the MSC-modified process.

3.1.4. Micro-wave radiant time

To get the most suitable micro-wave radiant time, we investigated the micro-wave radiation time during 1–9 min, with 25% (vol) phosphoric acid soaking 24 h, at the micro-wave radiation power of 630 W.

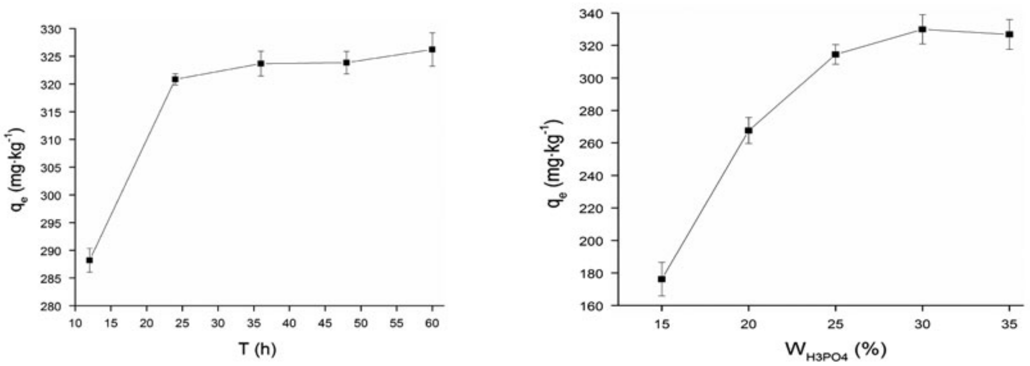
As can be seen from Fig. 1(D), the absorption capacity initially increased with radiant time increased, and then decreased monotonically. Therefore, the optimum radiation is around 3 min.

As a result, the optimal modification was summarized as follows: MMSC was prepared by soaking MSC with 25% phosphoric acid in a volume ratio of 1 (MSC):4 (phosphoric acid) in Bunsen beaker at 25℃ for 24 h. After micro-wave radiating 3 min at the radiation power of 630 W, MMSC was filtrated and washed with distilled water until the pH reached near 7.0 and dried in an oven at 50℃ until constant weight for further use. The color of MSC showed no obvious difference with MMSC.

3.2. Effect of MMSC dosage and contact time

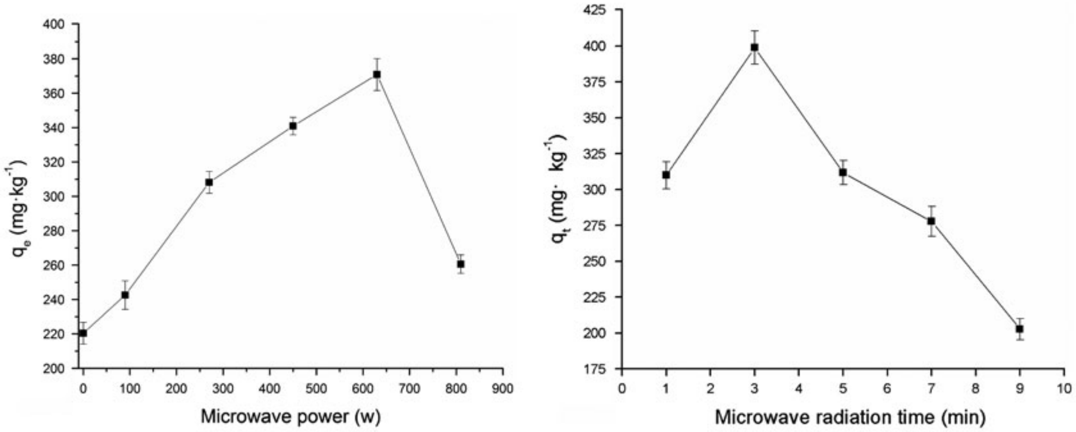
The use of high dosage of MMSC (7.2 g/100 mL solution) could reduce the fluoride concentration from 20 mg L^{-1} to below the recommended value (1.5 mg L^{-1}) (Fig. 2(A)). However, it was found that the pH in the solution after treatment was much lower than the recommended value (6.5–8.5 mg L^{-1}). Thus, the pH adjustment was needed if the high adsorbent dosage was used. But when the low dosage of MMSC (1.8 g/100 mL, 20 mg L^{-1} F$^-$ solution) was used, the MMSC could not effectively remove fluoride. So the optimal dosage of MMSC was 3.6 g/100 mL, which was employed in the following experiments.

Effects of contact time on adsorption capacity were also investigated. The equilibration time is normally chosen as the experiment time in most fluoride adsorption experiments [20], but we would like to choose the most optimum contact time. It was very clear from the results in Fig. 2(B) that the oscillation time required for maximum uptake of F$^-$ ions depended on the initial F$^-$ concentration. It was observed that the adsorption capacity initially increased rapidly and then to a lesser extent. Consequently, 80 min was chosen as the experimental contact time required to reaching excellent absorption for a short time in the present adsorption experiments.



(A) Effect of the phosphoric acid soaking time

(B) Effect of the phosphoric acid concentration



(C) Effect of the micro-wave radiant power

(D) Effect of the radiant time

Fig. 1. Modified conditions.

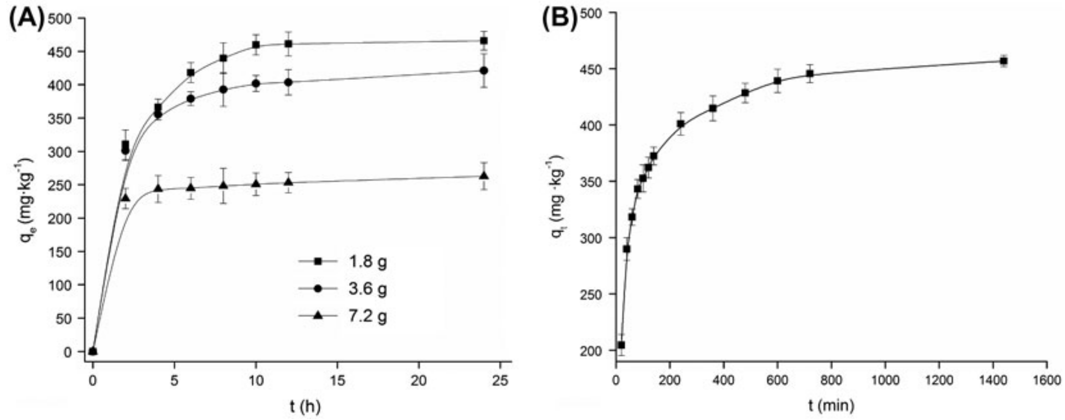


Fig. 2. Effect of the dosage of MMSC and the contact time.

3.3. Fluoride removal

3.3.1. Static adsorption

First, we tried MSC with or without micro-wave radiant during the modified process to remove fluoride, as a result, fluoride removal performance of MSC without micro-wave radiant cannot removal fluoride as effectively as MSC with micro-wave radiant.

Fig. 3(A) illustrated the static F^- adsorption process of MMSC ($m = 3.6$ g, $C_0 = 5,\ 10,\ 20\ \mathrm{mg\ L^{-1}}$, $V = 100$ mL,

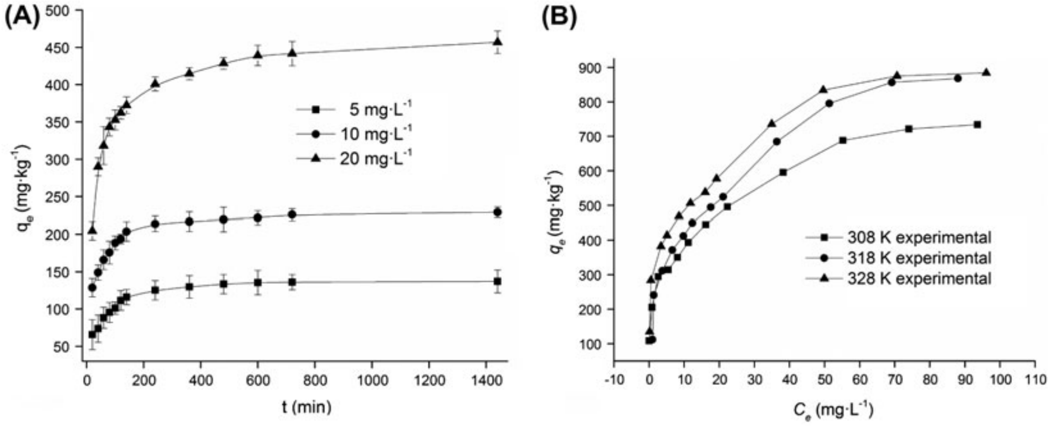


Fig. 3. Static adsorption process of F⁻ by MMSC.

$T = 298$ K). It was found that when the initial concentration was 5, 10, and 20 mg·L^{-1}, the F⁻ removal rate was 82, 71, and 63%, respectively. The color of MSC showed no obvious difference with MMSC. The adsorption capacity of MMSC can reach 885 mg L^{-1} kg^{-1} for F⁻ in high-fluoride resource water. This indicated that MMSC had good F⁻ adsorption capacity. It was also observed that equilibrium occurred relatively early in the solution containing the lower F⁻ concentrations than the higher ones. It also showed that the amount of F⁻ adsorbed by per unit weight of MMSC increased as the F⁻ concentration increased.

What's more, the bigger adsorptive capacities for F⁻ of MMSC were also observed in the higher temperature range ($m = 3.6$ g, $C_0 = 0$–100 mg L^{-1}, $V = 100$ mL, $T = 308$, 318, 328 K) (Fig. 3(B)). This indicated that the adsorption of F⁻ onto MMSC was endothermic in nature. So the adsorptive process may be chemical process [21].

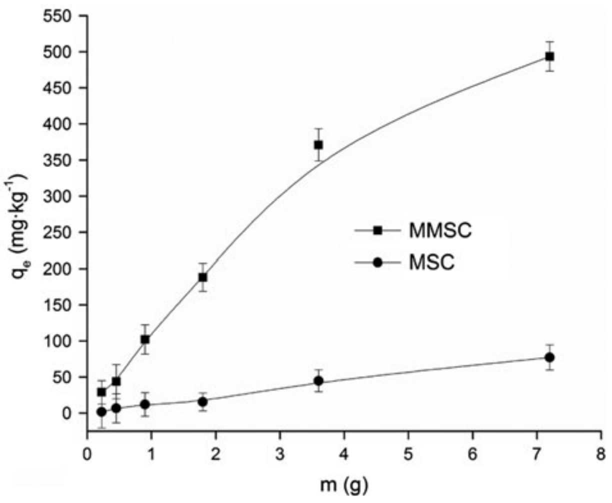


Fig. 4. F⁻ adsorption capacity of MSC and MMSC.

3.3.2. Adsorption capacity of MSC and MMSC

The comparative uptake of F⁻ by MSC and MMSC at 298 K ($m = 3.6$ g, $C_0 = 20$ mg L^{-1}, pH 7.0) were shown in Fig. 4. It was observed that the F⁻ adsorption capacity (q_e) of MMSC was significantly higher than that of MSC. So MMSC favored the F⁻ removal from high-fluoride resource water, which might be suitable to be used as potential F⁻ adsorbent material.

3.4. Characterization of MMSC

3.4.1 FTIR of MSC and MMSC

The FTIR technique is an important tool to identify some characteristic functional groups, which are capable of adsorbing pollutants.

It was clear from experiments that FITR of MSC and MMSC displayed a number of absorption peaks, reflecting the complex nature of the materials examined. There were carbonyl group, olefin group, etc. on surface of MSC from FTIR analysis. The broad absorption peaks around 3440.85 and 1616.50 cm^{-1} were indicative of the existence of bonded hydroxyl (the stretch vibration and bending vibration groups on the surface of MSC). The peak at 2924.29 cm^{-1} was assigned to the stretch vibration of C–H bond in methylene group. The peaks located at 619.18 cm^{-1} were characteristics of C–Cl group stretching from aldehydes and ketones. The peak near 1112.10 cm^{-1} was also attributed to stretch vibration of C–O from carboxyl group. The peak at 1,600–1,450 cm^{-1} may be from stretch vibration in aromatic rings. The absorption peak of MSC was major from stretching vibration of several groups, such as O–H (from cellulose, lignin, and adsorbed water), C–H, C–O, etc. Comparison of FTIR between MSC and MMSC, the significant change was the peak at 3440.85 cm^{-1} from O–H was shifted to 3444.49 cm^{-1}, the relative strength became weaker after modification. The result showed that MSC had less O–H groups than MMSC. The decrease in O–H content and the change in FTIR for MSC indicated that the reactions proceeded efficiently and the F^- was easier adsorbed onto the surface of MMSC.

3.4.2. X-ray fluorescence

The X-ray fluorescence technique is an important tool for analyzing all the elements between F(9)-U(92). Table 1 showed the X-ray fluorescence of MSC and MMSC. It was clear from Table 1 that the content of CaO and K_2O in MMSC was lower than that of MSC. During the modified process, the chemical reactions were predicted as following:

$$CaO + H_2O = Ca(OH)_2 \tag{2}$$

$$10Ca(OH)_2 + 6H_3PO_4 = Ca_{10}(PO_4)_6(OH)_2 \downarrow + 18H_2O \tag{3}$$

In F^- aqueous solutions, the F^- molecule of basic F^- made a reaction with $Ca_{10}(PO_4)_6(OH)_2$, OH^-, and F^-, which belonged to the same lattice and could displace each other. Otherwise, $Ca_{10}(PO_4)_6(OH)_2$ had large free surface which could adsorb F^-.

$$Ca_{10}(PO_4)_6(OH)_2 + 2\,F^- = Ca_{10}(PO_4)_6(F)_2 \downarrow + OH^- \tag{4}$$

Table 1
X-ray fluorescence analysis of MSC and MMSC (content: %)

Formula	Z	MSC	MMSC
CaO	20	7.73	3.67
K_2O	19	4.56	0.61
SiO_2	14	2.71	4.33
Fe_2O_3	26	2.17	2.45
Al_2O_3	13	0.49	0.59
SO_3	16	0.34	0.21
MgO	12	0.27	0.13
BaO	56	0.12	0.09
TiO_2	22	0.09	0.27
MnO	25	0.09	0.07
SrO	38	0.08	0.05
ZnO	30	0.05	0.03
Cr_2O_3	24	0.04	0.10
Cl	17	0.04	0.03
CuO	29	0.02	0.03
NiO	28	0.02	0.03
Rb_2O	37	0.01	/

So the mechanism of defluorination included both adsorption and ion exchange reaction.

Another chemical reactions mechanism was predicated as follows:

The hydrolysis reaction of F^- was happened first:

$$F^- + H_2O = OH^- + HF \uparrow \tag{5}$$

Since the ionization constants of H_3PO_4 were $Ka_1 = 7.52 \times 10^{-3}$, $Ka_2 = 6.31 \times 10^{-8}$, and $Ka_3 = 4.40 \times 10^{-13}$. The ionization constant of HF was $Ka = 6.61 \times 10^{-4}$, so the following ionization equations existed in the adsorption process.

$$H_3PO_4 + F^- = HF + H_2PO_4^- \tag{6}$$

$$3Ca(OH)_2 + 2HF = CaF_2 \downarrow + 2H_2O \tag{7}$$

The mechanism was similar to the calcium salt precipitation, since the adsorption happened on MMSC, the process overcame the shortcomings in tradition process, for example, slowly sludge settling and difficulty dehydrations.

As a result, F^- existed in sediment $Ca_{10}(PO_4)_6(F)_2$ and CaF_2, and gathered together into larger diameter which was easily adsorbed onto MMSC.

3.4.2. Elemental analysis

Synthesis of C, H, O, S in MSC and MMSC, the results were shown in Table 2. It can be seen from Table 2 that the content of C, N, and H increased after modification. Perhaps the C, N, H elements were fixed in the MMSC from CO, CO_2, H_2O, and NH_3 during the modified process.

3.4.4. X-ray powder diffraction

From XRD Spectra of MSC and MMSC, we learned that the main diffraction peak of MSC is 26.5°, its crystal diffraction peak of C_{111}. After modified, the diffraction peak in 26.5° disappeared, indicated that the crystallite structure of MSC changed (from order to disorder) during the modified process. This may be due to the reaction between MSC and phosphoric acid, or changed by microwave radiation.

3.4.5. Specific surface area and pore size distribution

The specific surface area and pore size distributions of MSC and MMSC were detected (Table 3). As a result, the specific surface area increased from 7.7 to

Table 2
Elemental analysis of MSC and MMSC

Sample name	Nitrogen (%)	Carbon (%)	Hydrogen (%)	Sulfur (%)
MSC	0.09	59.76	3.53	0
MMSC	0.11	61.93	3.47	0

Table 3
Determination of specific surface area and pore diameter distribution

Material	MSC	MMSC
Specific surface area	$7.68\,\mathrm{m^2/g}$	$389.95\,\mathrm{m^2/g}$
Pore diameter distribution	16.99 Å	0.93 Å

$339.0\,\mathrm{m^2\,g^{-1}}$ after modification, while the average pore diameter decreased from 17.0 to 0.9 Å, which indicated that the increasing specific surface area made great contributions to F^- adsorption.

3.4.6. Scanning electron microscope

We made the SEM micrographs under 250, 500, and 1,000 times electron microscopy.

It can be seen from scanning electron micrographs of MSC and MMSC that there were many impurities and sedimentation adsorption layer on MSC surface, blocking surface pore and fracture. Furthermore, the surface of MMSC is rougher than that of MSC.

After modification, the sedimentation adsorption layer was removed by phosphate-microwave, and formed a lot of hole through etching, so, based on the morphology, it can be concluded that this material presents an adequate morphological profile to retain precipitation adsorption, may be $Ca_{10}(PO_4)_6(F)_2$ and CaF_2.

4. Conclusions

MMSC, which was fabricated by acid-microwave method from MSC, had higher capacity for binding F^- and can be used as a new novel for the removal of F^- from high fluoride resource water. The optimal modifications were summarized as follows: MMSC was prepared by mixing MSC with 25% (vol) phosphoric acid by 1:4 (MSC: phosphoric acid, volume ratio) in Bunsen beaker at 25℃ for 24 h. After microwave radiated for 3 min (Radiation power 630 W), MMSC was filtrated and washed with distilled water until the pH reached around 7.0, then dried in an oven at 50℃ till constant weight for further fabrication. The color of MMSC showed no obvious difference with MSC. The F^- adsorption capacity of MMSC can reach $885\,\mathrm{mg\,kg^{-1}}$ in high-fluoride resource water. Compared with MSC, the adsorption capacity of MMSC implied it might be suitable as potential material as F^- adsorbent of aqueous solution, which provides a new way for high-fluoride resource water treatment. The characterization of MSC and MMSC indicated that the main reason of the increasing F^- adsorption including chemistry reaction and the increasing specific surface area. The process was spontaneous and endothermic in nature. Therefore, MMSC may be a desirable material for fluoride removal in water with high F^-concentrations, For example, it could be applied in constructed wetlands in high fluoride area. The analysis of removal mechanism provided a theoretical basis for further application. Further studies will be required to detect the practical application of MMSC.

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References

[1] C.B. Dissanayake, The fluoride problem in the groundwater of Sri Lanka environmental management and health, Int. J. Environ. Res. 19 (1991) 195–203.

[2] T. Tsutsui, N. Suzuki, M. Ohmori, H. Maizumi, Cytotoxicity, chromosome aberrations and unscheduled DNA synthesis in cultured human diploid fibroblasts induced by sodium fluoride, Mutat. Res. 139 (1984) 193–198.

[3] World Health Organization, Guidelines for Drinking Water Quality, WHO Press, Geneva, 2004.

[4] F. El-Gohary, A. Tawfik, U. Mahmoud, Comparative study between chemical coagulation/precipitation versus coagulation/dissolved air flotation for pretreatment of personal care products wastewater, Desalination 252 (2010) 106–112.

[5] P. Sehn, Fluoride removal with extra low energy reverse osmosis membranes: Three years of large scale field experience in Finland, Desalination 223 (2008) 73–84.

[6] M. Tahaikt, R. EiHabbani, A. AitHaddou, I. Achary, Z. Amor, M. Taky, A. Alami, A. Boughriba, M. Hafsi, A. Elmidaoui, Fluoride removal from groundwater by nanofiltration, Desalination 212 (2007) 46–53.

[7] F. Elazhar, M. Tahaikt, A. Achatei, F. Elmidaoui, M. Taky, F. El Hannouni, I. Laaziz, S. Jariri, M. EI Amrani, A. Elmidaoui, Economical evaluation of the fluoride removal by nanofiltration, Desalination 249 (2009) 154–157.

[8] M. Tahaikt, I. Achary, M.A. Menkouchi Sahli, Z. Amor, M. Taky, A. Alami, A. Boughriba, M. Taky, A. Alami Boughriba, M. Hafsi, A. Elmidaoui, Defluoridation of Moroccan ground water by electrodialysis: Continuous operation, Desalination, 189 (2006) 215–220.

[9] N. Kabay, O. Arar, F. Acar, A. Ghazal, U. Yuksel, M. Yuksel, Removal of boron from by electrodialysis: Effect of feed characteristics and interfering ions, Desalination 223 (2008) 63–72.

[10] C.Y. Hu, S.L. Lo, W.H. Kuan, Y.D. Lee, Removal of fluoride from semiconductor wastewater by electrocoagulation-flotation, Water Res. 39 (2005) 895–901.

[11] P.I. Ndiaye, P. Moulin, L. Dominguez, J.C. Millet, F. Charbit, Removal of fluoride from electronic industrial effluent by RO membrane separation, Desalination 173 (2005) 25–32.

[12] A.J. Karabelas, S.G. Yiantsios, Z. Metaxiotou, N. Andritsos, A. Akiskalos, G. Vlachopoulos, S. Stavroulias, Water and materials recovery from fertilizer industry acidic effluents by membrane processes, Desalination 138 (2001) 93–102.

[13] K. Hanninen, A.M. Kaukonen, L. Murtomaki, J. Hirvonen, Mechanistic evaluation of factors affecting compound loading into ion-exchange fibers, Eur. J. Pharm. Sci. 31 (2007) 306–317.

[14] R.X. Liu, J.L. Guo, H.X. Tang, Adsorption of fluoride, phosphate, and arsenate ions on a new type of ion exchange fiber, J. Colloid Interface Sci. 248 (2002) 268–274.

[15] X. Xu, Q. Li, H. Cui, J. Pang, L. Sun, H. An, J. Zhai, Adsorption of fluoride from aqueous solution on magnesia-loaded flyash cenospheres, Desalination 272 (2011) 233–239.

[16] A.A.M. Daifullah, S.M. Yakout, S.A. Elreefy, Adsorption of fluoride in aqueous solutions using $KMnO_4$-modified activated carbon derived from steam pyrolysis of rice straw. J. Hazard. Materi. 147 (2007) 633–643.

[17] D. Mohan, S. Rajput, C.U. Pittman Jr., Modeling and evaluation of chromium remediation from water using low cost bio-char, a green adsorbent, J. Hazard. Mater. 188 (2011) 319–330.

[18] L.J. Zhang, D. Ma, G.Y. Mao, M.M. Zhang, R.P. Han, Adsorption of neutral red from solution by bio-chars produced from pyrolysis of wheat straw, Adv. Mater. Res. 322 (2011) 72–76.

[19] C.S. Zhang, R.Q. Zhang, X.P. Li, Y.W. Li, W. Shi, X.T. Ren, X.M. Xu, Bench-scale fluidized-bed fast pyrolysis of peanut shell for bio-oil production, Environ. Prog. Sustainable Energy 30 (2011) 11–18.

[20] S. Vinitnantharat, S. Kositchaiyong, S. Chiarakorn, Removal of fluoride in aqueous solution by adsorption on acid activated water treatment sludge, Appl. Surf. Sci. 256 (2010) 5458–5462.

[21] R.P. Han, W.H. Zou, W.H. Yu, S.J. Cheng, Y.F. Wang, J. Shi, Biosorption of methylene blue from aqueous solution by fallen phoenix tree's leaves, J. Hazard. Mater. 141 (2007) 156–162.