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Performance of a novelly-defined zirconium metal-organic frameworks adsorption membrane in fluoride removal

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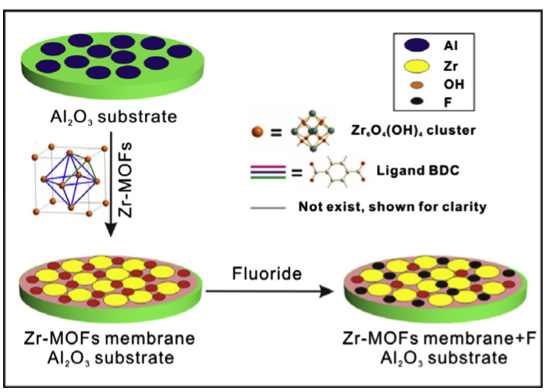
GRAPHICAL ABSTRACT



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ABSTRACT

A novelly-defined adsorption membrane for rapid removal of fluoride from drinking water was prepared. Both zirconium metal-organic frameworks (Zr-MOFs) adsorbent and membrane with large specific surface area of 740.28 m^2/g were used for fluoride removal for the first time. For adsorption technique, fluoride adsorption on Zr-MOFs was studied on a batch mode. The adsorption data could be well described by Langmuir isotherm model while the adsorption kinetic followed pseudo-second-order model. The maximum of adsorption capacity was 102.40 mg/g at pH 7.0 when the initial fluoride concentration was 200 mg/L. The FT-IR and XPS analyses of Zr-MOFs revealed that both surface hydroxyl groups and Zr(IV) active sites played important roles in fluoride adsorption process. The as-prepared Zr-MOFs adsorbent was suitable for practical treatment of drinking water and regeneration by sodium hydroxide solution (3 wt%). For membrane experiments, Zr-MOFs membrane supported on Alumina substrate could remove fluoride efficiently through dynamic filtration. The fluoride removal capability of Zr-MOFs membrane depended on flow rate and initial concentration of fluoride. The fluoride removal abilities of Zr-MOFs membrane with 20 µm thickness could reach 5510, 5173, and 4664 L/m^2 when fluoride

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concentrations were 5, 8 and 10 mg/L, respectively. This study indicated that Zr-MOFs membrane could be developed into a very viable technology for highly effective removal of fluoride from drinking water.

1. Introduction

Fluoride (F) is an essential element for both human and animals while it is also one of the World Health Organization (WHO) classified contaminants in ground water, maximum acceptable concentration limiting in 1.5 mg/L [1]. In a narrow concentration ranged of 0.5–1.5 mg/L, fluoride contained water would be good for the health of teeth and bones [2–4]. However, excess ingested of fluoride through food and drinks can cause a series of diseases such as dental/skeletal fluorosis, fetal cerebral function, and neurotransmitters [5–7]. Taking the serious health effects into account, many technologies have been developed and evaluated for the removal of excess amounts of fluoride from drinking water: precipitation [8], electro-coagulation [9–11], membrane techniques [12,13] and adsorption [2,7,8,14–17]. Despite the availability of above mentioned processes for fluoride removal, adsorption and membrane separation still remain to be two of the best methods.

Commonly in the removal process of fluoride, the two methods of adsorption and membrane separation were used separately. Adsorption can be defined as the immobilization of target molecules by adsorbents through biological recognition, electrostatic interactions, chemical reactions and hydrophobic interactions. Developing high-capacity and selective adsorbents was essential to facilitate fluoride removal in order to meet the requirement for the drinking water. So far, different adsorbents have been exploited for fluoride removal, such as alumina [18] and alumina based adsorbents [19,20], mixed oxides [21–23], activated carbon [24], clay like materials [25,26], bio-polymer based composites [27] and ion-exchange resins [28]. This method can remove soluble and insoluble organic pollutants easily and effectively without generation of hazardous by-products [29]. However, the adsorbents were sometimes difficult to be separated from water in practical application [8,30]. Membrane separation was defined as the rejections of target molecules by size exclusion [31]. In the traditional membrane separation processes, size exclusion was difficult to achieve, but the membrane can be easily separated from water [32,33]. Thus, the combination of adsorption and membrane separation can remove fluoride more effectively and will not cause secondary pollution [34]. It was highly important to find materials that can be used as both adsorbent and membrane.

Recently, a new class of fluoride adsorbent, named metal organic frameworks (MOFs), attracts great attention because of their tunable crystalline organic-inorganic hybrid networks [35–37]. MOFs can exhibit superior physical and chemical characteristics and have been applied in various adsorption-related areas, including hydrogen storage [38–40], CO_2 adsorption [41,42] and removal of toxic gases [43,44]. Due to the promising potential in the areas mentioned above, researchers started to investigated the capability of MOFs to remove compounds in aqueous environment. A number of researches have been conducted including removal of metal ions [45], toxic dyes [46,47], herbicides [48], oil droplets [49], humic acid [50]. These studies unveiled that several types of MOFs can remain intact in aqueous solutions and show exceptional capacities to remove pollutants from water compared to traditional adsorbents. Lately, MOFs has also been evaluated for defluoridation in water [51–53]. It was found that MOFs exhibited high adsorption capacity for fluoride compared to other adsorbents. However, there were very few researches about MOFs membrane for fluoride removal.

In the present study, a novelly-defined adsorption membrane for rapid removal of fluoride from aqueous solution was prepared for the first time. Both adsorption and membrane techniques were used for fluoride removal. Zr-MOFs adsorbent and Zr-MOFs membrane were prepared and used for fluoride removal, respectively. For adsorption experiments, fluoride adsorption isotherms and kinetics of Zr-MOFs adsorbent were investigated. The effects of pH and co-existing anions were examined. The mechanism of fluoride removal was studied by FT-IR and XPS analyses. The as-prepared adsorbent was also used for treatment of underground water with high fluoride concentration in Xingwang Village, Inner Mongolia of China. For membrane experiments, the effects of temperature, flow rate and initial concentration of fluoride on fluoride removal were studied, the amount of fluoride contaminated water that Zr-MOFs membrane can deal with was also tested.

2. Experimental

2.1. Synthesis of Zr-MOFs membrane and Zr-MOFs adsorbent

The Zr-MOFs membrane was fabricated on alumina substrate (diameter: 3.0 cm, thickness: 0.1 cm) by an in-situ solvothermal synthesis method in Fig. S1 (see in Supporting Information). 1,4-benzenedicarboxylic acid was used as a surface modifier of the substrate during the synthesis via constructing coordination bonds between the carboxylate oxgens and aluminum atoms from substrate. The optimized recipe is: $ZrCl_4$ (>99.5%, Sigma Aldrich), 1,4-benzenedicarboxylic acid (BDC, 98%, Sigma Aldrich) were dissolved in 60 mL N,N-Dimethylformamide (DMF, 99.8%, VWR) under stirring to give a molar composition: Zr^{4+}/BDC/DMF = 1:1:500. The resulting mixture was transferred into a Teflon-lined stainless steel autoclave which an alumina ceramic was hung in. Afterwards the autoclave was placed in a convective oven (UF30, Memmert) and heated at 120 °C for 3 days. After cooling, the membrane was washed with ethanol (99.85%, VWR) and dried at 25 °C overnight under vacuum (Fistreem Vacuum Oven).

The Zr-MOFs adsorbent was collected from the mother solution in the above mentioned autoclave after membrane synthesis. The Zr-MOFs powder was washed by ethanol with the assistance of centrifuge (Thermo Scientific Legend X1R) for later use.

2.2. Characterization methods

The obtained powder was characterized by X-ray diffraction (X'Pert ProMPD, Cu Kα radiation, wavelength 1.5418 Å). Field-emission scanning electron microscopy (FE-SEM) image was taken by a Sirion 200 field-emission scanning electron microscopy. The textural properties of the adsorbent (specific area, pore volume and average pore diameter) were tested on a Coulter Omnisorp 100CX Brunauer-Emmett-Teller (BET) using nitrogen adsorption with a degassing temperature of 80 °C. Thermo-gravimetric analyses (TGA) were performed on a SDT-Q600 DTG-TGA instrument by heating rate 10 °C/min in nitrogen flow. The EDS pattern and elemental mapping were analyzed with Zeiss Auriga microscope. X-ray photoelectron spectrometry (XPS) was carried out on an ESCALab MK II using non-monochromatized Mg Ka X-ray beams as the excitation source. Fourier transform infrared (FT-IR) spectra were recorded in KBr pellets on a Nexus-870 spectrophotometer.