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Performance of an optimized Zr-based nanoparticle-embedded PSF blend hollow fiber membrane in treatment of fluoride contaminated water

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ABSTRACT

Consumption of water that has excessive fluoride can cause adverse health impacts on human beings. A Zr-based nanoparticle-embedded PSF blend hollow fiber membrane was successfully prepared and optimized for removal of fluoride from the aqueous solution. Both static and dynamic adsorption of fluoride on the membrane was investigated. It was showed that the membrane could effectively remove fluoride within a wide pH ranging from 3 to 10. At neutral pH, the adsorption equilibrium was reached within 24 h. The maximum adsorption capacity of the optimized membrane was 60.65 mg/g, much higher than many commercial adsorbents. The presence of NO_3^-, SiO_3^{2-} or HA has insignificant effects on the fluoride removal. However, the removal was retarded as the concentration of HCO_3^- or PO_4^{3-} was increased. Furthermore, the membrane could remove fluoride efficiently through the continuous filtration, even in presence of natural organic matters. The spent membrane could be regenerated and then reused for the removal of fluoride with great efficiency. The adsorption history could be well described by an intraparticle diffusion model. The XPS analysis showed that the adsorption of fluoride was mainly associated with the ion-exchange between SO_4^{2-} and F^- ions. Finally, the toxicity analysis revealed that the treated water was safe for human consumption.

1. Introduction

Fluoride contamination of drinking water has raised great concerns, because excess uptake of fluoride can cause adverse health impacts on human beings such as dental and skeletal fluorosis, and fetal cerebral function (Meenakshi and Maheshwari, 2006; Viswanathan et al., 2009). As a result, the US EPA has set a concentration of 1.5 mg/L as the maximum allowable fluoride concentration level (MCL) for drinking water.

The WHO estimates that more than 200 million people worldwide consume drinking water containing fluoride with concentration above 1.5 ppm (WHO, 2006). High fluoride concentration in groundwater can be found in many parts of the world, particularly in parts of India, China, Central Africa

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and South America (Mohapatra et al., 2009). Therefore, it is important to bring down the fluoride concentration to meet the MCL.

Several technologies are employed to remove fluoride from water, including precipitation, coagulation, ion-exchange, adsorption, membrane filtration through nanofiltration membrane (NF) or reverse osmosis (RO) and electrodialysis (Adhikary et al., 1989; Meenakshi and Maheshwari, 2006; Mohapatra et al., 2009). These technologies have shown certain degrees of success in fluoride removal; however, they have their own limitations in operations in treating contaminated surface water or groundwater.

Among these technologies, adsorption has been considered as the most promising technology due to ease in operation, low cost, and good industrial track record (Bhatnagar et al., 2011; Mohapatra et al., 2009). The adsorbents available for treatment of fluoride include alumina-based sorbents (Mohapatra et al., 2009), iron-based sorbents (Chai et al., 2013), zirconium-based sorbents (Dou et al., 2011), manganese-based sorbents (Bhatnagar et al., 2011; Maliyekkal et al., 2006), zeolite-based sorbents (Sun et al., 2011), and nano-hydroxyapatite (Sairam Sundaram et al., 2008).

The zirconium-based sorbents have received more attentions due to their high affinities for fluoride and acceptable cost (Dou et al., 2012, 2011). However, they are often prepared in forms of fine powder or particles. As a result, the separation of spent particles is rather challenging. The particles could penetrate through the treatment trains and stay in the treated water, which may cause safety issues for human consumption.

NF and RO filtration seem effective in fluoride removal (Chakrabortty et al., 2013; Dolar et al., 2011; Nasr et al., 2013; Ndiaye et al., 2005). However, it has to be operated under high pressure. The requirement of energy is rather high. On the other hand, microfiltration (MF) and ultrafiltration (UF) operated under lower pressure cannot efficiently remove fluoride.

In order to overcome disadvantages of adsorbent and MF/UF membranes, we developed an innovative approach to combine both technologies together to achieve excellent adsorption performance for fluoride removal as well as ease in recycle and reuse of spend material. In our previous study, we successfully embedded an adsorbent in a PVDF membrane, which demonstrated good performance for the arsenic removal (Zheng et al., 2011). The study revealed that the membrane was applicable for the water treatment. However, there is still room for further improvement as the embedded adsorbent can be changed to reach higher adsorption capacities for removal of contaminants.

A powerful Zr-based nano-particle (NP) was synthesized by an one-step precipitation approach in our laboratory (Ma et al., 2011). It was found that it was able to remove arsenic from contaminated water with an extremely high efficiency. As both fluoride and arsenic are anionic, this similar nature had led us to use the membrane for fluoride removal. In our preliminary study, we found that its removal efficiency for fluoride was quite high. Hence, the NP was further used to fabricate a NP-embedded membrane for fluoride treatment.

It is noted that the commercial resins and adsorbents for water treatment may be less costly than the new membrane developed in this study. However, the treatment efficiency of the membrane developed in this study may be much higher than the resins and adsorbents. The membrane can serve as a separation medium for removal of suspended solids and microorganisms. In addition, the membrane can be packed as modules with different scales, ranging from smaller water filters for households to larger filtration systems in water treatment plants. These advantages would make the membrane to outperform the commercial resins and adsorbents.

In this study, a Zr-based nanoparticle-embedded PSF blend hollow fiber membrane (HFM) was successfully fabricated. The static adsorption and dynamic filtration experiments were studied in order to obtain the key parameters in treating fluoride-containing surface and groundwater. The mechanism for the removal of fluoride was studied by X-ray photoelectron spectroscopy (XPS). Finally, the toxicity effect of the HFM on the human cell was investigated to evaluate the safety of the material for water treatment.

2. Materials and method

2.1. *Materials*

All the chemicals used were of analytical grade. Polysulfone (PSF) and Zirconium (IV) oxychloride were purchased from Tianjin Chemical Co., Ltd. (China). 1-Methyl-2-pyrrolidone (NMP), polyvinylpyrrolidone (PVP), sodium fluoride, sulfate acid and the other chemicals used in this study were purchased from Sigma–Aldrich (Singapore).

2.2. *Synthesis of Zr-based nano-particles*

The synthesis of the Zr-based NPs was conducted according to the method reported in our paper (Ma et al., 2011). The newborn particles were collected and washed by deionized (DI) water, followed by drying in an oven for the subsequent experiment.

2.3. *Preparation of hollow fiber membrane*

In this work, the PSF was used as membrane matrix. The PVP and NMP were used as additive and solvent, respectively. Different amounts of the Zr-based NPs were added into the casting solution. The compositions of casting solutions used for the fabrication of four types of membranes (M0, M0.5, M1.0 and M2.0) were shown in Table 1. To get a homogenously

Table 1 – Composition and viscosity of casting solutions.

Membrane	Dope solution composition (wt%)[a]			Zr-based NPs/PSF (w/w)	Viscosity (mPa·s)
	PSF	PVP	NMP		
M0	13	3	84	0:1	247.9
M0.5	13	3	84	0.5:1	398.6
M1.0	13	3	84	1:1	475.6
M2.0	13	3	84	2.0:1	640.8

[a] Composition without NPs.