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Research article

# Fluoride removal from water using a magnesia-pullulan composite in a continuous fixed-bed column

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ABSTRACT

A magnesia-pullulan composite (MgOP) was previously shown to effectively remove fluoride from water. In the present study, a continuous fixed-bed column was used to examine the application of the composite at an industrial scale. The influencing parameters included bed mass (4.0, 6.0 and 8.0 g), influent flow rate (8, 16 and 32 mL/min), inlet fluoride concentration (5, 10 and 20 mg/L), reaction temperature (20, 30 and 40 °C), influent pH (4, 7 and 10) and other existing anions ($HCO_3^-$, $SO_4^{2-}$, $Cl^-$ and $NO_3^-$), through which the breakthrough curves could be depicted for the experimental data analysis. The results indicated that MgOP is promising for fluoride removal with a defluoridation capacity of 16.6 mg/g at the bed mass of 6.0 g, influent flow rate of 16 mL/min and inlet fluoride concentration of 10 mg/L. The dynamics of the fluoride adsorption process were modeled using the Thomas and Yan models, in which the Yan model presented better predictions for the breakthrough curves than the Thomas model. Moreover, the concentration of magnesium in the effluent was monitored to determine Mg stability in the MgOP composite. Results indicated the effluent concentration of $Mg^{2+}$ ions could be kept at a safe level. Calcination of fluoride-loaded MgOP effectively regenerated the material.



## 1. Introduction

Fluoride is an essential micronutrient because a trace intake of fluoride (0.4–0.6 mg/L) is helpful for normal mineralization of bones and formation of dental enamel. However, excessive concentrations of fluoride in drinking water may result in a progressive crippling disease known as fluorosis. The optimum fluoride level in drinking water set by the World Health Organization (WHO) is < 1.5 mg/L (WHO, 2011). Fluoride in the aquatic environment is derived mainly from natural weathering of fluorine-containing minerals such as fluorapatite and fluorite, industrial activities such as the production of glass and semiconductors, and mineral processing (Wang et al., 2017). More than 200 million people globally are exposed to drinking water containing >1.5 mg fluoride/L (Chai et al., 2013). Fluoride contamination has serious effects on the geo-environment in many countries, and especially in developing countries (Mohan et al., 2017).

Various technologies for defluoridation based on the principle of adsorption, precipitation-coagulation and the membrane separation process have been developed or are at the development stage. Primarily lime and aluminum salts are utilized to remove fluoride from water in the precipitation-coagulation process; the resulting fluoride-based precipitates achieve satisfactory fluoride removal. However, the method may also produce an excessive quantity of surplus sludge and thus increase the overall operation costs. Moreover, the use of aluminum salts may release some aluminum ions to the water in the defluoridation process. Consequently, human health can be detrimentally affected because the excessive aluminum concentrations (>0.2 mg/L) may cause diseases such as dementia (Shrivastava and Vani, 2009).

Membrane separation processes can effectively concentrate the negatively charged and highly hydrated fluoride ions within the

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reactor (Chakrabortty et al., 2013; Shen and Schäfer, 2014). Membrane separation can reduce costs and offer a viable treatment option in locations where resources or access to technology are limited (Jadhav et al., 2015). A major challenge is fluoride removal from the reactor after treatment and further research is needed to solve this problem.

Thus, adsorption is probably the most promising method for fluoride removal in drinking water treatment because of its simple design and operation, high efficiency and low costs compared with other methods (Kameda et al., 2015; Ye et al., 2016). More importantly, adsorption is more likely to be utilized for fluoride removal in less developed countries, where advanced wastewater treatment is unavailable.

Effective low-cost materials, including activated alumina and carbon, rare earths and magnesia (MgO), have been examined for defluoridation (Jadhav et al., 2015; Kameda et al., 2017; Loganathan et al., 2013). MgO is one of the most widely used materials and, unlike alumina, does not introduce potentially harmful substances to the water during treatment. However, MgO has disadvantages that may inhibit its commercial application for defluoridation (Thergaonkar and Nawalakhe, 1971) including: (i) pressure drop in the column due to its use in powder form; (ii) long time required to achieve equilibrium; and (iii) high pH of the treated water. Many researchers have developed MgO-based adsorbents for fluoride removal by adding other materials. For example, Xu et al. (2011) prepared MgO-loaded fly ash cenospheres that achieved maximum defluoridation capacity of approximately 6.0 mg/g at the initial fluoride concentration of 100 mg/L, but fluoride adsorption was inhibited by increasing pH. Granular matrix-supported nano-MgO was developed that could achieve effective fluoride removal from water; however, the fluoride adsorption on the adsorbent required more than 350 min to reach equilibrium when the initial fluoride concentration was 2.5–30 mg/L (Oladoja et al., 2015). Sundaram et al. (2009) revealed that the combination of chitosan and MgO resulted in a bio-composite adsorbent that was shown to have high adsorption capacity for fluoride ions and short equilibrium time due to a large number of hydroxyl groups in the chitosan.

In the previous study, pullulan (a biodegradable extracellular water-soluble microbial polysaccharide) was found to have highly biocompatible and non-toxic properties; thus, the material potentially could be employed as an adsorbent (Kang et al., 2011). More hydroxyl groups were found in the pullulan saccharide unit than in the chitosan saccharide unit, for which the number of potential sites for adsorption could be increased. In the previous study (Kang et al., 2011), pullulan was spread on MgO to synthesize a magnesia-pullulan composite (MgOP) and fluoride adsorption on the MgOP was explored in a batch system. Compared to other similar adsorbents, the accessibility of the adsorbate-binding sites was increased and the defluoridation capacity of MgOP was hence enhanced to 7.17 mg/g at the initial fluoride concentration of 15 mg/L and an adsorbent concentration of 2 g/L. Moreover, the fluoride adsorption on MgOP reached equilibrium within 60 min at a wide range of initial fluoride concentrations. Furthermore, effective fluoride removal was achieved over a wide pH range (2–12).

A continuous flow system is required for fluoride removal at a treatment plant scale. A fixed-bed column filter is considered optimum for removing excess fluoride from water and has the advantages of operational simplicity, cost effectiveness, and regeneration capability (García-Sánchez et al., 2017; Roy et al., 2017).

The aim of this study was to evaluate MgOP performance with respect to fluoride removal in a continuous fixed-bed column and provide guidance for design and operation of the reactor. MgOP performance was evaluated under various operating parameters, including bed mass, volumetric flow rate, influent fluoride concentrations, reaction temperature, inlet pH and the presence of coexisting anions. Models developed by Thomas (1944) and Yan et al. (2001) were used to describe the breakthrough curves. Magnesium concentrations were determined to ensure high-quality treated water. MgOP regeneration was explored for process sustainability and economic feasibility.

## 2. Materials and methods

### 2.1. MgOP preparation

The MgOP was prepared according to the sol-gel method used in our previous study (Kang et al., 2011). This entailed adding 8.0 g of MgO (Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) and 12.0 g of pullulan (Shandong Freda Biotechnology Co., Ltd, Linxi, China) to deionized water in a 1000-mL polypropylene beaker (weight ratio MgO: pullulan = 2:3). After 24 h of stirring at room temperature, the aqueous mixture was dried at 105 °C in an oven for 12 h and then calcined at 450 °C in a muffle furnace for 2 h to obtain the composite MgOP. The MgOP was pulverized, sieved and stored in a sealed bag for later use.

### 2.2. Analytical methods

Sodium fluoride (NaF) was used to prepare a standard fluoride solution (1000 mg/L), which could be diluted to obtain the desired concentrations of working fluoride solutions. The fluoride concentrations were tested through the ion selective electrode method using an ion meter and electrodes (Shanghai branch pXS-215, Tianda Instrument Shanghai Co., Ltd., Shanghai, China). Furthermore, NaOH and HCl solutions (0.1 mol/L) were used to adjust the pH values of fluoride solutions, and a pH meter (pHS-3C, Shanghai REX Instrument Factory Co., Ltd., Shanghai, China) was utilized for monitoring pH changes. An atomic absorption spectrophotometer was utilized to measure the effluent magnesium concentrations (ZEEnit700P, Analytik Jena AG, Jena, Germany).

### 2.3. Fixed-bed column study

The performance of MgOP for fluoride removal from water was evaluated using duplicate laboratory-scale continuous fixed-bed columns. Each fixed-bed adsorption filter column consisted of an organic glass (i.e., poly(methyl methacrylate)) cylinder having an internal diameter and height of 4 and 20 cm, respectively. Prior to adding the MgOP adsorbent, glass wool (~10 cm) was fixed in place at the bottom of cylinder and then compacted using a glass rod. The glass wool served as packing to a) facilitate an even distribution of flow across the column cross-section; b) prevent loss of adsorbent; and c) ensure a closely packed arrangement of MgOP.

MgOP was first washed using deionized water to remove the powder from the MgOP surface and avoid subsequent blocking of the bed and glass filter. An appropriate mass (4.0, 6.0 or 8.0 g) of washed MgOP (particle size distribution ranging from 420 to 840 μm) was then added to the column and packed by fully immersing the material in deionized water. Using this procedure, MgOP was compacted by natural gravity settlement, forming a uniform bed and ensuring a complete expulsion of air bubbles.

The fluoride solution was pumped downward through the MgOP bed. The influent volumetric flow rate varied by experiment but was held constant throughout a given experiment using a variable flow peristaltic pump (BT 100-1F, Baoding Longer Precision Pump Co., Ltd., Baoding, China). Steady flow through the column was assured by periodically recording the time taken to collect 100 mL of treated solution. Effluent samples were collected at