



Efficient utilisation of flue gas desulfurization gypsum as a potential material for fluoride removal

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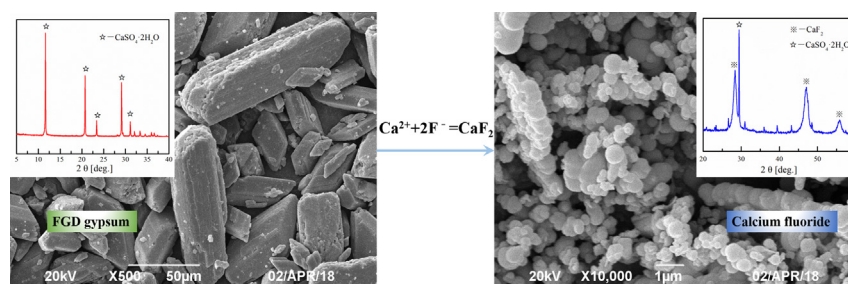
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HIGHLIGHTS

- An attractive material for fluoride removal from synthetic solution is presented.
- FGD gypsum exhibits satisfactory performance on calcium release and fluoride removal.
- FGD gypsum removes fluoride through combining with calcium to form calcium fluoride.
- By-product reuse improves the sustainable development of resource and environment.

GRAPHICAL ABSTRACT



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ABSTRACT

This study introduces the use of a waste by-product from wet limestone flue gas desulfurization as a potential material for fluoride removal. Systematic laboratory-scale experiments were tested to identify the fluoride removal performance and determine the underlying mechanism. Flue gas desulfurization (FGD) gypsum removes 93.31% of fluoride from 109 mg/L to 7.3 mg/L. Fluoride can be efficiently removed at the optimum pH range of 5–11. Kinetics analysis indicates that the theoretical fluoride capacity at 1 g/L FGD gypsum is 96.9 mg/g. Equilibrium speciation analysis indicates that the decrease of system pH to lower than 5 is unsuitable for the formation of calcium fluoride, and the increase of system pH to higher than 11 opposes calcium release from FGD gypsum. Thermodynamic analysis confirms the feasibility of converting calcium sulphate into calcium fluoride at pH > 5. FGD gypsum and precipitates were characterized to describe their surface morphology, elemental composition and crystalline phase. Results indicate that FGD gypsum removes fluoride through the combination of calcium with fluoride to generate calcium fluoride.

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1. Introduction

Fluoride-related human health hazards are a major environmental issue worldwide. The presence of trace amount of fluoride dissolved from surrounding geological materials are considered advantageous for preventing dental caries while an excess uptake is linked to chronic dental and skeletal fluorosis (Mahramanlioglu et al., 2002). However,

various industry productions, such as semiconductors, fertilizers, glass manufacturing and metal processing, produce effluents with high fluoride concentration that give rise to fluoride pollution (Reardon and Wang, 2000; Shen et al., 2003). Excessive fluoride in environmental matrixes, such as water, soil and air, poses severe threats to human health and development, resulting in many difficult miscellaneous diseases (Bhatnagar et al., 2011). Therefore, reducing the use of fluoride-containing raw materials and decreasing the emission of fluoride-containing wastewater are urgent tasks confronted by various industries.

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Effective techniques to remove fluoride from industrial effluents and drinking water mainly involve precipitation, reverse osmosis, adsorption, nanofiltration and electro dialysis (Araga et al., 2017; Mohapatra et al., 2009). Adsorption is an efficient process with ion exchange or surface chemical reaction (Yang and Dluhy, 2002). However, the contact bed needs regular back washing to eliminate deposited precipitates due to its limited adsorption capacities, which results in complicated operation and high cost. Activated alumina (Bulusu and Nawlakhe, 1990; Chatterjee and De, 2014), raw bauxite and gypsum (Thole et al., 2012), activated carbon (Araga et al., 2017; Roy et al., 2017), magnetic Fe_3O_4 -chitosan- $\text{Al}(\text{OH})_3$ beads (Hu et al., 2018), fly ash (Xu et al., 2011) and unconventional waste materials (Bhaumik and Mondal, 2015; Daifullah et al., 2007; Singh et al., 2016) have been tested for fluoride removal. However, the complicated preparation process of adsorbents and the high cost of raw materials restrict their practical application. Meanwhile, precipitation is widely used to treat high fluoride concentration wastewater attributing to its economic, efficient and simple operation. Calcium (Budyanto et al., 2015; Islam and Patel, 2007; Liu and Liu, 2016), magnesium (Huang et al., 2017) and aluminium salts (Gong et al., 2012; He et al., 2016) are common precipitation materials that exhibit efficient performances in removing fluoride. Cost is an important factor for industrial wastewater, but many available materials for fluoride removal are costly, non-operational and technically non-feasible. Therefore, new locally available alternatives need to be explored to realize high-efficiency and low-cost fluoride removal.

The process of wet limestone flue gas desulfurization produces gypsum as a waste by-product, which has been utilised to remove lead (Yan et al., 2015), cadmium (Yan et al., 2014) and silicate (Kang et al., 2018) from wastewater. FGD gypsum exhibits efficient adsorption and precipitation ability. Many steelworks, smelting plants and coal-fired power plants adopt the FGD process to control emissions of sulphur dioxide because of its high desulphurization performance, reliability and low-utility consumption (Yu et al., 2011), thus generating high amounts of FGD gypsum (Liu et al., 2010). Recent studies have demonstrated the use of FGD gypsum to manufacture high-strength building materials (Lei et al., 2017), fire-resistant panels (Li et al., 2015) and calcium sulphoaluminate cement (Xu et al., 2017). However, the unexploited FGD gypsum not only causes resource waste but also poses serious environmental risks. Enormous FGD gypsum deposits occupy land, which pollutes the water when eroded by rainwater and results in dust pollution when forced by wind. The waste by-products, such as cement kiln dust (Mackie and Walsh, 2012), waste lime (Tolonen et al., 2014) and calcined marble wastes (Haddad et al., 2015), have been utilised as substitutes of commercial materials for wastewater treatment. Calcium-containing compounds, such as calcium chloride, fluorapatite, quicklime and limestone, are widely used for fluoride removal. The removal mechanism is mainly attributed to the complexation of fluoride with calcium to generate calcium fluoride. The utilisation of FGD gypsum as a new-style material for fluoride removal has not been evaluated. FGD gypsum might be an attractive material for fluoride removal considering its wide distribution. In addition, the efficient utilisation of FGD gypsum has a great significance on environmental protection and resource utilisation, which not only promotes the development of the cycle economy, but also greatly reduces the exploitation of natural gypsum and protects the natural mineral resource.

The study testified the feasibility of utilising FGD gypsum for fluoride removal from a synthetic solution at different operating parameters. The mechanism underlying fluoride removal was investigated through equilibrium speciation, kinetics and thermodynamic analyses. FGD gypsum and the generated precipitates were characterized by scanning electron microscopy coupled with energy dispersive spectrometry (SEM-EDS), X-ray fluorescence (XRF), X-ray diffraction (XRD) and Fourier transform infrared (FTIR) analyses.

2. Materials and methods

2.1. Materials

FGD gypsum was taken from a steel plant located in Panzhihua, China. The dust-removed sulphur dioxide flue gas passes through a scrubber and reacts with lime-limestone slurry to generate FGD gypsum. The gypsum slurry is filtrated and dehydrated to make into FGD gypsum powder. The FGD gypsum samples were collected from different locations in the storage bin to ensure representativeness. The samples were adequately homogenized and prepared for the experiment.

2.2. Experimental methods

The synthetic fluoride solution was prepared with sodium fluoride (NaF) acquired from Xilong Chemical Co. Ltd., Guangdong, China. A stock fluoride aqueous solution of 1090 mg/L was prepared with distilled water and diluted to the desired concentration at different tests. The experiments of operating parameters on fluoride removal were conducted at room temperature ($25 \pm 2^\circ\text{C}$) in 200 mL beakers. The reaction mixture was stirred with a magnetic stirrer. The supernatant (10 mL) in the breakers was collected with a syringe filter (0.45 μm) for fluoride analysis. pH of synthetic fluoride solution was controlled using a pH meter (pHS-3C, China) with NaOH or HCl (1% and 10%) aqueous solution. Contact time was calculated with a chronograph. The detailed experimental procedures are as following.

(1) FGD gypsum dose on fluoride removal: Different doses (0.2–4 g/L) of FGD gypsum was added to the synthetic fluoride solution (200 mL) at the nature pH of 7, the initial fluoride concentration of 109 mg/L and the contact time of 600 s. The reaction mixture was separated with the syringe filter for fluoride analysis.

(2) Solution pH on fluoride removal: Initial fluoride solution pH was adjusted from 1 to 13 before the addition of FGD gypsum (1 g/L). Initial fluoride concentration is 109 mg/L and the contact time is 600 s. The reaction mixture was collected with the syringe filter for fluoride analysis.

(3) Contact time on fluoride removal: FGD gypsum (1 g/L) was added to fluoride solution (109 mg/L) at the nature pH of 7. Each experiment of contact time (30–1920 s) was relatively independent, and contact time was calculated from adding gypsum to separating fluid for analysis from the mixture. The fluid was separated with the syringe filter for fluoride analysis at a located contact time.

(4) Initial fluoride concentration on fluoride removal: FGD gypsum (1 g/L) was added to fluoride solution with different initial concentrations (109–1090 mg/L) at the nature pH of 7 and contact time of 600 s. The reaction mixture was collected with the syringe filter for fluoride analysis.

The dissolved calcium and pH level are key parameters that significantly affect fluoride removal from aqueous solutions. Experiments of solution pH (1–13) and FGD gypsum dose (0.5–5 g/L) on calcium release from FGD gypsum were conducted to evaluate the dissolution performance of FGD gypsum in aqueous solution. In order to characterize the micromorphological features and crystal structure of the precipitates, the sludge produced by FGD gypsum (1 g/L) and fluoride (109 mg/L) was washed in triplicate with distilled water and dried for SEM-EDS, XRF, XRD and FTIR analyses.

Fluoride removal (R , %) was calculated according to Eq. (1), where C_i and C_f (mg/L) refer to the initial and final fluoride concentration, respectively. Fluoride removal capacity (q , mg/g) of FGD gypsum was calculated by Eq. (2), where M (g) is the weight of added FGD gypsum, and V (L) is the volume of the fluoride solution.

$$R = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

$$q = \frac{C_i - C_f}{M} \times V \quad (2)$$

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