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Application of freeze concentration for fluoride removal from water solution

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ABSTRACT

A study on fluoride removal by freeze concentration was conducted using deionized and added dissolved substances to the water samples. Fluoride removal characteristics were evaluated in a batch system with reference to changes in freezing temperature, initial concentration, freezing rate and total dissolved solids (TDS). Fluoride removal was found to be freeze temperature-dependent and the optimal temperature range was −15 °C to approximately −20 °C. Fluoride removal rate ranged from 50 to 75% for added dissolved substances to water and from 75 to 85% for deionized water spiked with fluoride, which gives a more satisfactory result. The decline of salinity was consistent with the decline of fluoride concentrations. However, from the perspective of fluoride removal rate, TDS played an inverse role in the fluoride removal efficiency. The removal efficiency by freeze concentration was finally validated using the high fluoride groundwater samples collected from 5 monitoring wells in the field, which showed a good correlation. Our results show that freeze concentration is possible to develop as a feasible technology for fluoride removal from aqueous environment in remote and small areas.

1. Introduction

Fluoride removal from contaminated drinking water has been the focus of hydrochemistry and hygiene studies in recent years, since fluorosis is one of the significant issues worldwide and poses a major health risk to people and pets [1,2]. Fluoride in minute quantity is an essential component and intimately related with human life activity, tooth and skeleton constitution metabolism [3]. However, excess ingestion of fluoride is responsible for dental fluorosis or crippling fluorosis. Data from World Health Organization (WHO) indicate that, the desirable and permissible limit range of fluoride content of drinking water is 0.5–1.0 mg/L [4]. Endemic fluorosis occurring on account of consumption of groundwater with high-concentration fluoride has become a worldwide problem, particularly in the United States, Africa, Asia, the Middle East and China [5,6]. For example in China, the endemic fluorosis is mainly distributed in the northwestern, northern and northeastern China, most of which are arid and semi-arid areas [7]. Recent research on fluoride of groundwater in northwestern arid region is mainly concentrated on the Junggar Basin, the Tarim Basin, Heihe River Basin [8] and the Ningxia region, however little research in the Ulan Buh Desert. Concerning the toxic effects of fluoride on human health, it is imperative to find out a cost-effective and feasible method for the removing excessive fluoride from drinking water. Accordingly, sustainable management of that water resources requires proper evaluation of fluoride removal efficiency.

A substantial and growing researches have been conducted on the removing excessive fluoride from drinking water. The fluoride removal technique based on the mode of action includes adsorption, ion-exchange, precipitation, membrane separation process, electrochemical process, and electrodialysis [3,9–12] and so on. However, the major limitations for these methods are high investment in infrastructure and equipment, secondary pollution, unpleasant taste of treated water and bad maneuverability in the treatment, particularly in rural areas of developing countries. Therefore, such problems limit the further application and promotion of fluoride removal technique.

Nowadays an increasing number of people are beginning to concern about freeze concentration, which is an economically feasible, little pollution, free of corrosion and scaling technique. This technique can be used for decontaminating water during the formation of ice crystals, especially in the regions where natural cool energy is available. It has been reported that it is effective to remove various organic and inorganic contaminants from industrial wastewater/liquid waste [13–15]. Three basic concentration techniques are available: suspension crystallization, film freeze concentration and freeze-thaw method (also known as block freeze concentration). The last one of them includes freezing, thawing and separation steps, which was discussed in our study [16]. Although the theory of impurity separation by freeze concentration has been studied [2,17–19], more work is needed to be explored the fluoride separation rules on the basis of the theory of crystallization kinetics.

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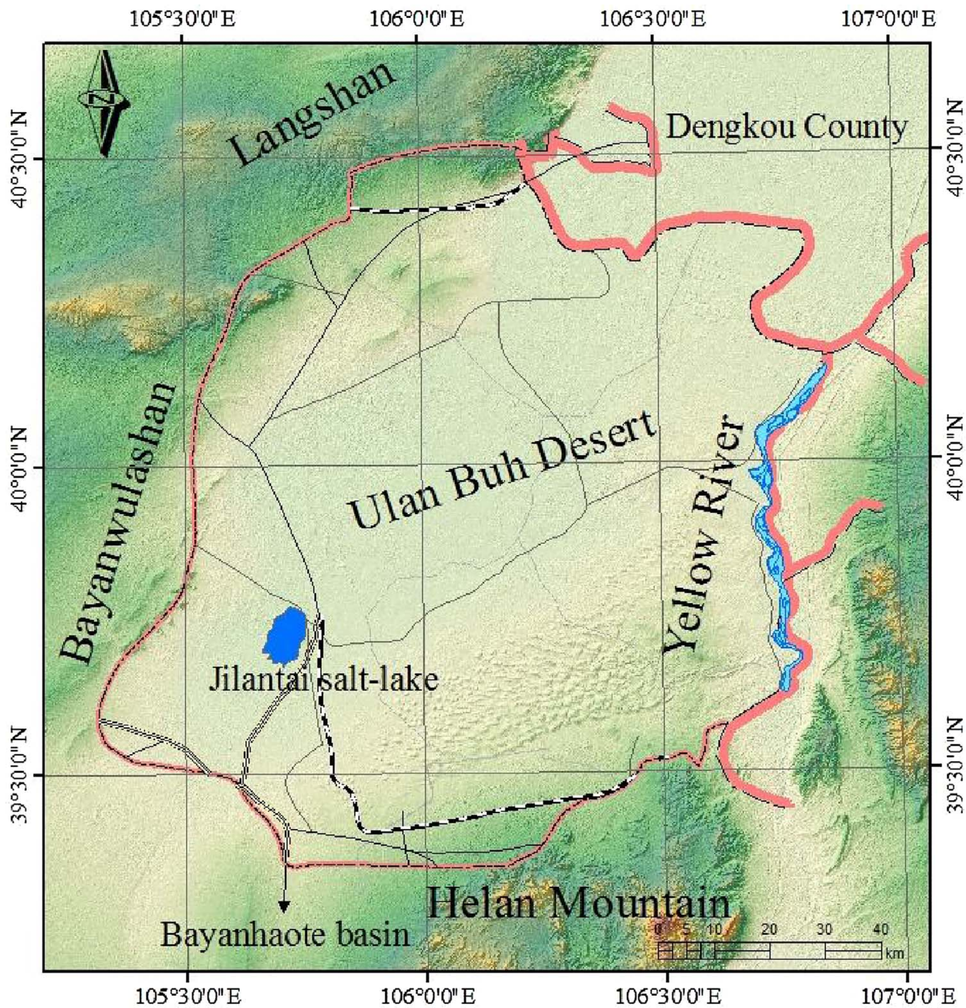

Fig. 1. The location of the study area.

Batch experiments with deionized and added dissolved substances water samples were performed to investigate fluoride separation capacity by freeze concentration in the artificial refrigeration system. The influence of several significant experimental parameters were subsequently examined, including initial fluoride concentration, freezing temperature, freezing rate and the presence of other salinities on fluoride removal efficiency. The regularity of desalination by freeze-thaw method was also experimentally assessed in our study. Furthermore, the results were validated using field data for fluoride removal and desalination efficiency. It is hoped that the results of this study will allow for a better understanding of the performance of freeze concentration for fluoride removal in similar semi-arid basin globally; a topic of vital importance to water supply and human health.

2. Study area

The study area located in the southwest edge of Ulan Buh Desert, Alashan league in Inner Mongolia, is an intra-continental rift basin spreading in the NE–SW direction. It is bounded by longitudes 105°15′ − 106°40′ E and latitudes 39°10′ ∼40°30′ N, covering an area of 9200 km^2 (Fig. 1). According to climate statistics between 1955 and 2010 from weather station of Jilantai, the average annual precipitation is roughly 108.1 mm, and the mean evaporation rate is about 1734.2 mm per year. Extensive evaporation and prolonged rock–water interaction cause the enrichment of fluoride in groundwater at Jilantai [20].

Previous survey data have shown that shallow groundwater containing excess fluoride is common in the Jilantai Basin, reaching levels of up to 4 mg/L. Studies have identified the fluoride present in the phreatic aquifer as being sourced from aeolian sandy soil and fluorine minerals from the surrounding mountainous sedimentary and magmatic rocks. The hydrochemical types of phreatic groundwater are Cl-Na and Cl·SO_4-Na primarily.

3. Materials and methods

3.1. Materials

Experiment reagents were selected including sodium fluoride, sodium chloride, calcium chloride, magnesium sulfate, sodium bicarbonate, sodium citrate and hydrochloride. Laboratory instruments mainly contain deionized water, temperature controlled refrigeration freezer -FYL-YS-128 (Beijing Fu Italian Electric Co., Ltd.), fluoride selective electrode, ion meter or pH meter, saturated calomel electrode, magnetic stirrer, volumetric flask, polyethylene beaker, pipette, and conductivity meter DDS-11A. All the instruments were calibrated before use. The desired initial fluoride concentration of 2 mg/L, 3 mg/L, 4 mg/L, 5 mg/L, 6 mg/L, 8 mg/L, 10 mg/L, 15 mg/L, 20 mg/L (by preparation with deionized water and sodium fluoride) were used in this work. Field water samples were collected in October 2013, from the monitoring wells S5-06, S4-09, S4-24, S4-02 and S2-06 with high fluorine content or high salinity. Sampling, preservation, transportation and analytical protocols were conducted by technical regulations and standards for groundwater samples (HJ493-2009).