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Treatment of fluoride concentrates from membrane unit using salt solutions

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ABSTRACT

A detailed study has been carried out for the removal of fluoride from concentrated retentate stream by precipitation overcoming the drawback of membranes. Calcium hydroxide ($Ca(OH)_2$), magnesium hydroxide ($Mg(OH_2)$) and calcium chloride ($CaCl_2$) used for fluoride precipitation, have shown effective results in the pH range varying from 4 to 14. Kinetic studies have shown that the reaction between F and Ca ions in aqueous phase is fast and completed within 20 min at stoichiometric ratio. Reactions carried out with method of excess (keeping calcium concentration very high) showed pseudo-first order kinetics for both $Ca(OH)_2$ and $CaCl_2$.

Parameters such as effect of reactant loading, reactant ratio and temperature which affect the particle size were studied. The maximum particle size of calcium fluoride (CaF_2) was observed to be around 1 μm and 0.5 μm for $Ca(OH)_2$ and $CaCl_2$ respectively. The reactant ratio studies showed that an increase in the calcium dose decreases final fluoride concentration upto USEPA and WHO standards. Temperature showed an accelerating effect on reaction kinetics for both the reactions. The CaF_2 particle size essentially remained unaltered with an increase in temperature for both the reactions. The study showed a successful reduction of fluoride concentration in the concentrated stream of the membrane and can be applied as relatively inexpensive assisting treatment to isolate large amount of fluoride precipitate.

1. Introduction

Although almost 70% of total earth is occupied by water, however, there is limited water available which can be used for domestic and industrial purposes. Groundwater has appropriately been described as the 'hidden sea' because groundwater constituting 97% of global freshwater is used for drinking by more than 50% of the world population and serves as the only economically viable option for many communities. This is true to a greater extent in the case of developing countries like India where an estimated 80% of domestic consumption in rural and 50% in urban areas are met by groundwater sources alone. Groundwater has become a source of drinking water since last few decades, due to the scarcity, non-availability and bacteriological pollution of surface waters in many developing and transition countries. As per UNICEF and WHO assessments, it has been concluded that a large proportion of the world's population does not have access to adequate or microbiologically safe sources of water for drinking and other essential purposes [1]. Thus, the supply of qualitatively and quantitatively safe water is regarded as a "human right" rather than a "human need". The presence of various hazardous contaminants such as fluoride, arsenic, nitrate, sulfate, pesticides, other heavy metals etc. in ground water has been reported from different parts of world [2–10]. These contaminants are introduced into the water through (i) erosion and dissolution of rocks, minerals, and ores, and, (ii) anthropogenic processes such as infiltration or runoff from mining, groundwater abstraction etc.

Fluoride is one of the constituents of drinking water and the disease fluorosis is caused by an element known as fluorine, the 13th most abundant element available in the earth crust. In contrast to arsenic, fluoride contamination of drinking water receives much less attention. However, fluoride, as a dissolved constituent of drinking water, is perhaps the only substance causing contrary health effects on the consumer depending upon its relative extent. Excessive fluoride consumption leads to the loss of calcium from the tooth matrix, aggravating cavity formation throughout life. The dental or skeletal fluorosis is irreversible and no treatment exists. In India, about 17 states have been identified as epidemic for fluorosis [11]. Table 1 shows the percentage of districts affected by fluorosis in India.

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Table 1
Percentage of districts affected by fluorosis in India.

% Affected	District
50–100	Andhra Pradesh, Tamil Nadu, Uttar Pradesh, Gujarat, Rajasthan
30–50	Bihar, Haryana, Karnataka, Maharashtra, Madhya Pradesh, Punjab, Orissa, West Bengal
<30	J & K, Delhi, Kerala

Fluoride in groundwater is one of the most harmful pollutants to the human health, recognized worldwide by the World Health Organization (WHO). The guideline value of WHO standards and BIS: 10500 permits the optimum concentration of fluoride ion in drinking water ranged from 0.5 to 1.5 mg/L for the good health of teeth and bones of mammals [12,13]. USEPA established the effluent standard of 4 mg/L for fluoride from the wastewater treatment plant [14]. Various techniques such as coagulation and electrocoagulation [15,16], adsorption [17–20], ion exchange [21–25], and membrane processes [26–29] have been reported in literature for the removal of fluoride from groundwater. However, membrane technology has found to be the best suitable treatment and presently, membrane units are in operation in villages at domestic level, which generates fluoride free water and concentrated fluoride retentate. The major problem associated with membrane technology is the treatment of retentate stream containing very high concentration of fluoride (typically in the range of 150 mg/L) which again contaminating the ground water [30]. Tahaikt et al. [30] managed to remove nearly 99% fluoride using NF90 and NF270 membranes on Moroccan ground waters where initial fluoride concentrations were as high as 20 mg/L. As the large part of fluoride was discarded to recycling retentate stream, it is safe to predict that at given permeate flow rate (700 L/h) and pressures (10–40 bar), the feed and retentate will reach extremely high fluoride concentration very quickly. The membrane units are designed to work up to certain operating conditions. Thus, in order to avoid frequent maintenance activities and to ensure longer membrane life it is needed to treat this retentate stream and develop a process which will operate at village places. Also, previously reported reviews of Mohapatra et al. [31], Emamjomeh and Sivakumar [32], and Meenakshi and Maheshwari [33] do not mention the data available on the precipitation reaction kinetics as well as particle size of the fluoride precipitate which is required for design of thickeners.

The objectives of this work are to study the removal of fluoride from concentrated retentate stream using calcium hydroxide ($Ca(OH)_2$) and calcium chloride ($CaCl_2$) overcoming the drawbacks of membrane. Additionally, the focus of this work is to produce better knowledge on reaction progression and particle size at a range of operating conditions. Comparison between above two stated materials with $Mg(OH)_2$ is also provided for better removal of fluoride based on experimental results.

2. Materials and methods

2.1. Chemicals and reagents

All reagents were pure and analytical grade and used as received. Sodium fluoride (NaF) (M. W. 41.9881) and anhydrous granular calcium chloride (M. W. 110.99) and magnesium hydroxide (M. W. 58.32) LR grade were procured from s.d. Fine Chem. Ltd., Mumbai, India. Calcium hydroxide (M. W. 74.093) was obtained from Central Drug House (P) Ltd., New Delhi, India. Ultra-pure Deionized (DI) water of conductivity 0.054 μS/m was used for all the washing purpose and to prepare the solutions of desired concentration. DI water was prepared by purification of distilled water of conductivity 18 μS/m using sartorius stedim arium® water purifier system.

2.2. Experimental

A series of laboratory scale jar experiments were executed on simulated water samples. All the tests were conducted in 1 L volume of aqueous phase and at ambient temperature (30 ± 2 °C) except temperature studies. The temperature of the system was controlled using temperature controlled bath. At each experimental run, aqueous solution of 500 mL of desired concentration (150 mg/L) of fluoride and calcium/magnesium was prepared. A rapid stirring (400 rpm) was applied for initial 10 min followed by slow stirring (100 rpm) for 5 min. The parameter studies were carried out by varying the pH, reactants ratio, reactants concentration (from 20 mg/L to 120 mg/L), and temperature to see effect on particle size and final fluoride concentration. Kinetics studies have also been carried out with method of excess (keeping calcium concentration very high) to find out the order of reaction. All experiments were repeated in thrice for their reproducibility and the average values have been reported in figures along with standard deviation.

2.3. Analysis

The fluoride concentration in water was analyzed by using the USEPA ion selective electrode method. This method electrochemically determines the concentration of fluoride in drinking water in the range of 0.1–1000 mg/L [34]. The electrode used was an Orion 9609BNWP ionplus® Sure-Flow fluoride electrode, coupled to an Orion Dual Star pH/ISE benchtop electrometer which also measures pH values of the solution. Standards solutions (1–100 mg/L) were prepared from a stock solution (100 ppm F ions) of sodium fluoride. Total ionic strength adjusting buffer (Orion ionplus® application solution TISAB-III) solution was added to samples and standards in the ratio 1:10. TISAB-III solutions regulate the ionic strength of samples and standard solutions adjusting the pH (5–5.5) and also avoid interferences by polyvalent cations such as Al, Fe, Ca and Si, which form complex or precipitate with fluoride and reduce the free fluoride concentration in the solution. Therefore, the electrode is selective for the fluoride ion over other common anions by several orders of magnitude.

Particle size analysis of residual calcium fluoride precipitate (CaF_2) was carried out on the Malvern Zetasizer nano series ZS90. The Zetasizer Nano series of particle characterization systems can measure particle size in the range from 0.3 nm to 5 μm at a 90 degree scattering angle using dynamic light scattering, also with the ability to measure zeta potential.

3. Results and discussion

3.1. Reaction feasibility

Addition of lime compounds to fluoride rich water at ambient temperature (30 ± 2 °C) initiates the reaction. Calcium/magnesium reacts with fluoride impurities such as NaF, HF, etc. to form insoluble calcium/magnesium fluoride.

$$Ca^{++} + 2F^{-} \rightarrow CaF_2 \tag{1}$$

For calcium hydroxide,

$$Ca(OH)_2(aq) + 2NaF(aq) \rightarrow CaF_2(s) + 2NaOH(aq) \tag{2}$$

Alternatively, for calcium chloride,

$$CaCl_2(aq) + 2NaF(aq) \rightarrow CaF_2(s) + 2NaCl(aq) \tag{3}$$

If the ionic product of the reactants is greater than the solubility product (Ksp) of product, then precipitation of product occurs [35]. Since, the solubility product calculated for CaF_2 (3.9×10^{-11}) was found to be smaller than its ionic product (6.275×10^{-6}), the