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Separation of fluoride from aqueous solution by electrodialysis: Effect of process parameters and other ionic species

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Abstract

Removal of fluoride from aqueous solution by electrodialysis was studied. Applied voltage, feed flow rate, fluoride concentration in the solution and effect of the other anions as sulfate, chloride were investigated as experimental parameters on fluoride removal from aqueous solution. The separation performance was evaluated in terms of mass transfer and energy consumption. It was obtained that the separation performance increased when the initial concentration of fluoride in the feed solution increased. Percent removal of fluoride increased as the applied potential increased. However, the effect of feed flow rate was not apparent in the range of applied feed flow rate. Separation of fluoride was influenced by chloride but not by sulfate ions.

Keywords: Electrodialysis; Fluoride; Separation; Ion exchange membranes; Water; Wastewater

1. Introduction

Fluoride in the environment occurs through natural presence in the earth's crust and industrial activities, especially, semiconductor, electroplating, aluminum, glass, ceramic and fertilizers industries [1,2]. The discharge of such wastewater leads to the fluoride contamination of surface and ground water. The optimum fluoride ion level in drinking water for general good health is considered to be between 0.5 and 1.0 mg/L [3]. The optimum fluoride level in drinking water for general good health set by WHO is considered to be between 0.5 and 1.0 mg/L [4]. US EPA recently established a discharge standard of 4 mg/L for fluoride from wastewater treatment plant. Beijing is working toward this standard value although the national fluoride discharge standard for industrial wastewater is 10 mg/L in China [5]. High concentrations of fluoride in drinking water result in fluorosis (dental/skeletal abnormalities) and several neurological damages in severe cases.

Various treatment technologies based on precipitation [6], ion exchange [7–9], adsorption [10–12], and membrane process such as reverse osmosis [13,14], nanofiltration [15], Donnan dialysis [16] and electrodialysis [17,18] have been suggested for fluoride removal. Most methods for the fluoride removal suffer from one of the following drawbacks: high initial cost, lack of selectivity, low capacity, and complicated or expensive regeneration. Of the many membrane processes available for the separation of ions from solutions, only two, reverse osmosis (RO) and electrodialysis (ED), have reached the practical application stage for the removal of inorganic contaminants from drinking water and wastewater. Both processes remove salts from seawater and brackish water and thus are commonly classified as desalination processes [19].

The electrodialysis is a widely used electro-membrane process especially for desalination of brackish water and sodium chloride recovery from seawater. The removal of ionic components from aqueous solution through ion exchange membranes is carried out under the driving force of an electrical field [20]. When a direct current potential is applied between two electrodes, the positively charged cations move to the cathode, passing through the negatively charged cation exchange membrane and retained by the positively charged anion exchange membrane. While the negatively charged anions move to the anode, passing through the anion exchange membrane and retained by the cation exchange membrane. At the end,

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ion concentrations increase in alternate compartments with a simultaneous decrease of ions in other compartments [21,22]. Previously, we studied the separation performances of monovalent and divalent salts by electrodialysis as a function of applied voltage, flow rate, and pH [23–26]. Elsewhere, separations of Na^+, K^+, Ca^{2+} and Mg^{2+} ions from ternary mixtures prepared from NaCl–$CaCl_2$ and KCl–$MgCl_2$ mixtures were investigated by the electrodialysis (ED) method using batch mode of operation as a function of solution concentration, applied voltage and flow rate [27]. In addition, separation of monovalent (Na^+, K^+) and divalent ions (Ca^{2+}, Mg^{2+}) from unary and binary mixtures by electrodialysis were compared using various salt combinations (NaCl, $NaNO_3$, KCl, KNO_3, K_2SO_4, Na_2SO_4, $CaCl_2$, $Ca(NO_3)_2$, $MgCl_2$, $Mg(NO_3)_2$) [28].

The interest in using electrodialysis processes to remove excess fluoride from drinking water has increased world wide principally because it is a simple process and does not have many of the defects of chemical processes [29]. Some studies were conducted to reduce fluoride by electrodialysis from brackish water and it was demonstrated that electrodialysis is a reasonable process for removing fluoride from brackish water. Because of higher concentration of bivalent salts in the brackish water, the risk of precipitation of these salts, especially sulfate and carbonate in the concentrate compartment by exceeding solubility, became very important. The membranes can be damaged by scaling and fouling. To avoid these risks, the ED operation was carried out according to two methods as without and with a chemical pretreatment. Without pretreatment, ACS-CMX membranes were used especially to stop the transport of bivalent anions in order to prevent the possible precipitation of bivalent salts. ACS membrane transports the anions in the following order $Cl^- > F^- > HCO_3^- > SO_4^{2-}$. As the second method, before ED operation, a chemical pretreatment of the brackish water was carried out to precipitate the calcium ions. Since this method requires chemical additives in the pretreatment step, it has more impact on the environment than the first one [17,30]. Recently, removal of fluoride from underground brackish water was studied by adsorption on natural chitosan and by ED [31]. Another study was reported on removal of fluoride and nitrate removal from groundwater by ED [32].

Types of co-existing anions play important roles in defluoridation in ED process. The aim of this study is to elucidate the effects of various co-existing anions on defluoridation in ED process. Two kinds of common anions, chloride and sulfate, were tested to discern the effects of different co-existing anions. In addition, the effects of process parameters such as applied voltage, flow rate and initial fluoride feed concentration were investigated.

2. Experimental

TS-l-l0 electrodialysis equipment (Tokuyama) was employed for experimental studies. A schematic view of the experimental set-up is shown in Fig. 1. This equipment contains a stack with 10 pairs of Neosepta® CMX (cation exchange) and AMX (anion exchange) membranes providing for each a membrane area of 1 dm^2, respectively. A rectifier is provided to supply a DC

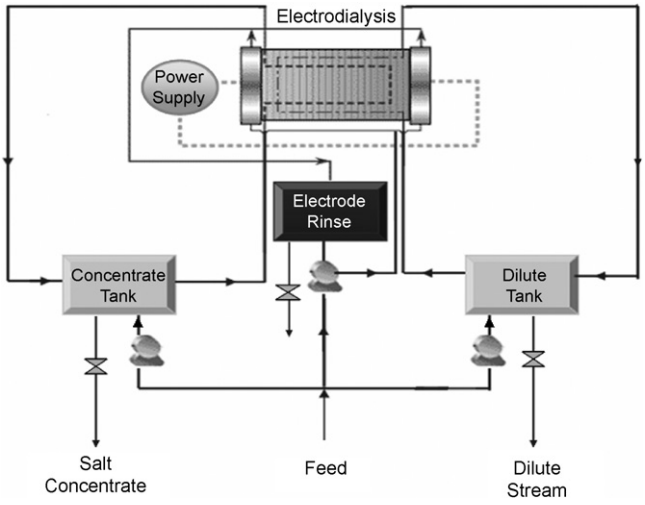

Fig. 1. Batch-mode operation of electrodialysis system.

power at constant voltage (max. 18 V) or constant current (max. 3 A). Three pumps have capacities of max. 1.8 L/min. Three solution tanks (each 1 L) are used for holding the diluted, the concentrated, and the electrode rinse solutions. The electrodes are platinum plated titanium (anode) and stainless steel (cathode) [33]. When a direct current potential is applied, fluoride ions migrates towards the anode. Fluoride ions leave the dilute compartment and move through the anion exchange membrane and retained by the cation exchange membrane in the concentrate compartment. Samples were taken periodically from dilute and concentrate compartments. The batch tests were carried out with NaF solutions prepared in deionized water at different concentrations (25, 50, 75, 100, 200 mg F/L) and using various potentials (5, 7 and 10 V) and flow rates (0.8, 1.2 and 1.6 L/min). The solutions of sulfate and chloride were prepared through the dissolution of Na_2SO_4 and NaCl in deionized water. The concentrations of anions were determined by ion chromatography (Shimadzu LC 10 A*i*).

3. Results and discussion

3.1. Effect of initial feed concentration on separation performance

The effect of initial feed concentration on separation performance of fluoride from aqueous solution was investigated using aqueous solutions at various concentrations of fluoride. Before performance tests, limiting current measurement were carried out for each concentration. The applied currents were changed keeping the solution concentration constant. The feed and permeate solutions pumped from the same reservoir were circulated through the feed and permeate compartments, respectively, and then recycled to the reservoir at a flow rate of 0.8 L/min. By doing this way, the solution concentration in the feed could be maintained constant at a desired level during the experiments. If the applied current is changed, obtained potential values will change linearly until limiting current point has been reached. After this point, there is a sharp change in slope. This switch-