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Fluoride removal from drinking water by electrocoagulation in a continuous filter press reactor coupled to a flocculator and clarifier

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ABSTRACT

This investigation is about fluoride removal from synthetic drinking water (10 mg L^{-1} F^- in 0.5 g L^{-1} Na_2SO_4 and 1.5 mg L^{-1} ClO^- at pH 7.7 and conductivity 410 μS cm^{-1}), by electrocoagulation (EC) using aluminum as the sacrificial anode in a continuous filter press reactor coupled to a flocculator and clarifier (sludge settler). The influence of current density (j) and linear flow velocity in the EC reactor (u_r) on the fluoride removal efficiency was analyzed. The EC tests that satisfy the WHO norm for fluoride ($C_F \leqslant 1.5$ mg L^{-1}) were obtained at $0.91 \leqslant u_r \leqslant 1.82$ cm s^{-1} and $5 \leqslant j \leqslant 7$ mA cm^{-2}, giving aluminum doses between $19.28 \leqslant C_{Al(III)} \leqslant 52.67$ mg L^{-1}. Scanning Electron Microscopy (SEM), Energy Dispersive Analysis of X-rays (EDA-X) and Fourier Transform Infrared Spectroscopy (FTIR) analyses were performed to confirm the presence of fluoride in the flocs. The best EC tests in terms of energy consumption was obtained at 5 mA cm^{-2}, with a mean linear flow velocity in the EC reactor of 1.82 cm s^{-1}, which gives an energy consumption of 0.37 kW h m^{-3}, during the removal of fluoride from 10 to 1 mg L^{-1}. EC at $j > 7$ mA cm^{-2} did not improve the EC process any further owing to massive generation of electrolytic gases which promote the breaking of the flocs.

1. Introduction

The problems related to water scarcity in Mexico and many regions in the world are due to geographical location, low rainfall and uncontrolled consumption. They have forced communities to use groundwater which contains fluoride concentrations above the maximum level recommended by the World Health Organization (WHO) (1.5 mg L^{-1}). Fluoride pollution in the environment occurs though two different ways: natural sources and anthropogenic sources [1]. Waters with high fluoride content are usually found at the foot of high mountains and in areas with geological deposits of marine origin. The discharge of industrial wastewater containing fluoride, such as semiconductor, glass and fertilizers industries, also contributes to water pollution, especially in groundwater [2,3].

Recent studies performed in Mexico have demonstrated the presence of fluoride in Central and Northwestern regions, mainly in Chihuahua, Durango, Zacatecas [4], Aguascalientes [5], San Luis Potosí [6] and Guanajuato with concentrations between 1 and 9.5 mg L^{-1} (CONAGUA). The level of fluoride in drinking water is an important factor in human health. It has both beneficial and harmful effect. When an optimum amount ranged between 0.5 and 1.5 mg L^{-1} is present in the drinking water fluoride helps prevent teeth deterioration and dental caries but long-term consumption of water containing excess of fluoride (>4 mg L^{-1}) can lead to fluorosis of the teeth and bones as well as osteoporosis and serious problems in kidneys, lungs, liver, muscles, nerves, among others [7]. Considering this human health risk, the WHO has set a maximum acceptable level of 1.5 mg L^{-1} of fluoride in drinking water, which coincides with the recommendation of the Mexican authorities (NOM-127-SA1-1994).

The fluoride removal method most widely used is based on the precipitation–flocculation with the help of calcium and aluminum salts, which has become popular because of its low cost and because can be carried out in domestic scale, but the large amounts of sludge results in waste management problems. In chemical coagulation, aluminum chloride and sulfate salts are employed as coagulants, although the counter ion consumes the fifty percent of coagulant [8]. These facts have made chemical coagulation less acceptable compared to other processes. The electrocoagulation (EC) has been considered as an alternative to remove fluoride in drinking water treatment because it lowers the amount of sludge and also provides

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some significant advantages such as, quite compact and easy operation, no chemical additives needed, and high flow rates [9,10]. However, EC is an emergent technology and its application has been conducted in lab and pre-pilot scale only [11,12].

Aluminum and iron are the used materials as sacrificial anodes in electrocoagulation studies. For both electrode materials at the same current density, the efficiency has been found to be higher for the aluminum electrodes [13]. An improved efficiency using Al electrodes was achieved because of the reaction between aluminum hydroxide and fluoride to form aluminum fluoride hydroxide complexes $[Al_nF_m(OH)_{3n-m}]$ [14,15].

Since some raw water, especially underground water may contain high concentrations of co-existing ions, it is necessary to quantify the effects of such ions on drinking water defluoridation [10]. The co-existing anions such as SO_4^{2-} could dramatically affect the fluoride removal efficiency in the EC process [16], which is attributed to the negative effect of SO_4^{2-} on defluoridation owing to the inhibition of the localized electrodissolution of aluminum electrodes. When the anodic dissolution of aluminum is inhibited, the current efficiency decreases. This produces a decrease in defluoridation efficiency and it is also associated with the ion exchange competition between SO_4^{2-} and F^- with aluminum flocs [10,17]. Another co-existing ion is Cl^-, which can affect defluoridation by two ways, on one side, Cl^- is known to be able to corrode the passive films on the aluminum electrodes favoring the EC efficiency [10,16,18]; and on the other hand, Cl^- competes with F^- just like the case with SO_4^{2-}.

It was found that Ca^{2+} could enhance defluoridation owing to fluoride is able to form the precipitate of CaF_2 [10]. In the same way, the ion Mg^{2+} improved the fluoride removal, because Mg^{2+} is also a good coagulant (MgF_2) and it is frequently used as co-coagulant with aluminum salt [9,17–19].

It is important to mention that F^- removal, using Al electrodes, is strongly influenced with reactor geometry (and operation parameters such as current density and flow rate), flocculator and clarifier geometries (and operation parameters such as retention time) [20,21], in addition to the presence of chemical compounds above mentioned.

In our previous communication we characterized the performance of a continuous filter press reactor equipped with aluminum electrodes for arsenic removal from underground water [22]. In that study we put on evidence that the removal of arsenic is dependent of current density and mean linear flow rate; however, the flocculation and the sludge precipitation were performed by test jar in batch mode of operation. This did not allow assessing the performance of the overall process in a continuous mode.

The purpose of this paper is to remove fluoride from synthetic drinking water by a novel continuous EC method. The EC process consists in a continuous filter press reactor equipped with aluminum electrodes coupled to a flocculator and clarifier (sludge settler) in order to evaluate the performance of the overall process. The influence of current density and mean linear flow rate on the fluoride removal efficiency was analyzed. The energy consumption for electrolysis was also estimated.

This research analyzed the influence of current density and flow velocity on the removal of fluoride from a synthetic water sample by EC. It is well known that some ions present in real groundwater have positive or negative effects on the removal of fluoride. This last, was beyond of the scope of this paper; however, upcoming research will be conducted to study the removal of fluor by EC from a groundwater sample.

2. Fluoride removal by electrocoagulation process

EC involves *in situ* generation of coagulants by electrodissolution of aluminum electrodes. Aluminum cations are generated at the anode (1) and hydrogen gas is evolved at the cathode (2), as shown in Fig. 1.

The main reactions involved are as following:

At the aluminum anode:

$$Al_{(s)} \rightarrow Al^{3+} + 3e^- \quad (1)$$

At the aluminum cathode:

$$3H_2O + 3e^- \rightarrow 1.5H_{2_{(g)}} + 3OH^- \quad (2)$$

During the dissolution of Al at the anode various aqueous aluminum species are produced. The aluminum cations are transformed to polymeric species and form $Al(OH)_3$ precipitate:

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \quad (3)$$

At neutral pH (~7) the predominating aluminum species are $Al(OH)_3$ which act with the pollutants to form large size flocs [1,23]. The mechanism of fluoride removal by EC is carried out by means of a chemical substitution in which F^- replaces OH^- group from $Al(OH)_3$ flocs according to Eq. (4), [9].

$$Al(OH)_3 + xF^- \leftrightarrow Al(OH)_{3-x}F_x + xOH^- \quad (4)$$

The major problem with aluminum anodes is the passivation due to $Al(OH)_3$ and Al_2O_3 precipitation, which leads to high anode and cell potentials and increases the energy consumption and cost of EC [22,24]. Passivation can be controlled at low current densities in combination with convection (turbulent flow conditions), which favors Al^{3+} transport away from the surface to the bulk solution. In addition, cathodes of the same material can be used to electrodissolve $Al(OH)_3$ and Al_2O_3 by periodic current reversal [24] which allows even consumption of the aluminum electrodes during the process.

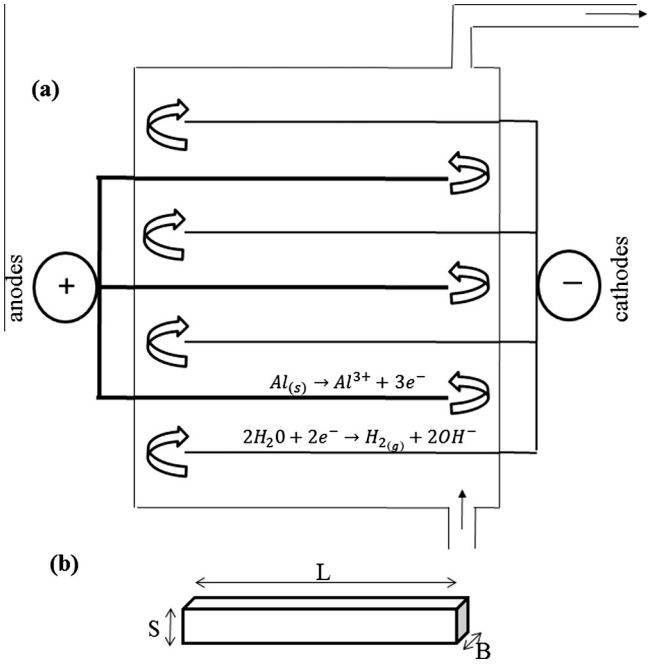

Fig. 1. 2D schematic view of the filter press reactor (a). 3D exploded view of a single channel of the reactor.