



Electrochemical generation of aluminum sorbent for fluoride adsorption

Chen-Lu Yang*, Robert Dluhy

*Advanced Technology and Manufacturing Center, University of Massachusetts Dartmouth,
151 Martine Street, Fall River, MA 02723, USA*

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Abstract

Aluminum sorbent (Al-sorbent) was produced in a parallel-plate electrochemical reactor by anodic dissolution of aluminum electrodes in a dilute sodium chloride (NaCl) aqueous solution. The NaCl in the solution effectively reduced the power consumption and promoted the sorbent generation by depassivating the aluminum–water electrochemical system. The freshly generated Al-sorbent was able to reduce fluoride concentration from 16 to 2 mg/l in 2 min. The final concentration was further reduced to 0.1 mg/l by partial neutralization of the mixture to pH 6.3. The sorbent generation and fluoride adsorption was integrated into a single electrochemical reactor. The system was able to reduce the fluoride concentration from 16 to 6 mg/l in 2 min of treatment and to about 2 mg/l in 4 min. The effluent from the electrochemical system needs pH adjustment to bring the fluoride concentration down to less than 1 mg/l.

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1. Introduction

Industries which discharge significant quantities of fluorides in process waste streams include fluorosilicone and fluorocarbon polymer synthesis, coke manufacture, electronics and semiconductor manufacture, electroplating operations, steel, glass and aluminum manufacture, metal etching, wood preservatives, and pesticide and fertilizer manufacture. Wastes from glass, electroplating and semiconductor manufacturing processes typically contain fluoride in the form of hydrogen fluoride (HF) or fluoride ion (F^-), depending upon the pH of the waste. Current treatment methods can be divided into two categories: precipitation and adsorption. Precipitation processes involve addition of chemicals and formation

* Corresponding author. Tel.: +1-508-910-9857.
E-mail address: cyang@umassd.edu (C.-L. Yang).

of fluoride precipitates or simultaneous coprecipitation of fluoride with a resulting precipitate. Chemicals employed in these processes include lime (calcium hydroxide, $\text{Ca}(\text{OH})_2$), dolomite (magnesium salts) and alum (aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$). Adsorption processes involve the passage of the wastewater through a contact bed where fluoride is removed by ion exchange [1] or surface chemical reaction with the solid bed matrix [2]. Due to the basic mechanism, adsorption processes are usually appropriate only for low-level fluoride wastes.

Precipitation processes are governed by the solubility of the forming salt while coprecipitation processes incorporate adsorption aspect. The lime reacts with fluoride in the wastewater to produce calcium fluoride (CaF_2) [3]. CaF_2 has a theoretical solubility of 8 mg/l fluoride at stoichiometric concentrations of calcium. Thus, concentrations of CaF_2 above the solubility limit will form a precipitate. Reported fluoride removals down to only 10–20 mg/l reflect the slow rate of precipitation. A 24 h contact time with lime is required to reduce fluoride to near the solubility limit. An additional difficulty with lime precipitation is the poor settling characteristics of the precipitate [4,5]. Recently, calcium chloride (CaCl_2) [6], limestone (calcium oxide, CaO) and magnesium oxide (MgO) [7] were studied to improve the precipitation process.

The removal of fluoride by alum addition is essentially a coprecipitation phenomenon whereby fluoride is removed by adsorbing on the surface of aluminum hydroxide ($\text{Al}(\text{OH})_3$) precipitate. With alum addition plus a small quantity of lime for pH control, the $\text{Al}(\text{OH})_3$ is able to reduce fluoride concentration to 1.7 mg/l. In recent years coagulants such as ferric chloride (FeCl_3), aluminum chloride (AlCl_3) [8] and $\text{Al}(\text{OH})_3$ [9–11] were studied to further lower the effluent concentration of fluoride. Final fluoride level was found to be independent of initial fluoride concentration, and was dependent only upon the AlCl_3 dosage and pH in the solution. Duffy et al. [12] found that the rate of reaction between freshly precipitated amorphous aluminum hydroxide and the reagent containing a reduced form of ferron may be used to quantify the aluminum reactivity. With increasing age between 1 min and 45 days, the reactivity of aluminum in the precipitate was found to steadily decrease. A t_{50} value, indicating the time for 50% recovery of the added aluminum, for a 1 min aged aluminum hydroxide was found to be nearly 10 min, while the t_{50} value for the 10,000 min aged sample was nearly 100 min. It is apparent that the freshly generated aluminum sorbent (Al-sorbent) significantly enhances the adsorption process by cutting the reaction time and by reducing sorbent dosage. Fresh Al-sorbent can be generated by neutralization of oversaturated aluminum salts [13–15], the dissolution of aluminum in caustic aqueous solutions [16,17] or by electrochemical dissolution of aluminum electrodes [18,19]. Even though recent studies of aluminum dissolution were focused on developing new processes for electronic component manufacturing, electrochemical methods were found to be effective in dissolving aluminum electrodes. One recent study shows that a wide range of fluoride concentrations (from 17 to 163 mg/l) in wastewater were reduced to about 8 mg/l by treating with 260 mg/l iron(II) coagulant and lime milk (calcium hydroxide solution). After sedimentation and removal of precipitates, hydrochloric acid was added to adjust the pH to about 10. After the acidification, the wastewater was further treated in an electrochemical reactor where aluminum anodes were used to produce Al-sorbent for fluoride removal. The effluent fluoride concentrations in the electrochemical reactor were about 1 mg/l [20].

The objective of this research is to study the electrochemical generation of Al-sorbent and the feasibility of the freshly generated sorbent for fluoride concentration reduction. The process involves adding a small amount of NaCl in the solution, running the solution through an electrochemical reactor where Al-sorbent is produced by dissolving aluminum electrodes, and adsorbing fluoride ions on the freshly generated sorbent. The advantage of the process over the others mentioned above is that the OH^- and aluminum ions necessary for Al-sorbent generation is acquired electrochemically and both precipitation and fluoride adsorption are achieved in a single electrochemical reactor.

2. Experimental

The study of freshly generated Al-sorbent for fluoride removal was conducted in a bench-scale electrochemical system, as shown in Fig. 1. The system consists of a DC power supply, a power control and measurement units, an electrochemical reactor, a reservoir, a feed pump, a flow control valve, a flow measuring unit, a circulation pump, and a magnetic stirrer. The reactor is made of PVC plastic with an active volume of 560 cm^3 . The electrode sets (anode and cathode) each consist of five pieces of aluminum sheets, situated approximately 4 mm apart from each other and submerged in the solution. The total electrode surface area is 1340 cm^2 for both cathodes and anodes. The production of Al-sorbent was studied using a simple batch recirculation system with magnetic stirrer to prevent the sedimentation of the sorbent.

A spectrophotometer was used to determine the sorbent content and fluoride concentration. The wave length at 720 nm was sensitive to suspended particles in the aqueous solution but not to fluoride ions. A certain amount of Al-sorbent was produced in the electrochemical reactor. The solution was transferred to an Imhoff settling cone to determine its sorbent content. The solution served as a stock solution to prepare a

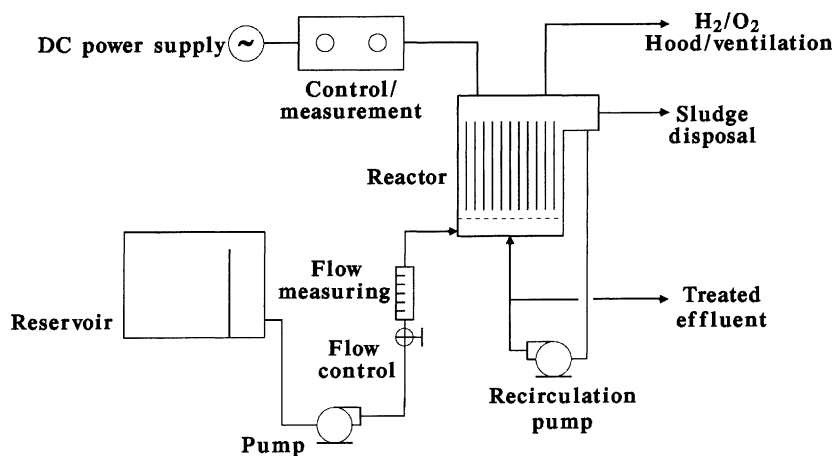


Fig. 1. Flow diagram of the electrochemical system.

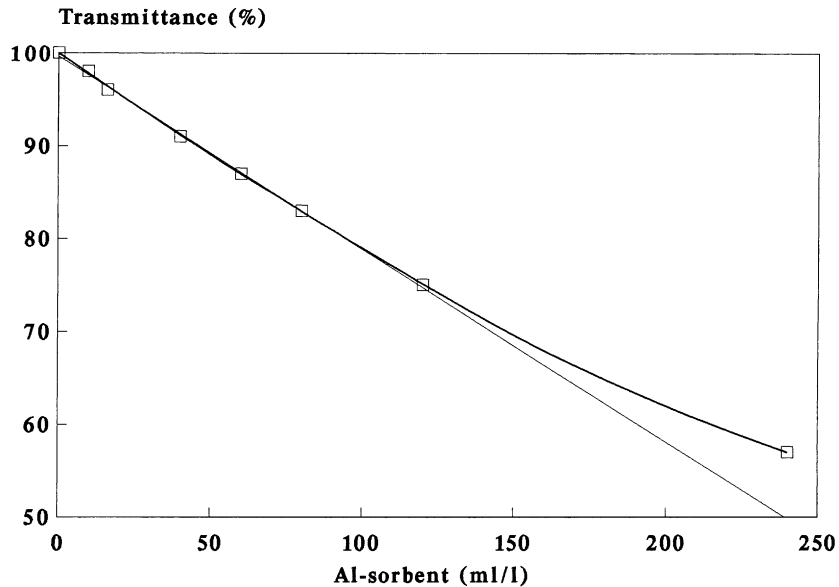


Fig. 2. Calibration curve of Al-sorbent content vs. transmittance at 720 nm.

calibration. Fig. 2 shows the relationship between sorbent content and transmittance at 720 nm. The data in this figure is derived by sequential dilution of the stock solution with a clean solution. Theoretically, concentrations are proportional to absorbance rather than to transmittance. However, the Al-sorbent content was found to be inversely proportional to transmittance. The thin line in Fig. 2 is the linear regression of all the data except the final one. The calibration curve was used to determine sorbent production in the following experiments. The Imhoff settling cone was used to confirm the measurement from this calibration curve.

Fluoride solutions were prepared by mixing hydrofluoric acid with deionized water. The solution was then checked by the spectrophotometer. Fluoride is colorless and will not absorb any light wave in the UV-VIS range. However, Hach Company has developed a method to analyze fluoride in water by adding a SPADNS reagent to the solution and to determine the fluoride concentration by absorbance at 580 nm. This method is accepted by the US EPA and is equivalent to EPA's method 340.1 for drinking water and wastewater. The duration of each treatment was 12 min. Samples were taken at certain time intervals. Measurement of fluoride concentration was done after membrane filtration to prevent the interference of fine particles.

3. Results and discussion

The results of the bench-scale research on electrochemical treatment are given in this section. Sodium chloride (NaCl) was added to the aqueous solution to promote the generation

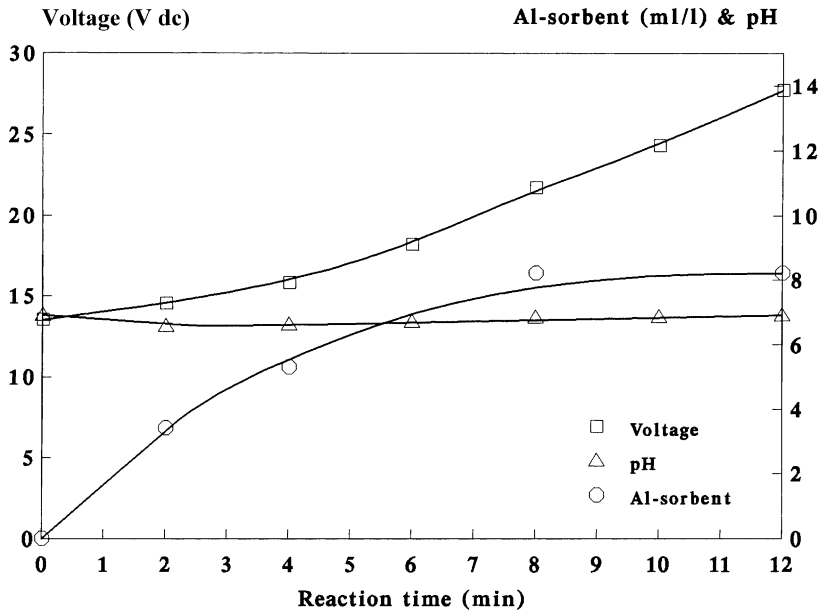


Fig. 3. Sorbent generation and pH change in water by anodic dissolution of aluminum electrodes.

of Al-sorbent in the electrochemical reactor. The fluoride containing aqueous solution was then treated with the freshly generated Al-sorbent. Finally, the fluoride-containing solution was treated in the electrochemical reactor. Parameters, such as fluoride concentration, pH, voltage, sorbent content, were monitored and quantified along with the treatment time.

3.1. Aluminum sorbent generation

Tap water was pumped into the electrochemical reactor to produce Al-sorbent. Due to the low conductivity, the cell needed 14 V to sustain a current of 1 A in the reactor. Fig. 3 shows the changes of all the parameters in the cell during the operation. The applied voltage increased with reaction time. Towards the end of the operation, the applied voltage was increased from 14 to 27 V in order to induce a 1 A current in the reactor. The pH remained constant at about 6.2 through out the operation. After 12 min, a trace amount of Al-sorbent was produced. This is due to the passivation of aluminum electrode in water. A common type of polarization curve for metal dissolution has an active dissolution region, a passivation region and an oxygen evolution region. In the active region, the electrode reaction is the desired metal dissolution, but on increasing the current density or the overpotential above a critical value, the surface becomes covered with an oxide film which passivates the anode and causes the current for the corrosion reaction to drop to a low level. In a constant-current operation, the potential of the anode will shift into the transpassive region where oxygen evolution is the major reaction on the anode. It is essential to maintain the anode potential

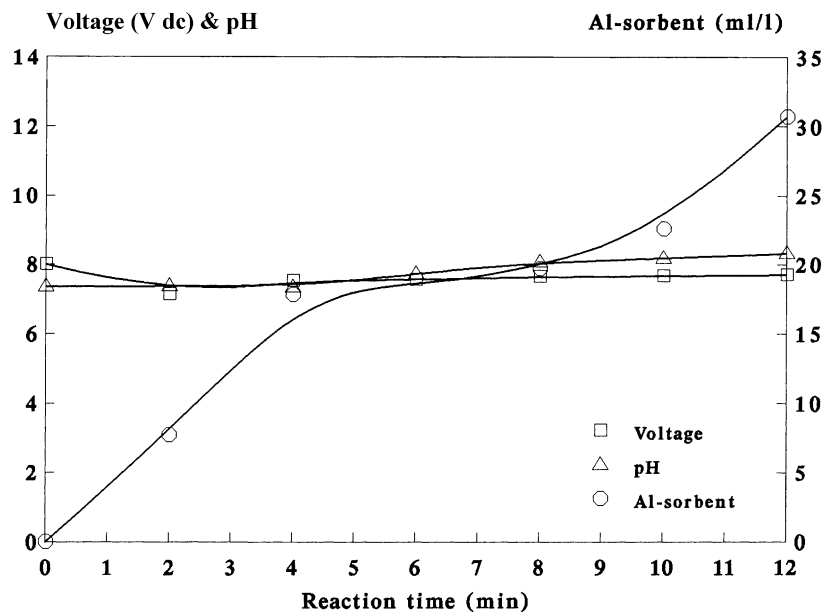


Fig. 4. Sorbent generation and pH change in NaCl aqueous solution.

in the active region to ensure smooth and uniform dissolution. This can be achieved by using a large anode surface area to maintain a suitably low current density at the anode or adding halide ions in the solution. The halide ions can cause sufficient pitting of the oxide film for dissolution to continue. A trace amount of NaCl was added to the tap water and the test of sorbent generation was repeated. Fig. 4 shows the characteristics of the electrochemical reactor and the Al-sorbent generated with 50 ppm NaCl aqueous solution. It took only 7.5 V to induce a current of 1 A in the reactor. The voltage was stable throughout the 12 min operation. The production of sorbent in the solution, after settling, was about 30 ml/l of solution. NaCl is an effective depassivation agent. The 50 ppm NaCl reduced the operating voltages from 27 to 7.2 V to induce an 1 A current in the reactor. In a week, the alkaline solution of the aluminum ions generated by electrode dissolution, are hydrolyzed to form aluminum hydroxide.



Due to the amphoterism, aluminum hydroxide dissolves in acids to form aluminum salts:



and also dissolves in strong basic solutions to form aluminates:



The lowest solubility obtained is between pH 6.4 and 6.6. Therefore, pH is a crucial parameter in Al-sorbent formation.

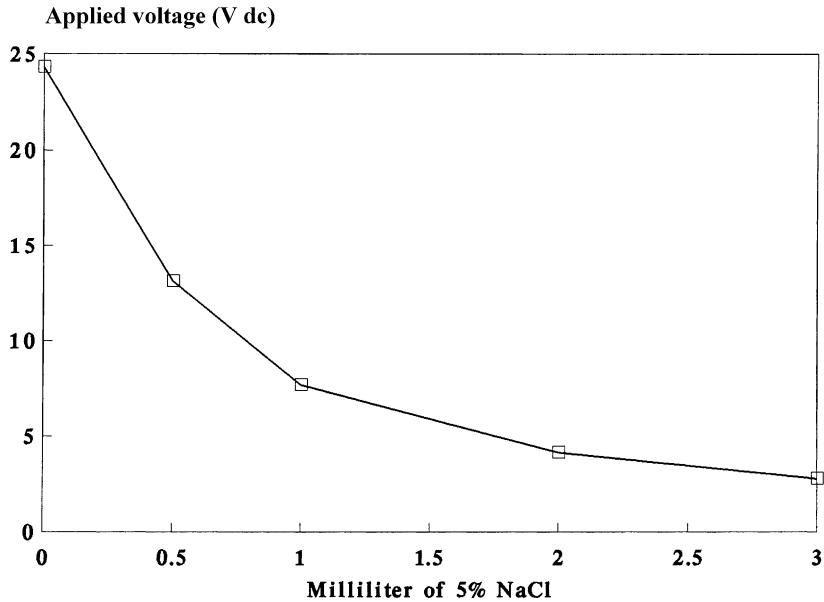


Fig. 5. Effect of NaCl concentration on applied voltage in the electrochemical reactor.

The previous test was repeated with solutions of 0.5, 1, 2, and 3 ml of 5% NaCl solution added to 1 l of DI water to study the effect of NaCl on sorbent generation and power consumption. The concentrations of these solutions were 25, 50, 100 and 150 ppm, respectively. Fig. 5 shows that the voltage required to draw 1 A current in the reactor decreases with the increasing of NaCl concentration in the solution. At constant current operation, power is proportional to the applied voltage. Fig. 5 also indicates that power consumption of the operation on 25 ppm NaCl solution is about 4.2 times more than that on the 150 ppm NaCl solution. Fig. 6 shows that with 2 A in the reactor, the system generates more than 80 ml/l of Al-sorbent in 12 min in a 150 ppm NaCl aqueous solution. The lower the NaCl concentration in the solution, the smaller the amount of the sorbent was generated in the operation. At low NaCl concentrations, the reactor consumes more energy to produce less Al-sorbent. This indicates that a larger portion of the electric energy is consumed in producing oxygen by water electrolysis.

3.2. Fluoride adsorption

A set of experiments was conducted to confirm that the mechanism of fluoride removal is due to the adsorption of the Al-sorbent. Fresh sorbent was produced in the electrochemical reactor by anode dissolution. After 12 min, the Al-sorbent is observed as a white gelatin-like amorphous sludge. The solution was placed in a separation funnel. Fig. 7 shows that it takes 3 h for the Al-sorbent to settle to the bottom of the separation funnel. The final volume of Al-sorbent is about 40% of the solution, which is about 350 ml in volume. 60 ml of

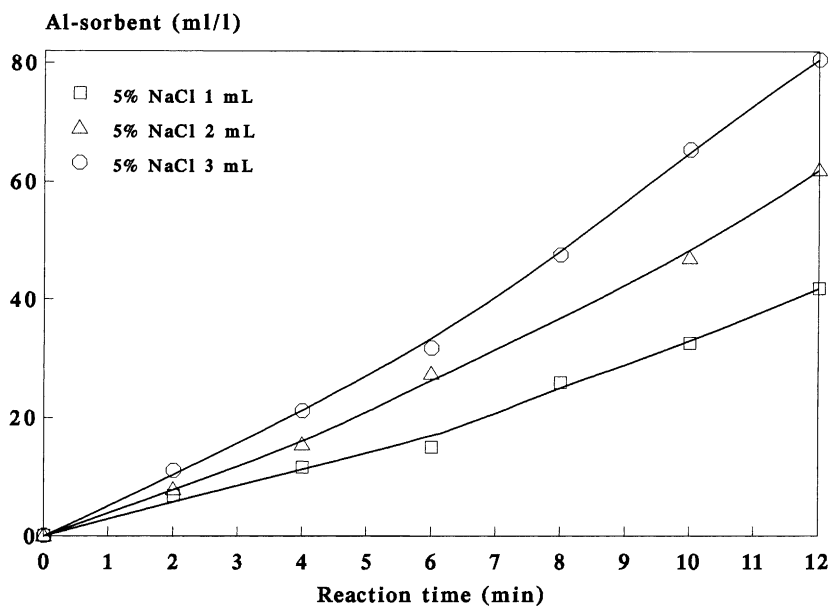


Fig. 6. Effect of NaCl concentration on sorbent generation.

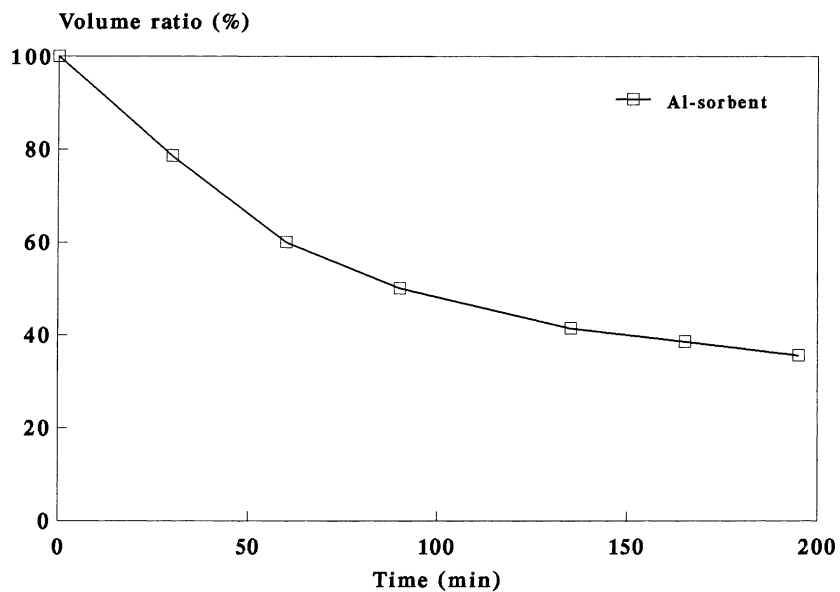


Fig. 7. Sedimentation of Al-sorbent generated in the electrochemical reactor.

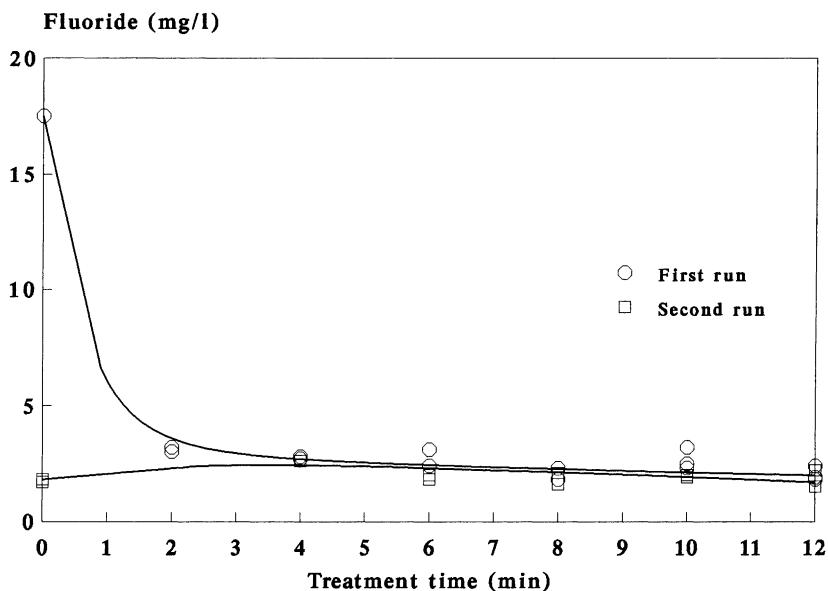


Fig. 8. Removal of fluoride ions in aqueous solution by electrochemically generated Al-sorbent.

the Al-sorbent was transferred from the separation funnel to a beaker containing a 600 ml fluoride-containing aqueous solution. After the mixing, the pH increased from 3.6 to 5.3. This is because the sorbent has a pH of 8.2. A magnetic stirrer was used to mix the mixture. Samples were collected for fluoride analysis. Fig. 8 shows that it takes only 2 min to reduce the fluoride concentration from 17 to 2 mg/l. It is believed that fluoride adsorbed is on the structure of $\text{Al}(\text{OH})_3$. However, the adsorption process stopped in 2 min, and the fluoride concentration remained at 2 mg/l in the solution for the remainder of the treatment time. At the end of the first run, another 60 ml of Al-sorbent was added to the solution. The fluoride concentration, considering dilution factor remained at 2 mg/l throughout the second run of treatment.

A test of 320 ml of Al-sorbent added to 600 ml of fluoride solution was conducted. After 12 min of treatment, the final fluoride concentration was about 2 mg/l and the pH was greater than 8. After the adsorption, HCl was added to obtain pH 7.3, 6.3, 5.3 and 4.3 in the Al-sorbent solution. Samples were taken at each pH stage to determine the concentration of fluoride in the solution. Fig. 9 shows the results of these tests. The final concentration of fluoride was further reduced by adding HCl to increase the adsorption capacity of the sorbent. Bottero et al. [21] reported that partially neutralized aluminum chloride solutions were effective coagulants for bentonite suspensions. A solubility diagram for aluminum in water [13] indicates that at alkaline pH values, $\text{pH} > 8$, the principal soluble species present at equilibrium with gibbsite is the monomeric anion, $\text{Al}(\text{OH})_4^-$. At lower pH levels, $\text{pH} < 6$, the dominant soluble species at equilibrium with gibbsite are cationic monomers such as Al^{3+} . The lowest solubility limit is at pH 6.5 where the solubility of aluminum compound is less than 10^{-6} mol/l [13]. Fresh Al-sorbent can

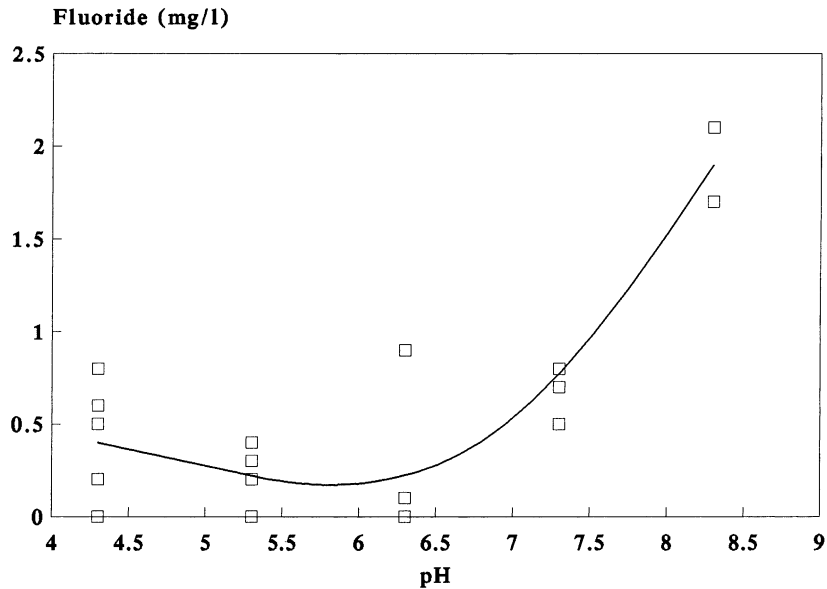


Fig. 9. Removal of fluoride ions by Al-sorbent adsorption enhanced by HCl in the solution.

be produced by neutralization of saturated solution from both high and low pH. It is apparent that the freshly generated Al-sorbent, gibbsite and amorphous, can be effectively produced at pH 6.5. Under the conditions, fluoride concentration can be reduced to 0.1 mg/l. Drondina and Drako [20] reported that an isoelectric point of aluminum hydroxide exists between pH 6.4 and 6.6 where the most effective fluoride adsorption take place.

3.3. Fluoride removal in electrochemical reactor

In view of the effectiveness of NaCl in depassivating an aluminum–water electrochemical system, there was an attempt to integrate both sorbent generation and fluoride adsorption in one reactor. A 40 l batch of 16 mg/l fluoride-containing solution was prepared for the study of fluoride removal in a 560 ml volume electrochemical reactor. Fig. 10 shows that the concentration of fluoride dropped from 16 to 6 mg/l in 2 min of treatment and dropped further to about 2 mg/l in 4 min and then stabilized at that concentration for the remainder of the treatment time. This confirmed the effectiveness of the aluminum-electrode electrochemical system for fluoride removal. The interaction between fluoride ions (F^-) and aluminum precipitate (P^{m+}) can lead to the formation of various products depending on the physico-chemical conditions of the solution [9]. The products of these reactions includes soluble complex ($PF^{(m-1)}$), precipitate ($PF_{n(S)}$), complexation of Al^{3+} (AlF^{2+} , AlF_2^+ , and AlF_3), cryolite ($Na_3AlF_6(s)$). In the electrochemical reactor, none of these reaction was able to reduce the fluoride concentration to less than 2 mg/l.

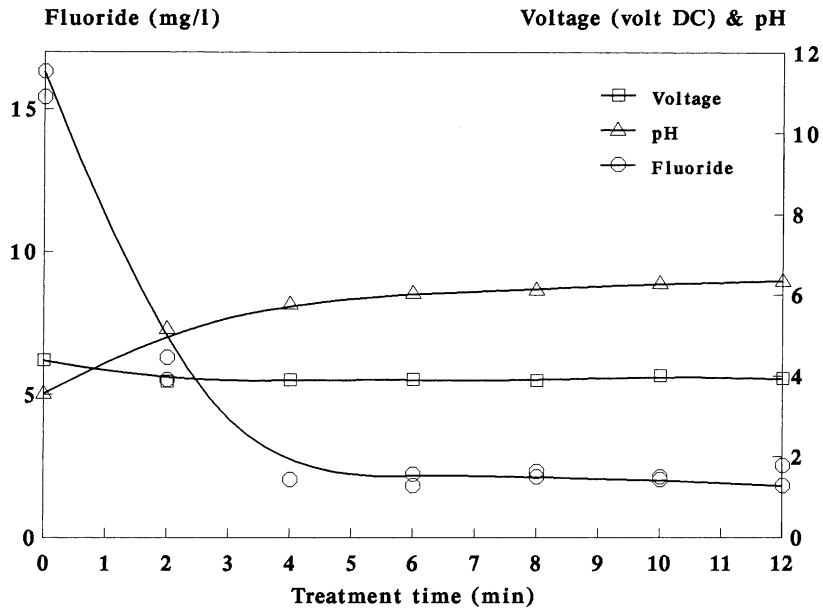


Fig. 10. Treatment of fluoride containing aqueous solution in electrochemical reactor.

In most of the electrochemical processes, current density is the most important parameter that governs the reaction rate in a reactor. Therefore, the first effort made to lower the fluoride concentration in the treated effluent is to increase the current density. The experimental results in the previous test showed that with 1 A in the reactor, the system is able to reduce fluoride concentration from 16 to 2 mg/l in 4 min. A second test was conducted under the same conditions with a current of 2 A. Fig. 11 shows the changes in the parameters fluoride, pH and applied voltages during the treatment. Because Al-sorbent is generated on the anode, the current density is calculated based on the surface area of the anode electrodes. The total surface of anode electrodes is 670 cm², a 1 A current in the reactor represents a current density of 1.5 mA/cm². In order to maintain a 2 A current in the reactor, the applied voltages were increased from 4 to 6.2 V. During 12 min of 2 A treatment, the pH in the solution increased from 3.7 to more than 8. Both the applied voltages and pH indicate that more vigorous conditions were provided to the reactor. However, the removal rate of fluoride from the solution remains the same. The concentration of fluoride was reduced from 16 to 2 mg/l in 4 min. After that, the concentrations leveled off at 2 mg/l for the rest of the treatment time. Another set of experiments was performed with a current further increased to 3 A. Fig. 12 shows that there is no difference in the removal of fluoride with respect to 1, 2, and 3 A in terms of treatment time and of the final concentrations in the treated effluent. It is believed that in order to increase current density, the applied voltage is increased. The high voltage triggers side reactions such as water electrolysis to occur. As a result of the side reaction, a significant increase of hydrogen bubbles was observed.

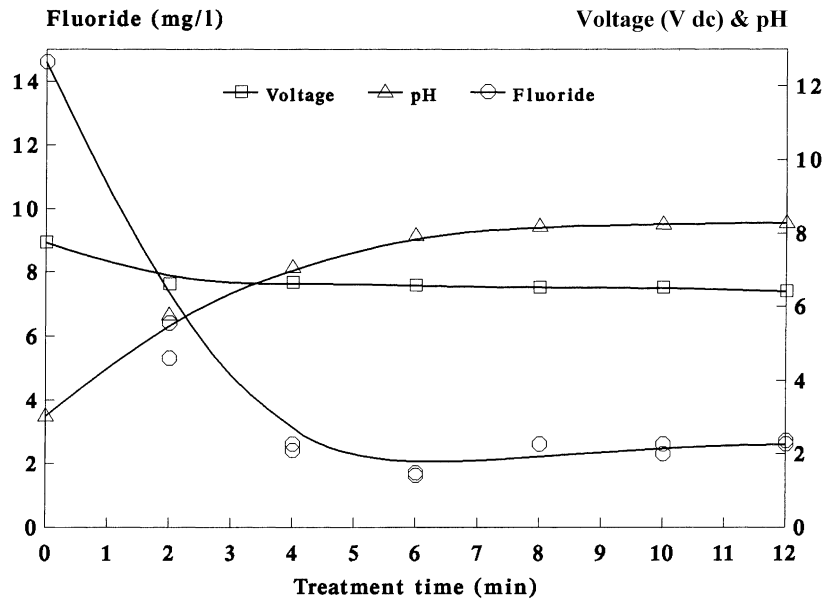


Fig. 11. Changes of fluoride concentration, pH and applied voltage during electrochemical treatment.

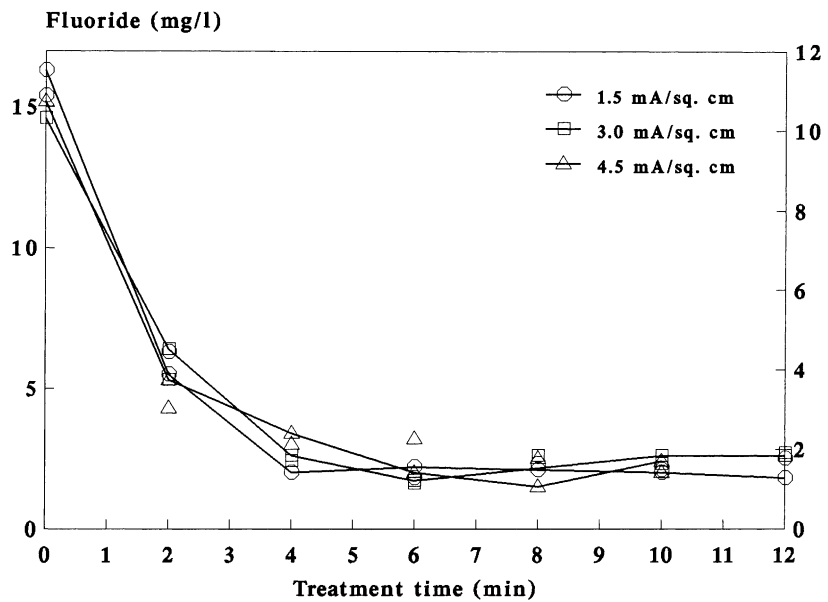


Fig. 12. Effect of current density on fluoride removal.

4. Conclusions

Electrochemical method is effective in producing fresh Al-sorbent by dissolving aluminum electrodes in dilute NaCl aqueous solutions. NaCl is essential to depassivate the aluminum–water electrochemical system. A trace amount of chloride ions in the solution is enough to penetrate the oxide film on the aluminum electrodes for dissolving to continue. By depassivating the system, the chloride is able to lower the power consumption and increase the sorbent production.

The freshly generated Al-sorbent is able to reduce fluoride concentration from 16 to 2 mg/l in 2 min. However, the fluoride ions and Al-sorbent reach an equilibrium at 2 mg/l throughout the 12 min treatment. This prevents the adsorption process to further reduce the fluoride concentration to less than 1 mg/l. Hydrochloric acid can be used to partially neutralize the mixture and open up new adsorption sites. The final fluoride concentration can be reduced to 0.1 mg/l by neutralizing the mixture to pH 6.3. Due to the amphoterism of aluminum hydroxide, the most important parameter for Al-sorbent formation is pH which turns out to be the crucial parameter for fluoride adsorption as well.

Al-sorbent generation and fluoride adsorption can be achieved simultaneously in a parallel-plate electrochemical reactor. The reactor is able to reduce fluoride concentration from 16 to 4 mg/l in 2 min and further down to 2 mg/l in 4 min. However, the effluent from the reactor also needs a pH adjustment to bring the fluoride concentration less than 1 mg/l.

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