2004

Fluoride removal by using a batch electrocoagulation reactor

Mohammad Emamjomeh

Muttucumaru Sivakumar
University of Wollongong, siva@uow.edu.au

Andrea Schafer

http://ro.uow.edu.au/engpapers/1650

FLUORIDE REMOVAL BY USING A BATCH ELECTROCOAGULATION REACTOR

M.M. EMAMJOMEH, M. SIVAKUMAR AND A.I. SCHÄFER

School of Civil, Mining and Environmental Engineering, Sustainable Earth Research Centre (SERC), Faculty of Engineering, University of Wollongong, Wollongong, NSW 2522, Australia.

SUMMARY: Ingestion of excess fluoride is a public health concern. It affects the teeth (fluorosis) and bones and in some areas of the world fluorosis is endemic. There are several methods for fluoride removal and one such method is electrocoagulation that has recently received attention as a suitable option. Colloid destabilizing agents that effect charge neutralization are produced by electrolysis in an electrocoagulation system. Reduced sludge production, no requirement for chemical handling and ease of operation are some of the advantages of this process. Experiments were undertaken to investigate the effects of the different parameters such as: current density ($6.25 - 31.25$ A/m^2), electrolysis time (5–60 min), electrolyte pH (5.5–8.5), and electrical conductivity (100 and 10000 μmhos/cm) on the fluoride removal efficiency in a batch electrocoagulator. The results obtained showed that the electrocoagulation technology is an effective process for defluoridation of potable water supplies and could also be utilized to the defluoridation of industrial wastewater.

1. INTRODUCTION

Fluoride has been found to have a significant effect against dental caries. However, ingestion of excess fluoride, most commonly through drinking water, can cause fluorosis that affects the teeth and bones (Lalumandier & Jones, 1999). Moderatly large amounts lead to dental problems, but long-term ingestion of large amounts can lead to potentially severe skeletal problems. Health impacts from long-term use of high fluoride concentration in drinking water have been summarized (NHMRC and ARMCANZ, 1996), as follows:

<0.5 mg/L   dental caries
0.5-1.5 mg/L   promotes dental health
1.5-4 mg/L   dental fluorosis
>4 mg/L   dental, skeletal fluorosis

    A study by UNICEF shows that fluorosis is endemic in at least 27 countries across the globe (Qian et al., 1999). These countries are: Iraq, Turkey, Syria, Jordan, Palestine, Morocco, Algeria, Libya, Egypt, Senegal, United Arabia Emirate, Iran, Pakistan, Sri lanka, India, Uganda, Kenya, Tanzania, Ethiopia, Japan, China, Bangladesh, Thailand, Australia, New Zealand, Mexico, Argentina. Fluoride in water is mostly of geological origin.

Waters with high levels of fluoride content are mostly found at the foot of high mountains and in areas where the sea has made geological deposits. The maximum acceptable concentration of fluorides in water is 1.5 mg/L (NHMRC and ARMCANZ, 1996). Fluoride also can be found industrial wastewaters, such as in glass manufacturing industries (Sujana et al., 1998) and in high concentrations in semiconductor industries (Toyoda & Taira, 2000). The discharge of these wastewaters without treatment in to the natural environment would contaminate groundwater.

There are several defluoridation processes that have been tested globally, such as adsorption (Lounici et al., 1997), chemical precipitation (Parthasarathy et al., 1986; Sujana et al., 1998; Toyoda & Taira, 2000), electrodialysis (Amor et al., 2001), and electrochemical method (Ming et al., 1983; Cheng, 1985; Mameri et al., 1998). In the precipitation technology, alum or combination of alum and lime are added respectively to water with low and high concentration of fluoride. Fluoride is then removed by flocculation, sedimentation and followed by filtration. Using chemical coagulants for precipitation is one of the most essential processes in conventional water and wastewater treatment. Generation of large volumes of sludge, the hazardous waste categorization of metal hydroxides, and high costs associated with chemical treatments have made chemical coagulation less acceptable compared to other processes. If a new process can replace the conventional chemical coagulation, the process efficiency would increase with little modification to present infrastructure in water and wastewater treatment plants and many problems caused by chemical coagulation would also be solved. This new process, called electrocoagulation (EC), is an electrochemical technique with many applications and more recently it has been suggested that EC as an alternative to conventional coagulation (Mills, 2000). Some researchers (Ming et al., 1983; Cheng, 1985; Drondina & Drako, 1994; Mameri et al., 1998; Yang & Dluhy, 2002; and Shen et al., 2003) have demonstrated that electrocoagulation using aluminum anodes is effective for defluoridation in water and industrial wastewater treatment. It has been suggested that the electrocoagulation process for fluoride removal does not require a big investment (Mameri et al., 1998).

This research is directed towards improving a new removal technology, for removing fluoride concentration in water and wastewater treatment processes by electrocoagulation. This study elucidates the effects of current density, contact time, solution pH, and electrolyte conductivity(E_c) on the fluoride removal efficiency of the process in a batch scale.

2. FUNDAMENTALS OF ELECTROCOAGULATION

2.1 Principle

Electrocoagulation is an electrochemical technique, in which a variety of unwanted dissolved particles and suspended matter can be effectively removed from an aqueous solution by electrolysis. Electrocoagulation is a process of passing a steady electric current through a liquid. When aluminum electrodes are used, the aluminum goes into solution at the anode and hydrogen gas is released at the cathode and dissolution of Al anodes produces aquous aluminum species. The coagulating agent combines with the pollutants and form large size flocs. The bubbles also float to the top of the tank; they collide with particles suspended in the water on the way up, adhere to them and float them to the surface of the water.

Indeed, the pollutants can be removed usually by either settling or flotation (electrocoagulation/electroflotation). In its simplest form, an electrocoagulating reactor is made up of an electrolytic cell with one anode and one cathode. The conductive metal plates are commonly known as 'sacrificial electrodes'. The sacrificial electrodes may be made up of the same or of different materials as the anode (Mollah et al., 2001). Interactions occurring within an electrocoagulation reactor is shown in Figure 1.
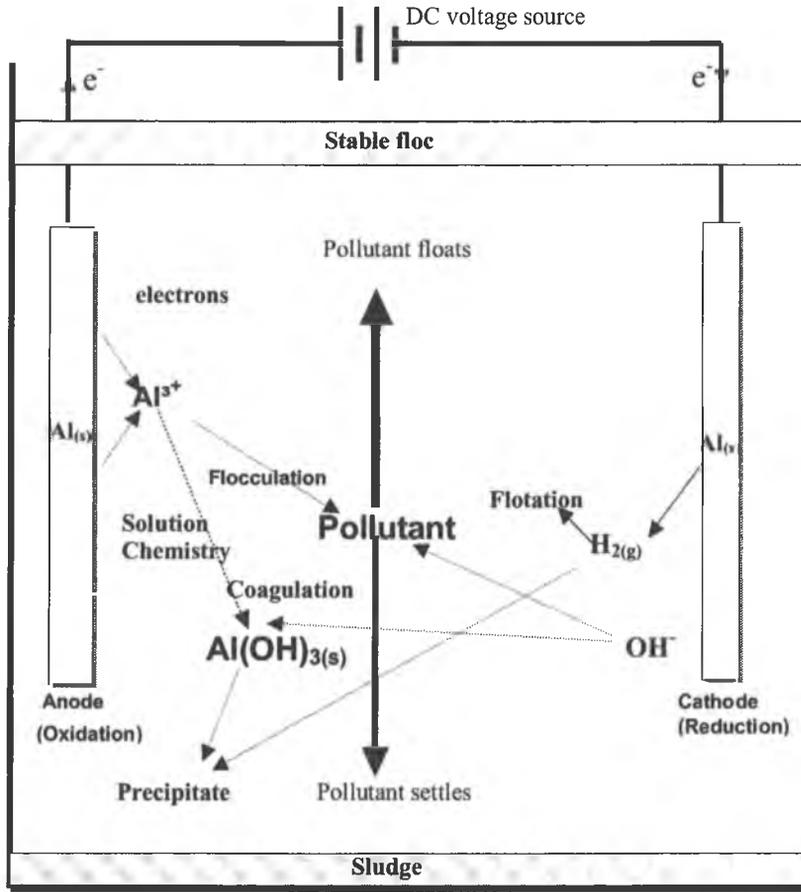
Figure1. Processes in an electrocoagulation reactor (Adapted from Holt et al., 2002)

Electrocoagulation has many advantages:
- It requires simple equipment, easy to operate and less maintenance.
- Treated water will be clear, colorless and odourless.
- Sludge formed by EC tends to be readily settable and easy to de-water.
- Flocs formed by EC can be separated faster by filtration.
- EC produces effluent with less total dissolved solids.
- The smallest colloidal particles are easily removed.
- The pollutants are both raised to the surface and settled to the bottom.

2.2   Mechanisms of electrocoagulation

The electrolytic dissolution of Al anodes in water produces aqueous Al^{3+} species:

Anodes: $$Al_{(s)} \longrightarrow Al^{3+} + 3e^-$$ (1)
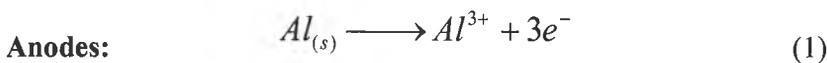
At the aluminum cathode hydrogen bubbles are produced by the following reaction:

Cathodes: $$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$ (2)
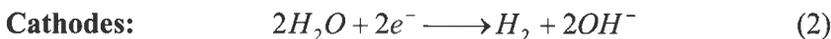
The bubbles float some of the flocs formed between water contaminants and a range of coagulant species and metal hydroxides formed by hydrolysis:

$$Al^{3+} + 3H_2O \longleftrightarrow Al(OH)_{3(S)} + 3H^+ \qquad (3)$$

These coagulants destabilise and aggregate suspended particles or precipitate and adsorb dissolved contaminants. The destabilization mechanism of the contaminants, particulate suspension, and breaking of emulsions has been summarized (Mollah et al., 2001) as follows:
- Colloid destabilizing agents that effect charge neutralization are produced by electrolysis in an electrocoagulation system.
- The floc formed as a result of coagulation creates a sludge blanket that entraps and bridges colloidal particles.

3. EXPERIMENTAL STUDY

3.1 Apparatus

A laboratory batch electrocoagulation reactor was designed and constructed to the dimension shown in Figure 2. In the electrochemical cell, five aluminum (purity of Al 95−97%) plate anodes and cathodes (dimension 250×100×3 mm) were used as electrodes. Figure 2 also shows the electrode arrangement; three aluminum cathodes were interspersed with two aluminum anodes. The electrodes were connected using monopolar configuration in the electrocoagulation reactor. These were dipped 200 mm into an aqueous solution (3.6 L) in a perspex box (dimension 300×132×120 mm). In the reactor, stirring was achived using a magnetic bar placed between the bottom of the elecrodes and the box. There was a draining tube at the bottom of the box for cleaning. Samples of treated water or wastewater were collected from a port located 50 mm above the bottom of the box.

The gap between the two neighboring electrode plates was 5 mm. Direct current (0−30 V, 0−2.5 A) from a DC power supply was passed through the solution via the five electrodes. Cell voltage and current, were readily maintained using the digital power display. The pH of the feed and product water and temperature were measured for each experiment run. Fluoride analysis was determined using SPADNS method (AWWA and WEF, 2000). Fluoride is colorless and will not absorb any light wave. The fluoride concentration was determined by adding a reagent consisting of acid zirconyl and SPADNS to the solution and mixed well. This method is subject to errors due to interfering ions such as aluminum and chloride concentration. These interfering ions were not present in excess of the accepted tolerance for this method. Aluminum concentration was measured using an Atomic Absorption Spectrophotometer.

3.2 Experimental procedure

The influence of the experimental parameters on the defluoridation process was achieved with synthetic water in a batch mode. Fluoride solutions were prepared by mixing sodium fluoride (NaF) in deionized water. Sodium chloride (NaCl) was added to the aqueous solution to promote conductivity in the electrocoagulator. Sodium hydroxide and hydrochloric acid solutions were also added for pH adjustment between 5.5 and 8.5. Sodium bicarbonate was added to maintain alkalinity. Electrocoagulation experiments were performed for 60 min for each run and samples were taken every five-minutes.

1. Electrolytic Box
2. Aluminum electrodes
3. Magnetic bar-stirrer
4. Drain tube
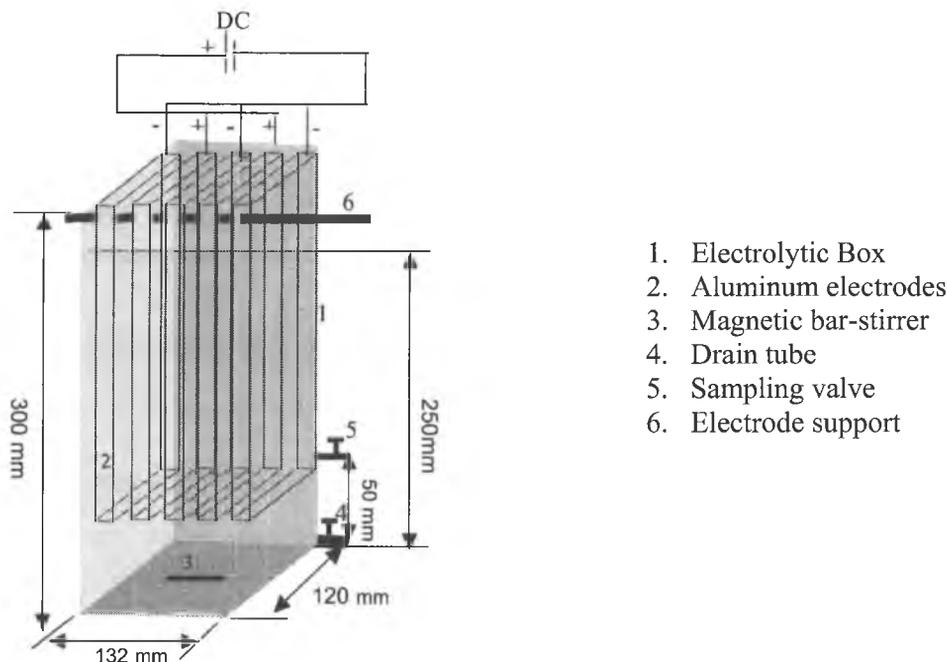5. Sampling valve
6. Electrode support

Figure 2. Schematic diagram of an electrocoagulation reactor.

Fluoride, Al concentration and pH were then measured using a visible Spectrophotometer, Atomic Absorption Spectrophotometer and a calibrated pH meter, respectively. All experiments were conducted at 20°C with an initial F^- concentration of 10 mg/L . Current was changed over the range 0.5 – 2.5A, however, it was held constant for each run.

4. RESULTS AND DISCUSSION

4.1 Effect of electrolysis time

Figure 3 shows the influence of electrocoagulation time on F^- and Al^{3+} concentrations. Electrolysis time determined the rate of dissolution of Al^{3+} ions, as it strongly depends on the current range. According to Figure 3, the fluoride removal percentage is increased (22– 92.7%) by increasing respectively the electrolysis time and aluminum concentration from 5 to 60 min and from 18.18 to 146.89 mg/L at a constant current of 1.5 A. Variation of fluoride concentration with time at different current densities has been shown in Figure 4.

4.2 Effect of current density

In most electrochemical process, current density is the most important parameter for controlling of the reaction rate in the reactor. The influence of the current density on the defluoridation experiments was studied with two monopolar electrodes. Figure 4 shows fluoride removal behaviour when current was varied from 0.5 to 2.5 A. Fluoride residual concentration decreases with the increase in current density. However, between currents densities 6.25 –12.5 A/m², the decrease was very low. The current range determines the rate of dissolution of Al^{3+} concentration. The lower the current, the less aluminum is released from the anode and hence the fluoride reduction is low.
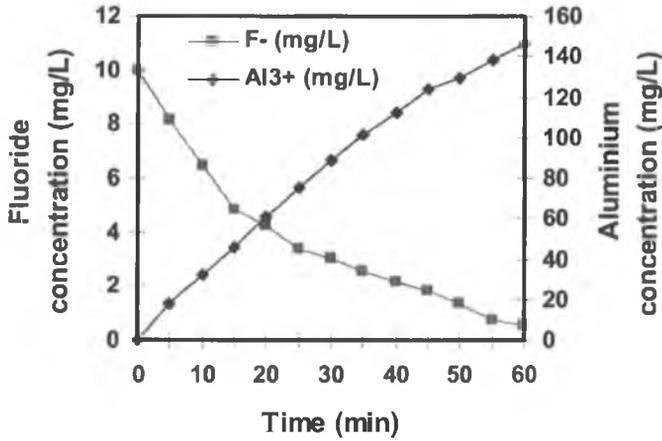
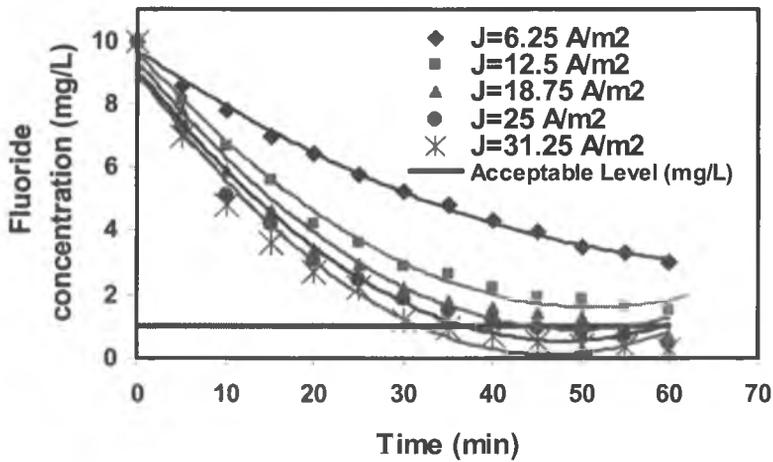Figure 3. Influence of electrolysis time on the fluoride and aluminum concentrations (I=1.5A, d=5 mm, T=20°C)

Figure 4. Variation of fluoride concentration with time at different current densities (d=5 mm, T=20° C, Ec=100 μmhos/cm)

The highest current (2.5A) produced the quickest fluoride removal due to the ready availability of Al^{3+} ions for coagulation. The experimental results show that the mass ratio Al^{3+}/F^- was between 10-16 in the pH range 5.5−8.5. This result is in agreement with the results obtained by Cheng (1985); Ming et al., (1983); and Mameri et al., (1998).

The rate of change of F^- concentration can be expressed, as follows:

$$\frac{dC}{dt} = -k_i C_t \qquad (4)$$

Equation 4 can be arranged by simple integration to give:

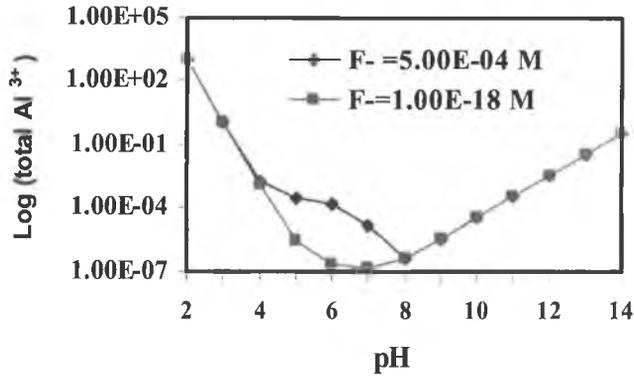$$C_t = C_\circ.e^{-k_i t} \qquad (5)$$

148

Figure 6. Influence of different concentration of F⁻ on the solubility of Gibbsite at various pH values.

In the anodic adsorption layer, the concentration of OH⁻ ions is higher than the concentration of F⁻, so the production of the complex AlF_6^{3+} ion becomes difficult; therefore, the reduction of fluoride from water and wastewater at a range of pH>7 is affected by the formation of aluminum hydroxide floc.

4.4   Effect of electrical conductivity

The conductivity of a suspension can be adjusted by varying its salinity. In this experiment, the fluoride removal efficiency was investigated for a sample conductivity of 100 μmhos/cm and 10000μmhos/cm. At currents of 1.5, 2, and 2.5A, the required electrolysis times were 55, 40 and 30 min, respectively, to achieve a fluoride residual concentration ≤1.5mg/L at 100 μmhos/cm conductivity. For the same experimental conditions, the contact times were marginally decreased to 50, 35 and 30 min when conductivity increased to 10000 μmhos/cm. The decrease in electrolysis time was not significant.
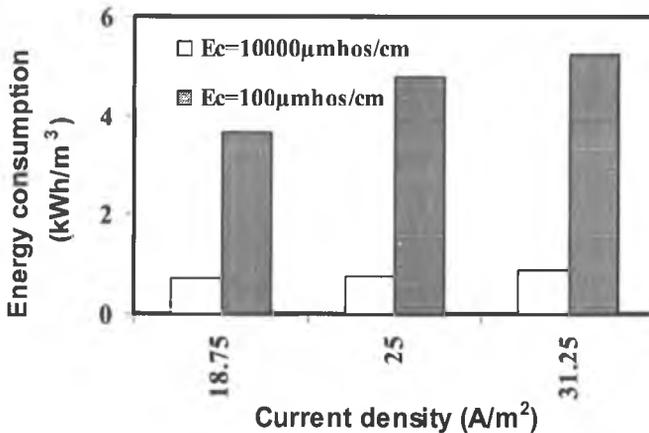

Figure 7. Effects of conductivity on the energy consumption at different current densities.

REFERENCES

AWWA and WEF (1998) Standard methods for the examination of water and wastewater, American Water Works Association and Water Environment Federation, Washington, D. C.

Amor Z., Bariou B., Mameri N., Taky M., Nicolas S. & Elmidaoui A. (2001) Fluoride removal from brackish water by electrodialysis, *Desalination*, vol.133, pp. 215-223.

Cheng S.L. (1985) Electro-chemical method to remove fluoride from drinking water, *Water Supply,* vol. 3, pp.177-186.

Drondina R.V. & Drako I.V. (1994) Electrochemical technology of fluorine removal from underground and wastewaters, *Journal of Hazardous Materials*, vol.37, n.1, pp. 91-100.

Holt P.K., Barton G.W., Wark M. & Mitchell C. A. (2002) A quantitative comparison between chemical dosing and electrocoagulation, *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* vol. 21, n. 2-3, pp. 233-248.

Lalumandier J. & Jones J. (1999) Fluoride concentrations in drinking water, *American Water Works Association Journal*, vol.91, n.10, pp. 42-51.

Lounici H., Addour L., Belhocine D., Grib H., Nicolas S., Bariou B. & Mameri N. (1997) Study of a new technique for fluoride removal from water, *Desalination*, vol.114, n.3, pp. 241-251.

Mameri N., Yeddou A.R., Lounici H., Belhocine D., Grib H. & Bariou B. (1998) Defluoridation of septentrional Sahara water of North Africa by electrocoagulation process using bipolar aluminium electrodes, *Water Research*, vol.32, n. 5, pp.1604 –1612.

Mills D. (2000) A new process for electrocoagulation, *American Water Works Association Journal,* vol.92, n.6, pp.34-43.

Ming L., Yi S.R., Hua Z.J., Lei B.Y.W., Ping L. & Fuwa K.C. (1983) Elimination of excess fluoride in potable water with coarcervation by electrolysis using aluminium anode, *Fluoride,* vol 20, pp. 54-63.

Mollah M.Y.A., Schennach R., Parga J.R. & Cocke D. L. (2001), Electrocoagulation (EC) science and applications, *Journal of Hazardous Materials*, vol. 84, n. 1, pp. 29-41.

NHMRC and ARMCANZ (1996) Australian Drinking Water Guidelines, *National Health and Medical Research Council and the Agriculture and Resource Management Council of Australia and New Zealand .*

Parthasarathy N., Buffle J. & Haerdi W. (1986) Combined use of calcium salts and polymeric aluminum hydroxide for defluoridation of waste waters, *Water Research*, vol.20, n.4, pp. 443-448.

Qian J., Susheela A.K., Mudgal A. & Keast G. (1999) Fluoride in water: An overview, *Waterfront: A UNICEF Publication on Water, Environment, Sanitation and Hygiene*, n.13, pp.11-13.

Shen F., Chen X., Gao P. & Chen G. (2003) Electrochemical removal of fluoride ions from industrial wastewater, *Chemical Engineering Science*, vol. 58, n. 3-6, pp. 987-993.

Sposito G (1996) *The environmental chemistry of aluminum*, Baca Raton.

Sujana M.G., Thakur R.S. & Rao S. B. (1998) Removal of fluoride from aqueous solution by using alum sludge, *Journal of Colloid and Interface Science*, vol. 206, pp. 94-101.

Toyoda A & Taira T. (2000) A new method for treating fluorine wastewater to reduce sludge and running costs, *IEEE Transactions on semiconductor manufacturing*, vol. 13, no. 3, pp. 305-309.

Yang C. & Dluhy R. (2002) Electrochemical generation of aluminum sorbent for fluoride adsorption, *Journal of Hazardous Materials*, vol. 94, n. 3, pp. 239-252.