Fluoride Removal from Aqueous Media by Electrogenerated Al(OH)$_3$

Monica Ihos[*] and Ladislau Andres

National R&D Institute for Industrial Ecology - ECOIND - Timisoara Branch, P-ta Regina Maria Nr.1, Et.2, 300004 Timisoara, Romania, e-mail: monica_ihos@yahoo.com

Abstract

The removal of fluoride from aqueous media was carried out by electrocoagulation with aluminium sacrificial anode. The electrogenerated Al(OH)$_3$ has high fluoride adsorption capacity. The applied current density was of 10, 30 and 50 A/m^2, respectively, the initial fluoride concentration was of 5 mg/L and 10 mg/L, respectively and pH of 7. The supporting electrolyte was 0.01 M Na Cl. Concentrations of fluoride in the electrolysed solutions of about 0.20 mg/L were obtained.

Introduction

Fluoride (F$^-$) is widespread in the geologic medium and is released in the groundwater, usually, by the slow dissolution of fluorine-containing rocks. The fluoride is known as one of the contaminants for drinking water that causes serious health concerns and the World Health Organization (WHO) recommendation regarding the limit of the fluoride in drinking water is 1.5 mg/L [1]. The fluoride is an essential element in a narrow range of concentration, between 0.5 and 1 mg/L, but it is harmful for the human health when exceeds 1.5 mg/L.

Groundwater, an important source of drinking water, is also a very important source of fluoride for human intake. Long term ingestion of fluoride rich drinking water causes serious health disorders such as fluorosis, which causes mottling of teeth in mild cases and embrittlement of bones and neurological damage in severe cases [2]. The high concentrations of fluoride can also interfere with carbohydrates, lipids, proteins, vitamins and mineral metabolism [3, 4]. Excess intake of fluoride leads to various diseases such as osteoporosis, arthritis, brittle bones, cancer, infertility, brain damage, Alzheimer syndrome, and thyroid disorder [2].

Because of the harmful effects of fluoride upon human health it is necessary to develop technologies that can effectively remove fluoride from the groundwater used for drinking purposes.

Among the processes studied for fluoride removal from aqueous media, adsorption [5-13], membrane techniques [14-17] and electrochemical processes can be mentioned. The third approach is a versatile and effective method and also a sustainable way to remove the fluoride from aqueous media.

The aim of this paper was to assess the removal of fluoride from aqueous media by using Al(OH)$_3$ generated during the electrocoagulation with aluminium sacrificial anode.

Experimental

Fluoride removal from aqueous media by electrocoagulation was carried out in a plexiglass cell with horizontal electrodes. The sacrificial anode was made of aluminium with an active surface area of 78.4 cm^2. The cathode was a wire mesh grid made up of 3 mm diameter stainless steel wires. The distance between the electrodes was 5 mm.

Volumes of 500 ml solution were introduced in the cell, and the applied current densities were 10, 30 and 50 A/m^2, respectively. Electrolysis duration was 60 minutes and samples were taken at every 10 minutes.

Stock solution of 1000 mg/L F^- was obtained by dissolving the appropriate quantity of NaF (Merck) p.a. in distilled water. Working solution of 5 and 10 mg/L F^- and pH of 7 were prepared freshly for each experiment by diluting stock solution and adjusting pH with NaOH p.a. The supporting electrolyte was 0.01 M Na Cl.

The fluoride content was determined by using a Thermo Scientific Orion fluoride ion selective electrode. TISAB II solution was used as a buffer to maintain the pH and background ion concentrations.

Results and discussion

In Table 1 are listed the working conditions during the electrocoagulation and the concentration of F^- in the electrolysed solutions.

Table 1. Working conditions and F^- concentration; $pH_{ini}=7$

Time/ min	Current density/ A/m^2	*Cell voltage/ V	*F^- conc./ mg/L	*F^- removal efficiency / %	**Cell voltage/ V	**F^- conc./ mg/L	**F^- removal efficiency / %
10		1.0	2.32	53.6	1.0	8.57	14.3
20		1.0	2.28	54.4	0.9	7.62	23.8
30	10	1.1	2.27	54.6	0.9	6.44	35.6
40		1.1	1.96	60.8	0.9	5.11	48.9
50		1.0	1.63	67.4	0.9	3.92	60.8
60		0.9	1.37	72.6	0.9	3.79	62.1
10		1.6	2.63	47.4	1.4	5.97	40.3
20		1.5	1.50	70.0	1.4	4.21	57.9
30	30	1.5	1.12	77.6	1.4	2.66	73.4
40		1.7	0.77	84.6	1.4	1.76	82.4
50		1.7	0.65	87.0	1.4	1.11	88.9
60		1.4	0.54	89.2	1.4	0.65	93.5
10		1.9	2.17	56.6	2.0	2.33	76.7
20		1.9	0.80	84.0	2.0	0.82	91.8
30	50	1.8	0.35	93.0	2.0	0.54	94.6
40		1.8	0.22	95.6	2.0	0.37	96.3
50		1.9	0.19	96.2	1.9	0.22	97.8

* c_{ini}: 5 mg/L F^-; ** c_{ini}: 10 mg/L F^-

The limit of 1.5 mg/L fluoride recommended by WHO was achieved by applying a current density of 30 and 50 A/m^2 whatever the initial concentration of fluoride. The electrolysis time to achieve the recommended limit was higher for 30 A/m^2 as the initial concentration of the fluoride increased, but the same at 50 A/m^2 for both concentrations. The explanation of this behaviour can follow that one given by Gosh et al. [18]. In the first instances of electrogeneration, aluminium cations contributed to charge neutralization of the pollutant particles as part of a sorption coagulation mechanism, the result was formation of loose aggregates. As the time progresses, further aluminium cation addition resulted in amorphous aluminium hydroxide precipitation that promotes pollutant aggregation. If the current density had remained at 30 A/m^2 so the production of the aluminium cation had remained fixed and therefore with the increase in initial fluoride concentration, the complex formation process between the amorphous aluminium hydroxide and fluoride would have been insufficient.
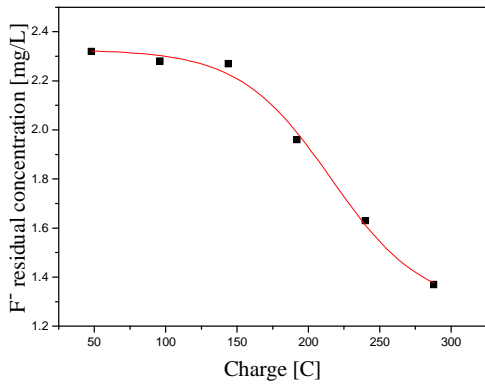
Figure 1. Dependence of F⁻ residual concentration versus charge; c_{ini}: 5 mg/L F⁻, pH_{ini}: 7, current density: 10 A/m²
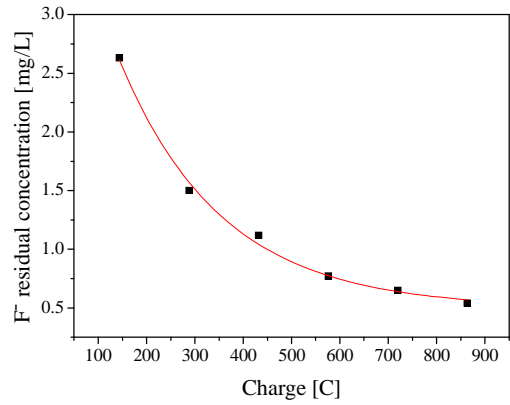

Figure 2. Dependence of F⁻ residual concentration versus charge; c_{ini}: 5 mg/L F⁻, pH_{ini}: 7, current density: 30 A/m²
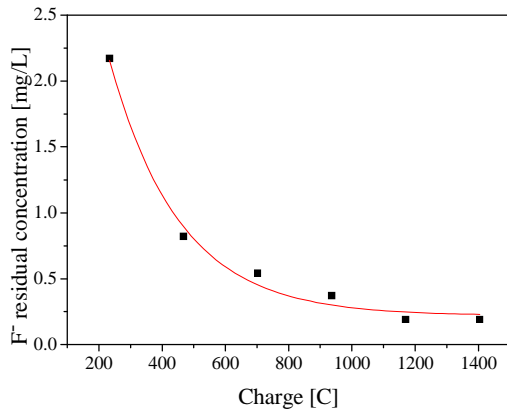

Figure 3. Dependence of F⁻ residual concentration versus charge; c_{ini}: 5 mg/L F⁻, pH_{ini}: 7, current density: 50 A/m²
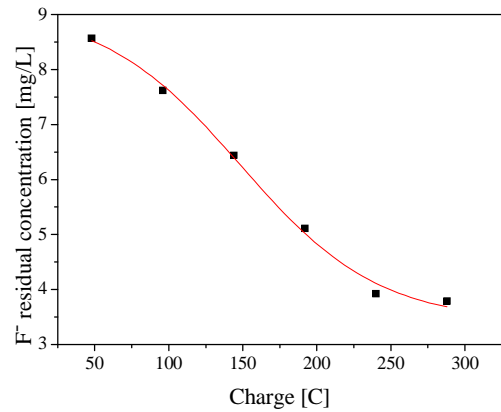

Figure 4. Dependence of F⁻ residual concentration versus charge; c_{ini}: 10 mg/L F⁻, pH_{ini}: 7, current density: 10 A/m²
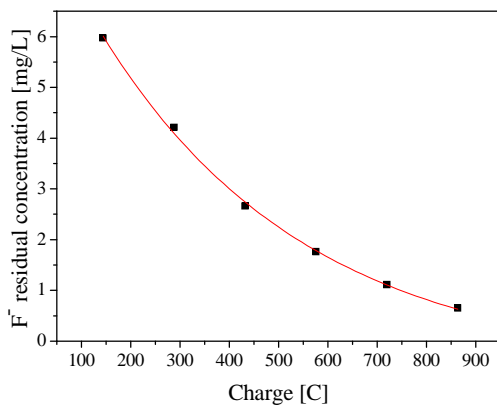

Figure 5. Dependence of F⁻ residual concentration versus charge; c_{ini}: 10 mg/L F⁻, pH_{ini}: 7, current density: 30 A/m²
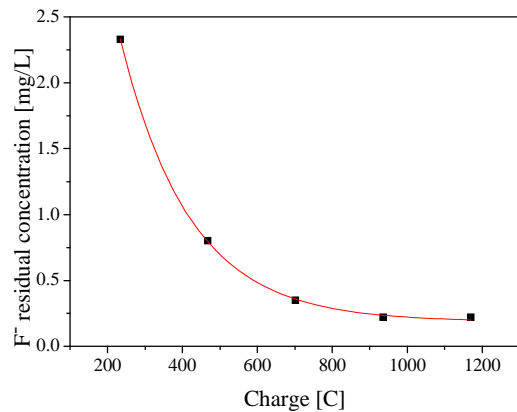

Figure 6. Dependence of F⁻ residual concentration versus charge; c_{ini}: 10 mg/L F⁻, pH_{ini}: 7, current density: 50 A/m²

241

As it is shown in Figures 1-6, the shapes of the curves for fluoride dependence versus charge are different at 10 A/m^2 from those at 30 and 50 A/m^2 for both concentrations. This finding suggested that the removal process of fluoride by electrocoagulation with aluminium sacrificial anode occurred faster as the applied charge increased when the applied current density was 10 A/m^2, for both fluoride concentrations. Also for both concentrations and applied current densities of 30 and 50 A/m^2, the process was faster at the beginning, which was in accordance with the electrocoagulation process progress.

Conclusions

Electrocoagulation with aluminium sacrificial anode was effective in fluoride removal from aqueous media both at fluoride initial concentration of 5 mg/L and 10 mg/L. The fluoride concentration was under 1.5 mg/L, the recommended limit of the fluoride in drinking water by WHO, for an applied current density of 30 A/m^2 and 50 A/m^2, respectively.

As the electrolysis time increased the removal efficiency of fluoride increased for any applied current density and initial concentration of fluoride. The best results were obtained at 50 A/m^2 and 50 minutes of electrolysis and the fluoride removal efficiency for initial concentration of fluoride of 5 mg/L and 10 mg/L was 96.2% and 97.8%, respectively.

Acknowledgements

References

[1]   W.H.O., Guidelines for Drinking Water Quality, fourth edition, 2011.
[2]   A. Bhatnagar, E. Kumar, M. Sillanpaa, Chem. Eng. J. 171 (2011) 811.
[3]   S.K. Swaina, S. Mishrab, T. Patnaikc, R.K. Pateld, U. Jhaa, R.K. Deye, Chem. Eng. J. 184 (2012) 72.
[4]   M. Islam, R.K. Patel, Chem. Eng. J. 169 (2011) 68.
[5]   A. Bansiwal, P. Pillewan, R.B. Biniwale, S.S. Rayalu, Micropor. Mesopor. Mat. 129 (2010) 54.
[6]   J. Kang, B. Li, J. Song, D. Li, J. Yang, W. Zhan, D. Liu, Chem. Eng. J. 166 (2011) 765.
[7]   S. Lunge, D.Thakre, S.Kamble, N.Labhsetwar, S.Rayalu, J. Hazard. Mater. 237–238 (2012) 161.
[8]   V.Tomar, S. Prasad, D. Kumar, Microchem. J. 111, (2013) 116.
[9]   J. Wang, W. Xu, L. Chen, Y. Jia, L. Wang, X.-J. Huang, J. Liu, Chem. Eng. J. 231 (2013) 198.
[10]   A. L.Srivastav, P. K. Singh, V.Srivastava, Y. C. Sharma, J. Hazard. Mater. 263 (2013) 342.
[11]   C. Yang, L.Gao, Y. Wang, X.Tian, S.Komarneni, Micropor. Mesopor. Mat. 197 (2014) 156.
[12]   I. Ali, Z. A. ALOthman, M. M.Sanagi, J. Mol. Liq. 211 (2015) 457.
[13]   B.-S. Zhu, Y. Jia, Z. Jin, B. Sun, T. Luo, X.-Y. Yu, L.-T. Kong, X.-J. Huang, J.-H. Liu, Chem. Eng. J. 271 (2015) 240.
[14]   N. Kabay, O. Arar, S. Samatya, U. Yuksel, M. Yuksel, J. Hazard. Mater. 153 (2008) 107.
[15]   F. Elazhar, M. Tahaikt, A. Achatei, F. Elmidaoui, M. Taky, F. El Hannouni, I. Laaziz, S. Jariri, M. El Amrani, A. Elmidaoui, Desalination 249 (2009) 154.
[16]   D. Dolar, K. Kosutic, B. Vucic, Desalination 265 (2011) 237.
[17]   N. Drouiche, S. Aoudj, H. Lounici, M. Drouiche,T. Ouslimane, N. Ghaffour, Procedia Eng. 33 (2012) 385.
[18]   D. Gosh, C.R. Medhi, M.K. Purkait, Chemosphere 73 (2008) 1393.