DEVELOPMENT OF GROUNDWATER MANAGEMENT BY USING ELECTROCOAGULATION FOR REMOVAL OF FLUORIDE AND COEXISTING ANIONS

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Abstract

The electrocoagulation was applied to removal of fluoride and coexisting anions from simulated groundwater. The concentration of fluoride, chloride and sulfate was of 5 ppm, 347 ppm and 199 ppm, respectively. The influence of pH, current density, electrolysis time and sulfate presence were studied. Fluoride and sulfate removal efficiency, chloride concentration and specific energy consumption were calculated.

Introduction

Groundwater represents about 30% of world's fresh water. From the other 70%, nearly 69% is captured in the ice caps and mountain snow/glaciers and merely 1% is found in rivers and lakes. Groundwater counts in average for one third of the fresh water consumed by humans, but at some parts of the world, this percentage can reach up to 100% [1].

Taking into account the importance of groundwater as one of the main part of the existing freshwater resources and source of supply for drinking water, irrigation and industry, it is necessary to apply an appropriate groundwater management. Thus, the unadvised exploitation of groundwater and depletion of groundwater storages is avoided [2,3].

One of the important tools of groundwater management is represented by the technical aspects that suppose groundwater treatment technology especial for drinking purposes. The chemical characteristics of groundwater quality are responsible for the decision to treat the groundwater for drinking waters purposes. Among the challenges related to the groundwater quality, the presence of fluoride and coexisting anions above the limits allowed by the regulations in use require finding the technological solutions.

The processes and methods reported for removal of fluoride itself or along with coexisting anions from groundwater are various [4-12]: adsorption, membrane distillation, electrodialysis, micellar ultrafiltration, capacitive deionization, electrochemical processes and coagulation.

The aim of this study was to apply the electrocoagulation process for removal of fluoride and coexisting anions from a simulated groundwater in order to provide a reliable experimental model to developing an efficient groundwater management.

Experimental

The electrocoagulation experiments were carried out in a Plexiglas cell with horizontal electrodes. The sacrificial anode of 5.6 x 14 cm was made on aluminium and 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 working solutions were introduced in the cell, and the applied current densities were 10, 50, 100 and 150 A/m^2, respectively. Electrolysis duration was 60 minutes and samples were taken at every 15 minutes. The experiments were carried out with simulated groundwater with concentration of 5 ppm fluoride, 347 ppm chloride and 199 ppm sulfate. All reagents were of analytical grade and the solutions were prepared with distilled water. The pH of initial solutions was adjusted to 5.3 and 7, respectively.

The fluoride concentration was determined by using a Thermo Scientific Orion fluoride ion selective electrode (range: from 0.02 ppm to concentration at saturation). TISAB II solution was used as a buffer to maintain the pH and background ion concentrations.

The chloride and sulfate concentration was carried in accordance with SR ISO 9297:2001, and EPA9038, respectively.

Results and discussion

For better understanding the experiments results some theoretical issues should be briefly presented.

When electrocoagulation is carried out with Al as sacrificial anode, the electrochemical reactions that occur at the electrodes are:

$$\text{anode } (+) \qquad Al(s) \leftrightarrow Al^{+3}(aq) + 3e^{-} \qquad (1)$$

$$\text{cathode } (-) \qquad 3H_2O_{(l)} + 3e^{-} \leftrightarrow 3/2H_{2(g)} + 3OH^{-}_{(aq)} \qquad (2)$$

During the electrocoagulation the reaction between Al^{+3} and OH^{-} lead to various monomeric and polymeric species of hydrated aluminium, such as: $Al(H_2O)_4(OH)^{2+}$, $Al(H_2O)_5(OH)^{2+}$, $Al(H_2O)_6^{3+}$, $Al(OH)^{2+}$, $Al(OH)_2^{+}$, $Al_2(OH)_2^{4+}$, $Al(OH)_4^{-}$, $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}(OH)_{34}^{5+}$, $Al_{13}O_4(OH)_{24}^{7+}$ [13]. These species are further transformed into in amorphous $Al(OH)_{3(s)}$:

$$Al^{+3}_{(aq)} + 3OH^{-}_{(aq)} \leftrightarrow Al(OH)_{3(s)} \qquad (3)$$

Near neutral pH the aluminium predominant species is $Al(OH)_{3(s)}$. The newly-formed precipitate of $Al(OH)_{3(s)}$ has a large surface that is beneficial to fast adsorption of soluble compounds and destabilization of colloidal particles.

Regarding the fluoride removal, one can notice that with the increase of the current density and the electrolysis time, at both initial pH, 5.3 and 7, the increase of removal efficiency of fluoride occured (Figures 1 and 2).

The applied current density is an important parameter for pollutants removal because it determines the rate of dosing of the coagulant, the yielding of gas bubbles, the size and growth of the flocks what influences the removal efficiency by electrocoagulation.

In accordance with Faraday's law the amount of dissolved aluminium is directly proportional to the quantity of electricity passed through the solution during the electrocoagulation. Therefore, the higher the amount of electricity, the higher the amount of coagulant and gas bubbles. Thus, by increasing the current density the yielding rate of Al^{3+} and OH^{-} ions will increase which will accelerate the removal of pollutants.

The fluoride removal efficiency was higher at initial pH of 5.3 because the pH of electrolised solutions ranged between 8.1 and 9.2 when the applied current densities ranged between 10-150 A/m^2. The pH of electrolised solutions of initial pH of 7 ranged between 8.6-9.5 when the applied current densities ranged between 10-100 A/m^2. At higher pH of 8, the solubility of amorphous $Al(OH)_{3(s)}$ increases and thus the anions removal efficiency decreases.

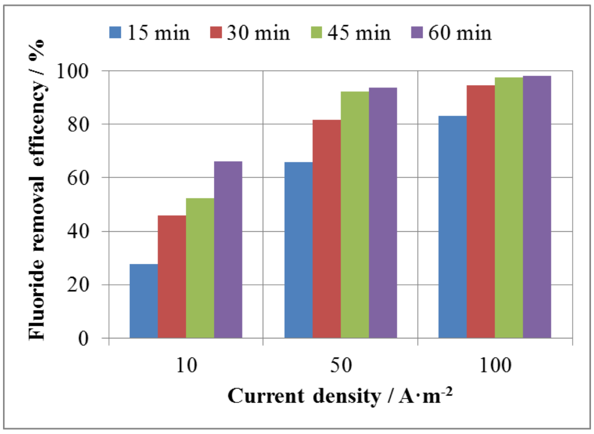

Figure 1. Fluoride removal efficiency by electrocoagulation at pH 5.3
C_F^- : 5 ppm, C_{Cl}^- : 347 ppm

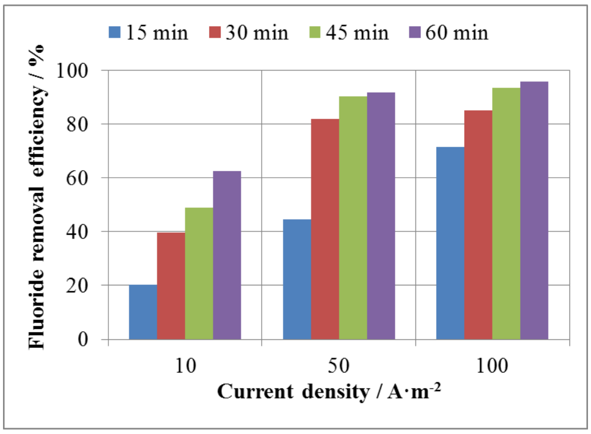

Figure 2. Fluoride removal efficiency by electrocoagulation at pH 7
C_F^- : 5 ppm, C_{Cl}^- : 347 ppm

Regarding the chloride concentration, the data listed in Table 1 did no show significant changes along with the increasing of current density, pH and electrolysis time.

It should be noticed that the presence of chloride is beneficial because it facilitates the electrical charge transport by increasing the solution conductivity and also, eliminates the aluminium passivation due to the precipitation of $Al(OH)_3$ and Al_2O_3 [14]. Besides the repercussion of passivation to block the electrode activity another important aspect is given by increasing the cell voltage and thus, the energy consumption and the cost of electrocoagulation are higher.

Table 1. Working conditions and chloride concentration variation
initial concentration: 5 ppm F^-; 347 ppm Cl^-

Current density / A/m^2	Cell voltage / V	Electrolysis time / min	Chloride concentration / ppm	
			pH 5.3	pH 7
10	1	15	333	333
		30	329	333
		45	329	333
		60	319	333
50	2.2	15	320	312
		30	320	312
		45	320	305
		60	305	298
100	3.7	15	319	305
		30	297	297
		45	287	279
		60	271	260

Examination of the data in Tables 2 and 3 showed that the presence of SO_4^{2-} ions led to a slight decrease of fluoride removal efficiency. This is probably due to a competitive adsorption effect.

Table 2. Working conditions and fluoride removal efficiency in presence of sulfate initial concentration: 5 ppm F^-, 347 ppm Cl^-, 199 ppm SO_4^-; pH=5.3; current density: 100 A/m^2

Electrolysis time / min	Cell voltage / V	Fluoride content / ppm	Fluoride removal efficiency / %	Chloride content / ppm	Sulfate content / ppm	Sulfate removal efficiency / %
15	2.9	0.97	80.6	312	149	25.1
30	2.9	0.40	92.0	294	140	29.6
45	2.9	0.21	95.8	276	142	28.6
60	2.9	0.12	97.6	259	124	37.7

Table 3. Working conditions and fluoride removal efficiency in presence of sulfate initial concentration: 5 ppm F^-, 347 ppm Cl^-, 199 ppm SO_4^-; pH=7; current density: 150 A/m^2

Electrolysis time / min	Cell voltage / V	Fluoride content / ppm	Fluoride removal efficiency / %	Chloride content / ppm	Sulfate content / ppm	Sulfate removal efficiency / %
15	4.0	0.59	88.2	301	142	28.6
30	4.2	0.28	94.4	266	133	33.2
45	4.2	0.19	96.2	245	122	38.7
60	4.2	0.06	98.8	239	119	40.2

The specific energy consumption is an important parameter in characterization of electrocoagulation performances regarding the removal of fluoride and coexisting anions from groundwater. This parameter was calculated according to equation (1) by using as working conditions: pH of 5.3, applied current density of 150 A/m^2 (1.17 A), electrolysis time of 45 minutes, cell voltage of 4.2 V, groundwater sample of 500 ml and it was of 7.4 kWh/m^3.

$$Q = U \cdot I \cdot t \cdot 10^{-3} / V \cdot 3600 \qquad (1)$$

where:

Q = specific energy consumption, kWh/m3; U = cell voltage, V; I = current intensity, A; t = electrolysis time, s; V = electrolyzed solution volume, m3

In the above conditions, the concentration of fluoride and chloride in the treated groundwater was under the threshold limits of 1.2 ppm and 250 ppm, respectively, stipulated in Romanian Law 458/2002 concerning the drinking water quality.

Conclusion

Electrocoagulation was applied to groundwater treatment for drinking water purposes and was focused on removal of fluoride and coexisting anions, chloride and sulfate. As a result, the fluoride concentration was 0.19 ppm and chloride concentration was 245 ppm in treated simulated groundwater, that are values under the limits stipulated in Romanian Law 458/2002 concerning the drinking water quality. The presence of sulfate influenced slightly fluoride removal efficiency. The results of this study showed that electrocoagulation should be considered for the development of efficient groundwater management.

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