

IMPROVEMENT OF WATER QUALITY WITH HIGH FLUORIDE CONTENT

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Abstract

The improvement of water quality with high fluoride content was carried out by precipitation of pollutant with $\text{Ca}(\text{OH})_2$ and post-treatment by electrocoagulation. The applied current densities were 100, 200 and 300 A/m^2 and the electrolysis time was 60 minutes. The fluoride concentration was lowered from 1000 mg/L to 407 mg/L after the precipitation and to 97 mg/L after the post-treatment by electrocoagulation at 300 A/m^2 . The specific energy consumption was calculated and it was in the range of 2.34 – 13.2 kWh/m^3 .

Introduction

High concentration of fluoride can be found in effluents originated from different industries such as glass, fertilizers, solar photovoltaic cells, semiconductor or metals manufacturing industries. In these effluents, the fluoride concentration may range from hundreds to thousands of ppm [1,2].

Because of these high concentrations of fluoride in the industrial effluents, it is necessary to treat them before discharge. Conventionally, precipitation with lime is used to remove high concentrations of fluoride as CaF_2 from wastewaters [3]. Experiments were also performed with magnesium salts [4] and it was found out that as precipitator they exhibited better settle ability when compared with calcium salts in fluoride precipitation.

However, the wastewaters treated by the precipitation do not meet the strict regulations requirements and post-treatment has to be done. Thus, processes like adsorption [5-8], electro dialysis [9] or coagulation [3] were able to reach this goal.

Alongside adsorption and membrane processes, electrocoagulation can be used as post-treatment of high fluoride concentration effluents and also this process exhibits some advantages from technical point of view: mechanical stirring is not necessary, reagents amount and settling time are lower than in other processes, high current efficiencies can be reached (~90%) in well-designed systems and short electrolysis time are required [10].

The aim of this paper was to remove the high concentration of fluoride from aqueous solutions envisaging the improvement of water quality by using the electrocoagulation as post-treatment.

Experimental

All reagents were of analytical grade and the solutions were prepared with distilled water. Aqueous solution of 1000 mg/L fluoride was prepared. $\text{Ca}(\text{OH})_2$ was used to remove the fluoride. The precipitate was removed by filtration and the pH of resulting solution was adjusted to 5 with HCl and it was sent to electrocoagulation.

The electrocoagulation experiments were carried out in a plexiglass 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 100, 200 and 300 A/m². Electrolysis duration was 60 minutes and samples were taken at every 10 minutes. The supporting electrolyte was 0.01 M NaCl.

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

Results and discussion

The fluoride concentration in the solution resulted after the precipitation with lime followed by filtration was 407 mg/L. This solution was post-treated by electrocoagulation and Tables 1-3 show the residual concentration of fluoride under various working conditions.

Regardless of current density the process was more effective as the electrocoagulation time increased and the best results were obtained at 60 minutes. This finding is in agreement with the theoretical aspects regarding the electrocoagulation.

Electrocoagulation is a process consisting of producing metallic hydroxide flocks within the solution by the electro-dissolution of soluble anodes, usually made of metallic iron or aluminium. Metallic cations are being generated at the anode, via the electrochemical oxidation of iron or aluminium, whereas at the cathode typically molecular H₂ evolves. The metallic ions react with the OH⁻ ions yield at cathode during the hydrogen evolution, and thus insoluble poly-oxo-hydroxides are generated. The pollutants from solution are adsorbed onto poly-oxo-hydroxides and the gas bubbles carry the pollutant to the surface solution. The increase of current density yields to higher amount of metallic hydroxide and as a consequence the adsorbed pollutant amount will be larger.

Table 1. Working conditions and fluoride residual concentration
 C_{fluoride ini}: 407 ppm; pH_{ini}=5; current density: 100 A/m²; cell voltage: 1.5 V

| Electrolysis time / min | Fluoride residual concentration / ppm | Fluoride removal efficiency / % |
|-------------------------|---------------------------------------|---------------------------------|
| 10 | 353 | 13.27 |
| 20 | 328 | 19.41 |
| 30 | 271 | 33.42 |
| 40 | 254 | 37.59 |
| 50 | 226 | 44.47 |
| 60 | 212 | 47.91 |

Table 2. Working conditions and fluoride residual concentration
 $C_{\text{fluoride ini}}: 407 \text{ ppm}; \text{pH}_{\text{ini}}=5; \text{current density: } 100 \text{ A/m}^2; \text{cell voltage: } 2.0 \text{ V}$

| Electrolysis time / min | Fluoride residual concentration / ppm | Fluoride removal efficiency / % |
|-------------------------|---------------------------------------|---------------------------------|
| 10 | 302 | 25.75 |
| 20 | 246 | 39.68 |
| 30 | 218 | 50.58 |
| 40 | 201 | 46.40 |
| 50 | 171 | 58.00 |
| 60 | 151 | 62.88 |

Table 3. Working conditions and fluoride residual concentration
 $C_{\text{fluoride ini}}: 407 \text{ ppm}; \text{pH}_{\text{ini}}=5; \text{current density: } 100 \text{ A/m}^2; \text{cell voltage: } 2.8 \text{ V}$

| Electrolysis time / min | Fluoride residual concentration / ppm | Fluoride removal efficiency / % |
|-------------------------|---------------------------------------|---------------------------------|
| 10 | 283 | 30.38 |
| 20 | 197 | 51.69 |
| 30 | 170 | 58.23 |
| 40 | 151 | 62.87 |
| 50 | 117 | 71.31 |
| 60 | 97 | 76.16 |

The specific energy consumption for 60 min of electrolysis is given in Table 4 and it was calculated according to equation 1. As it was expected the higher value was recorded for the current density of 300 A/m^2 .

$$Q = UIt \cdot 10^{-3} / V \cdot 3600 \quad (1)$$

where:

Q = specific energy consumption, kWh/m³

U = cell voltage, V

I = current intensity, A

t = electrolysis time, s

V = electrolysed solution volume, m³

Table 4. Specific energy consumption for 60 min of electrolysis

| Current density / A/m ² | Cell voltage / V | Current intensity / A | Treated groundwater / m ³ | Specific energy consumption / kWh/m ³ |
|------------------------------------|------------------|-----------------------|--------------------------------------|--|
| 100 | 1.5 | 0.78 | 0.0005 | 2.34 |
| 200 | 2.0 | 1.56 | | 6.24 |
| 300 | 2.8 | 2.35 | | 13.2 |

Conclusion

The electrocoagulation was effective for the removal of fluoride from aqueous solutions of 1000 mg/L fluoride as post-treatment stage.

The fluoride removal efficiency from an aqueous solution of 407 ppm fluoride originated from an aqueous solution of 1000 ppm fluoride after the precipitation with Ca(OH)₂ was of 47.91% at 100 A/m², 62.88 % at 200 A/m² and 76.16 % at 300 A/m².

The overall efficiency was of 78.8% at 100 A/m², 84.9 % at 200 A/m² and 90.3 % at 300 A/m².

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