



Fluoride removal from industrial wastewater using electrocoagulation and its adsorption kinetics

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ARTICLE INFO

Article history:

Received 3 November 2009

Received in revised form 25 February 2010

Accepted 28 February 2010

Available online 6 March 2010

Keywords:

Electrocoagulation

Fluoride removal

Treated industrial wastewater

Hydraulic retention time

Adsorption kinetic

ABSTRACT

Electrocoagulation (EC) process using aluminum electrodes is proposed for removing fluoride from treated industrial wastewater originated from steel industry. Effects of different operating conditions such as temperature, pH, voltage, hydraulic retention time (HRT) and number of aluminum plates between anode and cathode plates on removal efficiency are investigated. Experimental results showed that by increasing HRT, removal efficiency increases but after 5 min changes are negligible. Therefore, the total HRT required is only 5 min. The more HRT, the more electrical current is needed in order to achieve to constant voltage and temperature in system. In addition, it is found that pH value decreases from 6.91 to 4.6 during first 10 min but it increases up to 9.5 during 50 min. After treatment, the fluoride concentration was reduced from initial 4.0–6.0 mg/L to lower than 0.5 mg/L. The pH of the influent is found as a very important variable which affects fluoride removal significantly. The optimal range for the influent is 6.0–7.0 at which not only effective defluorination can be achieved, but also no pH readjustment is needed after treatment. Moreover, increasing number of aluminum plates between anode and cathode plates in bipolar system does not significantly affect fluoride removal. Finally, the kinetic analysis is done for the system which indicates that the adsorption system obeys the second-order kinetic model.

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1. Introduction

Fluoride in the environment occurs through natural presence in the earth's crust and industrial activities, specially semiconductor, electroplating, glass, steel, ceramic and fertilizers industries [1,2]. The discharge of such wastewaters lead to the fluoride contamination of surface and ground water. According to WHO standard, the optimum fluoride level in drinking water is considered to be between 0.5 and 1.0 mg/L [3,4]. US EPA recently established the effluent discharge standard of 4 mg/L for fluoride from wastewater treatment plant [5]. The effluent discharge standard of fluoride in Iran is 2 mg/L [6]. Depending on the discharge standards, a polishing step may be necessary. Various treatment technologies based on precipitation [7], ion exchange [8,9], adsorption [10,11], membrane process such as reverse osmosis [12,13], nanofiltration [14], Donnan dialysis [15] and electro dialysis [16,17] and electrochemical technology, including electrocoagu-

lation, electroflotation and electrochemical oxidation [18], have been proposed for removal of fluoride from wastewater. Some researchers [19,20] have demonstrated that EC using aluminum anodes is effective in defluorination. The combined electrocoagulation and electroflotation process is successfully applied in treating wastewater containing fluoride by Shen et al. [5]. The EC cell was a bipolar electrode having three aluminum electrodes. They reported that optimal retention time is 20 min. Moreover, higher charge loading resulted in good fluoride removal efficiency. EC has been used by Hu et al. [21] for fluoride removal wastewater from semiconductor manufacturers that contains large amounts of fluoride. They reported that such wastewater can be effectively treated using EC.

In previous studies on EC for fluoride removal, effects of using different numbers of aluminum plates in EC cell is not conducted. Moreover, polishing effluent of steel industrial wastewater for fluoride removal, which is a concerning environmental issue, is not evaluated. Besides, adsorption kinetic of the process is not addressed, especially for bipolar reactors. The objective of the present study is to examine the feasibility of using EC in fluoride removal from treated steel industrial wastewater, to determine the optimal operational conditions. In the first part, fundamentals of EC process are presented. Second, experimental methods are reported. Then, effects of different operational conditions consist of numbers of aluminum plates in EC cell, pH, temperature and charges load-

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ing are evaluated. Finally the adsorption kinetics of the process is analyzed.

2. Materials and methods

2.1. Electrocoagulation process

Electrocoagulation (EC) has been widely used for treating urban wastewater [22], oil wastes [23], dyes [24], suspended particles [25], chemical and mechanical polishing waste [26], organic contaminants from landfill leachates [27], defluoridation [28] and heavy metal containing solutions [29]. This process consists of creating metallic hydroxide flocs within the wastewater by electro dissolution of soluble anodes, usually constituted by iron or aluminum. This method has been practiced for most of the 20th century with limited success. Recently, there has been renewed interest in the use of electrocoagulation owing to the increase in environmental restrictions on effluent wastewater. It was found that anodized aluminum is more effective than the aluminum ion introduced in the form of aluminum sulfate solution. However, preliminary experience in laboratory showed that the hydrogen gas produced at the aluminum cathode in an electrocoagulation cell was not so fine that could float only about 60% of the total solids.

In the electrocoagulation unit, some aluminum plates placed between two aluminum electrodes having opposite charges will undergo anodic reactions on the positive side while on the negative side cathodic reaction takes place. When current passes through an electrochemical reactor, cathodic overpotential and ohmic potential drop of the solution. The anode overpotential includes the activation overpotential and concentration overpotential, as well as the possible passive overpotential resulted from the passive film at the anode surface, while the cathode overpotential is principally composed of the activation overpotential and concentration overpotential. When aluminum is used as electrode material, three major reactions occur in electrochemical reactor.

The oxidation reaction at the anode,



The reduction reaction at the cathode,



The hydrolysis reaction,



The hydrolysis and polymerization of Al^{3+} under appropriate pH conditions subsequently give rise to the formation of such species as $\text{Al}(\text{OH})_2^+$, $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}(\text{OH})_3$ and charged hydroxo cationic complexes which can effectively remove pollutants by adsorption to produce charge neutralization, and by enmeshment in a precipitate. Other reactions could be observed at the cathode surface and bring about the precipitation of the carbonate salt.



2.2. Experimental method

Experiments are conducted in a bipolar batch reactor with 2 Al electrodes and variable number of aluminum plates. A constant current is maintained using a potentiostat in intensiostat mode. Magnetic stirring at 400 rpm is maintained a homogenous solution in the batch reactor which contains 1.5 L of wastewater sample. In this investigation, samples from treated steel industrial wastewater are used, which is taken from the Mobarake Steel Complex (MSC)

Table 1

The characteristics of treated steel industrial wastewater from Mobarake Steel Complex.

Parameter	F ⁻	Cl ⁻	SO ₄ ²⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	BOD	COD
Concentration (mg/L)	5	219.6	180	135.4	4.9	16.6	56.1	8.5	35

located in Esfahan, Iran. Around 1500 m³/h of fluoride-containing wastewater, with fluoride concentration of 5–35 mg/L is generated by the rinsing and cleaning operations in a found process. Table 1 summarizes the characteristics of the treated industrial wastewater. The concentration of fluoride is normally 5 mg/L and the initial pH is 7. Experiments are carried out, at laboratory scale, in cell equipped by 2 aluminum electrodes (anode and cathode with 150 cm² area) in addition with some extra aluminum plates in order to improving coagulation. In other words, placing aluminum plates could result in producing more coagulant precursors which improves the treatment process. In each run, 1.5 L treated wastewater is fed to the electrolytic cell. At the end of the each experiment, the solution is filtered before analysis. The membrane filter used in this method is 0.2 μm. Fluoride is measured using Diar 5000 (SPANDS reagent) and pH of each sample after each runs is determined by a 720 A pH meter. The SPANDS method for fluoride determination involves the reaction of fluoride with a red zirconium-dye solution. The fluoride combines with part of the zirconium to the fluoride concentration. This method is accepted by the EPA for NPDES and NPDWR reporting purpose when the samples have been distilled [30]. The reported concentration for each sample is the average of 3 times measurement.

3. Results and discussion

3.1. Effect of HRT on fluoride removal in monopolar reactor

Electrocoagulation test is first performed at fixed potential of 30 V and at difference electrolysis times. Experiments are carried out in cell equipped with two Al electrodes (anode and cathode). The variation of fluoride with electrolysis time is shown in Fig. 1. Fluoride decreases with increasing electrolysis time and after 5 min fluoride concentration decreases from 4.84 to 0.48 mg/L with a removal efficiency of 90%. As shown in Fig. 1, fluoride removal increases with time until fifth minute when the removal of fluoride reached a plateau. Two stages can clearly be identified—namely, a reactive and a stabilizing stage. The rate of fluoride reduction decreases with time and eventually the fluoride becomes near zero.

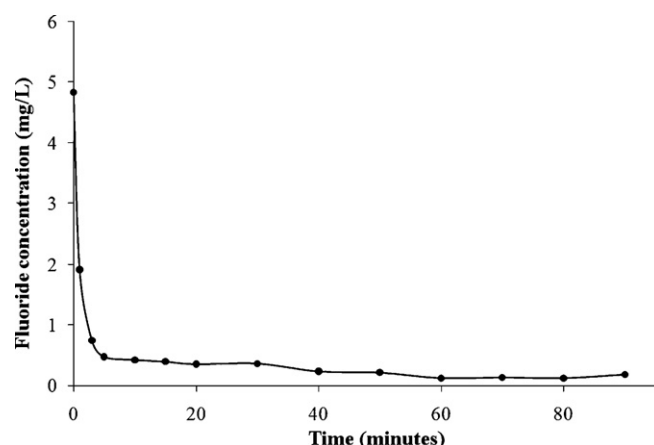


Fig. 1. Evaluation of fluoride removal with electrolysis time at $E = 30$ V.

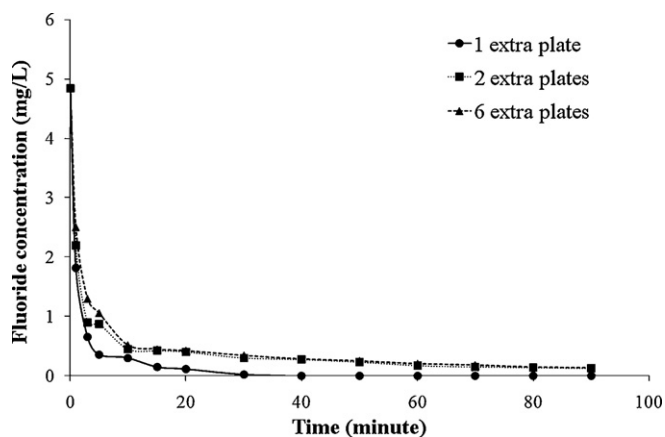


Fig. 2. Effect of varying number of extra plates on fluoride removal.

3.2. Effect of HRT on fluoride removal in bipolar reactor

Experiments are carried out in cell equipped with two Al electrodes (anode and cathode) and a variable number of Al plates that were located between two electrodes and performed at fixed potential of 30 V and at difference electrolysis times. The distance of between each plate was 1.5 cm. The variation of fluoride with electrolysis time and the effect of increasing number of plates between electrodes plates are shown in Fig. 2.

Fig. 2 shows that increasing number of aluminum plates in reactor increases the fluoride removal. When one extra plate is placed between electrodes, the final fluoride concentration after 5 min reaches to 0.35 mg/L. While, in monopolar reactor the final fluoride concentration after 5 min is 0.48 mg/L. Therefore, the fluoride removal efficiency increases from 90% to 93% by increasing number of aluminum plates in reactor. But increasing number of extra plates to 2 and 6 has negative effect on removal efficiency. After placing 2 and 6 plates in reactor, the final fluoride concentration after 5 min reaches to 0.87 and 1.06 mg/L, respectively. In other words, the fluoride removal efficiency decreases to 82.6% and 78.8% after placing 2 and 6 plates in reactor, respectively. Consequently, in operation of EC reactors, a special attention should be pay to optimum number of extra aluminum plates in order to optimizing removal efficiency. Because adding more plates may has negative effect on fluoride removal. This phenomenon could be explained regarding the fact that placing aluminum plates could result in producing more coagulant precursors and therefore, more coagulant is generated. Adding more plates results in increasing in resistance of solution and according to the Ohm rule, electric current is reduced. Therefore, although the active area increases, the concentration of coagulant precursors decreases.

3.3. Effect of electrocoagulation time on pH

The pH of a solution is one of the most important parameters that govern the removal of fluoride in electrocoagulation and in the performance of many electrochemical process and chemical coagulation operation [19]. Controlling the pH of the solution, however, is very difficult during the electrocoagulation process because the defluoridation reaction changes the pH. Moreover, controlling the initial pH in the electrocoagulation system is not very useful for varying the final pH. Because of the buffer capacity of aluminum hydroxide, the final pH and residual fluoride concentration did not change very much in the range of initial pH that is 4–8 in the electrocoagulation process [28]. Therefore, changes in pH value is measured during the test in different times and also, with different number of plates which is shown in Fig. 3a. It could be seen that

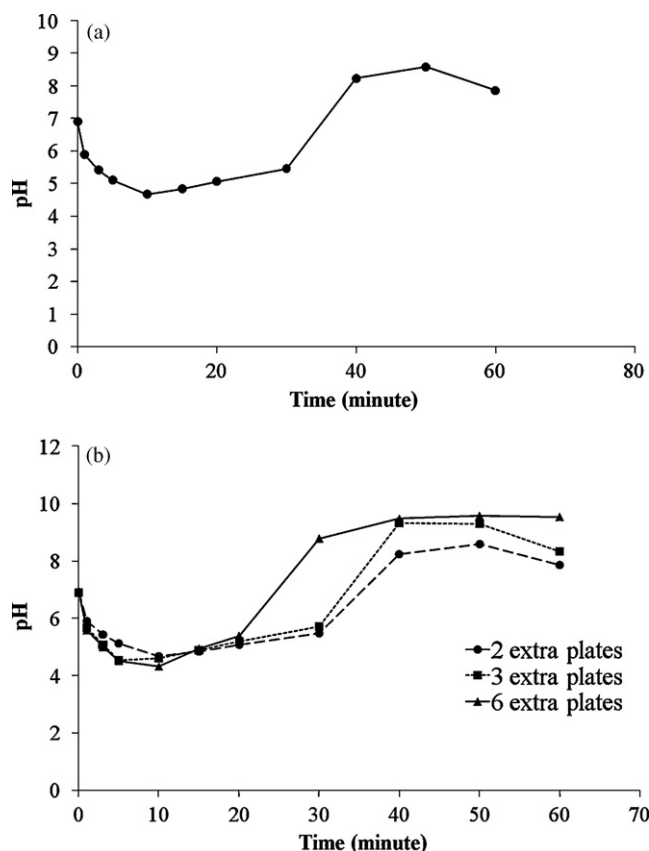


Fig. 3. (a) Variations of pH in monopolar EC reactor. (b) Variations of pH in bipolar EC reactor.

in both monopolar and bipolar cells, pH decreases from 7 to 4.68 in first 15 min and then increases until 40th minute. After 40 min the pH reaches to 9.48 and remains relatively constant. Main reasons of pH decreasing in first 15 min are alkalinity consumption by coagulant precursors and also, H^+ producing according to reactions (1)–(3).

In acidic medium, CO_2 is over saturated and released from the wastewater due to H_2 and O_2 bubble 'purge', which causes a pH increase. In addition, the chemical dissolution of Al (reaction (1)) will consume H^+ and gives rise to the pH. As shown in Fig. 3b, by increasing number of plates, the time of reaching to stable pH decreases but more fluctuations occur.

3.4. Effect of voltage on fluoride removal

Operating voltage and electric current are critical in batch electrocoagulation. According to Faraday's law, the amount of aluminum dissolved electrochemically is proportional to charge loadings. When 1 F (26.8 Ah) passes through the electric circuit, 0.0224 Nm^3 hydrogen gas will be evolved, which is much greater than the volume of gas released in traditional DAF. Consequently, increasing current density will give rise to an increase in charge loading and leading to increased removal of pollutants. Furthermore, better collection efficiencies could be reached during electroflotation by obtaining smaller bubbles with increasing current density [18].

Voltage is the only operational parameter which can be controlled directly because considering reactions (4)–(6), current will change with time. In other word, due to increase of ohmic resistance according to mentioned reactions, electric current would change. Moreover, generation of salt sediments like carbonate salts on aluminum plate could affect the electrical current.

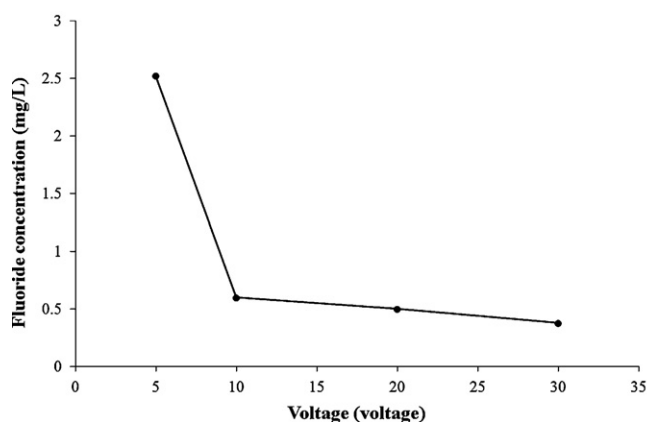


Fig. 4. Effect of voltage on fluoride removal.

In this system electrode spacing is fixed and voltage is a continuous supply. Voltage directly determines both coagulant dosage and bubble generation rates, as well as strongly influencing both solution mixing and mass transfer at the electrodes. Thus a set of experiments is carried out to quantify the impact of operating voltage on reactor performance. Fig. 4 shows the fluoride removal as a function of voltage. It is found that the removal of fluoride was increased with increasing voltage. In terms of evaluating batch electrocoagulation as a candidate technology for providing low-cost, low maintenance local wastewater treatment, this set of experiments clearly demonstrated two important results. First, that operating current density is the key operational parameter, affecting not only the system's response time but also strongly influencing the dominant pollutant separation mode. Second, these results indicate that running the reactor at the highest allowable current density may not be the most efficient mode of operation. For any specific application, the optimal current density will invariably involve a trade-off between operational costs and efficient use of the introduced coagulant. Moreover, changes in electrical current with fixed voltage are evaluated. With voltage of 5, 10, 20 and 30 V, the current would be 0.15, 0.49, 0.81 and 1.32 A, respectively.

3.5. Adsorption kinetics

The adsorption kinetic data of fluoride are analyzed using Lagergran rate equation. The first-order Lagergran model is [31]:

$$\frac{dq}{dt} = k_1(q_e - q) \quad (7)$$

where q is the amount of fluoride adsorbed on the adsorbent at time t (min), q_e is the amount of fluoride adsorbed at equilibrium and k_1 (min^{-1}) is the rate constant of first-order adsorption. The integrated form of the above equation is

$$\log(q_e - q) = \log(q_e) - \frac{k_1 t}{2.303} \quad (8)$$

The q_e and rate constant (k_1) were calculated from the slope of the plots of $\log(q_e - q)$ versus time (t). A straight line is obtained from the plots suggests the applicability of this kinetic model. It was found that the calculated q_e values are not compatible with the experimental values (figure not shown here). So the adsorption does not obey the first-order kinetics adsorption [32].

The second-order kinetic model is expressed as:

$$\frac{dq}{dt} = k_1(q_e - q) \quad (9)$$

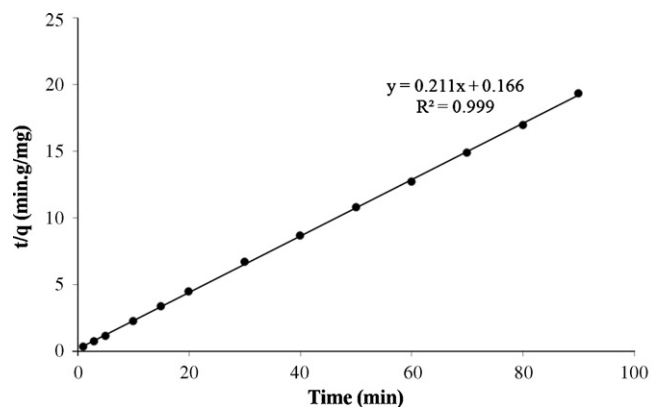


Fig. 5. Second-order kinetic model plot of monopolar reactor with electrolysis time at $E=30$ V.

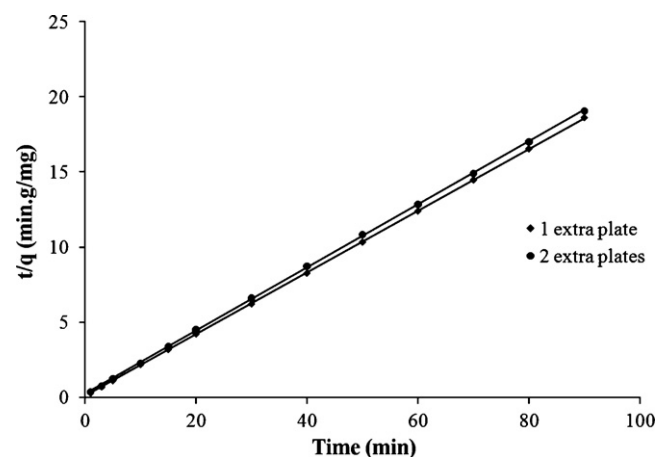


Fig. 6. Second-order kinetic model plot of bipolar reactor with electrolysis time at $E=30$ V.

where k_2 is the rate constant of the second-order adsorption. The integrated form of Eq. (7) is

$$\frac{1}{q_e - q} = \frac{1}{q_e} + k_2 t \quad (10)$$

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (11)$$

The plots t/q versus time (t) (Figs. 5 and 6) show the straight lines. The second-order kinetic values of q_e and k_2 are calculated from the slope and intercept of these plots. The correlation coefficient for the second-order kinetic model obtained in monopolar and bipolar reactor studies are above 0.99. Table 2 demonstrates the computed result obtained from the second-order kinetic model. These results indicate that the adsorption system belongs to the second-order kinetic model.

Table 2
Comparison between calculated q_e for different reactors in second-order adsorption isotherm at $E=30$ V.

Kind of reactor	q_e calculated (mg)	k_2 (g/(mg min))	R^2
Monopolar reactor	4.739	0.268	0.99
Bipolar reactor			
1 extra plate	4.878	0.396	1
2 extra plate	4.76	0.195	0.999
6 extra plate	4.76	0.161	0.999

4. Conclusion

In this research, performance of a parallel-plate electrocoagulation process with aluminum electrodes is investigated for the removal of fluoride from treated industrial wastewater originated from steel industry. Effect of various parameters like pH, voltage, hydraulic retention time (HRT) and number of aluminum plates between anode and cathode are studied in detail. Electrocoagulation is carried out for initial fluoride concentration 4.0–6.0 mg/L and satisfactorily, after 5 min 93% removal is obtained. The adsorption kinetic data of fluoride are analyzed using Lagergran rate equation. The adsorption process follows second-order kinetics.

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