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Removal of copper and fluoride from wastewater by the coupling of electrocoagulation, fluidized bed and micro-electrolysis (EC/FB/ME) process

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Abstract: Copper and fluoride ions were removed from wastewater by the coupling of electrocoagulation, fluidized bed and micro-electrolysis (EC/FB/ME) process. The results indicate that the use of aluminum electrode for simultaneous removal of copper and fluoride ions is better than iron electrode. By the orthogonal experiments study of the main factors influencing the efficiency of the treatment process, the best control parameters of this process were achieved in four aluminum electrodes, an initial pH of 5.0, a hydraulic retention time of 30 minutes, an applied voltage of 5V, a mass of iron-carbon (Fe/C) of 45g and the particle diameter of Fe/C of 20-27 mesh. With these conditions and the initial concentration of ions of 50mg/L, the residual concentration of copper and fluoride are 0.205 mg/L and 2.936 mg/L, respectively. The EC/FB/ME process is suitable for treatment of wastewater that fluoride concentration is less than 50 mg/L and copper concentration is less than 200 mg/L. This process was successfully applied to the treatment of a smelting wastewater sample.

Keywords: Electrocoagulation, Micro-Electrolysis, Iron Electrode, Aluminum Electrode, Copper and Fluoride Ions, Fluidized Bed

1. Introduction

Industrial effluents from electroplating, metallurgy and mining contain high concentration of fluoride, lead, zinc and copper, etc. The wastewater treatment methods such as biological method, membrane method, adsorption method are unsuitable for treating large amounts of wastewater with high concentration of heavy metal and fluoride ions. Currently, the most popular method for treating of heavy metal and fluoride ions is precipitation method by alkaline solutions. However, the treated wastewater by this method has some disadvantages such as deposition of coagulants is slow, the residual concentration of heavy metal ions is usually larger than 1 mg/L and fluoride removal efficiency is low, etc [1]. Thus, the study of a new method for simultaneous removal of heavy metal and fluoride ions from wastewater is necessary.

In this paper, the use of EC/FB/ME process for simultaneous removal of copper and fluoride ions from wastewater was studied. This process is the simultaneous combination of electrocoagulation, fluidized bed and micro-electrolysis. Where the electrocoagulation method used iron electrodes and aluminum electrodes. The micro-electrolysis method used particles of iron-carbon (Fe/C). The fluidized bed method was used to provide oxygen for the treatment system and prevent the clumping of Fe/C, therefore, reduce the passivation problem of the particles of Fe/C. The mechanism of EC/FB/ME process is summarized as follows as [2-4]:

* At the anode surface: The possible reactions that may occur on the anode surface (including iron or aluminum anode and iron of Fe/C) are metal dissolution and oxygen evolution. The half-cell reactions may be expressed as:

$$Al \rightarrow Al^{3+} + 3e^-,\ E^0(Al^{3+}/Al) = -1.66V \quad (1)$$

$$Fe \rightarrow Fe^{2+} + 2e^-,\ E^0(Fe^{2+}/Fe) = -0.44V \quad (2)$$

$$2H_2O \rightarrow O_2\uparrow + 4H^+ + 4e^-,\ E^0(O_2/H_2O) = 1.23V \quad (3)$$

$$2OH^- \rightarrow O_2\uparrow + 2H^+ + 4e^-,\ E^0(O_2/OH^-) = 0.40V \quad (4)$$

* At the cathode surface: including iron or aluminum

cathode and carbon of Fe/C. The half-cell reactions can be represented as reduction in the cathode:

$$2H^+ + 2e^- \rightarrow H_2\uparrow \text{ (acidic), } E^0(2H^+/H_2)=0.00V \quad (5)$$

$$2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^- \text{ (neutral to alkaline), } E^0(2H^+/H_2O)= - 0.83V \quad (6)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \text{ (acidic), } E^0(O_2/H_2O)=1.23V \quad (7)$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \text{ (neutral to alkaline), } E^0(O_2/OH^-)=0.40V \quad (8)$$

$$Cu^{2+} + 2e^- \rightarrow Cu\downarrow \text{, } E^0(Cu^{2+}/ Cu) = 0.340V \quad (9)$$

* At the solution: oxidation of Fe^{2+} generates Fe^{3+}.

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \text{ (acidic)} \quad (10)$$

$$4Fe^{2+} + O_2 + 2H_2O \rightarrow 4Fe^{3+} + 4OH^- \text{ (neutral to alkaline)} \quad (11)$$

Fe^{2+}, Fe^{3+} and Al^{3+} react with H_2O and OH^- group to generate coagulants in the wastewater such as $Al(OH)_3$, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Fe(OH)_2$, $Fe(OH)_3$, $Fe(OH)_4^-$, etc. These coagulants are co-precipitation and adsorption with the heavy metal and fluoride ions. So, they separate heavy metal and fluoride ions from wastewater.

Recently, the electrocoagulation method and the micro-electrolysis method are widely used in wastewater treatment. Electrocoagulation has been successfully performed for decolorization treatment of dyes, remediation of the dye-house wastewaters [5], treatment of oil wastes [6], heavy metal bearing effluents [7], etc. The micro-electrolysis method has been successfully performed for improving the biodegradability before the bioprocess treatment [4], treatment of lead and zinc smelting wastewater [8], treatment of electroplating wastewater [9], etc. However, the disadvantages of electrocoagulation are large energy consumption and many sludges. The disadvantages of micro-electrolysis are speed slow, low efficiency, etc. Therefore, the study of a new process with the combination of electrocoagulation, fluidized bed and micro-electrolysis will promote the advantages and reduce disadvantages of each method.

2. Materials and methods

2.1. Materials

$CuSO_4.5H_2O$, NaF, HCl, H_2SO_4, HNO_3, NaOH, KCl are analytical grade (Merck). Specifications of iron and aluminum electrodes are: long 28cm, wide 4.7cm and thick 1mm. The particle of Fe/C bought at Weifang Yan Wal Yun Pu environmental technology company, China.

The actual wastewater was obtained from a smelting unit at Mengzi, Yunnan, China.

The equipments were used in the experiment include: self-made kit as Figure 1, water velocity meter LZB-25, water pump AP 1600, *atomic absorption spectroscopy* AA240FS, machine transforms from alternating current to direct KGF50A/50V, and other equipments.

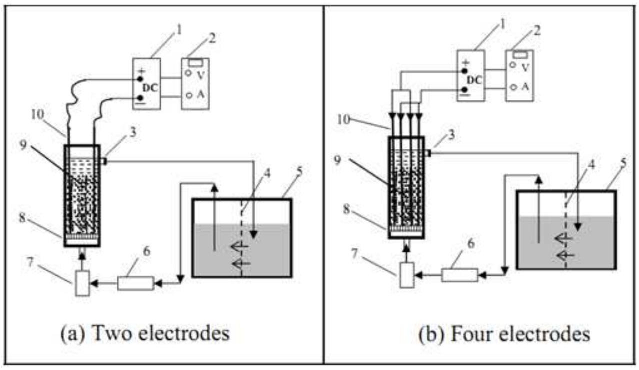

Figure 1. *Schematic diagram of EC/FB/ME process*

(1 - DC power supply, 2 - adjustment of voltage, 3 - water outlet, 4 – bulkhead, 5 - wastewater tank, 6 - water pump, 7 - adjustment of wastewater speed, 8 - EC/FB/ME reactor, 9 - Fe/C, 10 - electrode)

Where: the volume of wastewater tank was 3.5 liters. The volume of EC/FB/ME reactor was 0.66 liters. The electrocoagulation cell was a monopolar electrode having two electrodes (in Figure 1a) and four electrodes (in Figure 1b). The net spacing between two electrodes was 4.5 cm (in Figure 1a) and 1.4cm (in Figure 1b). The particles of Fe/C are put in the net spacing between electrodes.

2.2. Methods

The concentration of heavy metal ions was determined by an *atomic absorption spectroscopy*. Fluoride concentration was determined by using the ionometric standard method with a fluoride selective electrode [10]. Energy consumption was calculated from equation following [11]:

$$P = U \times I \times t \quad (12)$$

Where P - energy consumption (Wh); U - applied voltage (V); I - current intensity (A); t - time (hour).

By the orthogonal experiments study of the main factors influencing the efficiency of the treatment process, the factors and levels of experiments are shown in Table 1 and Table 2.

Table 1*. Arrangement of orthogonal experiment L_{16} $(4^5)^*$*

Level	Factor				
	A	B	C	D	E
1	3	45	75	5	14-17
2	4	60	100	10	18-19
3	5	75	125	15	20-27
4	6	90	150	20	28-34

*L_{16} (4^5) means 5 factors with 4 levels.

Where: A - initial pH, B - hydraulic retention time (minute), C - mass of Fe/C (g), D – applied voltage (V) and E - particle diameter of Fe/C (mesh). Other factors of the experiment are fixed such as distance of two electrodes of 4.5 cm, wastewater speed of 260 liters/hour, initial concentration of copper and fluoride ion of 50 mg/L.

Table 2. *Arrangement of orthogonal experiment $L_9\ (3^3)^{**}$*

Level	Factor		
	L	M	N
1	20	30	3
2	30	45	5
3	40	60	7

**$L_9\ (3^3)$ means 3 factors with 3 levels.

Where: L - hydraulic retention time (minute), M - mass of Fe/C (g), N - applied voltage (V). Other factors of the experiment are fixed such as distance of two electrodes of 1.4cm, wastewater speed of 260 liters/hour, particle diameter of Fe/C of 20-27 (mesh), initial pH of 5.0, KCl of 0.5g/L, initial concentrations of copper and fluoride ion of 50 mg/L.

The experiments used aluminum electrodes which are added KCl of 0.5 g/L. Because the chloride salt added to the solution can prevent the formation of the alumina layer on the anode and therefore reduce the passivation problem of the electrode [12].

3. Results and Discussion

3.1. Using EC/FB/ME Process with Two Electrodes

In this section, effect of experimental factors on energy consumption and residual concentration of ions are examined by orthogonal experiments. The experiments are conducted based on Table 1 and orthogonal design of $L_{16}\ (4^5)$ [4], and then use the variance analysis method to analyze results. Figure 2, Figure 3 and Figure 4 showed that experimental result:

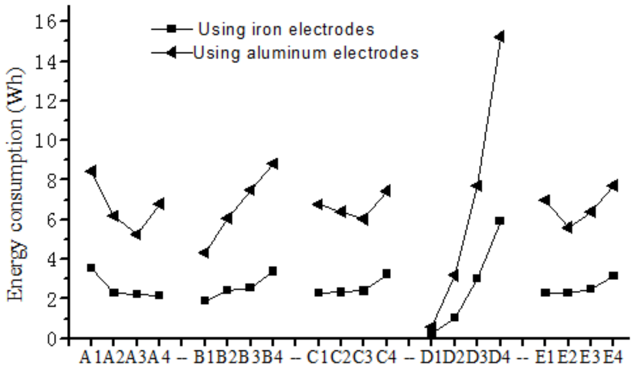

Figure 2. *Relationship between experimental conditions and energy consumption*

From Figure 2 noticed: Effect of factor D on energy consumption is largest. Therefore, we must be special attention to the factor D in choosing of the optimal condition for simultaneous removal of copper and fluoride ions. Energy consumption by the use of aluminum electrode is higher than iron electrode. Because the experiments used aluminum electrodes which are added KCl, so the electrical conductivity of solutions is increased.

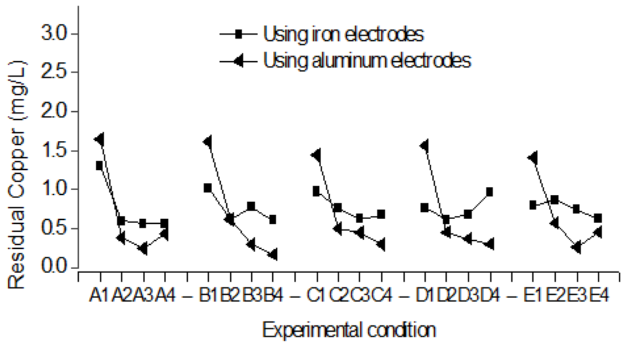

Figure 3. *The relationship between experimental conditions and residual concentration of copper*

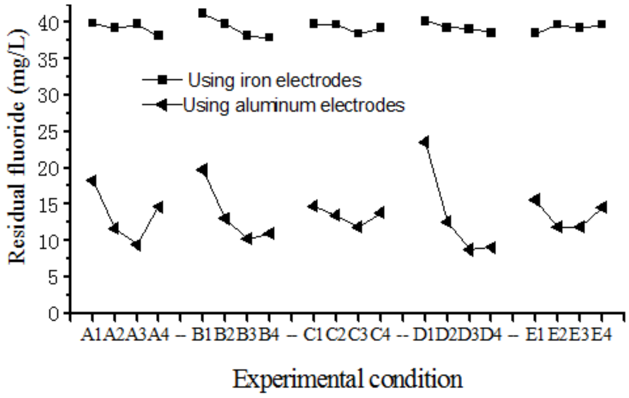

Figure 4. *The relationship between experimental conditions and residual concentration of fluoride*

From Figure 3 noticed: The EC/FB/ME process treated copper ion from wastewater with removal efficiency very high. All of the Cu^{2+} concentration in the treated wastewater is less than 2 mg/L. In the same experimental condition of level 2, 3 and 4, the copper removal efficiency of aluminum electrodes is better than iron electrodes.

From Figure 4 noticed: The EC/FB/ME process using iron electrodes treated fluoride from wastewater with removal efficiency very low. But when using aluminum electrodes treated fluoride with removal efficiency very high.

The optimal condition for simultaneous removal of copper and fluoride from wastewater to achieve high performance and low energy consumption are chosen based on Figure 2, Figure 3 and Figure 4. The result indicated that the use of aluminum electrode is better than iron electrode. The best control parameters of EC/FB/ME process were achieved in initial pH of 5.0, a hydraulic retention time of 75 minutes, a mass of Fe/C of 125g, an applied voltage of 15V and the particle diameter of Fe/C of 20-27 mesh, respectively.

With this optimal condition and the initial concentration of ions of 50mg/L, the residual concentration of copper and fluoride ions in the treated wastewater is 0.030mg/L and 7.655mg/L, respectively. Thus, copper ion was removed from wastewater with removal efficiency very high. But fluoride removal efficiency is not high. To overcome this weak point, the next experiment was the use of EC/FB/ME process with four aluminum electrodes (see Figure 1b).

3.2. Using EC/FB/ME Process with Four Aluminum Electrodes

In this section, effect of experimental factors on energy consumption and residual concentration of ions are examined by orthogonal experiments. The experiments are conducted based on Table 2 and orthogonal design of L_9 (3^3) [13], and then use the variance analysis method to analyze results. Experimental results are shown in Figure 5 and Figure 6.

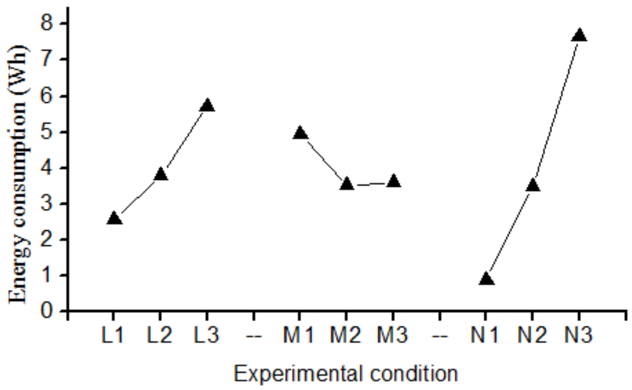

Figure 5. *Relationship between experimental conditions and energy consumption*

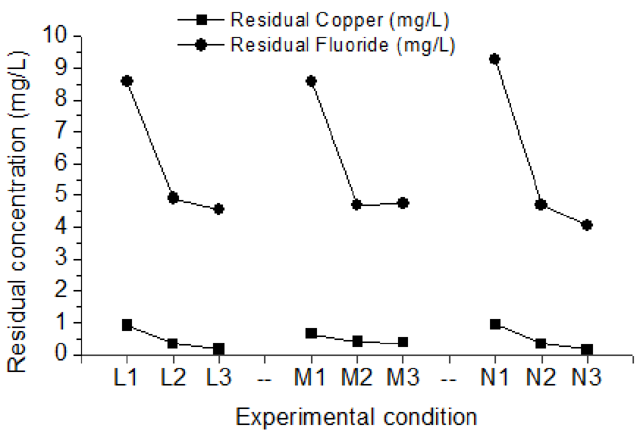

Figure 6. *The relationship between experimental conditions and residual concentration of Cu^{2+} and F^-*

From Figure 6 noticed: copper removal efficiency is very high. All of the Cu^{2+} concentration in the treated wastewater is less than 1 mg/L. In the same experimental condition, the removal efficiency of Cu^{2+} is better than fluoride. The optimal condition for simultaneous removal of copper and fluoride is $L_3M_3N_3$ or $L_3M_2N_3$.

From Figure 5 and Figure 6 noticed: energy consumption of L_2 and N_2 is much smaller than L_3 and N_3. But the ions removal efficiency of L_2 and N_2 is not much smaller than L_3 and N_3. In addition, when the use of factor N_3 is aluminum electrodes very hot and therefore is not safe for experimental equipments. Thus, the optimal condition for simultaneous removal of copper and fluoride from wastewater to achieve high performance and low energy consumption is $L_2M_2N_2$ with a hydraulic retention time of 30 minutes, a mass of Fe/C of 45g and an applied voltage of 5V, respectively.

With this optimal condition and the initial concentration of ions of 50mg/L, the residual concentration of copper and fluoride ions in the treated wastewater is 0.205mg/L and 2.936mg/L, respectively.

Thus, the EC/FB/ME process with four aluminum electrodes for fluoride removal efficiency is much better than EC/FB/ME process with two aluminum electrodes.

3.3. Current Efficiency

The current efficiency is defined as the ratio of the actual electrode consumption to the theoretical value. It is an important parameter in the electrocoagulation process because it affects the lifetime of the electrode. So, the both values, theoretical and experimental, consumed electrode are determined. The first one is calculated using Faraday's law [14, 15]:

$$m_{Fe} = AIt / nF \tag{13}$$

Where A - molecular weight (g/mol); I - current intensity (A); t - time (s); F - Faraday's constant (96500 C); n - the number of electrons corresponding to aluminum oxidation.

The experiment for simultaneous removal of copper and fluoride ions from wastewater are conducted in four aluminum electrodes, initial pH of 5.0, a hydraulic retention time of 30 minutes, a mass of Fe/C of 45g, an applied voltage of 5V and the particle diameter of Fe/C of 20-27mesh, the initial concentration of copper and fluoride ion of 50 mg/L. The result is shown that the current efficiency was 174.45%. This value is in the middle of the range of 120%- 220% reported in a recent study [16]. Thus, the actual aluminum electrode consumption is much larger than faradaic aluminum dosing. Because besides the electrochemical corrosion of the anode, also happened chemical corrosion of both the anode and cathode [2]. This is beneficial because it reduces wastewater treatment time.

3.4. Effect of Initial Concentration

To test the effect of initial concentration of copper and fluoride on the ions removal efficiency of the EC/FB/ME process, a set of experiments was conducted with three different solutions containing same concentrations of 10, 50 and 200 mg/L of each ion respectively. These experiments were conducted in four aluminum electrodes, an initial pH of 5.0, a hydraulic retention time of 30 minutes, a mass of Fe/C of 45g, an applied voltage of 5V and the particle diameter of Fe/C of 20-27 mesh. The experimental results are shown in Figure 7.

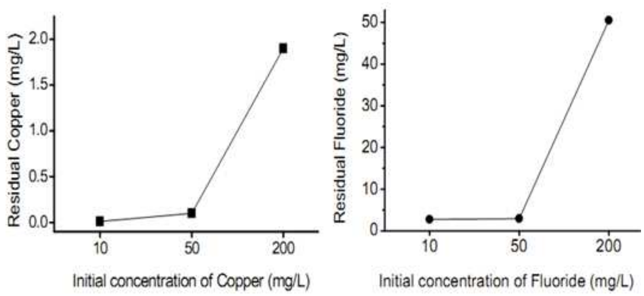

Figure 7. *Effect of initial concentration of copper and fluoride on removal efficiency.*

From Figure 7 noticed: if the initial concentration of copper is less than 50 mg/L, the residual concentration of copper in the treated wastewater will be less than 0.5 mg/L. If the initial concentration of copper is 200 mg/L, the residual concentration of copper in the treated wastewater will be 2.0mg/L. Thus, this EC/FB/ME process is suitable for treatment of wastewater that copper concentration is less than 200 mg/L.

Figure 7 was also shown that, this EC/FB/ME process is suitable for treatment of wastewater that fluoride concentration is less than 50 mg/L.

3.5. Treatment of Actual Wastewater

The applicability of the EC/FB/ME process for actual wastewater was validated by treating a smelting wastewater sample. The main characteristics of the effluent sample before and after treatment are shown in Table 3.

Table 3. *Characteristics of the smelting wastewater before and after treatment by the EC/FB/ME process.*

Parameter	Before treatment	After treatment	Removal rate (%)
pH	5.00	6.11	
Cu (mg/L)	4.680	< 0.001	100
F (mg/L)	22.177	3.833	82.7
Pb (mg/L)	3.046	< 0.001	100
As (mg/L)	1.302	0.004	99.7

From table 3 found that, the residual concentrations of heavy metal and fluoride are lower than the emission standards of pollutants. Thus, the EC/FB/ME process is a safe, reliable and efficient method for removal of heavy metals and fluoride from smelting wastewaters.

3.6. Analysis of Mechanism

In the EC/FB/ME process, the removal of copper ion depends on redox and adsorption. Copper ion, beyond hydroxide precipitation and absorption on the $Al(OH)_3$, $Al(OH)^{2+}$, $Al(OH)_2^{+}$, $Fe(OH)_2$, $Fe(OH)_3$, $Fe(OH)_4^-$ flocs, is also partially removed by direct electroreduction at the cathode or by electroless deposition according to the reaction as follows as [11, 17]:

$$3Cu^{2+} + 2Al \rightarrow 2Al^{3+} + 3Cu\downarrow \quad (14)$$

$$Cu^{2+} + Fe \rightarrow Fe^{2+} + Cu\downarrow \quad (15)$$

Cu generated from the reaction was adsorbed on the carbon surface of Fe/C and the aluminum cathode surface or deposited with coagulants; thus, it can be removed from wastewater.

The mechanism of the fluoride removal process was a chemical adsorption process with F^- replacing the OH^- group from the $Al_n(OH)_{3n}$ and $Fe_n(OH)_{3n}$ flocs. Because the affinity between fluoride and $Fe(OH)_3$ is much smaller than that of $Al(OH)_3$ [18, 19], so fluoride removal efficiency of the iron electrode is much smaller than the aluminum electrode. Fluoride ions and hydroxide ions can clearly co-precipitate with Al^{3+} ions to form $Al_nF_m(OH)_{3n-m}$ [18]:

$$nAl^{3+} + (3n-m)OH^- + mF^- \rightarrow Al_nF_m(OH)_{3n-m}\downarrow \quad (16)$$

However, the fluoride ions in the precipitate are very easily substituted for hydroxide ions.

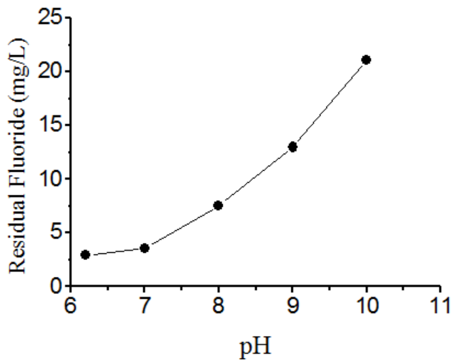

Figure 8. *Effect of pH on residual concentration of fluoride*

(This experiment is conducted at the optimal condition of the EC/FB/ME process for removal of copper and fluoride from wastewater, and then used NaOH to adjust the solution pH value, initial concentration of fluoride =50 mg/L).

Figure 8 was shown that, when the solution pH value is lager than 7 , OH^- group easily replaces F^- from the $Al_nF_m(OH)_{3n-m}$ flocs, the reaction as follows as:

$$Al_nF_m(OH)_{3n-m}\downarrow + xOH^- \rightarrow Al_nF_{m-x}(OH)_{3n-m+x}\downarrow + xF^- \quad (17)$$

3.7. Comparison of EC/FB/ME Process and Electrocoagulation (EC) Process

A test was conducted to compare the EC/FB/ME process and EC process at the same of experimental conditions, such as using four aluminum electrodes, an initial pH of 5.0, a hydraulic retention time of 30 minutes, an applied voltage of 5V, the initial concentration of Cu^{2+} and F^- of 50mg/L, KCl 0.5g/L, etc. The experimental result was shown in Figure 9.

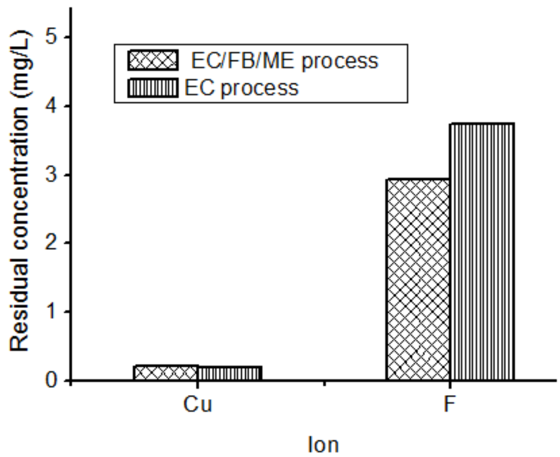

Figure 9. *Comparison of residual concentration of Cu^{2+} and F^- between the EC/FB/ME process and EC process.*

Figure 9 was shown that, the EC/FB/ME process significantly outperformed EC process for fluoride removal. But copper removal efficiency of the two processes is equivalent. The cause can be explained as follows as: Fe^{3+} is good coagulants. It is frequently used as co-coagulant with aluminum salt. Fengsheng, et al [18] have demonstrated that 50mg/L of iron ion in the EC process gives the best fluoride removal. Too low or high Fe^{3+} concentration are not good for fluoride removal of the EC process. In this EC/FB/ME process,

Fe^{3+} concentration is 67mg/L, so fluoride removal efficiency is better than EC process. But too high Fe^{3+} concentration may lead to the precipitation of $Fe(OH)_3$ onto the $Al(OH)_3$ flocs surface, the $Fe(OH)_3$ precipitates blind the $Al(OH)_3$ flocs [18-19].

Recently, some of scientific literatures reported that the EC process performed better than CC (chemical coagulation) process in defluoridation efficiency [20-23]. Thus, the EC/FB/ME process is the best suitable for treatment of fluoride ion in wastewater.

4. Conclusion

The optimal condition of the EC/FB/ME process for simultaneous removal of copper and fluoride from wastewater was achieved in four aluminum electrodes, an initial pH of 5.0, a hydraulic retention time of 30 minutes, a mass of Fe/C of 45g, an applied voltage of 5V and the particle diameter of Fe/C of 20-27mesh. This EC/FB/ME process is suitable for treatment of wastewater that fluoride concentration is less than 50 mg/L and copper concentration is less than 200 mg/L. The effluent wastewater by this process is very clear and its quality exceeds the direct discharge standard.

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