Simultaneous removal of Ni(II) and fluoride from a real flue gas desulfurization wastewater by electrocoagulation using Fe/C/Al electrode

Shinian Liu, Xiaokun Ye, Kuang He, Yuancai Chen and Yongyou Hu

ABSTRACT

Large amounts of anions and heavy metals coexist in flue gas desulfurization (FGD) wastewater originating from coal-fired power plants, which cause serious environmental pollution. Electrocoagulation (EC) with Fe/C/Al hybrid electrodes was investigated for the separation of fluoride and nickel ions from a FGD wastewater. The study mainly focused on the technology parameters including anode electrode type, time, inter-electrode distance (5–40 mm), current density (1.88–6.25 mA/cm^2) and initial pH (4–10). The results showed that favorable nickel and fluoride removal were obtained by increasing the time and current density, but this led to an increase in energy consumption. Eighty-six percent of fluoride and 98% of Ni(II) were removed by conducting the Fe/C/Al EC with a current density of 5.00 mA/cm^2 and inter-electrode distance of 5 mm at pH 4 for 25 min and energy consumption was 1.33 kWh/m^3. Concomitant pollutants also achieved excellent treatment efficiency. The Hg, Mn, Pb, Cd, Cu, SS and chemical oxygen demand were reduced by 90%, 89%, 92%, 88%, 98%, 99.9% and 89%, respectively, which met stringent environmental regulations.

Key words | current density, defluorination, electrocoagulation, Fe/C/Al, FGD wastewater, nickel removal

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INTRODUCTION

Flue gas desulfurization (FGD) wastewater is generated when wet scrubbers wash dirty exhaust streams in coal-fired power plants. During this process various hazardous substances are stripped off and go into liquid phase. FGD wastewater requires special attention mainly due to the combination of a high concentration of anions, such as Cl^-, SO_4^{2-}, F^- and NO_3^-, and many kinds of heavy metals like Ni, Pb, Cu and Hg, which makes the wastewater treatment complex and difficult. Among these, high concentrations of fluoride are very toxic and generally appear in coal-fired power plant effluents. It is also an essential trace element for organisms, but it can present perniciousness at concentrations above the tolerance level (>1.5 mg/L) (Muthu Prabhu & Meenakshi 2014). It causes some adverse effects such as teeth deterioration and dental caries in slightly contaminated drinking water, and osteoporosis and serious problems for organs in seriously polluted water (Palahouane et al. 2015). FGD wastewater also contains many kinds and large amounts of heavy metals like Ni, Pb, Cu and Hg. These heavy metals are non-biodegradable carcinogens and have a bioaccumulation effect. As the most common heavy metal element in the Earth's crust, nickel is frequently involved in industrial production, especially in coal combustion which generates vast amounts of FGD effluent containing Ni. In addition, nickel ions have stronger chelation with organics, like nucleic acids, than other heavy metals (Gupta 1998). Therefore, discharge of FGD wastewater into natural water without proper treatment

would endanger public health, threaten the survival of indigenous aquatic biota and even have a fatal effect (Kabuk *et al.* 2014). Recently, the Ni ion discharge standard in many industries was raised to 0.1 mg/L in China (DB 44/1597-2015).

Conventional technologies applied to remove fluoride and heavy metals from FGD wastewater include chemical precipitation, filtration and ion exchange (Guan *et al.* 2009; Khosa *et al.* 2013; Muthu Prabhu & Meenakshi 2014). However, chemical precipitation requires the addition of a large amount of chemicals such as lime, polyacrylamide, 2,4,6-trimercaptotriazine, trisodium salt, nonahydrate (TMT-15), which may produce secondary pollutants and a large amount of sludge (Guan *et al.* 2009). Expensive membrane filtration is often limited by the high concentration of suspended solids (SS). Ion exchange shows excellent performance in the laboratory, but it incurs high operation costs for an extremely complex FGD wastewater treatment. These methods are insufficient to meet elevated environment standards and achieve economic feasibility.

Electrocoagulation (EC) technology generated coagulants, created by an *in situ* electro-dissolution metal anode, have attracted much attention in the last two decades. Due to its fast reaction, reasonable cost and simple operation, EC has been employed successfully to treat fluoride-containing wastewater (Zhao *et al.* 2010), organic wastewater (Kuokkanen *et al.* 2015), and heavy metal wastewater (As (Balasubramanian & Madhavan 2001), Cr (Arroyo *et al.* 2009), Ni (Beyazit 2014)). However, to our knowledge, FGD wastewater treated by EC has not been reported in the literature. Nevertheless, many efforts have been made to develop the EC method in treating fluoride and nickel ions. Sandoval *et al.* (2014) found that aluminum as the sacrificial electrode was efficient for fluoride removal. Similar results have been obtained in many studies (Drouiche *et al.* 2009; Palahouane *et al.* 2015). Comparing the iron and aluminum anode, Bazrafshan *et al.* (2012) demonstrated higher efficiency for the aluminum electrode for the removal of fluoride. This is as a result of the precipitate formation of aluminum fluoride hydroxide complexes ($Al_nF_m(OH)_{3n-m}$). For the high removal efficiency of Ni ions, some controversies between iron and aluminum as the working electrode have developed; it is widely accepted that the iron hydroxide complexes have higher flocculation than aluminum for removal of most heavy metals (Khosa *et al.* 2013). However,

some studies indicated that a satisfactory Ni treatment efficiency can be achieved for an aluminum electrode rather than an iron one (Jagati *et al.* 2015). This may be related to aeration, target pollutant properties or coexisting substances, and so on. For example, Fe(III) hydroxide complex presented in aeration exhibited stronger coacervation than Fe(II) hydroxide (without aeration) for metals (Martinez-Huitle & Brillas 2009). Hence, more exploration needs to be carried out in order to determine optimum EC treatment conditions for FGD wastewater.

In this study, the treatment of real FGD wastewater by EC with the combination of iron and aluminum sacrificial electrode was investigated. Fluoride and nickel in the FGD wastewater are selected as the main target pollutants. Optimization of various parameters such as electrode material, electrode distance, initial pH and current density for fluoride and nickel removal efficiency were explored. Finally, we also assessed the effectiveness of the Fe/C/Al EC method for the removal of other concomitant substances in FGD wastewater and energy consumption.

MATERIALS AND METHODS

Chemical and samples

The samples of real FGD wastewater were collected from a coal-fired power plant located in Zhanjiang city, China. Some physicochemical characteristics of raw wastewater used in this experiments are listed in Table 1. All chemicals used in the experiments were analytical grade and purchased from Sigma. The graphite, iron ($\geq$99.9%) and aluminum ($\geq$99.9%) plates were arranged from Shenzhen Quanfu Metal Co. Ltd, China.

Experimental apparatus

The electrolytic system (Figure 1) consisted of a DC power supply (DF17315D3A, Zhongce Electronics Co. Ltd, China), aerator (Songbao SB-988, China), electrolytic cell and magnetic stirrer. The DC power supply (0–30 V, 0–3A) was used for providing steady current for the EC system. The aerator was designed for pumping the air into the solution of the electrolytic cell to accelerate the Fe(II)

Table 1 │ Physicochemical characteristics of FGD wastewater before and after EC treatment

Parameter	Raw water	Effluent	Average removal efficiency (%)
Conductivity (µS/cm)	20,723–21,309	18,630–19,055	8–10
pH	5.6–6.2	6.7–7.3	
Mercury (mg/L)	0.25–0.43	≤0.03	90
Manganese (mg/L)	2.73–3.45	≤0.4	89
Nickel (mg/L)	3.16–3.37	≤0.1	98
Lead (mg/L)	0.41–0.80	≤0.08	92
Cadmium (mg/L)	1.38–1.54	≤0.2	88
Copper (mg/L)	1.65–1.93	≤0.1	98
Sulfate (mg/L)	4,325–5,720	3,269–4,580	20–24
Chloride (mg/L)	6,400–8,432	4,012–6,974	18–32
Fluoride (mg/L)	39.7–52.2	≤7.3	86
SS (mg/L)	15,232–18,930	≤3.0	99.9
COD (mg/L)	575–827	≤ 95	89
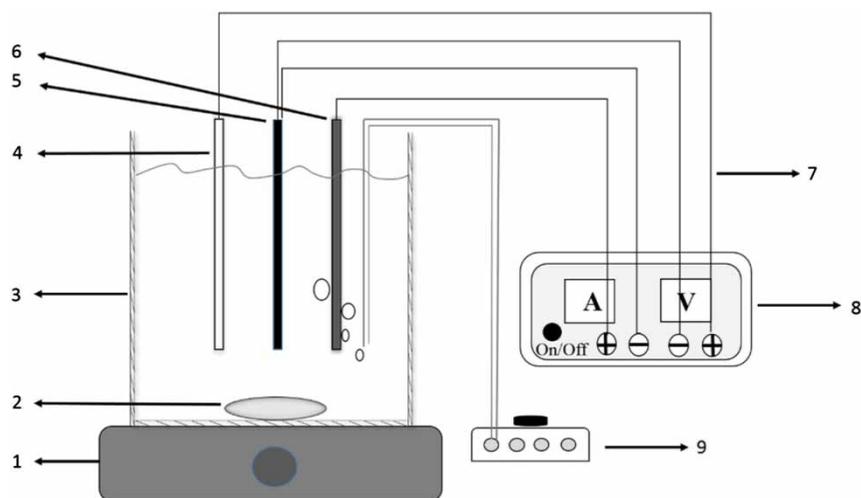
Figure 1 │ Schematic diagram of the EC apparatus: (1) magnetic stirrer, (2) magnetic bar stirrer, (3) electrolytic cell, (4) anode (aluminum plate), (5) cathode (graphite plate), (6) anode (iron plate), (7) circuit, (8) DC power supply, (9) aerator.

transform into Fe(III). The electrolytic cell was made from Plexiglas® of 2 mm thickness with dimensions of 100 mm × 110 mm × 120 mm and the inner wall of the cell had slots to introduce the electrodes. The iron and aluminum plates of rectangular geometry with the dimensions of 100 mm × 100 mm × 2 mm were used for the sacrificial anode electrode. The graphite plate of similar dimensions to the anode was employed for the cathode electrode. The total submerged surface area of the anode electrode was around 160 cm². The magnetic stirrer operated at 800 rpm during the EC experiment.

EC procedure

Before the experiments were carried out, the iron and aluminum plates were scrubbed with sandpaper to clean the surface passivation layer and washed with ultrapure water, then all electrodes were soaked in 0.25 M H_2SO_4 solution

for 10 min and rinsed with ultrapure water, before being finally dried in the vacuum drying oven and placed in a desiccator to cool down.

An electrolytic cell with a volume of 1,000 mL wastewater was used at room temperature ($25 \pm 0.8\,^{\circ}C$) for EC in batch experiments. In order to optimize the EC parameters, the different anode electrode types, like Fe/C/Fe, Al/C/Al and Fe/C/Al, different electrode distances from 5–40 mm, different current densities from 1.88–6.25 mA/cm^2 and different pH values from 4–10 were tested. The pH was adjusted to a desirable value by using 0.1 M HCl or NaOH solution. The samples were taken from the electrolytic cell at a given time and stored at $4\,^{\circ}C$. All experiments were carried out three times and the average values are reported here.

Analytical methods

The electrical conductivity and pH were measured by conductivity meter (DDSJ-308A, Rex Electric Chemical, China) and pH meter (sensION+ Ph1, HACH, USA), respectively. Chemical oxygen demand (COD), sulfate and chloride of the samples were tested by standard methods (Greenberg 2005). In detail, the COD values were calculated by the dichromate method and sulfate was measured by the gravimetric method. Concentration of chloride was analyzed using the silver nitrate titration method. An expandable ion analyzer (EA 940, Orion, USA) with fluoride ion selective electrode (PF-1-01, Rex Electric Chemical, China) was adopted for the quantitative analysis of fluoride (Palahouane *et al.* 2015). All samples for heavy metal analysis were filtered through a 0.45 µm glass fiber filter on site and measured by an Inductively Coupled Plasma-Atomic Emission Spectrometer (PerkinElmer, USA). SS of samples were analyzed using a turbidimeter (2100N, HACH, USA).

Calculations

The pollutants removal was determined in terms of removal efficiency defined as:

$$\omega\ (\%) = \frac{C_0 - C}{C_0} \times 100\% \tag{1}$$

where C_0 and C are concentrations of pollutants (Ni^{2+}, F^-, Hg^{2+}, Cu^{2+}, and so on) in the original FGD wastewater and treated one at given time (t), respectively. The amount of energy consumption for the EC treatment is a very important industrial parameter, which can be calculated as follows (Ardhan *et al.* 2014):

$$E = \frac{1.67 \times 10^{-5} UIt_{EC}}{V} \tag{2}$$

in which E is the electric energy consumption (kWh/m^3), U is the voltage across the circuit (V), I is the current (A), t_{EC} is the EC time (min) and V is the volume of given wastewater (m^3).

According to Faraday's law, the theoretically dissolved mass of aluminum or iron from the sacrificial electrode during the EC process can be calculated by the following equation (Mollah *et al.* 2004):

$$m = \frac{I \cdot M_r \cdot t_{EC}}{z \cdot F} \tag{3}$$

where m is the amount of the dissolved anode material (g), I is the applied current (A), t_{EC} is the reaction time of the EC process (s), M_r is the specific molecular weight of the anode metal (g/mol), z is the number of electrons involved in the reaction ($Z_{Fe} = 2$, $Z_{Al} = 3$), and F is the Faraday's constant (96,485.34 C/mol).

RESULTS AND DISCUSSION

EC has vast advantages compared with the conventional coagulation process, but the effective utilization of it depends highly on the conductive capability of the solution. For this reason, many researchers have added an electrolyte like NaCl, Na$_2$SO$_4$, KI or NaClO$_4$ into low electrical conductivity industrial wastewater and drinking water to limit the voltage drop (Sahu *et al.* 2014). They have reported that a solution with low conductivity increases the electrical consumption and decreases the life span of machine. However, as shown in Table 1, FGD wastewater with a high conductivity of 20,723–21,309 µS/cm met the working condition of EC without additional chemicals. The presence

of chloride ions of 5,400–6,432 mg/L could also increase the dissolution of the anode metal due to pitting corrosion to improve the removal efficiency of the Ni and fluoride from FGD wastewater (Yetilmezsoy *et al.* 2009).

Effect of anode electrode type and time

Choice of the anode electrode material plays a key role in the maximum efficiency of the EC process. The iron and aluminum are generally polyvalent metals used as sacrificial anode due to their cheaper, excellent coagulating properties and numerous sources. In the study, three kinds of different double anode configurations, including Fe/C/Fe, Fe/C/Al and Al/C/Al, were used to conduct the EC process for real FGD wastewater treatment and the experiment results are shown in Figure 2. It can be seen that the removal efficiencies of both fluoride and Ni increased with the increasing time for all electrode combinations. For fluoride removal (Figure 2(a)), there is only a small significant difference between Fe/C/Al and Al/C/Al, and the maximum removal of 77% and 78% were obtained at 25 min and 30 min, respectively. Compared with the Fe/C/Al and Al/C/Al electrode types, a poor treatment efficiency of 66% was obtained by the Fe/C/Fe combination. This is because flocs produced from the Fe anode only provided adsorption for fluoride, while the flocs produced from Al anode provided adsorption and coprecipitation (Kuokkanen *et al.* 2015). For nickel removal (Figure 2(b)), the significant removal of 96% was found with the Fe/C/Al or Fe/C/Fe electrodes after 20 min of the EC process. However, only 91% nickel removal efficiency was achieved with the Al/C/Al electrodes at 30 min. Hence, it can be concluded that higher fluoride and Ni treatment efficiency can be obtained with the combination of Al and Fe anode, and the optimized time was 25 min.
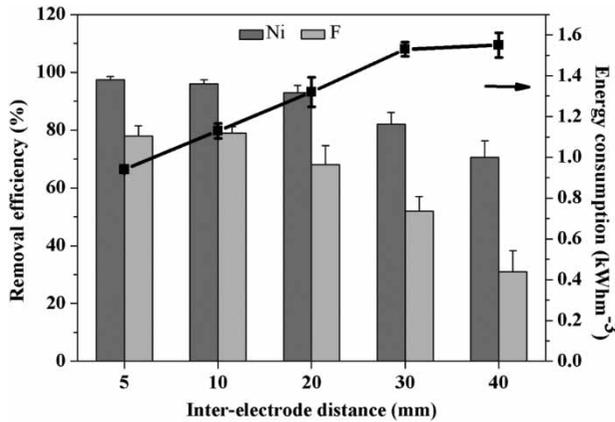
Effect of electrode distance

In order to improve the availability and safety performance of EC devices, the energy consumption needs to be reduced during use. According to Hernandez *et al.* (2012)'s report, adoption of appropriate measures can cut down the energy consumption, such as reduction of the gap between parallel electrode plates and increasing the solution
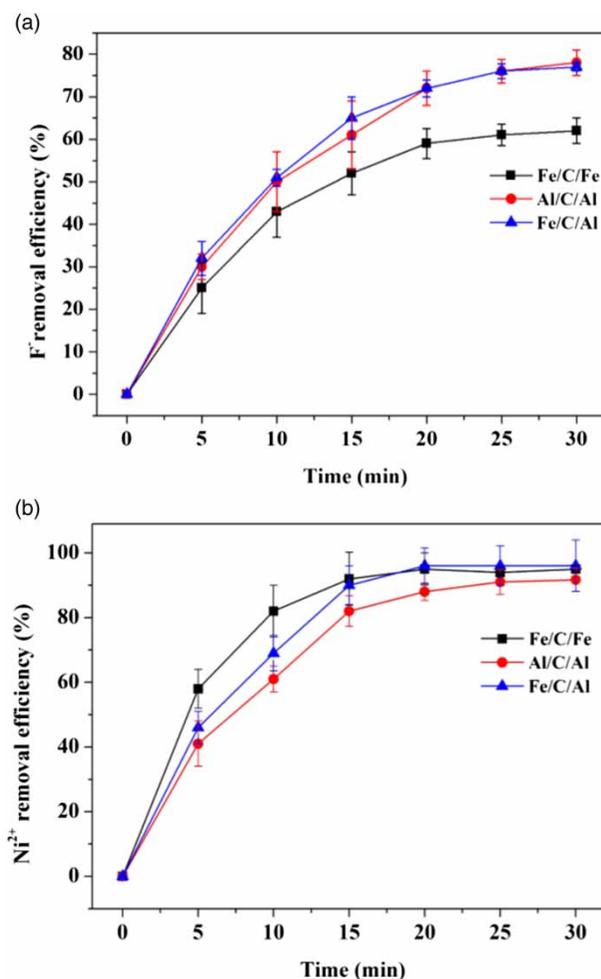
Figure 2 │ Effects of electrode type on fluoride (a) and Ni (b) removal efficiency. Conditions: inter-electrode distance of 5 mm, current density of 5.00 mA/cm^2, pH = 5.

conductivity. In the present study, the FGD wastewater possessed tremendous conductivity, which did not require additional chemical agents. Therefore, reduction of the gap between the parallel electrode plates became the only way to save electrical energy. Batch experiments were conducted by controlling the inter-electrode distance for FGD wastewater with current density of 5.00 mA/cm^2 at pH = 5 for 25 min. Figure 3 shows that the removal efficiency of fluoride and Ni increased from 32% to 78% and 70% to 97%, respectively, when the electrode distance decreased from 40 mm to 5 mm. However, the energy consumption of the EC system increased rapidly from 0.94 to 1.53 kWh/m^3 with the increasing of electrode distance from 5 mm to 30 mm and then became stable after 30 mm. Obviously,

Figure 3 | Effect of inter-electrode distance on fluoride and Ni removal efficiency. Conditions: current density of 5.00 mA/cm², pH = 5, Fe/C/Al electrodes, time of 25 min.

the optimal inter-electrode distance parameter was 5 mm. The phenomenon can be explained by the following equation (Vasudevan *et al.* 2011):

$$\eta_{opd} = \frac{I_{EC}d}{k_{aq}A} \qquad (4)$$

where η_{opd} is the Ohmic potential drop (voltage drop, V), I_{EC} is the applied current of the EC system (A), d is the inter-electrode distance (m), k_{aq} is the specific conductivity of the aqueous solution (10^3 mS/m) and A is the active anode surface (m²).

It is clear that a small space between electrodes will lead to a small IR-drop when the other parameters are fixed in the equation. Nevertheless, as small inter-electrodes distance as possible may not be optimal because short-circuit faults happen and the difficult dispersion of concentrated iron or aluminum ion or precipitates beside the electrode plates would reduce the pollutants removal efficiency. However, the result that energy consumption became stable after 30 mm seems difficult to explain directly by Equation (4). It might be explained by the high electrical conductivity k_{aq} playing a key role beyond a certain range of inter-electrode distance (d) in small volume of solution (Attour *et al.* 2014).

Effect of current density

Applied current (current density) is a very important parameter in the EC system because it determines the yield of

coagulants and electric energy consumption. To study the effect of current density for pollutants removal from FGD wastewater, batch experiments were carried out with the current density varying from 1.88 to 6.25 mA/cm² and electrode distance of 5 mm at initial pH = 5. Figure 4(a) shows that the fluoride removal efficiency increased with the increase of applied current density. The highest defluorination efficiency of 84% was obtained with a current density of 6.25 mA/cm² at 25 min, but defluorination efficiency of only 69% was achieved with the current density of 1.88 mA/cm² at 30 min. In the same conditions, Ni removal efficiency shows a significant difference between different applied currents in Figure 4(b). It only needed 15 min to reach the highest removal efficiency of 96% at 6.25 mA/cm², whereas
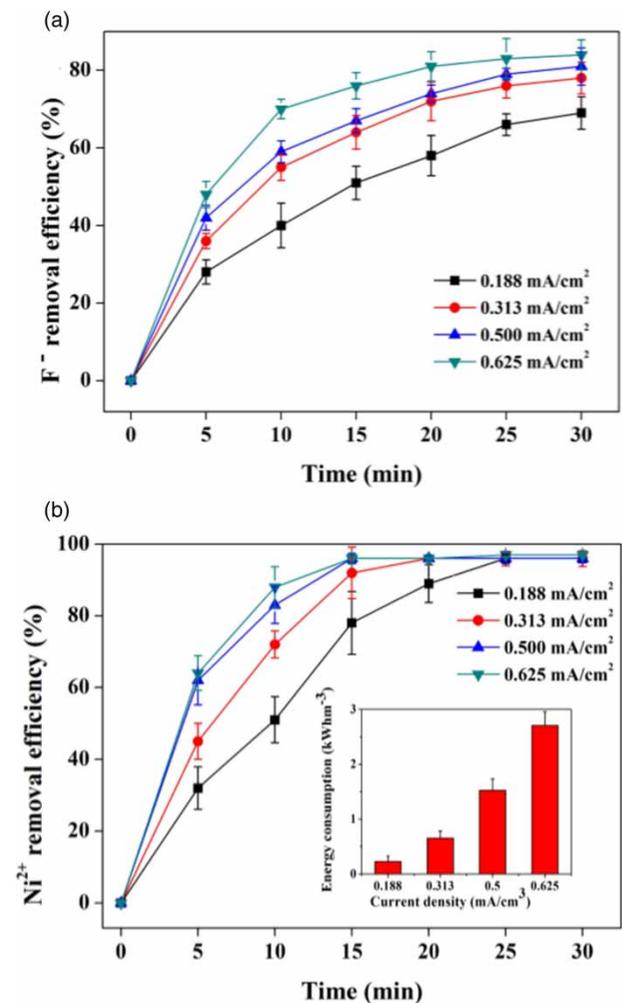
Figure 4 | Effect of current density on fluoride (a) and Ni (b) removal efficiency. Conditions: pH = 5, inter-electrode distance of 5 mm, Fe/C/Al electrodes.

20 and 25 min were needed at 3.13 and 1.88 mA/cm^2, respectively. It was also found that at 30 min the energy consumption grew exponentially with the current density varying from 1.88 to 6.25 mA/cm^2.

It can be seen from Equation (3) that the amount of dissolved iron and aluminum is proportional to the applied current and reaction time. Hence the achievement of a certain amount of dissolved metal can be obtained through increased time under a small applied current or increased applied current under a short time.

Effect of initial pH

In the EC process, the pH of the solution is a significant technical parameter since it influences the electrochemical reaction of electrodes and speciation of metal hydroxides (Chen *et al.* 2000). The experiments investigating effects of pH on Ni and F$^-$ removal efficiency by hybrid Fe and Al anode EC were performed. The removal efficiency of the fluoride decreased when the initial pH was varied from 4 to 10 and the maximum removal efficiency of 68.9% was obtained with pH 4 at 10 min (Figure 5(a)). The results are in accordance with the fluoride removal of pretreated photovoltaic wastewater by Al sacrificial electrode EC (Palahouane *et al.* 2015). Ni removal efficiency decreased firstly from 92% to 49% when initial pH was varied from 4 to 8 and then increased slowly to 61% when the initial pH was further increased to 10 through 10 min EC treatment (Figure 5(b)). This is because the dissolution of iron and aluminum were accelerated at acidic pH and the precipitates of Ni(OH)$_2$ were generated by the reaction between OH$^-$ and nickel (Equation (15)) at alkaline pH. The optimal pH 4 obtained was consistent between Ni and fluoride.

Similar removal tendencies of fluoride and nickel were found after 25 min. All of the EC processes achieved a high fluoride and Ni removal efficiency and the maximal removal efficiency of fluoride and Ni were 85.8% and 98.1% at pH 4, respectively. Besides, since the system initial pH was 5.6–6.2 and after the EC process increased to 6.7–7.3, Al(OH)$_3$ and Fe(OH)$_3$ were able to be deposited according to their solubility product ($K_{sp(Al(OH)3)} = 4.57 \times 10^{-33}$ and $K_{sp(Fe(OH)3)} = 4.0 \times 10^{-38}$, 25 °C). The results showed that the effect of initial pH on the pollutants removal from FGD wastewater was not neglectable.
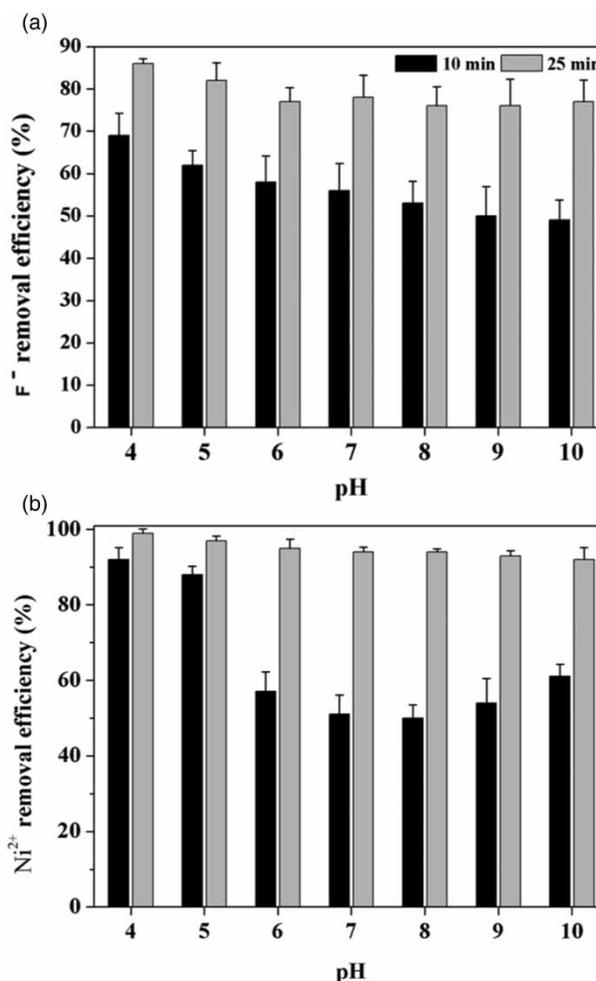
Figure 5 | Effect of initial pH on fluoride (a) and Ni (b) removal efficiency. Conditions: current density 5.00 mA/cm^2, inter-electrode distance of 5 mm, Fe/C/Al electrodes.

Removal efficiency of concomitant pollutants

Significant removal of fluoride and Ni(II) were obtained after the optimization, but the removal efficiency for the concomitant pollutants in the FGD wastewater was not clear. Hence, the removal of concomitant pollutants was tested. Table 1 describes the removal efficiency of pollutants from FGD wastewater by EC using Fe/C/Al electrode combination with the current density of 5.00 mA/cm^2 and inter-electrode distance of 5 mm at pH 4 for 25 min. The results confirmed that the EC treatment system can effectively achieve a broad spectrum of pollutants removal. Remarkable efficiency for toxic heavy metals was obtained such as Hg ($\leq$0.03 mg/L, 88%), Mn ($\leq$0.4 mg/L, 89%), Pb ($\leq$0.08 mg/L, 92%), Cd

($\leq$0.2 mg/L, 88%) and Cu ($\leq$0.1 mg/L, 98%). These indicated iron and aluminum hydroxide species generated from Fe/C/Al EC had excellent absorption performance for heavy metals in the optimal condition. The effluent concentration of Fe and Al was 1.22–0.73 mg/L and 0.53–0.22 mg/L, respectively, which met China's industrial wastewater emission standards.

The electrical conductivity is mainly attributed to the presence of SO_4^{2-} and Cl^- in the FGD wastewater. Hence low treatment efficiency of the SO_4^{2-} (20–24%) and Cl^- (18–32%) resulted in low decrease in conductivity. At present, removal of high concentrations of SO_4^{2-} and Cl^- remains a challenge to wastewater treatment plants, but is not considered as a component of major concern for FGD wastewater (Huang *et al.* 2013). However, the large amount of SO_4^{2-} ($\sim$1,800 mg/L) and Cl^- ($\sim$2,400 mg/L) removal were achieved by adsorption of colloids in the present study. Moreover, excellent removal of 99% was achieved in SS by the EC process, which made turbid water instantaneously become clear. The concentration of COD was reduced to below 95 mg/L, because most of the organics were absorbed or coprecipitated by the iron and aluminum hydroxide species and flocs. In addition, COD can be treated by oxidation of active chlorine species (Cl_2, HClO, OCl^-) derived from Equations (5)–(7) when chloride is present in the solution and the anode potential is sufficiently high (Kuokkanen *et al.* 2015).

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{5}$$

$$Cl_2 + H_2O \rightarrow HOCl + Cl^- + H^+ \tag{6}$$

$$HOCl \rightarrow OCl^- + H^+ \tag{7}$$

These experiment results demonstrated the feasibility of the EC technology in treating real FGD wastewater. Another advantage for FGD wastewater with the EC process was better energy consumption due to the high electrical conductivity in the raw solution without additional electrolyte. In this condition, the energy consumption was 1.34 kWh/m^3, which was much less than in some other studies, such as 3.9 kWh/m^3 for As-containing groundwater (Flores *et al.* 2014), 7.19 kWh/m^3 for egg processing effluent (Sridhar *et al.* 2014), and 8 kWh/m^3 for phenolic-simulated effluent (Fajardo *et al.* 2014). Moreover, the power supplement was convenient

for treatment of FGD wastewater from a coal-fired power plant.

Removal mechanism

It is generally believed that EC is the interaction of three main mechanisms including electrochemical coagulation, electro-oxidation and electro-flotation. Electrochemical coagulation, relying on the dissolution of the Al or Fe anode, is the most important influence for fluoride and nickel removal. According to the literature (Sahu *et al.* 2014; Sandoval *et al.* 2014), the equations involved in electrochemical coagulation of Al and Fe are listed below.
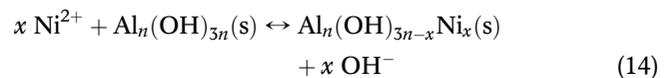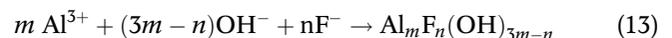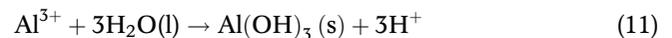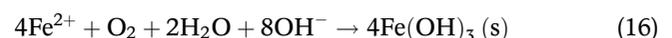
Anode:

$$Fe(s) \rightarrow Fe^{2+} + 2e^- \tag{8}$$

$$Al(s) \rightarrow Al^{3+} + 3e^- \tag{9}$$

Cathode:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^- \tag{10}$$

Solution: for aluminum,

$$Al^{3+} + 3H_2O(l) \rightarrow Al(OH)_3 (s) + 3H^+ \tag{11}$$

$$Al_n(OH)_{3n}(s) + xF^- \leftrightarrow Al_n(OH)_{3n-x}F_x(s) + xOH^- \tag{12}$$

$$m\,Al^{3+} + (3m - n)OH^- + nF^- \rightarrow Al_mF_n(OH)_{3m-n} \tag{13}$$

$$x\,Ni^{2+} + Al_n(OH)_{3n}(s) \leftrightarrow Al_n(OH)_{3n-x}Ni_x(s) + x\,OH^- \tag{14}$$

and for iron,

$$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 (s) + 2H^+ \tag{15}$$

$$4Fe^{2+} + O_2 + 2H_2O + 8OH^- \rightarrow 4Fe(OH)_3 (s) \tag{16}$$

$$Fe(OH)_3(s) + 3F^- \rightarrow FeF_3 + 3OH^- \tag{17}$$

$$x \, Ni^{2+} + Fe_n(OH)_{3n}(s) \leftrightarrow Fe_n(OH)_{3n-x}Ni_x(s) + x \, OH^- \tag{18}$$

$$Ni^{2+} + OH^- \rightarrow Ni(OH)_2 \, (s) \tag{19}$$
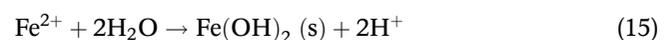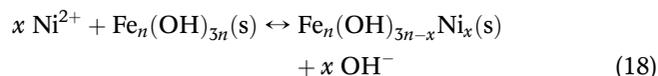
In the EC system, the rapid dissolution of the submerged Al and Fe electrode *in situ* happened in an energized state, which transferred the Al and Fe ions into the solution. Then, Fe^{2+} and Al^{3+} produced the precipitates and flocs through Equations (11), (15) and (16). The precipitates and dissolved metal ions in the solution play an important role in the treatment of pollutants. According to the study, the fluoride removal was attributed to adsorption of $Al(OH)_3$ particles (Equation (12)) and coprecipitation of Al^{3+} (Equation (13)). Another pathway for fluoride removal by means of coprecipitation between ferric oxyhydroxides and fluorine ions has been proposed (Martinez-Miranda *et al.* 2011). On the other hand, the major nickel removal was the result of absorption and coprecipitation of iron or aluminum polyhydroxide species (Equations (14), (18) and (19)). From this, it can be seen that the Fe/C/Al have a satisfactory performance for fluoride removal in the EC system. Therefore, to simultaneously remove F^- and Ni^{2+}, the Fe/C/Al electrodes combination was chosen in the EC system for further FGD wastewater treatment. However, the reasonable disposal of heavy metal-containing sludge generated from the EC process should be considered, such as the utilization of lime or cement for stabilization/solidification or usage as raw material for production of ceramics (Butt *et al.* 2014; Verbinnen *et al.* 2015).

CONCLUSIONS

This paper investigated the use of Fe/C/Al hybrid electrodes in an EC system for FGD wastewater treatment which allowed for simultaneous removal of Ni(II), fluoride and most toxic pollutants to improve the effluent quality. The effect of parameters like anode material type, time, inter-electrode distance, current density and initial pH on the removal of fluoride and nickel was evaluated. Results showed that the optimum removal of fluoride and Ni achieved was 85.8% and 98.1%, respectively, in current density of 5.00 mA/cm^2 and inter-electrode distance of 5 mm with pH 4 for 25 min. Meanwhile, excellent removal efficiency was also observed for some concomitant pollutants of Hg, Mn, Pb, Cd, Cu, SS and COD and reasonable energy consumption was used. In conclusion, the EC process with the Fe/C/Al electrode type is an effective method for removal of fluoride, nickel and most pollutants in FGD wastewater to meet the stringent environmental regulations.

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