Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2016.1186567

57 (2016) 28417–28425
December

A study on continuous and batch electrocoagulation process for fluoride removal

Jun Lu*, Qing Tang, Zhong-Ru Wang, Chao Xu, Sheng-Ling Lin

School of Environmental and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang, Jiangsu 212003, China, emails: jluabc@163.com (J. Lu), tq19901003@163.com (Q. Tang), wangzhongru@126.com (Z.-R. Wang), 764384760@qq.com (C. Xu), linshl5757@sina.com (S.-L. Lin)

Received 9 December 2015; Accepted 14 April 2016

ABSTRACT

Continuous and batch electrocoagulation processes (CEC and BEC) for treating fluoride-containing solution were investigated and compared. The poor mixture and uneven distribution of flocs during BEC lead to a lower removal efficiency, when compared with CEC. Under whole range of current densities, the superiority of CEC is obvious. However, at high residence time, CEC process, which has intense back mixing has a lower removal efficiency when compared with BEC. Also it was found that even at same charge loading, the CEC differ a lot with BEC. The influences of charge loading and initial pH on CEC process were investigated with the consideration of utilization rate of electro-generated Al element. The molar ratio of F/Al in sludge presents a trend of gradual decline with the increment of charge loading. The molar ratio of (OH + F) to Al element in sludge conforms the fact that the F^- is removed not only by $Al(OH)_{3-x}F_{x(s)}$ precipitation but also by the absorption of aluminum flocs. The influent at the condition of weak acid leads to a maximum production of aluminum hydroxide flocs along the whole electrolysis channel from inlet to outlet. This leads to the maximum removal efficiency. This was also proved by the fact that the utilization rate of Al element in sludge reaches its maximum under weak acid condition.

Keywords: Electrocoagulation; Fluoride removal; Continuous; Batch; Back mixing

1. Introduction

The emission of industrial wastewaters containing fluorides increases with the development of semiconductor, electroplating, glass-manufacturing, and fertilizer industries [1]. These wastewaters containing fluorides without careful treatment will pollute surface and ground water. The excessive fluorides in drinking water will cause dental fluorosis, neurological damage, and even skeletal damage [2]. There are several treatment options to remove fluorides from wastewater, such as chemical precipitation [3,4], selective ion exchange [5], reverse osmosis [6], and electrochemical methods [7] (electrodialysis [8]). However, these methods can’t be widely used because of some disadvantages such as the generation of large volumes of sludge, secondary pollution, and high cost. Electrocoagulation (EC) which has the advantages of *in situ* formation of coagulants, high efficiency, low sludge generation, and easy operation [9], has been studied by more and more researchers.

---

*Corresponding author.

In EC with aluminum electrode, the electro-generated Al^{3+} will react with OH^- (originated from cathode surface) to form various aluminum hydroxide products such as $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_2^{4+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}(OH)_{34}^{5+}$, which will finally transform into amorphous $Al(OH)_{3(s)}$ [10]. The amorphous $Al(OH)_{3(s)}$ which has abundant surface hydroxyl groups could have complexation reaction with fluoride ions (through ligand exchange complexation). In addition, the amorphous $Al(OH)_{3(s)}$ with high surface area could also absorb fluoride ions directly. The fluoride removal is mainly attributed to the above two removal mechanisms, which was also proved by other researchers [11].

During the past years, EC has been used for treating various kinds of wastewaters [12–16]. For fluoride removal, EC with aluminum anode shows high removal efficiency [17–19]. Emamjomeh and Sivakumar studied batch experiments with monopolar aluminum electrode for fluoride removal [20]. It was found that the fluoride removal efficiency increases steadily with the increment of current density and reaction time. Many researchers discussed the effect of other factors such as charge loading, solution pH, fluoride concentration, and electrolyte concentration on the energy consumption and fluoride removal efficiency [21–23].

A batch EC process combined with chemical coagulation was proposed to remove fluoride from drinking water [24]. It was found that the highest efficiency would be obtained when the molar ratio of alkalinity and fluoride to Al(III) of the initial solution was controlled at 3.0. Emamjomeh et al. [25] analyzed the dry sludge of EC process for separating F^- and found that the residual fluoride occurs in various dissolved forms (F^-, AlF_2^+, AlF_4^-) or finally formed to solid (cryolite, $Al(OH)_{3-x}F_x$). The mechanism of the fluoride removal was confirmed to be not only the competitive adsorption between OH^- and F^- but also the formation of solid cryolite. Although EC technology was used for defluoridation widely with batch process, researchers gradually turned their attentions to continuous EC process to treat wastewater [26,27]. With advantage of easy operation, continuous EC is more suitable for industrial application. However, there are few discussions about the continuous EC process.

The objective of this work was to investigate the difference between BEC and CEC process. The influences of current density, charge loading, residence, and reaction time on BEC and CEC were discussed. The advantage and disadvantage of CEC and BEC were studied. The influences of back mixing and uneven distribution of hydroxide flocs on CEC and BEC performance were discussed, respectively. The continuous EC process for treating fluoride wastewater was investigated. The effects of charge loading and initial pH on CEC process were investigated with the consideration of utilization rate of electro-generated Al element.

2. Experimental

2.1. Materials and methods

The electrocoagulation reactor was made of Pyrex glass. The effective volume is 220 mL. Two aluminum (Al) plates (305 mm × 46 mm × 2 mm) with effective surface area of 120 cm^2 were used as anode/cathode pair. The electrodes were installed parallelly. The distance between the anode and cathode was 10 mm. The electrode plates were connected to a DC power supply (APS3005DM, Atten, China) at constant current mode (2.5–12.5 A/m^2). In CEC process, the model wastewater was continuously pumped into the EC cell by peristaltic pump (BT100-1F, Longer, China). In BEC process, in order to mix the solutions in EC channel, the fluent is externally circulated from outlet to inlet. The process was shown in Fig. 1.

2.2. Model wastewater and analytical techniques

The model water containing F^- (10 mg/L) was used as the wastewater. The fluoride solution was prepared by dissolving NaF (AR) in tap water. Solution conductivity was adjusted to 1 ms/cm by adding anhydrous sodium sulfate (Na_2SO_4, AR). The conductivity was measured by conductivity meter (DDS-11A, LIDA, China). Sodium hydroxide and hydrochloric acid solutions with different concentration were added for pH adjustment. The pH value was measured by pH meter (pHS-3C, Shanghai REX Instrument, China).

In continuous EC process, four samples were taken from the bulk solution in the direction of streamline at $X = 0$, 100, 200, and 300 mm (from inlet to outlet). Samples were taken from the reactor after the process reached steady state. Four parallel experiments were taken to get the error bar. Fluoride concentration was determined using the ionometric standard method with a fluoride selective electrode (PF-1-01, Shanghai REX Instrument, China). TISAB II buffer solution was prepared to prevent the interference by other ions (Al^{3+}, Fe^{3+}, etc.) [29]. The sludge of the effluent was dissolved by chlorhydric acid. The concentration of aluminum element of the effluent and the dissolved solution (EC's sludge) was measured by ICP-AES (VISTA-MPX, Varian).

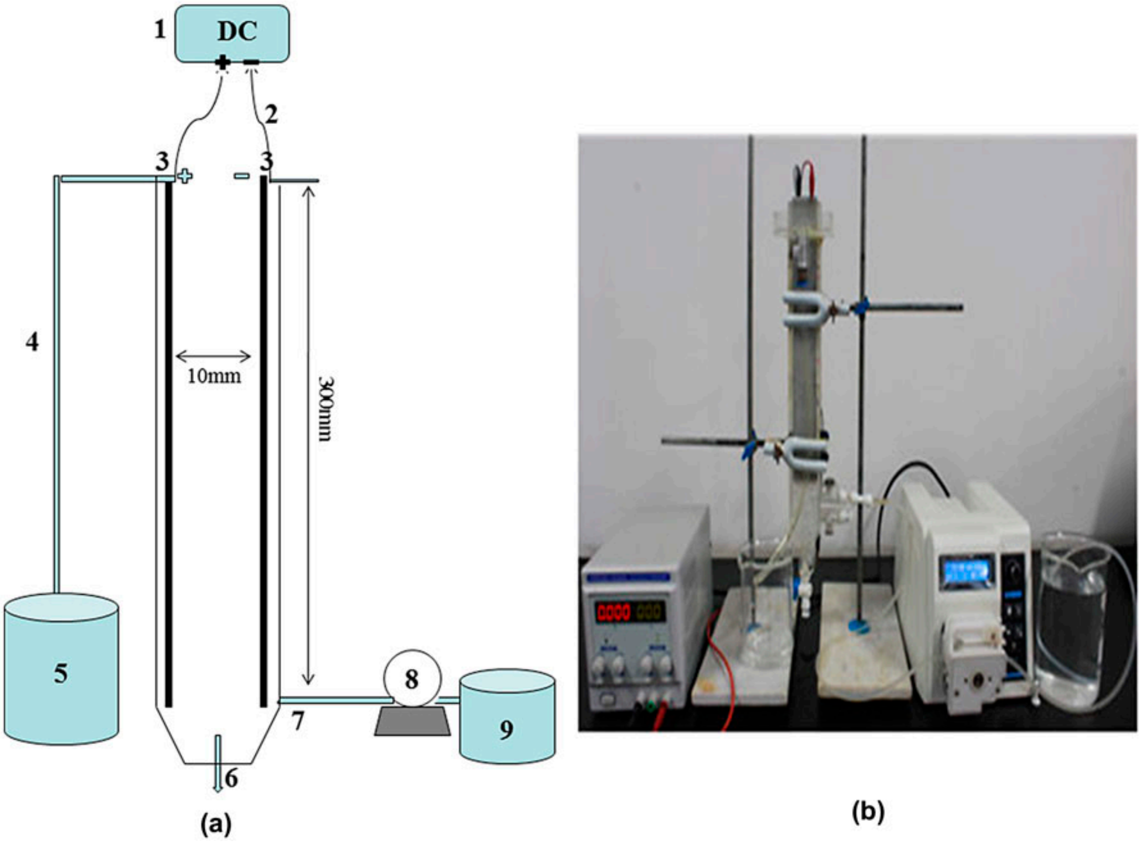

Fig. 1. Schematic diagram of EC reactor (a) and bench-scale EC process (b).
Notes: (1) constant-current power supply, (2) wire, (3) aluminum electrodes, (4) outlet, (5) treated water tank, (6) drainage valve, (7) inlet, (8) peristaltic pump, and (9) raw water tank [28].

3. Results and discussion

3.1. The comparison between CEC and BEC process

The continuous and batch EC processes for fluoride removal were investigated and compared.

3.1.1. The comparison based on current densities

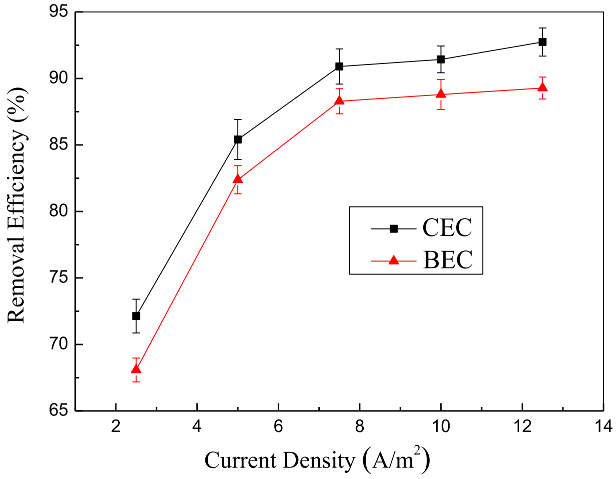

Fig. 2. Removal efficiency of CEC and BEC at different current densities (residence and reaction time: 20 min; initial pH of influent: 6).

It can be found from Fig. 2 that the performance of CEC is superior to that of BEC on the whole range of current densities. The aluminum hydroxide flocs could absorb the H_2 which is generated from the cathode reaction. The flocs with bubbles will slowly rise up to the top of the channel by buoyancy [30]. Therefore, in BEC process a large proportion of flocs will distribute at the top of the channel. The flocs with abundant surface hydroxyl groups and high specific surface area could remove the F^- through adsorption and specific adsorption (ligand exchange complexation reaction with F^-), which are the main mechanisms of F^- removal. Thus at the top of the channel, large amount of flocs will lead to higher removal efficiency. There are fewer flocs in the middle and the bottom of the channel. The fewer flocs will lead to lower adsorption effect. The result is that the poor mixture and the uneven distribution of flocs lead to lower removal efficiency in BEC process. In addition, although the solution of BEC process is externally circulated, the flocs with H_2 bubbles are accumulated at the top of EC channel. However, in CEC process, the flocs with H_2 bubbles transport in the direction of streamline. The flocs are distributed along the channel and removed out of the channel at the outlet. Thus, compared with the CEC, BEC has lower removal efficiency.

3.1.2. The comparison based on residence time and reaction time

At short residence time, the removal efficiency of CEC is also larger than that of BEC (Fig. 3). It is attributed to the uneven distribution of flocs, which is discussed above. However, the difference of removal efficiency between CEC and BEC gradually decreases with the increment of residence and reaction time, respectively. At long residence time, the removal efficiency of CEC becomes lower than that of BEC (Fig. 3). This could be explained by two facts. For one thing, in CEC system, the back mixing could lead to the decrement of removal efficiency. In BEC and CEC process, there are three phases in electrolysis channel: floc phase, solution phase, and gas phase. In CEC, the mutual movement between these phases causes intense fluid turbulence and this in turn will lead to back mixing. The back mixing will cause the mixture of fluorides which have different residence times. Therefore, the removal efficiency of F^- at the outlet will decrease. The proportion of volume fraction of floc phase and gas phase will increase with the increment of residence time. Thus, at long residence time (CEC) and reaction time (BEC), the removal efficiency of CEC will be lower than that of BEC with the same residence and reaction time. For another, at long residence time, the flow velocity is low. Thus compared with the forced convection flux, the ionic diffusion flux is relatively high. This will improve the intensity of back mixing. It could also be explained by the Peclet number, which is the ratio of convection to diffusion. With the increment of residence time, high diffusion flux and low forced convection will lead to a low Peclet number, which means high intensity of back mixing [28] (i.e. high residence time will lead to back mixing). This will cause the degradation of the CEC’s performance a lot.

3.1.3. The comparison based on the same charge loading

The energy consumption is proportional to the charge loading. In order to study the energy consumption of continuous and batch operation, the continuous and batch EC, the removal efficiency of CEC and BEC under same charge loading was studied. Fig. 4 is the variation of removal efficiency of CEC and BEC with different residence and reaction times under same charge loading. The charge loading (Q_e, C/m^3) is defined as the charge applied per cubic meter of solution. The Q_e equation for BEC and CEC can be written as follows [31]:

$$Q_{e_{BEC}} = \frac{n \cdot I \cdot t}{V} \tag{1}$$

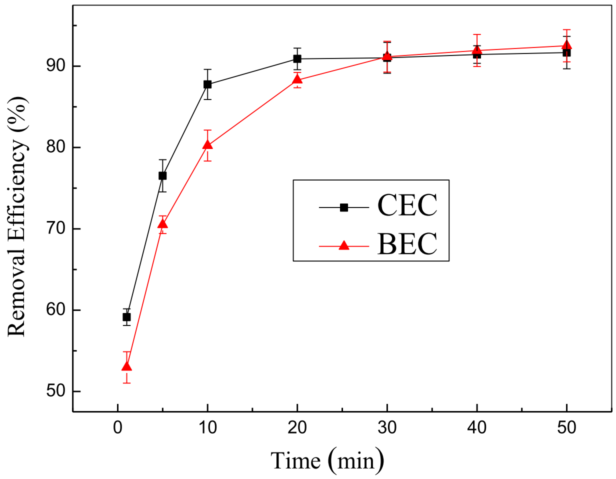

Fig. 3. Removal efficiency of CEC and BEC at different residence and reaction times (current density j: 7.5 A/m^2; initial pH of influent: 6).

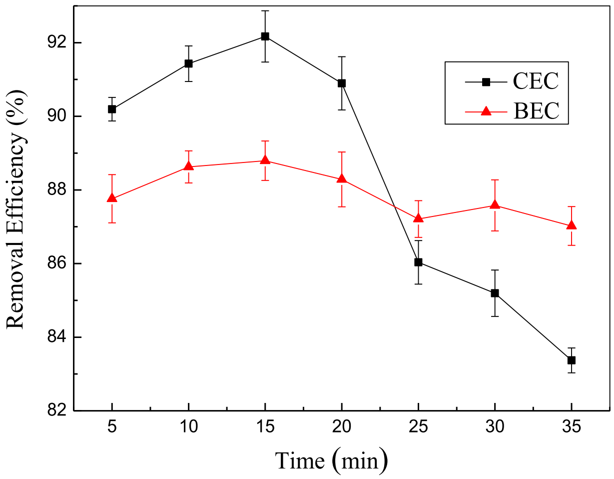

Fig. 4. Variation of removal efficiency of CEC and BEC under same charge loadings (charge loading Q_e: 4.9×10^5 C/m^3; initial pH of influent: 6).

$$Q_{e_{\mathrm{CEC}}} = \frac{n \cdot I}{q_{\mathrm{v}}} \qquad (2)$$

where n refers to the number of cells; I is the total current applied to EC process; V represents the effective volume of BEC process; q_{v} is influent flow rate of CEC process.

The charge loading of both CEC and BEC is set as 4.9×10^5 C/m^3. As Fig. 4 displays, under the same charge loading, the removal efficiency of BEC varies slightly with the reaction time. The removal efficiency of CEC shows a different tendency. It decreases significantly with the increment of residence time. At short residence time, the back mixing in CEC is negligible. Thus, the CEC shows a higher removal efficiency. At long residence time, the high intense back mixing in CEC leads to a lower removal efficiency. According to Faraday's law, BEC or CEC with same charge loading will produce approximately same amount of coagulants and flocs. However, the performance of BEC and CEC under same charge loading differs a lot. It is attributed to the back mixing and uneven distribution of flocs in continuous and batch operations, respectively.

3.2. *CEC process for fluoride removal*

3.2.1. *Influence of charge loading*

The charge loading determines the generation of coagulants and flocs during CEC. Thus, it will be the most important factor that determines the removal efficiency. The removal efficiency of fluoride ions along the streamline was measured and illustrated in Fig. 5. As can be seen from Fig. 5, an increase in the charge loading from 1.6×10^5 to 8.2×10^5 C/m^3 yields an increment of fluoride removal (from 72.13 to 92.74%). At charge loading (1.6×10^5 C/m^3), the removal efficiency increases linearly along the streamline from inlet to outlet (from $X = 0$ to $X = 300$). However, at charge loading larger than 3.3×10^5 C/m^3, the increment of removal efficiency slows down along the streamline. Especially after $X = 100$, the removal efficiency increases more slightly. At the rear part of the channel, the residence time of F$^-$ and aluminum hydroxides is high. As discussed above, the high residence time will improve the degree of back mixing. Thus, in the direction of streamline, the degree of back mixing gets intense from inlet to the outlet. In addition, the accumulation of flocs and bubbles at the rear part of the channel also improves the degree of back mixing. The result is that back mixing at the rear part leads to the mixture of F$^-$ and an even distribution of removal efficiency.

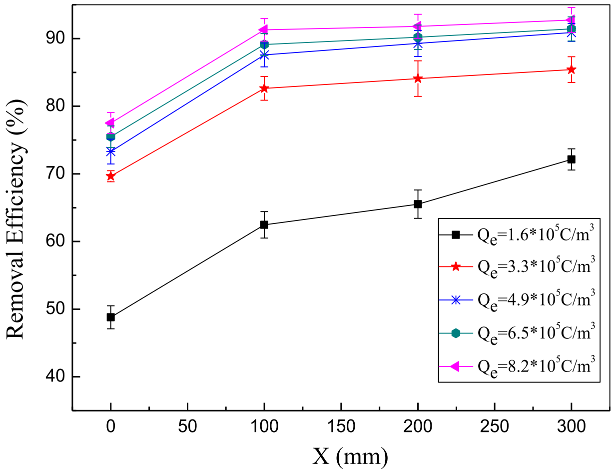

Fig. 5. Distribution of the removal efficiency of F$^-$ in the direction of streamline at different charge loadings (initial pH of influent: 6).

The pollutant removal by EC process consists of many complicated processes, such as complexation reaction, sweep coagulation, co-precipitation, and electrical neutralization. The fluoride ions are mainly removed through ligand exchange complexation reaction with flocs and direct adsorption by flocs [25]. It could be considered that defluorination efficiency is proportional to the amount of aluminum hydroxide flocs. Meanwhile, the amount of electro-generated coagulants Al^{3+} is approximately proportional to the charge loading, which is related to the energy consumption. Thus, the utilization rate of electro-generated coagulants should be considered as an important parameter during EC process. A universal parameter named as molar ratio of F to Al element was introduced to quantify the utilization rate of *in situ* electro-generated Al ions in previous paper [28]. The ratio of F/Al was calculated and shown in Fig. 6. The utilization rate of electro-generated Al ions could be considered as the amount of F element absorbed by per Al element [28]. In this work, the molar ratio differs with the previous work by Hu [32]. Hu defined an initial molar ratio of OH$^-$ and F$^-$ to the total electro-generated Al^{3+}, the amount of which is calculated from the applied current. However, in actual CEC and BEC, only parts of electro-generated Al^{3+} could be hydrolyzed to aluminum hydroxide flocs.

It could be found from Fig. 6 that the molar ratio of F/Al decreases with the increment of charge

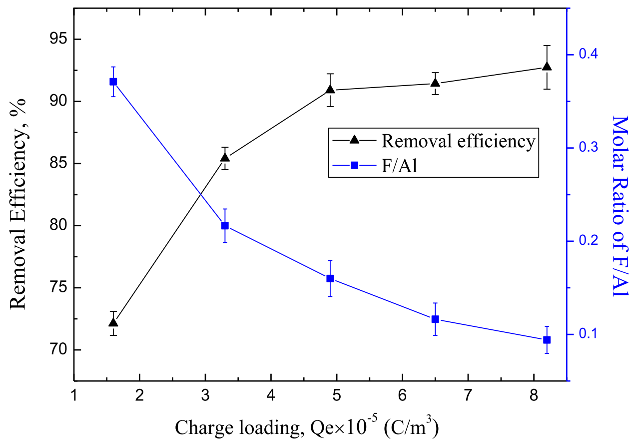

Fig. 6. Removal efficiency of F^- at the exit and F/Al ratio in the sludge at different charge loadings (initial pH of influent: 6).

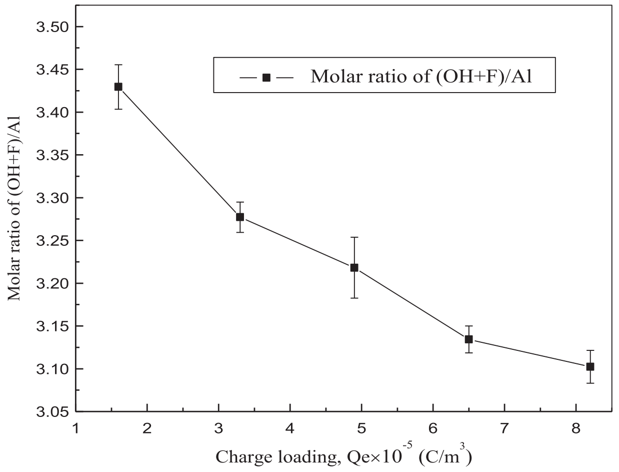

Fig. 7. The (OH + F)/Al ratio of flocs at different charge loadings (initial pH of influent: 6).

loading. The molar ratio decreases from 0.4 to 0.1. The amount of flocs increases with the charge loading proportionally. The concentration of residual fluoride ions reduces at the same time. This will lead to the competitive adsorption effect among aluminum hydroxide flocs [28]. The mechanism of the fluoride removal was confirmed to be the competitive adsorption between OH^- and F^- [25]. Thus, the F/Al ratio presents a trend of gradual decline and the curve becomes relatively smoother.

The removal mechanism of fluoride is the formation of complexes and co-precipitation reaction with aluminum hydroxides as $Al(OH)_{3-x}F_x$. Thus, the sludge is mainly composed of flocs and $Al(OH)_{3-x}F_{x(s)}$. The molar ratio of (OH + F) to Al was calculated and shown in Fig. 7. This ratio could be considered as the ratio of the average amount of OH^- and F^- combined by per Al element. As seen in the Fig. 7, with the increment of charge loading, the molar ratio of (OH + F) to Al decreases from 3.45 to 3.10. This proves the fact that the F^- is removed not only by the formation of $Al(OH)_{3-x}F_{x(s)}$ precipitation but also by the absorption of aluminum flocs. Also, it could be speculated from Fig. 7 that at high charge loading, the ratio approaches to 3.0, which is the composition of amorphous $Al(OH)_{3(s)}$. With the increment of charge loading, the amount of generated aluminum hydroxide flocs increases proportionally, but the absorbed F^- increases much slowly.

3.2.2. Influence of initial pH

It has been proved that initial pH has a sensitive effect on the efficiency of the EC process [33,34]. The influence of initial pH on CEC process was investigated. EC processes with a reasonable initial pH range (3–8) were studied. It can be found in Fig. 8 that the removal efficiency is low when influent's initial pHs are 4, 7, and 8. The removal efficiency is high at weak acid initial pH (5 and 6). The reason could be explained by the relationship between pH condition and the hydrolysis behavior of aluminum ions [34]. During CEC process, the pH value of the channel in steady sate was measured in the direction of streamline. In Fig. 9, it was found that in the direction of streamline, the pH value of the solution increases from

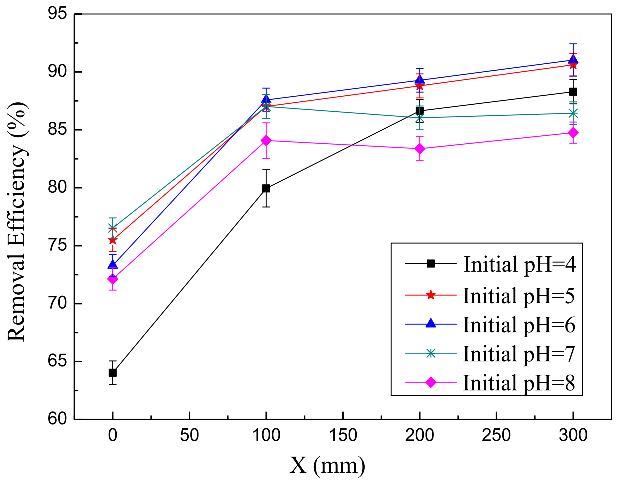

Fig. 8. Distribution of the removal efficiency of F^- in the direction of streamline under different initial pH conditions (current density *j*: 7.5 A/m^2; Residence time RT: 20 min; Charge loading Q_e: 4.9 × 10^5 C/m^3).

inlet to outlet. For the weak acid initial pH (5 and 6), the pH condition at the outlet is close to neutral. In addition, for the whole channel from inlet to outlet, the pH value of the solution is between 6 and 7. The whole channel is in weak acid condition. This pH range is necessarily favorable for the formation of aluminum flocs [35]. Thus for the whole channel from inlet to outlet, the pH condition is favorable for formation of aluminum flocs. Thus, the amount of flocs will increase to maximum at weak acid initial pH value (5 and 6).

The effect of influent's initial pH on the F/Al ratio was shown in Fig. 10. It was concluded that initial pH determines the generation and transportation of the flocs and there are more flocs when the initial pH of influent is weak acid (initial pH 5–6). Thus, the adsorption and complexation effects of flocs under weak acid initial pH condition are more intense than that in other initial pH condition. The result is that the utilization rate of electro-generated Al element reaches its maximum under weak acid initial pH condition.

The weak acid initial pH condition leads to maximum utilization rate of electro-generated Al^{3+}. The molar ratio of (OH + F) to Al under different initial pH conditions was shown in Fig. 11. The ratio of initial weak acid condition (initial pH 6) reaches its maximum (about 3.3). It is higher than that under acid and alkaline conditions. CEC with initial pH 6 has a higher flocs and complex formation rate. The electro-generated Al element could combine more hydroxyl group and F^{-}.

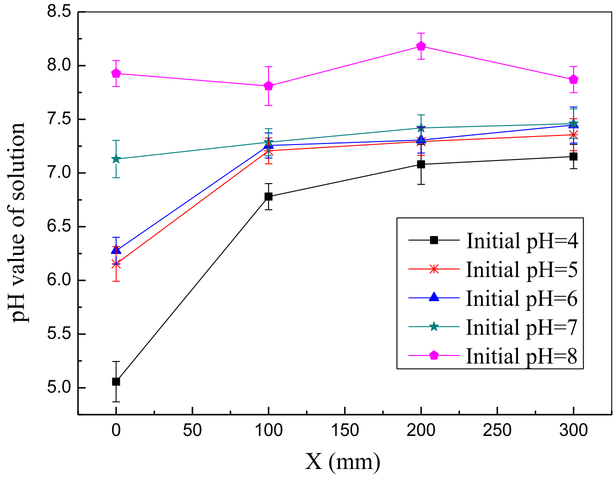

Fig. 9. Distribution of pH value in the direction of streamline at different initial pH conditions (current density *j*: 7.5 A/m^2; residence time RT: 20 min; charge loading Q_e: 4.9 × 10^5 C/m^3).

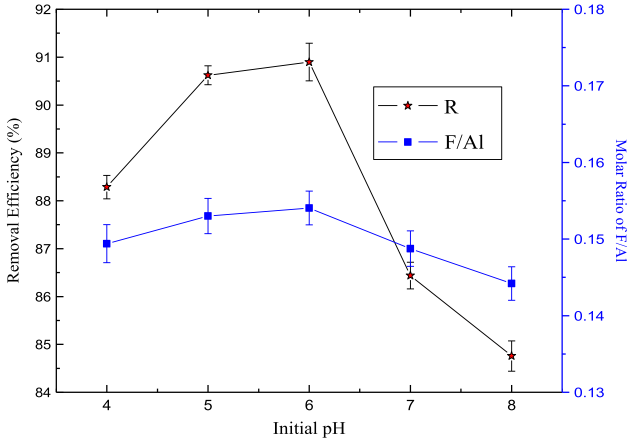

Fig. 10. Removal efficiency of F^{-} and F/Al ratio in the sludge at different initial pH conditions (current density *j*: 7.5 A/m^2; residence time RT: 20 min; charge loading Q_e: 4.9 × 10^5 C/m^3).

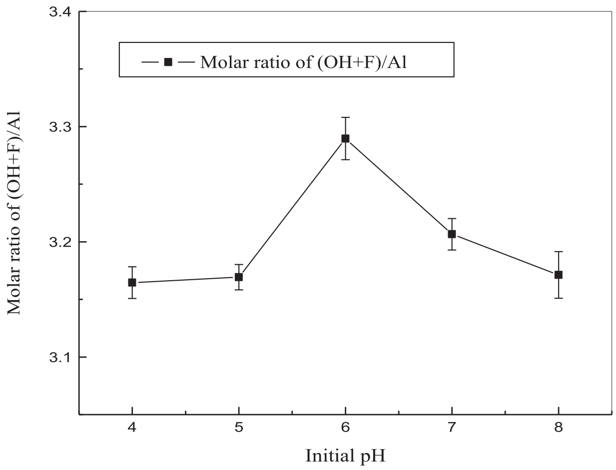

Fig. 11. The (OH + F)/Al ratio of flocs under different initial pH conditions (current density *j*: 7.5 A/m^2; residence time RT: 20 min; charge loading Q_e: 4.9 × 10^5 C/m^3).

4. Conclusions

The continuous and batch electrocoagulation processes were investigated and compared. The poor mixture and the uneven distribution of flocs in BEC lead to a lower removal efficiency. Under whole range of current densities, the superiority of CEC is obvious. High residence time is not suitable for continuous operation. High residence time will lead to intense back mixing in CEC process. At the direction of streamline, the degree of back mixing gets intense from inlet to the outlet. The performance of BEC and CEC under same charge loading differs a lot. It is attributed to the back mixing and uneven distribution of flocs in continuous and batch operations, respectively.

The influences of charge loading and initial pH on CEC process were investigated with the consideration of utilization rate of electro-generated Al element. The molar ratio of F/Al in sludge gradually decreases with the increment of charge loading. The ratio of (OH + F)/Al decreases from 3.45 to 3.10. This conforms the fact that the F^- is removed not only by Al $(OH)_{3-x}F_{x(s)}$ precipitation but also by the absorption of aluminum flocs. Under weak acid initial pH condition, the solution of the whole channel from inlet to outlet is also under weak acid pH condition. The production of aluminum hydroxide flocs will reach its maximum. This is proved by the utilization rate of F/Al and (OH + F)/Al in sludge.

The comparison between pilot-scale BEC and CEC process should be studied in future works. Also more works are required elucidating the influence of types and concentrations of pollutants and electrolyte on the utilization rate of electro-generated Al ions.

Acknowledgments

This study was supported by the National Natural Science Foundation of China (NSFC, No. 51208233) and the Natural Science Foundation of Jiangsu Province, China (No. BK2012079). This is also supported by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

References

[1] A. Mazighi, H. Lounici, N. Drouiche, R. Leenaerts, N. Abdi, H. Grib, N. Mameri, Economic study of groundwater defluoridation of the North African Sahara, Desalin. Water Treat. 54 (2015) 2681–2691.

[2] S. Vasudevan, J. Lakshmi, G. Sozhan, Studies on a Mg-Al-Zn Alloy as an anode for the removal of fluoride from drinking water in an electrocoagulation process, Clean—Soil Air Water 37 (2009) 372–378.

[3] E.J. Reardon, Y. Wang, A limestone reactor for fluoride removal from wastewaters, Environ. Sci. Technol. 34 (2000) 3247–3253.

[4] V. Khatibikamal, A. Torabian, F. Janpoor, G. Hoshyaripour, Fluoride removal from industrial wastewater using electrocoagulation and its adsorption kinetics, J. Hazard. Mater. 179 (2010) 276–280.

[5] H. Kodama, N. Kabay, Reactivity of inorganic anion exchanger $BiPbO_2(NO_3)$ with fluoride ions in solution, Solid State Ionics 141–142 (2001) 603–607.

[6] P.I. Ndiaye, P. Moulin, L. Dominguez, J.C. Millet, F. Charbit, Removal of fluoride from electronic industrial effluentby RO membrane separation, Desalination 173 (2005) 25–32.

[7] S. Vasudevan, M.A. Oturan, Electrochemistry: As cause and cure in water pollution—An overview, Environ. Chem. Lett. 12 (2014) 97–108.

[8] M. Tahaikt, I. Achary, M.M. Sahli, Z. Amor, M. Taky, A. Alami, A. Boughriba, M. Hafsi, A. Elmidaoui, Defluoridation of Moroccan groundwater by electrodialysis: Continuous operation, Desalination 189 (2006) 215–220.

[9] T. Harif, M. Khai, A. Adin, Electrocoagulation versus chemical coagulation: Coagulation/flocculation mechanisms and resulting floc characteristics, Water Res. 46 (2012) 3177–3188.

[10] A. Akyol, Treatment of paint manufacturing wastewater by electrocoagulation, Desalination 285 (2012) 91–99.

[11] U.T. Un, A.S. Koparal, U.B. Ogutveren, Fluoride removal from water and wastewater with a bach cylindrical electrode using electrocoagulation, Chem. Eng. J. 223 (2013) 110–115.

[12] N. Drouiche, S. Aoudj, H. Lounici, H. Mahmoudi, N. Ghaffour, M.F. Goosen, Development of an empirical model for fluoride removal from photovoltaic wastewater by electrocoagulation process, Desalin. Water Treat. 29 (2011) 96–102.

[13] R. Kamaraj, D.J. Davidson, G. Sozhan, S. Vasudevan, Adsorption of herbicide 2-(2,4-dichlorophenoxy)propanoic acid by electrochemically generated aluminum hydroxides: An alternative to chemical dosing, RSC Adv. 5 (2015) 39799–39809.

[14] S. Vasudevan, J. Lakshmi, G. Sozhan, Simultaneous removal of Co, Cu, and Cr from water by electrocoagulation, Toxicol. Environ. Chem. 94 (2012) 1930–1940.

[15] K.A. Vakil, M.K. Sharma, A. Bhatia, A.A. Kazmi, S. Sarkar, Characterization of greywater in an Indian middle-class household and investigation of physicochemical treatment using electrocoagulation, Sep. Purif. Technol. 130 (2014) 160–166.

[16] S. Cotillas, J. Llanos, O.G. Miranda, G.C. Díaz-Trujillo, P. Cañizares, M.A. Rodrigo, Coupling UV irradiation and electrocoagulation for reclamation of urban wastewater, Electrochim. Acta 140 (2014) 396–403.

[17] M.A. Sandoval, R. Fuentes, J.L. Nava, I. Rodríguez, Fluoride removal from drinking water by electrocoagulation in a continuous filter press reactor coupled to a flocculator and clarifier, Sep. Purif. Technol. 134 (2014) 163–170.

[18] G. Ghanizadeh, G. Shariati Neghab, M. Salem, K. Khalagi, CFD simulation of heat and mass transport for water transfer through hydrophilic membrane in direct-contact membrane distillation process, Desalin. Water Treat. (2015) 1–11, doi: 10.1080/19443994.2015.1094675.

[19] S. Aoudj, A. Khelifa, N. Drouiche, M. Hecini, HF wastewater remediation by electrocoagulation process, Desalin. Water Treat. 51 (2013) 1596–1602.

[20] M.M. Emamjomeh, M. Sivakumar, An empirical model for defluoridation by batch monopolar electrocoagulation/flotation (ECF) process, J. Hazard. Mater. 131 (2006) 118–125.

[21] N. Drouiche, S. Aoudj, H. Lounici, M. Drouiche, T. Ouslimane, N. Ghaffour, Fluoride removal from pretreated photovoltaic wastewater by electrocoagulation: An investigation of the effect of operational parameters, Procedia Eng. 33 (2012) 385–391.

[22] E. Bazrafshan, K.A. Ownagh, A.H. Mahvi, Application of electrocoagulation process using iron and aluminum electrodes for fluoride removal from aqueous environment, J. Chem. 9 (2012) 2297–2308.

[23] M.M. Emamjomeh, M. Sivakumar, Fluoride removal by a continuous flow electrocoagulation reactor, J. Environ. Manage. 90 (2009) 1204–1212.

[24] H. Zhao, W. Yang, J. Zhu, J. Ni, Defluoridation of drinking water by combined electrocoagulation: Effects of the molar ratio of alkalinity and fluoride to Al(III), Chemosphere 74 (2009) 1391–1395.

[25] M.M. Emamjomeh, M. Sivakumar, A.S. Varyani, Analysis and the understanding of fluoride removal mechanisms by an electrocoagulation/flotation (ECF) process, Desalination 275 (2011) 102–106.

[26] N. Drouiche, S. Aoudj, M. Hecini, N. Ghaffour, H. Lounici, N. Mameri, Study on the treatment of photovoltaic wastewater using electrocoagulation: Fluoride removal with aluminium electrodes—Characteristics of products, J. Hazard. Mater. 169 (2009) 65–69.

[27] B. Merzouk, B. Gourich, K. Madani, C. Vial, A. Sekki, Removal of a disperse red dye from synthetic wastewater by chemical coagulation and continuous electrocoagulation. A comparative study, Desalination 272 (2011) 246–253.

[28] J. Lu, Y. Li, M. Yin, X. Ma, S. Lin, Removing heavy metal ions with continuous aluminum electrocoagulation: A study on back mixing and utilization rate of electro-generated Al ions, Chem. Eng. J. 267 (2015) 86–92.

[29] E.W. Rice, L. Bridgewater, P.H.A. American, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, Washington, DC, 2012.

[30] R. Sinha, A. Singh, S. Mathur, Multiobjective optimization for minimum residual fluoride and specific energy in electrocoagulation process, Desalin. Water Treat. (2014) 1–11, doi: 10.1080/19443994.2014.990929.

[31] C.Y. Hu, S. Lo, W. Kuan, Y. Lee, Treatment of high fluoride-content wastewater by continuous electrocoagulation–flotation system with bipolar aluminum electrodes, Sep. Purif. Technol. 60 (2008) 1–5.

[32] C.Y. Hu, S.L. Lo, W.H. Kuan, Effects of the molar ratio of hydroxide and fluoride to Al(III) on fluoride removal by coagulation and electrocoagulation, J. Colloid Interface Sci. 283 (2005) 472–476.

[33] R. Kamaraj, S. Vasudevan, Evaluation of electrocoagulation process for the removal of strontium and cesium from aqueous solution, Chem. Eng. Res. Des. 93 (2015) 522–530.

[34] Y. Ae, F. Ba, K. Karakasz, A new adsorbent for fluoride removal: The utilization of sludge waste from electrocoagulation as adsorbent, Global Nest J. 17 (2015) 186–197.

[35] G. Mouedhen, M. Feki, M.D.P. Wery, H.F. Ayedi, Behavior of aluminum electrodes in electrocoagulation process, J. Hazard. Mater. 150 (2008) 124–135.