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Electro-coagulation-flotation process for algae removal

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ABSTRACT

Algae in surface water have been a long-term issue all over the world, due to their adverse influence on drinking water treatment process as well as drinking water quality. The algae removal by electro-coagulation–flotation (ECF) technology was investigated in this paper. The results indicated that aluminum was an excellent electrode material for algae removal as compared with iron. The optimal parameters determined were: current density = 1 mA/cm^2 , pH = 4-7, water temperature = $18-36 \degree C$, algae density = 0.55×10^9 – 1.55×10^9 cells/L. Under the optimal conditions, 100% of algae removal was achieved with the energy consumption as low as 0.4 kWh/m^3 . The ECF performed well in acid and neutral conditions. At low initial pH of 4-7, the cell density of algae removal worsened when the PH increased (7–10), and the main mechanism shifted to sweeping floculation and enmeshment. The mechanisms for algae removal at different pH were also confirmed by atomic force microscopy (AFM) analysis. Furthermore, initial cell density and water temperature could also influence the algae removal. Overall, the results indicated that the ECF technology was effective for algae removal, from both the technical and economical points of view.

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1. Introduction

The removal and control of algae in water treatment industry is a worldwide issue, especially in tropical and semi-tropical zone. Algae in surface water cause many problems such as color, odour, taste and toxins compounds [1], which would pose potential hazards to human and animal health. Furthermore, the algae would also adversely affect the drinking water treatment process [2,3]. Traditionally, pre-oxidation by ozone, chlorine dioxide, chlorine or permanganate is usually employed to enhance algae removal in the coagulation process [2,4,5].

As an alternative method to the coagulation/sedimentation process, electrocoagulation combined with electroflotation (ECF) technology has attracted considerable attentions in water and wastewater treatment. Usually, the following processes take place in the ECF system: (a) metal ions release at sacrificial anode through electrolytic oxidation, which are considered as efficient coagulants; at the same time, the oxygen and hydrogen microbubbles are generated at the anode and cathode, respectively; (b) the coagulants react with pollutants and bigger flocs are formed; (c) the flocculated particles are removed through sedimentation or lifted to the surface by the microbubbles adhered to them [6,7]. Besides, the anodic oxidation, cathodic reduction and electrophoretic migration of the

ions may also promote the pollutants removal [6]. Compared with conventional coagulation, the coagulants produced in situ in the ECF could offer many advantages, i.e. (i) no anions such as sulfates and chlorides would be introduced in the ECF system, which are always coupled with traditional coagulants [8]; (ii) the coagulants produced by electrolytic oxidation are of high efficiency, and less dosage would be required as compared with conventional coagulants [9]; (iii) pH adjustment is unnecessary since ECF performs well in a large pH range [10]; (iv) alkalinity is not consumed during ECF process as the OH⁻ ions are generated at cathode. Moreover, in ECF process, the microbubbles produced at the anode and cathode could also contribute to the separation of pollutants through flotation [11]. The main reactions occurring in ECF process with different electrode materials are as follows [12]:

When aluminum is used as electrode material, Anode:

$$AI \rightarrow AI^{3+} + 3e^{-} \tag{1}$$

$$2H_20 \to 0_2 + 4H^+ + 4e^-$$
 (2)

In solution:

$$Al^{3+} + 3H_2O \leftrightarrow Al(OH)_3 + 3H^+$$
(3)

Cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$
 (4)

When iron is used as electrode material,

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Anode:

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

$$2H_2O \to O_2 + 4H^+ + 4e^- \tag{6}$$

In solution:

$$Fe^{2+} + 2OH^- \leftrightarrow Fe(OH)_2$$
 (7)

If dissolved oxygen is presented in the solution, the reaction would be:

In solution:

$$Fe^{2+} + 4H^+ + O_2 \rightarrow Fe^{3+} + 2H_2O$$
 (8)

$$Fe^{3+} + 3OH^- \leftrightarrow Fe(OH)_3$$
 (9)

Cathode:

$$2H_2O + 2e^- \to H_2 + 2OH^- \tag{10}$$

It has been demonstrated that ECF was very effective for the treatment of a broad range of water and wastewater, such as colored water [13], fluoride-containing water [14,15], heavy metal-containing water [16,17], laundry wastewater [10], restaurant wastewater [18], oil wastewater [19], chemical mechanical polishing wastewater [20], and textile wastewater [21,22].

Generally, cyanobacteria (often called blue-green algae) have a lower density than that of water due to their gas vacuoles for adjusting the content of water [23]. Thus, it is difficult to remove the cyanobacteria through sedimentation. On the other hand, the ECF process with the combination of coagulation and flotation might be an effective technology for the algae removal. Poelman et al. found that excellent separation of cyanobacteria (>90%) could be achieved by electrolytic flocculation, with relatively low energy consumption (0.3 kWh/m³) [24]. Alfafara et al. demonstrated that the electroflotation alone also exhibited a maximum algae removal of 40–50% [25]. While complete removal of algae was obtained by Ghernaout et al. when treating Keddara raw water by the electrocoagulation using aluminum electrodes [26].

Few investigations, however, focused on the influence of the key parameters, including electrode material, initial pH, initial cell density of algae, and solution temperature, on the algae removal by ECF treatment; and the removal mechanisms were also not fully understood yet. In this research, the effects of these parameters on algae removal in the ECF process were systematically examined. Furthermore, scanning electron microscopy (SEM) coupled with energy-dispersive X-ray (EDX) analysis and atomic force microscopy (AFM) were also employed to investigate the removal mechanisms of algae in the ECF.

2. Materials and methods

2.1. Preparation of the algal suspension

The target algae used in the experiments was *Microcystis aeruginosa*, one of the dominant cyanobacteria, which occurs frequently in most eutrophic water bodies in China. *M. aeruginosa* was supplied by Wuhan Institute of Hydrobiology of Chinese Academy of Sciences, and was incubated as described by Xu et al. [27]. The testing water used in the study was prepared by diluting the culture solution of *M. aeruginosa* with deionized water. The algae solution was incubated for 7 days after inoculation; pre-experiments showed that the *M. aeruginosa* were at the log growth phase at this time. The initial cell density used in the experiments was controlled at 1.2×10^9 – 1.4×10^9 cells/L, except the experiments investigating the effect of initial cell density.



Fig. 1. Schematic diagram of the batch reactor system.

2.2. The ECF system

As shown in Fig. 1, the experiments were carried out in a polyethylene column (diameter = 10 cm; height = 16 cm) with an effective volume of 1000 mL. Aluminum or iron was used as the electrode material with the effective area of 60 cm², and the electrode gap of 1.0 cm. The voltage and current were provided with a digital direct current power supply (WYY 30V 3A, China), and measured by two digital multimeters (UT70B UTI-T, China). The cell was stirred with a magnetic stirrer (781 CJJ, China) at 200 rpm. All the experimental runs were performed at room temperature except experiments about the effect of temperature.

2.3. Experimental procedure

The comparison between aluminum and iron electrodes was performed for the treatment of algae-containing water. The pH of raw water was adjusted to desirable values using 0.1 M NaOH or 0.1 M HCl. The effects of current density and initial cell density on the algae removal in the ECF were also examined. At the end of each experiment, the solution was allowed to settle for 20 min for flotation or sedimentation; and then water sample was taken at 5.0 cm below the water surface, followed by the algae counting with a microscope (BX51 Olympus, Japan) according to the method used by Brookes et al. [28]. The algae removal efficiency was calculated as:(11)Algae removal efficiency (%) = $\frac{C_o - C_t}{C_o} \times 100$ where C_0 was the initial cell density of algae (cells/L) and C_t was the final cell density of algae (cells/L).

Furthermore, the electrical energy consumption of the ECF process for algae removal was evaluated. The energy consumption W (kWh/m³) was calculated as:

$$W = \frac{UIt_{\rm ECF}}{V_{\rm ECF}} \tag{12}$$

where *U* was the voltage (V), *I* was the applied electrolysis current (A), t_{ECF} was the electrolysis time (h) and V_{ECF} was the reactor volume (m³).

2.4. The characterization of the algal flocs

The algal flocs floated at the surface of the water in the ECF process were observed with a high-resolution scanning electron microscopy (SEM) (S-4700 HITACHI, Japan) coupled with energydispersive X-ray (EDX) analysis (AMETEK, USA). 10 mL of the algal flocs was concentrated by a centrifuger (SIGMA 2-16PK, GER-MANY) at 8000 rpm for 10 min. After discarding the supernatant,



Fig. 2. Removal efficiency of algae as a function of electrolysis time using different electrode materials. Conditions: current density, 1 mA/cm^2 ; room temperature; initial pH, 7.0; volume, 1.0 dm^3 ; initial cell density 1.2×10^9 – 1.4×10^9 cells/L.

the sample was fixed and dehydrated according to [29]. Then the sample was gold-coated and examined under the SEM. In addition, EDX was used for analyzing the element composition of the algal flocs.

Atomic force microscopy (AFM) (Bioscope Veeco, USA) was employed to further confirm the mechanisms for algae removal at different pH. 1 mL of flocs was fixed on a glass slide. After airdrying for 2 h, the images of the algal flocs were obtained under the tapping mode using a probe made by etched single crystal silicon.

3. Results and discussion

3.1. The comparison of different electrode materials

It has been established that the electrode material plays an important role in ECF process. Aluminum and iron have both been widely used as electrode materials in this process by many investigators [30-32]. However, little information about the comparison of electrode material on algae removal could be found in the literature up to now. In this investigation, comparative experiments were carried out using aluminum and iron as the electrode material, under the same operation conditions. Algae removal as a function of treatment time was shown in Fig. 2. Iron electrodes were observed to be less efficient as compared with aluminum electrodes, as demonstrated by the difference between the removal efficiencies (78.9% vs. 100%) at 45 min, probably due to the much higher current efficiency generated by aluminum electrodes than that by iron [33,34]. Also, under the experimental pH of 7, the amount of aluminum hydroxide was much higher than that of ferric/ferrous hydroxide, which might be another reason accounting for the better algae removal with aluminum electrodes [35]

In addition, in the case of aluminum electrodes, it was observed that a layer of greenish flocs floated at the surface of water, which might be composed of aluminum hydroxide and algae cells, as discussion in detail in Section 3.6. While in the case of iron electrodes, the water in the whole ECF reactor only appeared yellowish green at the beginning, and turned reddish-brown gradually, due to the presence of Fe (II) and Fe (III) species (Eqs. (7)-(9)). After 20 min of settlement, tiny flocs produced by iron electrodes still remained in the water. Overall, aluminum was considered as the better one for the algae removal and selected as the electrode material in the following experiments.



Fig. 3. Removal efficiency of algae as a function of electrolysis time at different current densities. Conditions: room temperature; initial pH, 7.0; volume, 1.0 dm^3 ; initial cell density $1.2 \times 10^9 - 1.4 \times 10^9$ cells/L.

3.2. Effect of current density

It is expected that current density exerts a significant influence on reaction kinetics and energy consumption of ECF process [11,17]. In this investigation, to optimize the current density, the experiments for algae removal were carried out with a wide range of current densities $(0.5-5 \text{ mA/cm}^2)$ at initial pH of 7. As shown in Fig. 3, when current density was 0.5 mA/cm², the removal efficiency increased gradually with the operating time, and 75 min of electrolysis time would be required to achieve complete removal. When current densities increased from 1 to 5 mA/cm², the removal efficiencies were shown to follow comparable variations with electrolysis time, as exhibited by the existence of a rapid increase at the initial stage, followed by a steady increase up to the complete algae removal. However, it could be seen that the higher the current density was, the more rapid the ECF treatment for algae removal would be. For example, 25 min was demonstrated to be enough for complete removal at the current density of 5 mA/cm²; while 45 min was needed at 1 mA/cm².

This could be attributed to the fact that the dissolved aluminum from anode increased with the current density and electrolysis time according to the Faraday's law. As the concentration of aluminum ions increased in the ECF, the coagulant surface area and number of active sites increased correspondingly [36], which promoted algal aggregation and flocs formation. Besides, it was shown that microbubble density increased and their size decreased with increasing current density [37], leading to a faster upward flow and the algae flotation.

In addition, the pH change of water during the ECF treatment with different current densities was investigated. As could be seen in Fig. 4, the pH increased gradually with the increased current density and electrolysis time. At the time that complete removal of algae was obtained, the final pH was about 9.2 when the current intensities were 2.0-5.0 mA/cm², and pH was about 8.3 with the current intensities of $0.5-1.0 \text{ mA/cm}^2$. The pH of the water increased from 7 to about 8-9 after ECF treatment, which could be attributed to the continuous production of OH- ions at the cathode with the generation of Al^{3+} at anode. According to Eqs. (1) and (4), the OH^- and Al^{3+} were generated with the molar ratio of 3:1; however, this ratio were between 2 and 2.5 when treating solutions of dyes and humic substances [38,39]. For algae solution, it might be reasonable to infer that the Al³⁺/OH⁻ ratio was also less than 3. As a result, OH⁻ ions accumulated in the algae solution, which resulted in the increase of solution pH after ECF treatment.



Fig. 4. Variation of pH as a function of electrolysis time at different current densities. Conditions: room temperature; initial pH, 7.0; volume, 1.0 dm³; initial cell density 1.2×10^9 – 1.4×10^9 cells/L.

In spite of more effective removal of algae with the higher current density, increasing the current density could also lead to the increase of applied potential, which resulted in the sharp increase of the energy consumption of the ECF system (Eq. (12)). According to Fig. 5, it could be observed that as current densities varied from 0.5 to 5.0 mA/cm², the energy consumption increased dramatically from 0.20 to 2.28 kWh/m³, correspondingly.

Therefore, it might be important to optimize the current input for the ECF process, to avoid the post pH adjustment and extrahigher energy consumption. In this investigation, the current density of 1 mA/cm² was found to be the optimum value when considering the energy consumption, the removal efficiency, and the effluent pH simultaneously.

3.3. Effect of initial pH

It has been long recognized that the solution pH is one of the key parameters influencing the performance of ECF process [12,16]. Initial pH exhibited different effects on the ECF for different target pollutants, such as turbidity and Eriochrome Black T [8,17]. However, the influence of pH for algae removal has not been made clear yet. Thus, in this study, the effect of initial pH on the algae removal was also examined, with the pH varied in the range of 4–10.



Fig. 5. Electrical energy consumption as a function of current density for complete removal of algae. Conditions: room temperature; initial pH, 7.0; volume, 1.0 dm^3 ; initial cell density $1.2 \times 10^9 - 1.4 \times 10^9$ cells/L.



Fig. 6. Removal efficiency of algae as a function of electrolysis time with different initial pH. Conditions: room temperature; current density, 1 mA/cm^2 ; volume, 1.0 dm^3 ; initial cell density, $1.2 \times 10^9 - 1.4 \times 10^9$ cells/L.

From Fig. 6, it could be found that low initial pH was beneficial to algae removal. For the first 15 min, the ECF exhibited low efficiency for the algae removal when initial pH was in the alkaline range. The treatment efficiency decreased with the increase of initial pH. When t_{ECF} = 55 min, the ECF removed the algae in the raw water completely with the pH of 4–7; while the removal efficiencies were 99%, 90% and 87.2% when initial pH was 8, 9 and 10, respectively.

It was observed from Fig. 6 that the algae removal could be improved by decreasing the initial pH and/or increasing the electrolysis time. This might be explained by the aluminumspecies in the solution, which relies significantly on the pH and aluminum concentration according to the concentrationpH aluminum-species diagram [35]. In acidic and neutral pH range (4–7), aluminum hydroxide precipitates and monomerichydroxoaluminum cations, as well as polymeric species such as $Al_{13}O_4(OH)_{24}^{7+}$ are the primary species in the solution according to [40]. As a result, positively charged precipitates could be formed (i.e. aluminum hydroxide together with the adsorbed hydroxoaluminum cations). Therefore, the negatively charged algae would be easily adsorbed onto the positively charged precipitates, which facilitated the removal of algae through subsequent flotation.

In alkaline conditions, monomeric-hydroxoaluminum anions dominated in solution, which led to negative charges of the aluminum hydroxide precipitates [8], and consequently reduced the adsorption capacity of negatively charged algae. Thus, the ECF exhibited worse algae removal under alkaline condition as compared with that under acid and neutral conditions. Nevertheless, as the electrolysis time increased, the efficiency of algae removal improved significantly as a result of the sweeping and enmeshment effect through the continuous generation of aluminum coagulants. The results obtained in this investigation were similar to that obtained by Zhu et al. for the virus removal [36].

To better understand the removal mechanisms of algae in the above experiments, two samples of algal flocs with the similar removal efficiency (about 70%) were collected for AFM analysis. As shown in Fig. 7a, the fresh algae cells before ECF treatment appeared to have smooth surface; while after ECF treatment under initial pH of 6, a number of small floccules were adsorbed on the algae (Fig. 7b), which was due to the charge neutralization between the positively charged floccules and the negatively charged algae. Fig. 7c shows that the treated algae were covered almost completely with a large amount of flocs under the initial pH of 9; thus the algae cells were considered to be removed through the mechanism of sweeping flocculation and enmeshment.



Fig. 7. AFM topographic images of algal flocs, scan rate: 0.5003 Hz. (a) Algae in fresh culture before treatment, (b) after ECF treatment, conditions: initial pH, 6; current density, 1 mA/cm²; electrolysis time, 5 min; effluent pH, 7.4; the algae removal efficiency, 70.2% (c) after ECF treatment, conditions: initial pH, 9; current density, 1 mA/cm²; electrolysis time, 35 min; effluent pH, 8.9; the algae removal efficiency, 71.4%.

Besides, variation of the solution pH during the ECF process was investigated. It could be observed in Fig. 8 that when the initial pH was 4–8, the solution pH increased gradually with the electrolysis time. The increase of pH was mainly due to the continuous formation of OH[–] ions at the cathode as a consequence of the H₂ evolution process (Eq. (4)). In addition, Eq. (3) would shift towards the left, which could also lead to the increase of pH [41]. On the other hand, when the initial pH was increased to 9 and 10, a slight decrease of the pH was observed at the beginning, which might be explained by the consumption of OH[–] as a consequence of the formation of Al(OH)₄[–]; and then almost a constant pH level was maintained, probably due to the buffer effect of Al(OH)₃/Al(OH)₄[–] (Eq. (13)).

$$Al(OH)_3 + OH^- \leftrightarrow Al(OH)_4^-$$
(13)

As shown in Fig. 6, when the initial pH varied in the range of 4–7, the electrolysis time for complete algae removal was 45 min under the experimental conditions. Thus, the energy consumption was almost constant at the level of about 0.3 kWh/m³ (Fig. 9). However, as the initial pH further increased from 7 to 9, the electrolysis time for complete algae removal increased from 45 to 75 min correspondingly, which led to the increase of energy consumption



Fig. 8. Variation of pH as a function of electrolysis time at different initial pH. Conditions: room temperature; current density, 1 mA/cm²; volume, 1.0 dm³; initial cell density 1.2×10^9 - 1.4×10^9 cells/L.

from 0.29 to 0.53 kWh/m³. On the other hand, the similar energy consumption was observed for the initial pH values of 9 and 10 (0.53 kWh/m³ vs. 0.60 kWh/m³), mainly due to the same electrolysis time of 75 min required for complete algae removal.

In conclusion, higher efficiency of algae removal could be obtained in acidic and neutral conditions. With lower pH, low aluminum dosage would be required for algae removal through the charge neutralization mechanism; while at higher pH, higher aluminum dosage was needed to achieve the similar removal efficiency, through the mechanism of enmeshment and sweeping flocculation. And both coagulation mechanisms were equally important for algae removal in ECF process.

3.4. Effect of initial algae cell density

In natural waters, different algae cell densities might occur in different regions and different seasons. Thus, the effectiveness of ECF for algae removal with different initial algae cell densities was evaluated. Fig. 10 shows the influence of initial cell density on algae removal, which decreased notably with the increase of cell density. This behavior could be attributed to the fact that no sufficient aluminum was available for the removal of excessive algae cells with short electrolysis time. Furthermore, the reaction rate



Fig. 9. Electrical energy consumption as a function of initial pH for complete removal of algae. Conditions: room temperature; current density, 1 mA/cm^2 ; volume, 1.0 dm^3 ; initial cell density $1.2 \times 10^9 - 1.4 \times 10^9$ cells/L.



Fig. 10. Removal efficiency of algae as a function of electrolysis time with different initial cell densities. Conditions: initial pH, 7.0; current density, 1 mA/cm²; volume, 1.0 dm³.

decreased when the initial cell density was increased according to Emamjomeh and Sivakumar [42]. The similar results were also obtained by Ghosh et al. [43].

In the experiments, when the cell densities were 0.55×10^9 , 1.10×10^9 , 1.55×10^9 and 2.10×10^9 cells/L, the energy consumption of the ECF process for complete algae removal were 0.20, 0.21, 0.30 and 0.26 kWh/m³, respectively. The initial cell density did not seem to greatly influence the energy consumption.



Fig. 11. Removal efficiency of algae as a function of electrolysis time under different temperature. Condition: initial pH, 7.0; current density, 1 mA/cm^2 ; volume, 1.0 dm^3 ; initial cell density $1.2 \times 10^9 - 1.4 \times 10^9$ cells/L.

3.5. Effect of temperature

Water temperature is one of the most important environmental factors that might influence algae removal in the ECF. However, previous studies showed that water temperature exerted different effects on electrocoagulation for the removal of different pollutants [44,45]. Thus, it is necessary to examine the effect of water temperature on algae removal. As shown in Fig. 11, it was found



Fig. 12. SEM-EDX analysis of the algal flocs produced by ECF. (a and b) SEM micrograph at different magnifications; EDX analysis of elemental compositions (c) on the algae cells and (d) on the agglutinant.

342 Table 1

Flemental	composition	and relative	contents of	atoms of	on the f	locs by	SFM-FD	(analysi
Licificitai	composition	and relative	contents of	atoms	JII LIIC I	IUCS Dy	JLIVI-LD/	s analysi

Element	СК	NK	OK	AlK	PK	SK	NaK	FeK	MgK	Total
Spectrum 1	65.40%	9.49%	16.17%	3.78%	2.99%	1.21%	0.36%	0.49%	0.11%	100%
Spectrum 2	42.57%	9.85%	22.15%	14.27%	6.89%	2.05%	0.55%	1.39%	0.28%	100%

that the algae removal was dramatically improved at the initial stage with increased temperature. When t_{ECF} = 15 min, the removal efficiencies of 46%, 86%, and 98% were obtained at the temperature of 18 °C, 27 °C and 36 °C, respectively. The increase of algae removal at higher temperature might be attributed to the increase of particle transport and collision rate through the reduction of viscosity [44,46]. Besides, the dissolving rate of aluminum electrode increased when the solution temperature increased [47], which could also accelerate the algae removal and shorten the electrolysis time.

To achieve the complete removal of algae, 0.36, 0.24 and 0.16 kWh/m³ of electrical energy would be consumed when the temperature was 18 °C, 27 °C and 36 °C, respectively. On one hand, higher temperature could increase the electrical conductivity of the water, thus the applied voltage would be reduced. On the other hand, the higher water temperature was able to enhance the algae removal, thus shorten the electrolysis time. As a result, less energy would be required at higher water temperature for complete algae removal.

3.6. The characterization of the algal flocs

SEM coupled with EDX analysis was used to examine the surface morphology and elemental composition of the greenish algal flocs floated at the surface of the ECF. It could be observed from Fig. 12a that the algal flocs were mainly composed of algae cells, which were flocculated together by some agglutinant. To better understand the formed algal flocs, two sites on the algal flocs were further investigated through EDX analysis. One site was on the algae cells (spectrum 1), the other was on the agglutinant (spectrum 2) (Fig. 12b), and the obtained values were reported in Table 1. As shown in Fig. 12c and Table 1, the peaks indicated that carbon, nitrogen and oxygen were the main elements in the algae cells, which accounted for 65.4%, 9.5% and 16.2% of the total weight, respectively. On the other hand, EDX analysis for the agglutinant (Fig. 12d and Table 1) revealed that the carbon content reduced to 42.6%; while high content of aluminum (14.3%) was detected in the agglutinant. Therefore, it might be considered that the agglutinant was the aluminum hydrolysis together with the flocculated pollutants on it. It was also observed that 22.2% of oxygen and 6.9% of phosphor were presented in the aluminum floccules. The increase of oxygen might be due to the aluminum hydroxide formed in the ECF; while the increase of phosphor might result from the coagulation of phosphate in the raw water by the aluminum coagulants.

4. Conclusions

In this study, the effects of various parameters on algae removal in an ECF system were investigated, including electrode material, current density, initial pH, algae cell density and water temperature. The following conclusions could be drawn according to the experimental results.

- (1) Much better algae removal could be achieved by aluminum electrodes than that by iron electrodes, as indicated by the less electrolysis time required for complete algae removal and clearer treated water.
- (2) The current density should be optimized when considering the algae removal, energy consumption and effluent pH simulta-

neously. In this investigation, the current density of 1 mA/cm² was found to be optimum under the experimental conditions.

- (3) The ECF exhibited higher algae removal efficiency under the initial pH of 4–7 as compared with that under 7–10. This might be due to that the dominant mechanism for algae removal was charge neutralization under acidic and neutral conditions, which shifted to sweeping flocculation and enmeshment under alkaline condition. These behaviors were further confirmed by atomic force microscopy (AFM) analysis. As a result, the energy consumption for complete algae removal increased from 0.29 to 0.60 kWh/m³ when the initial pH varied from 7 to 10.
- (4) Longer electrolysis time would be required when the initial cell density was increased. On the other hand, higher water temperature could accelerate algae removal in the ECF and thus shorten electrolysis time.

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References

- [1] D. Elke, W. Claudia, Cyanobacterial toxins-occurrence, biosynthesis and impact on human affairs, Mol. Nutr. Food Res. 50 (2006) 7–17.
- [2] J.D. Plummer, J.K. Edzwald, Effect of ozone on algae as precursors for trihalomethane and haloacetic acid production, Environ. Sci. Technol. 35 (2001) 3661–3668.
- [3] H. Liang, W.J. Gong, J. Chen, G.B. Li, Cleaning of fouled ultrafiltration (UF) membrane by algae during reservoir water treatment, Desalination 222 (2008) 267–272.
- [4] J.J. Chen, H.H. Yeh, I.C. Tseng, Effect of ozone and permanganate on algae coagulation removal-pilot and bench scale tests, Chemosphere 74 (2009) 840–846.
- [5] R. Henderson, S.A. Parsons, B. Jefferson, The impact of algal properties and preoxidation on solid–liquid separation of algae, Water Res. 42 (2008) 1827–1845.
- [6] M.Y.A. Mollaha, P. Morkovskyb, J.A.G. Gomesc, M. Kesmezc, J. Pargad, D.L. Cockec, Fundamentals, present and future perspectives of electrocoagulation, J. Hazard. Mater. B 114 (2004) 199–210.
- [7] M.M. Emamjomeh, M. Sivakumar, Review of pollutants removal by electrocoagulation and electrocoagulation/flotation processes, J. Environ. Manage. 90 (2009) 1663–1679.
- [8] P. Caizares, F. Martnez, C. Jimnez, J. Lobato, M.A. Rodrigo, Coagulation and electrocoagulation of wastes polluted with dyes, Environ. Sci. Technol. 40 (2006) 6418–6424.
- [9] F. Ilhan, U. Kurt, O. Apaydin, M.T. Gonullu, Treatment of leachate by electrocoagulation using aluminum and iron electrodes, J. Hazard. Mater. 154 (2008) 381–389.
- [10] J.T. Ge, J.H. Qu, P.J. Lei, H.J. Liu, New bipolar electrocoagulation–electroflotation process for the treatment of laundry wastewater, Sep. Purif. Technol. 36 (2004) 33–39.
- [11] A.Y. Hosny, Separating oil from oil-water emulsions by electroflotation technique, Sep. Technol. 6 (1996) 9–17.
- [12] S. Vasudevan, G. Sozhan, S. Ravichandran, J. Jayaraj, J. Lakshmi, S.M. Sheela, Studies on the removal of phosphate from drinking water by electrocoagulation process, Ind. Eng. Chem. Res. 47 (2008) 2018–2023.
- [13] J.Q. Jiang, N. Graham, C. Andre, H.K. Geoff, N. Brandon, Laboratory study of electro-coagulation-flotation for water treatment, Water Res. 36 (2002) 4064–4078.
- [14] Q.H. Zuo, X.M. Chen, W. Li, G.H. Chen, Combined electrocoagulation and electroflotation for removal of fluoride from drinking water, J. Hazard. Mater. 159 (2008) 452–457.
- [15] M. Bennajah, B. Gourich, A.H. Essadki, Ch. Vial, H. Delmas, Defluoridation of Morocco drinking water by electrocoagulation/electroflotation in an electrochemical external-loop airlift reactor, Chem. Eng. J. 148 (2009) 122–131.

- [16] P. Gao, X.M. Chen, F. Shen, G.H. Chen, Removal of chromium (VI) from wastewater by combined electrocoagulation–electroflotation without a filter, Sep. Purif. Technol. 43 (2004) 117–123.
- [17] B. Merzouk, B. Gourich, A. Sekki, K. Madani, M. Chibane, Removal turbidity and separation of heavy metals using electrocoagulation–electroflotation technique. A case study, J. Hazard. Mater. 164 (2009) 215–222.
- [18] G.H. Chen, X.M. Chen, P.L. Yue, Electrocoagulation and electroflotation of restaurant wastewater, J. Environ. Eng. 126 (2000) 858–863.
- [19] R.M. Bande, B. Prasad, I.M. Mishra, K.L. Wasewar, Oil field effluent water treatment for safe disposal by electroflotation, Chem. Eng. J. 137 (2008) 503–509.
- [20] C.Y. Hu, S.L. Lo, C.M. Li, W.H. Kuan, Treating chemical mechanical polishing (CMP) wastewater by electro-coagulation-flotation process with surfactant, J. Hazard. Mater. A 120 (2005) 15-20.
- [21] L. Szpyrkowicz, Hydrodynamic effects on the performance of electrocoagulation/electroflotation for the removal of dyes from textile wastewater, Ind. Eng. Chem. Res. 44 (2005) 7844–7853.
- [22] A.H. Essadki, M. Bennajah, B. Gourich, Ch. Vial, M. Azzi, H. Delmas, Electrocoagulation/electroflotation in an external-loop airlift reactor—application to the decolorization of textile dye wastewater: a case study, Chem. Eng. Process. 47 (2008) 1211–1223.
- [23] T. Nakamura, Y. Adachi, M. Suzuki, Flotation and sedimentation of a single microcystis floc collected from surface bloom, Water Res. 6 (1993) 979–983.
- [24] E. Poelman, N.D. Pauw, B. Jeurissen, Potential of electrolytic flocculation for recovery of microalgae, Resour. Conserv. Recycl. 19 (1997) 1–10.
- [25] C.G. Alfafara, K. Nakano, N. Nomura, T. Igarashi, M. Matsumura, Operating and scale-up factors for the electrolytic removal of algae from eutrophied lakewater, J. Chem. Technol. Biotechnol. 77 (2002) 871–876.
- [26] D. Ghernaout, A. Badis, A. Kellil, B. Ghernaout, Application of electrocoagulation in *Escherichia coli* culture and two surface waters, Desalination 219 (2008) 118–125.
- [27] Y.F. Xu, J. Yang, M.M. Qu, Y.L. Wang, J.P. Jia, Study of *Microcystis aeruginosa* inhibition by electrochemical method, Biochem. Eng. J. 36 (2007) 215–220.
- [28] J.D. Brookes, G.G. Ganf, M.D. Burch, The separation of forms of *Microcystis* from Anabaena in mixed populations by the application of pressure, Aust. J. Mar. Freshwater Res. 45 (1994) 863–868.
- [29] J.Y. Tian, H. Liang, J. Nan, Y.L. Yang, S.J. You, G.B. Li, Submerged membrane bioreactor (sMBR) for the treatment of contaminated raw water, Chem. Eng. J. 148 (2009) 296–305.
- [30] M. Zaied, N. Bellakhal, Electrocoagulation treatment of black liquor from paper industry, J. Hazard. Mater. 163 (2009) 995–1000.
- [31] A.A. Bukhari, Investigation of the electro-coagulation treatment process for the removal of total suspended solids and turbidity from municipal wastewater, Bioresour. Technol. 99 (2008) 914–921.
- [32] I.A. Alaton, I. Kabdash, D. Hanbada, E. Kuybu, Electrocoagulation of a real reactive dyebath effluent using aluminum and stainless steel electrodes, J. Hazard. Mater. 150 (2008) 166–173.

- [33] I. Zongo, A.H. Maiga, J. Wethe, G. Valentin, J.P. Leclerc, G. Paternotte, F. Lapicque, Electrocoagulation for the treatment of textile wastewaters with Al or Fe electrodes: compared variations of COD levels, turbidity and absorbance, J. Hazard. Mater. 169 (2009) 70–76.
- [34] P. Caizares, M. Carmona, J. Lobato, F. Martnez, M.A. Rodrigo, Electrodissolution of aluminium electrodes in electrocoagulation processes, Ind. Eng. Chem. Res. 44 (2005) 4178–4185.
- [35] J. Duan, J. Gregory, Coagulation by hydrolysing metal salts, Adv. Colloid Interface Sci. 100–102 (2003) 475–502.
- [36] B. Zhu, D.A. Clifford, S. Chellam, Comparison of electrocoagulation and chemical coagulation pretreatment for enhanced virus removal using microfiltration membranes, Water Res. 39 (2005) 3098–3108.
- [37] P.H. Holt, G.W. Barton, M. Wark, A.A. Mitchell, A quantitative comparison between chemical dosing and electrocoagulation, Colloids Surf. A 211 (2002) 233-248.
- [38] A.S. Koparal, Y.S. Yildiz, B. Keskinler, N. Demircioglu, Effect of initial pH on the removal of humic substances from wastewater by electrocoagulation, Sep. Purif. Technol. 59 (2008) 175–182.
- [39] O.T. Can, M. Bayramoglu, M. Kobya, Decolorization of reactive dye solutions by electrocoagulation using aluminum electrodes, Ind. Eng. Chem. Res. 42 (2003) 3391–3396.
- [40] N. Adhoum, L. Monser, N. Bellakhal, J.E. Belgaied, Treatment of electroplating wastewater containing Cu²⁺, Zn²⁺ and Cr(VI) by electrocoagulation, J. Hazard. Mater. B 112 (2004) 207–213.
- [41] X.M. Chen, G.H. Chen, P.L. Yue, Separation of pollutants from restaurant wastewater by electrocoagulation, Sep. Purif. Technol. 19 (2000) 65–76.
- [42] M.M. Emamjomeh, M. Sivakumar, An empirical model for defluoridation by batch monopolar electrocoagulation/flotation (ECF) process, J. Hazard. Mater. B 131 (2006) 118–125.
- [43] D. Ghosh, H. Solanki, M.K. Purkait, Removal of Fe(II) from tap water by electrocoagulation technique, J. Hazard. Mater. 155 (2008) 135–143.
- [44] A.E. Yilmaz, R. Boncukcuoglu, M.M. Kocakerim, M.T. Yilmaz, C. Paluluoglu, Boron removal from geothermal waters by electrocoagulation, J. Hazard. Mater. 153 (2008) 146–151.
- [45] Y.O.A. Fouad, A.H. Konsowa, H.A. Farag, G.H. Sedahmed, Performance of an electrocoagulation cell with horizontally oriented electrodes in oil separation compared to a cell with vertical electrodes, Chem. Eng. J. 145 (2009) 436– 440.
- [46] Z. Zaroual, H. Chaair, A.H. Essadki, K. El Ass, M. Azzi, Optimizing the removal of trivalent chromium by electrocoagulation using experimental design, Chem. Eng. J. 148 (2009) 488–495.
- [47] M. Vepsalainen, M. Ghiasvand, J. Selin, J. Pienimaa, E. Repo, M. Pulliainen, M. Sillanpaa, Investigations of the effects of temperature and initial sample pH on natural organic matter (NOM) removal with electrocoagulation using response surface method (RSM), Sep. Purif. Technol. 69 (2009) 255–261.