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Could the optimization of electrocoagulation simply be based on the maximization of flocs yield?

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ABSTRACT

Electrocoagulation (EC) is a promising and moderately environmentally-friendly electrochemical wastewater treatment method. Since a wide range of pollutants are present in wastewater, it has become tedious to optimize the operation parameters of EC for every single kind of pollutant. In this work, we tried to prove that the optimization of EC could be simply based on the maximization of flocs yield that determines the hydroxide flocs' adsorption effect. The influence of some crucial operation parameters on flocs yield was investigated. It was found that flocs yield reaches its maximum at no aeration condition and flocs yield steadily decreased with the increment of extra time after electrolysis. Weak acid and neutral initial pH lead to a higher flocs yield. The impacts of flocs yield on EC efficiency were investigated. Three typical pollutants (anions (F^-), organics (MO), and heavy metal ions (Ni^{2+})) were chosen as the target pollutant. It was found that higher flocs yield resulted in higher removal efficiency of anions and organics apart from heavy metal ions. Hence, the optimization of operation parameters of the EC process could be simply based on the maximization of flocs yield.

Keywords: Electrocoagulation; Hydroxide flocs; Flocs yield; Electrochemical wastewater treatment; Adsorption

1. Introduction

Electrocoagulation (EC) process is considered to be an environmentally friendly and efficient electrochemical technology for treating wastewater containing heavy metal ions, inorganic contaminants, or toxic organic compounds [1–3]. Many other methods have been reported for these pollutants from wastewater such as chemical coagulation (CC), adsorption, and membrane filtration [4,5]. Although CC is one of the most used technology for contaminants removal, this process produces too much sludge and needs to add extra coagulants compared to the EC process [6]. The EC technique is based on the electrochemical reaction at the anode, which couples hydroxide precipitation, coagulation, and adsorption [7]. During the EC process, the sacrificial anodes such as iron (Fe) or aluminum (Al) release metal ions Fe^{2+} or Al^{3+} whereas cathodes generate OH^- by water electrolysis (Fig. 1). The electro-generated Fe^{2+} ions (or Al^{3+}) and OH^- transfer in the electrolyte and undergo further spontaneous hydrolysis reactions to form various monomeric and polymeric species, part of which will finally transform into hydroxide flocs [8,9]. The *in-situ* generated hydroxide flocs possess a high specific surface area and high density of hydroxyl radicals to adsorb several pollutants by physical adsorption, surface complexation reaction, coordination adsorption, etc. [10].

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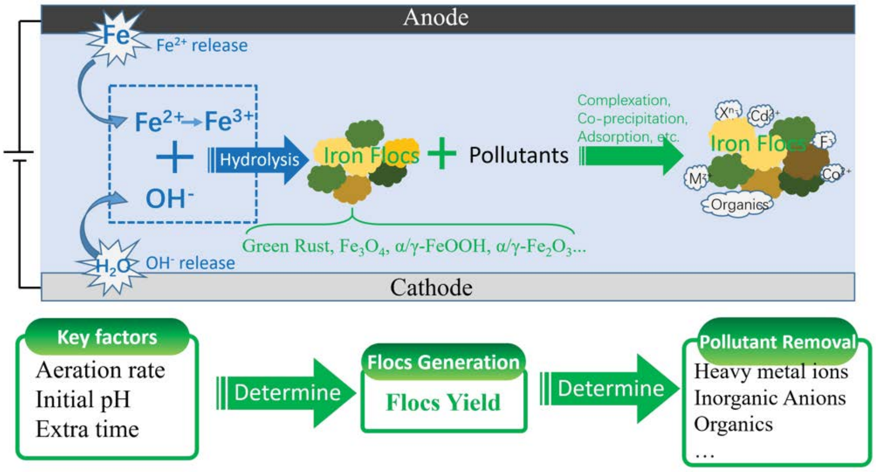


Fig. 1. Schematic diagram and key factors of flocs generation.

The pollutant removal through flocs adsorption is considered to be the most important removal mechanism in the EC process [11–15].

The pollutant removal mechanism of flocs during the EC process for treating kinds of pollutants was studied recently. Phosphate anions removal in the EC process was reported in three aspects: removal from effluents by complexation, precipitation, and/or adsorption by metallic hydroxides [12]. The removal mechanism of boron was verified via sweep flocculation of flocs [13,16]. The removal mechanisms of fluorine ions were confirmed to be co-precipitation and surface ligand exchange reactions [6,15]. Removal mechanisms of heavy metals ions from wastewater using electrocoagulation were reported as redox reactions and/or complexation reactions and/or adsorption by hydroxides [17]. Studies also proved that green rust plays a crucial role in Cd^{2+} removal by strong adsorption and ion exchange [18]. Nuñez et al. [19] also found arsenic could be eliminated by two steps: (i) adsorption by flocs; (ii) co-precipitation with flocs. The *in-situ* electro-generated flocs were proved to be responsible for the pollutant removal, especially the inorganic anions and cations.

There are various kinds of iron hydroxide (or oxyhydroxide and oxide) generated during the EC process. The XRD results reported in the literatures [20–27] showed the fact that iron flocs like α-FeOOH, γ-FeOOH, α-Fe_2O_3, γ-Fe_2O_3, Fe_3O_4, green rust, etc. exist during the EC process. The effects of EC operation conditions on the structure of generated flocs were studied by a few researchers. The growth and structure of iron precipitate flocs produced in a bench-scale EC system were investigated by Lee and Gagnon [21]. The results revealed that higher current leads to larger flocs with irregular and amorphous structures. Dubrawski et al. [22] investigated the formation pathways of mixed-valent Fe hydro(oxide) phases generated by the iron EC process under different aeration conditions. The generated green rust only exists at the condition of the N_2 atmosphere (DO absent) and only exists in several seconds and finally transforms to Fe_3O_4. At the condition of aeration (DO present), the flocs are in the state of α-FeOOH and γ-FeOOH. The effect of electrolyte composition on flocs' structure generated in EC was studied by van Genuchten et al. [23]. Electrolyte composition strongly determines the structure, ion uptake behavior, and colloidal stability of the Fe(III) flocs. The adsorption ability of hydroxide flocs with different structures and compositions differs. FeOOH with more surface hydroxyls may have a higher ligand exchange capacity and higher adsorption capacity. The green rust which has a layered structure also may have a higher pollutants adsorption when compared with the other iron (oxy) hydroxide or oxide flocs. However, there were few studies about the adsorption ability of flocs (*in-situ* generated in the EC process) with different structures.

A lot of literatures have focused on the optimization of EC's operating parameters to get the high removal efficiency for certain pollutants [2,8,6,12,20,24–27]. It is hard to investigate on the optimization of operating parameters to get the highest removal efficiency for every kind of pollutant. This work aims to prove the fact that instead of the optimization of the EC process's operation parameters for getting the highest removal for every kind of pollutants, the optimization could be based on the maximization of flocs yield.

It was proven above that freshly generated hydroxide flocs play a key role in contaminants removal during EC. The optimization of EC operation conditions should be based on maximizing the hydroxide flocs' adsorption effect, which is determined by the flocs yield. However, few literatures discussed about the flocs yield. In our previous study [9,28], the flocs generation and yield during the continuous EC process were studied with the aid of mathematical modeling. A steady-state model considering electrochemical hydrolysis reaction, mass, and momentum transfer was established to simulate the generation of hydroxides during the continuous EC process. The production of various kinds of aluminum hydroxide flocs were simulated and discussed.

After treatment, another important consideration in the EC process is the disposal of sludge containing pollutants. The amount of sludge produced by EC is less than sludge produced by CC, which can be settled by several methods, such as landfilling, incineration, compost, and cement-based solidification stabilization. Sludge containing iron or aluminum can be an appropriate raw material for manufacturing building blocks due to its compressive strength. Manufacturing brick or ceramic materials is another method for disposing of sludge driven by environmental protection [4].

It is generally known that a high electrolyte conductivity and a low inter-electrode distance can reduce ohmic losses (potential drop) in the solution, which reduces the cell potential [29]. In this work, the generation and yield of flocs during the real batch EC process were studied (Fig. 1). The effect of some key operation conditions on the flocs yield was analyzed and the optimization condition for higher or maximum flocs yield was discussed. Heavy metal, fluoride, and dye are three major pollutants in wastewater derived from metal-finishing, textile industry, electroplating industry, and other manufacturing and processing industries, which have been proved that can be efficiently removed by EC technology [4,29,30]. This wastewater causes severe environmental problems and serious human issues even in small quantity. For instance, organic dye depletes aquatic fauna and flora and are carcinogenic in nature; wastewater containing heavy metals has a chance to enter the food chain and tends to accumulate in living organisms; fluoride causes thyroid disorder, neurological damage, and mottled teeth, etc., once its concentration exceeds 4 mg/L [5,6,30]. Therefore, Ni^{2+}, F^{-}, and methyl orange (MO) were chosen as the target pollutants, which could be generalized as heavy metal ions, inorganic anions, and organic pollutants, respectively. The role of flocs in the EC process for treating three typical kinds of pollutants was studied. The removal mechanism of these three kinds of pollutants were discussed and studied, respectively. The variations in removal efficiency were explained and analyzed with the consideration of *in-situ* electro-generated flocs yield.

2. Materials and Methods

2.1. Chemicals

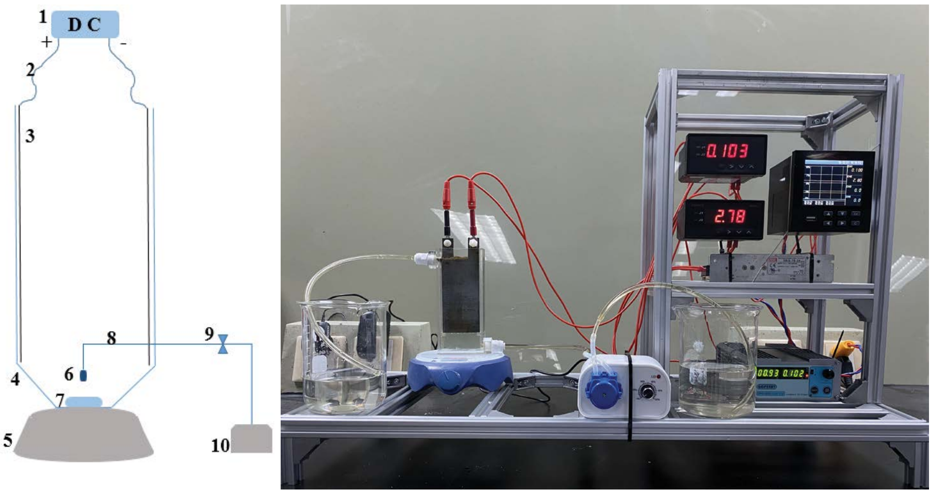
The electrolyte was composed of 0.2 M sodium sulfate (Na_2SO_4) and 0.1 M sodium chloride (NaCl). Heavy metal ions (Ni^{2+}) or organics (MO) or anions (F^{-}) were selected as the pollutant. The concentrations of three kinds of model wastewater (Ni^{2+}, MO, or F^{-}) were both set as 100 mg/L. $NiSO_4{\cdot}6H_2O$, MO, and NaF were dissolved in the electrolyte, respectively, to get the model wastewater. In the experiments, the pH values were adjusted by NaOH (0.5 M) and/or HCl (20%). All chemicals used were analytical grade reagents. All solutions were prepared with ultrapure water (resistivity > 18.2 MΩ*cm).

2.2. Measurements

The pH value was measured with a pH meter. Pure electrolyte solution (without pollutant) was used for experiments conducted in section 3.1 (Flocs yield during batch EC process). Model wastewater were prepared for studies conducted in section 3.2 (Role of flocs yield in pollutant removal during batch EC process). Model wastewater were prepared for studies conducted in section 3.3. Three parallel experiments were taken to get the error bar. At the end of EC treatment, the solution with flocs was filtered by an aqueous phase micro-filtration membrane (0.22 μm × 50mm) to get the flocs. Then the flocs were dried at 110°C. The weight of generated flocs was calculated with an electronic balance.

2.3. Experimental apparatus and procedure

The batch EC reactor was self-designed and constructed with Pyrex glass with the following dimensions: two rectangular plates (Fe, 126 mm × 46 mm × 2 mm) with 50 cm^2 effective surface area and a constant gap of 10 mm was maintained between them. Prior to the experiments, the electrode plates were polished with sandpaper, etched



(a) (b)

Fig. 2. (a) Schematic diagram of EC reactor: (1) constant-current power supply, (2) wire, (3) electrodes, (4) electrolytic cell, (5) magnetic stirrers, (6) air inlet, (7) magnetic stir bar, (8) airway tube, (9) flowmeter instrument, and (10) air pump and (b) bench-scale EC process.

with diluted HCl solution (5% by weight) for 20 min, and rinsed three times with ultrapure water. 60 mL electrolyte or wastewater was used in each experiment. The electrodes were directly connected to a constant direct current (DC) power supply as shown in Fig. 2. During the EC process, the batch reactor was stirred at 300 rpm with a magnetic stir bar. A constant current density of 10 A/m^2 was maintained on the iron electrodes by the DC power supply.

3. Results and discussion

3.1. Flocs yield during batch EC process

During the EC process, the *in-situ* generated Fe^{2+} and OH^- undergo spontaneous hydrolysis reactions to form various monomeric and polymeric hydroxide or oxyhydroxide flocs such as goethite (α-FeOOH), maghemite (Fe_2O_3), lepidocrocite (γ-FeOOH), and magnetite (Fe_3O_4) [22,31]. The newly formed metal hydroxide flocs possess a large specific surface area and abundant surface hydroxyl groups that could remove various pollutants. The pollutants could be removed through flocs' complexation reaction adsorption, physical adsorption, and electric-static adsorption, etc. [32]. Theoretically, a higher flocs yield means higher removal efficiency of contaminants. Therefore, the flocs yield may determine the pollutants' removal. The flocs yield generated during the EC process was investigated.

The influence of aeration rate conditions on flocs yield was investigated (Fig. 3a). It was found that under different aeration rates the flocs yield of EC varies slightly. The flocs yield without aeration is a bit higher than that with aeration. EC at no aeration condition has the maximum flocs yield. At the condition of no aeration, the flocs generated are temporarily in the state of green rust (GR) and then transform to the magnetite Fe_3O_4 [22]. The GR which has the layered structure also may have a higher pollutants adsorption when compared with the other iron (oxy) hydroxide or oxide flocs. At the condition of aeration, the flocs yield increased only slightly with the increasing aeration rate. This could be explained by the oxidation of Fe^{2+} through aeration and the transformation of hydroxide flocs. With the increment of aeration rate, Fe hydroxides are in the state to α-FeOOH and γ-FeOOH [22], which lead to an increase in flocs yield. Furthermore, the structure of iron hydroxide changes at aeration conditions, subsequently resulting in a change of flocs weight. To sum up, from the aspect of flocs yield, aeration maybe not necessary since maximum flocs yield was observed at no aeration.

The flocs are generated *in-situ* during the electrolysis time. The extra time after electrolysis which may determine the hydrolysis depth of the electro-generation Fe ions could affect the yield of flocs. The influence of extra time on the flocs yield in the EC process was studied and the results are shown in Fig. 3b. As can be seen from the curve, flocs yield firstly decreases sharply and then increase slightly with the increment of extra time and reaches its minimum at 120 min. The variation of flocs yield with an increment of extra time could be explained by the hydrolysis of the flocs. A small amount of the formed flocs will decompose to soluble Fe hydroxides due to the equilibrium after electrolysis. The maximum flocs yield was generated in the condition of no extra time, however, the extra time after electrolysis may improve the pollutant adsorption, which will be discussed in section 3.3.

The initial pH of the solution controls the amount of electro-generated Fe^{2+} and OH^- and affects the hydrolysis of Fe ions and the structure of flocs as well. Also, the flocs could dissolve in strongly alkaline conditions, affecting the formation of flocs. As a consequence, EC with these initial pH conditions may result in a lower production of flocs. The initial pH condition is therefore a key operation parameter on the formation and production of flocs. The effect of initial pH on the flocs yield was studied and illustrated in Fig. 3c. It could be found that flocs yield reaches its maximum at neutral pH conditions while the flocs yield decreases with the increase of initial pH at both acid and alkaline conditions. It has been reported that the alkaline condition and strong acid condition greatly impede the formation of hydroxide flocs. Thus, flocs yield decreased with increment of basic pH. Additionally, OH^- released from the cathode surface could increase the risk of anode passivation (which will lead to oxygen evolution and the formation of dense oxides on the surface of the anode, preventing the release of Fe^{2+}). However, initial weak acidic pH conditions could prevent the passivation of the anode. The weak acidic pH condition is suitable for the formation of Fe flocs. In conclusion, from the aspect of flocs yield and technical issues, the optimized initial pH range is from weak acidic to neutral (pH 5–7).

3.2. Role of flocs yield in pollutant removal during batch EC process

Pollutants can be removed through flocs complexation reaction, electro-static attraction, bridging adsorption, and sweep coagulation. For different pollutants (such as inorganics and organics), the role of flocs in pollutant removal differs. The complexation adsorption of flocs plays a major role in the removal of cationic metal ions and anions. Physical adsorption accounts for the removal of organics. Thus, in this section, the removal efficiency and mechanisms of synthetic wastewater pollutants (nickel ions, fluoride, and methyl orange) were explained from the aspect of flocs yield.

3.2.1. Ni^{2+} removal during EC process

The adsorption process of heavy metal ions by metal hydroxide flocs contains many complicated processes, such as complexation reaction, sweep coagulation, co-precipitation, and electrical neutralization. Among these removal approaches, the surface complexation reaction [Eqs. (1) and (4)] and (co-)precipitation [Eqs. (2), (3), and (5)] is the most important approach [8,9].

For Iron-EC process, the surface complexation reaction of Fe hydroxide flocs is:

$$z \equiv \mathrm{Fe-OH} + \mathrm{Me}^{z+} \leftrightarrow \left(\equiv \mathrm{FeO}\right)_z \mathrm{Me} + z\mathrm{H}^+ \qquad (1)$$

where ≡ is the surface of the particle; Me is the heavy ions; → is coordinate bonds.

The (co-)precipitation reaction is:

$$\mathrm{Fe(OH)_2 + Me^{z+} \leftrightarrow Fe(OH)_{(2-z)}(O)_z Me_{(s)} + zH^+} \tag{2}$$

$$\mathrm{Fe(OH)_3 + Me^{z+} \leftrightarrow Fe(OH)_{(3-z)}(O)_z Me_{(s)} + zH^+} \tag{3}$$

For aluminum-EC process, the surface complexation reaction of Al hydroxide flocs is [32]:

$$z \equiv \mathrm{Al-OH + Me^{z+} \leftrightarrow (\equiv AlO)_z Me + zH^+} \tag{4}$$

The (co-)precipitation reaction is:

$$\mathrm{Al(OH)_3 + Me^{z+} \leftrightarrow Al(OH)_{(3-z)}(O)_z Me_{(s)} + zH^+} \tag{5}$$

Fig. 4 shows the removal efficiency of nickel ions under various operation conditions. As can be seen from Fig. 4a, the removal efficiency at no aeration and low aeration rate are much higher than that at other aeration rates. The variation of removal efficiency and flocs yield shows a similar trend, revealing a proportionality relationship between flocs yield and Ni^{2+} removal. However, aeration didn't increase flocs yield, indicating that aeration does not have an impact on the heavy metal ions removal. The heavy metal ions are removed by flocs' direct complexation, surface complexation reactions, and adsorption. It can be concluded that aeration is not necessary for the removal of heavy metal ions. Another factor needed to be mentioned is the adsorption capacity of flocs with different structures. At no aeration condition, the *in-situ* electro-generated flocs are temporarily in the state of GR and then transform to the magnetite Fe_3O_4 [22]. The GR which has the layered structure may also have a higher pollutants adsorption compared with the other iron (oxy)hydroxide or oxide flocs. Thus, at the condition of no aeration, the removal efficiency of Ni^{2+} reaches its maximum induced by the higher flocs yield and the flocs structure.

Effects of extra time (after electrolysis) on removal efficiency of Ni^{2+} were studied and the results are shown in Fig. 4b. As stated above, extra time hardly affects the structure of flocs but affects the complexation reactions and flocs adsorption to pollutants. It was concluded above that the flocs yield controls the removal efficiency of heavy metals. From Fig. 4b it was found that the relationship between removal efficiency and extra time is contrary to that between flocs yield and extra time. This can be explained by the adsorption equilibrium of flocs. It was found that at the low extra time (0–30 min) the removal efficiency increases with the increment of extra time and reached the maximum at 30 min extra time. This is due to the fact that as time goes, flocs yield decreases but the adsorption time of flocs for pollutant removal increases, which causes a higher removal efficiency. At the high extra time (60–500 min), the removal efficiency decreased slightly with the increment of extra time (Fig. 4b). Despite the longer adsorption time, the desorption time is augmented simultaneously. Therefore, further increase of extra time has little effect on removal of Ni^{2+} on account of adsorption equilibrium.

Fig. 4c shows the effect of initial pH on Ni^{2+} removal. It was found that the removal efficiency of Ni^{2+} increased with the increment of initial pH. At weak acidic initial pH conditions, the variation trend of removal efficiency is consistent with that of floc yield, which indicates that the removal efficiency increases with the increase of flocs yield. However, at neutral and alkaline conditions, the trends are inconsistent. Although a low flocs yield was observed at alkaline pH conditions, the high concentration of generated OH^- facilitated the precipitation reaction of Ni^{2+} in solution leading to higher removal efficiency. Therefore, the metal ions can be removed through precipitation and co-precipitation regardless of the low flocs yield [33]. Hence, when treating heavy metal ions by EC process with initial basic pH condition, the precipitation reaction of OH^- plays a major role and thus the flocs yield has limited influence on heavy metal ion removal.

3.2.2. *Methyl orange (MO) removal during EC process*

In this section, the organic pollutants removal by EC process was discussed from the aspects of *in-situ* electro-generated flocs yield and structure. The main removal mechanisms of organic pollutants through the EC process are direct/indirect (electro-)oxidation, flocs adsorption, surface complexation reaction (Eq. (6)), and a combination of the above [34]:

$$\begin{aligned}&\mathrm{M(OH)_2^+ + dye-SO_3-Na \rightarrow}\\&\quad\mathrm{\left[M(OH)_2 - 2(SO_3 - dye)\right]_{(particle)} + Na^+}\end{aligned} \tag{6}$$

The removal efficiency of methyl orange (MO) under various operating conditions is shown in Fig. 5. It was found from Fig. 5a that with the change of aeration rate, the variation of removal efficiency is also consistent with flocs yield. No aeration or high aeration rate (0.4 L/min) was beneficial for MO removal. The above analysis showed the fact that the flocs yield is much higher under no aeration or high aeration rate condition, which leads to the higher adsorption capacity of flocs. Compared with the Ni^{2+} removal, the removal mechanism of MO is more complicated. MO not only could be removed by the adsorption of flocs but also could be oxidized and mineralized directly at the electrode by the breakage of carbon chains after oxidation. Furthermore, MO can also be oxidized by highly oxidizing substances such as hydroxyl radicals generated during the EC process. Therefore, these complicated mechanisms together lead to a larger error bar of MO removal efficiency (Fig. 5). Also, at no aeration condition, due to the temporarily generated GR (green rust) that presents layered structure [22], the flocs have higher adsorption capacity. This fact also makes the EC process get the highest removal efficiency at no aeration condition.

The variation of MO removal efficiency with extra time after electrolysis is shown in Fig. 5b. The removal efficiency of MO increases with the increment of extra time and reaches the maximum at 60 min extra time. After reaching the maximum removal efficiency, removal efficiency stops increasing and begins to flatten, which could

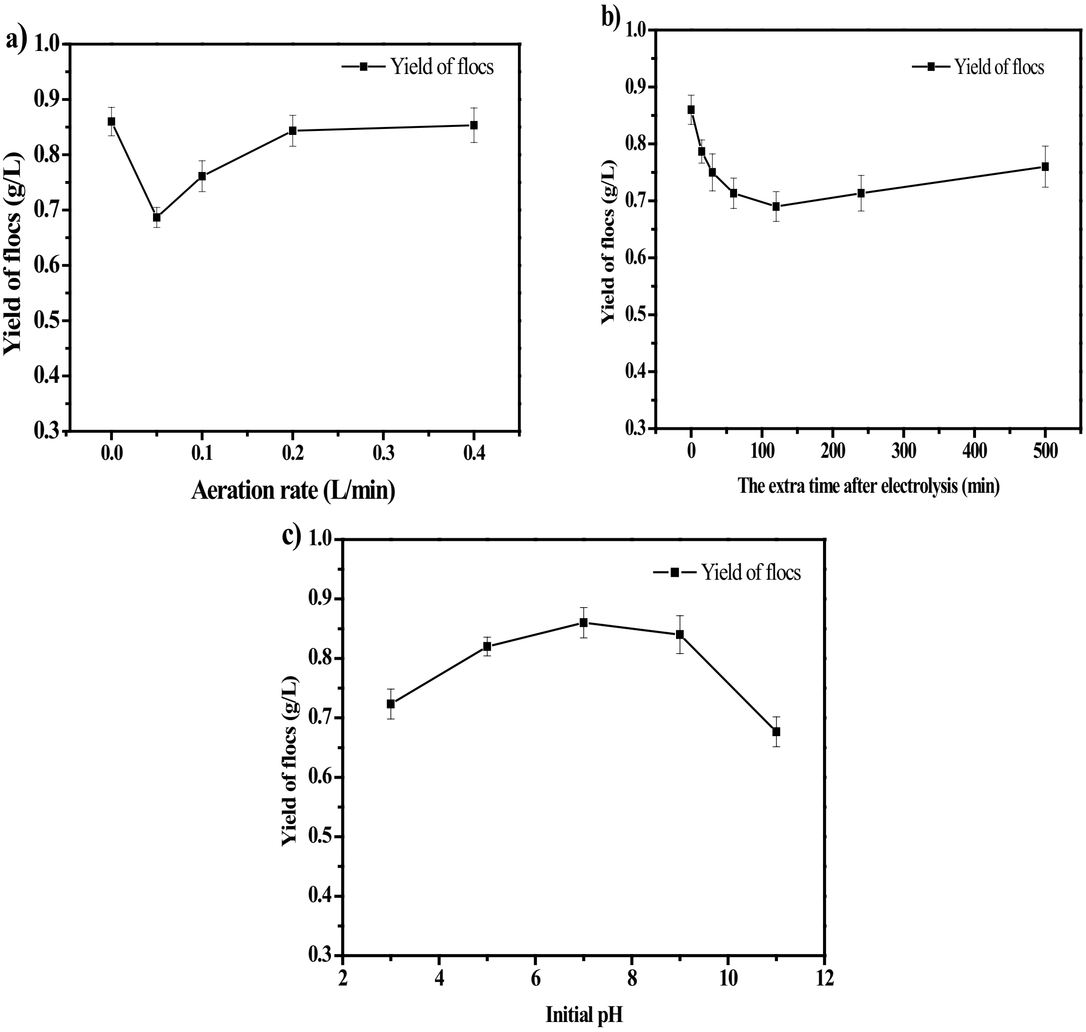


Fig. 3. Yield of iron hydroxide flocs under different operation conditions: (a) aeration rate = 0/0.05/0.1/0.2/0.4 L/min, extra time = 0 min, pH = 7; (b) extra time = 0/15/30/60/12/240/500 min, aeration rate = 0 L/min, pH = 7; (c) initial pH = 3/5/7/9/11, aeration rate = 0 L/min, extra time = 0 min. Conditions: j = 10 A/m^2, electrolysis time = 30 min, r = 300 rpm, and electrolyte: 0.1 M NaCl + 0.2 M Na_2SO_4.

also be explained by the adsorption equilibrium of flocs. Appropriate extra time is critical for both flocs adsorption and MO/organics removal. When comparing Fig. 4b with 5b, it could be found that the variation of MO removal efficiency with extra time is similar to that of Ni^{2+}. It is worth noting that the removal efficiency of MO reaches its maximum at 60 min extra time, which is longer than that of Ni^{2+} (30 min). It is owing to that the size of MO is larger than that of heavy metal ions, which could be concluded that the longer extra time to adsorb pollutant with large size. Furthermore, the variation trend of removal efficiency with extra time is contrary to that of flocs yield with extra time, which is triggered by the same mechanism that has been expounded in the removal of Ni^{2+}. Obviously, the optimization of organic pollutant removal by EC process should also be based on the maximization of flocs yield, and appropriate extra time after electrolysis is crucial for flocs adsorption.

The removal efficiency of MO under different initial pH is shown in Fig. 5c. It was found that the variation of removal efficiency with initial pH value is similar to the variation of flocs yield. With the increment of initial pH value, both the flocs yield and the removal efficiency of MO demonstrate maximum peaks, in which the flocs yield gets its maximum in initial neutral pH condition and the removal efficiency of MO gets its maximum in weak acid pH condition. Actually, besides the flocs adsorption, direct anodic oxidation, and hydroxyl radical oxidation also contribute to the organics removal during the EC process, which results in such a difference. During the EC process, reactive oxygen species (ROS, such as reactive hydroxyl) could be generated. In addition, it is necessary to mention that the redox potential of the electro-generated ROS is much higher than that at the neutral or basic condition. Thus, at the acid or weak acid initial pH condition, the flocs yield is lower and flocs adsorption capacity is limited, but the MO removal through ROS oxidation should not be neglected.

To sum up, for the MO or organic pollutant, the variation of MO removal efficiency is in accordance with the flocs yield. The optimization of the EC process for treating

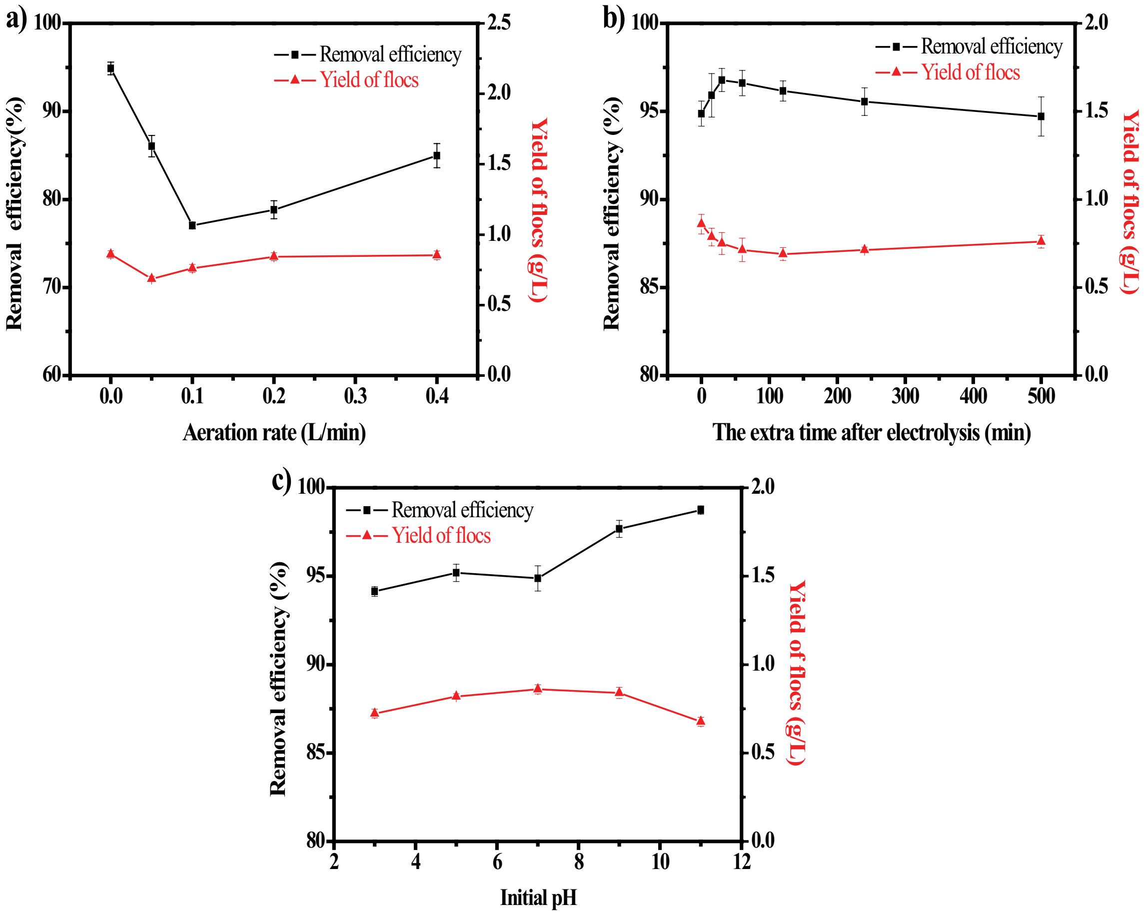


Fig. 4. Removal efficiency of wastewater containing Ni^{2+} under different operation conditions: (a) aeration rate = 0/0.05/0.1/0.2/0.4 L/min, extra time = 0 min, pH = 7; (b) extra time = 0/15/30/60/12/240/500 min, aeration rate = 0 L/min, pH = 7; (c) initial pH = 3/5/7/9/11, aeration rate = 0 L/min, extra time = 0 min. Conditions: j = 10 A/m², electrolysis time = 30 min, r = 300 rpm, and electrolyte: 0.1 M NaCl + 0.2 M Na_2SO_4.

organic pollutants or refractory organic pollutants should be based on maximizing the flocs yield.

3.2.3. Fluoride removal during EC process

During the EC process the removal mechanisms of fluoride have been proven to be direct adsorption, co-precipitation, and flocs adsorption [15]. Iron hydroxide flocs or aluminum hydroxide flocs could combine with fluoride ions to form various hydroxide complexes and co-precipitates in solution [4,35,36]. The co-precipitation and flocs complexation reaction during EC process for treating fluoride is shown in Eqs. (7)–(10).

$$\mathrm{Al}\left(\mathrm{OH}\right)_3 + x\mathrm{F}^- \leftrightarrow \mathrm{Al}\left(\mathrm{OH}\right)_{3-x}\mathrm{F}_x + x\mathrm{OH}^- \tag{7}$$

$$n\mathrm{Al}^{3+}_{(\mathrm{aq})} + 3n - m\mathrm{OH}^-_{(\mathrm{aq})} + m\mathrm{F}^-_{(\mathrm{aq})} \rightarrow \mathrm{Al}_n\mathrm{F}_m\left(\mathrm{OH}\right)_{3n-m(\mathrm{s})} \tag{8}$$

$$\mathrm{Al}_n\left(\mathrm{OH}\right)_{3n(\mathrm{s})} + m\mathrm{F}^-_{(\mathrm{aq})} \rightarrow \mathrm{Al}_n\mathrm{F}_m\left(\mathrm{OH}\right)_{3n-m(\mathrm{s})} + m\mathrm{OH}^-_{(\mathrm{aq})} \tag{9}$$

$$\mathrm{Fe}\left(\mathrm{OH}\right)_3 + 3\mathrm{F}^- \rightarrow \mathrm{FeF}_3 + 3\left(\mathrm{OH}\right)^- \tag{10}$$

The removal efficiency of fluorine wastewater under various aeration rates was studied and shown in Fig. 6a. The removal efficiency of fluorine presents a down- and up-trend with the increase of aeration rate, indicating that no aeration and high aeration rate (0.4 L/min) are beneficial to the removal of F^-. As discussed above, flocs yield was much higher under no aeration or high aeration rate condition which has a better adsorption capacity of pollutants. As illustrated in Eq. (10), fluorine clouds be partly eliminated by iron hydroxide. As a consequence, the degree of (co-)precipitation and complexation reaction are determined by the amount of flocs containing abundant surface hydroxyl and surface areas. In regard to the structure of flocs which was influenced by aeration, it almost had no influence on the removal efficiency of fluoride compared with the effect of flocs yield on removal efficiency. Thus, it could be concluded that the effect of aeration rate on removal efficiency of F^- is consistent with the effect of aeration rate on the flocs yield, revealing that the removal efficiency of F^- is mostly determined by the flocs yield.

The influence of extra time (after electrolysis) on removal efficiency of fluorine wastewater was studied and shown in Fig. 6b. The removal efficiency of F^- under different extra time reaches its maximum at extra time = 30 min, and

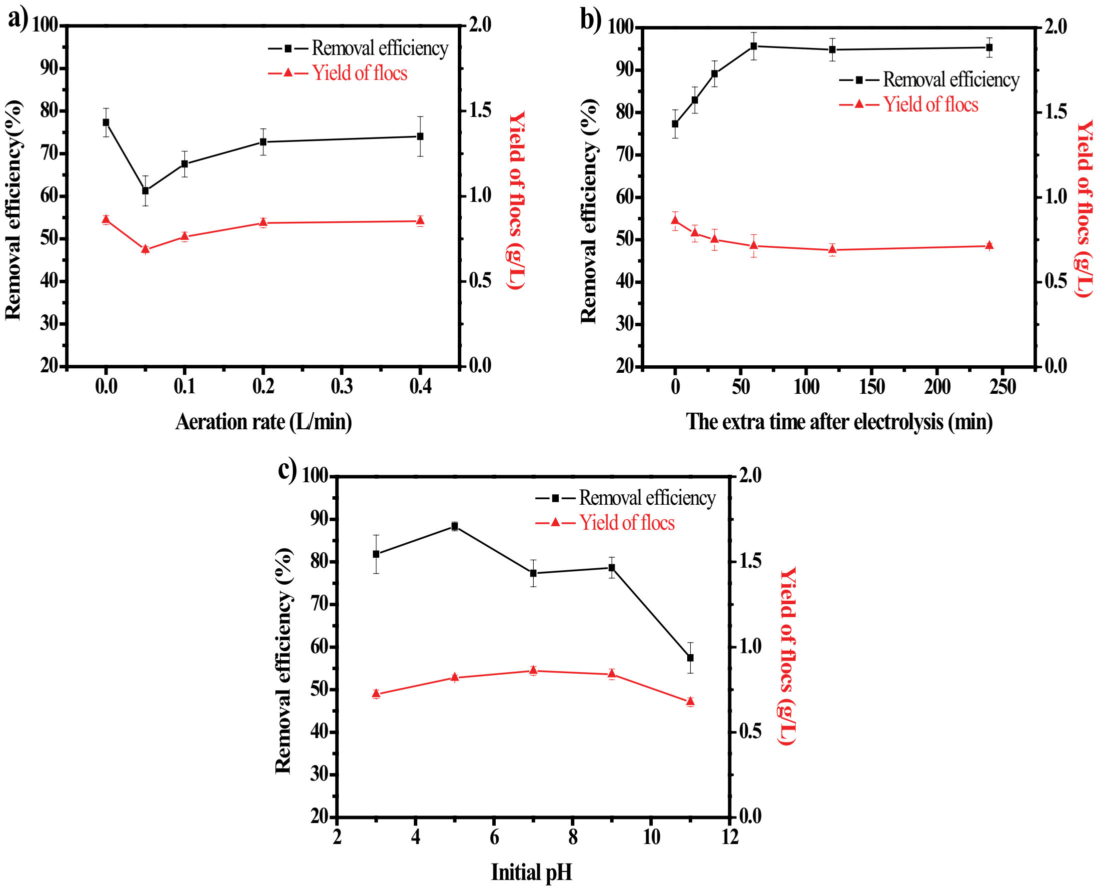


Fig. 5. Color removal of MO wastewater under different operation conditions: (a) aeration rate = 0/0.05/0.1/0.2/0.4 L/min, extra time = 0 min, pH = 7; (b) extra time = 0/15/30/60/12/240/500 min, aeration rate = 0 L/min, pH = 7; (c) initial pH = 3/5/7/9/11, aeration rate = 0 L/min, and extra time = 0 min. Conditions: *j* = 10 A/m^2, electrolysis time = 30 min, *r* = 300 rpm, and electrolyte: 0.1 M NaCl + 0.2 M Na_2SO_4.

thereafter gradually decreases, which is in consistent with that of Ni^{2+} and MO removal. For Ni^{2+} and F^-, removal efficiency was highest when extra time was 30 min, while the removal efficiency of MO reached a maximum when extra time was 60 min. The possible cause is that Ni^{2+} and F^- take shorter extra time to reach adsorption equilibrium because of the smaller ion size compared with MO. Thus for the inorganic pollutants which have a smaller size, the extra time after electrolysis is shorter. As mentioned above, a small amount of formed flocs decomposed to soluble Fe hydroxides after electrolysis, resulting in the decreasing tendency of removal efficiency with longer extra time. Therefore, advisable extra time is advantageous to fluorine removal.

The influence of initial pH on removal efficiency of fluorine wastewater was studied and is shown in Fig. 6c. It was found that the removal efficiency changes with initial pH and reaches its maximum at weak acid initial pH (pH = 5). With the change of initial pH, the variation of removal efficiency was found to be basically consistent with flocs yield. It was concluded that the weak acid and neutral initial pH range (5–7) which was favorable for the formation of iron flocs generated a higher amount of flocs. Therefore, the flocs complexation and adsorption effect under weak acid and neutral initial pH are more efficient than that under other initial pH conditions. The optimization of fluoride removal by EC should be based on the maximization of flocs yield.

In summary, the optimized operation conditions for three pollutant removal during the EC process are concluded in Table 1. For anionic pollutants (F^-) and organics (MO), the variation trends of removal efficiency with the change of initial pH condition and aeration rate are in accordance with that of flocs yield. The reason is that aeration rate and initial pH could affect the flocs yield which in turn influenced the adsorption capacity of flocs. Anionic and organic pollutants were mainly removed by flocs adsorption, indicating that the flocs yield determines the removal efficiency of anions and organics pollutants. Thus, the optimization of anionic and organic pollutant removal through the EC process can be based on the maximization of flocs yield. However, the heavy metal ions like Ni^{2+} could be removed by (co-)precipitation besides the flocs adsorption. Therefore, for heavy metal ions Ni^{2+}, the variations of removal efficiency were not in accordance with that of flocs yield. For heavy metal ions, the optimization should be based on the maximization of flocs yield and co-precipitation.

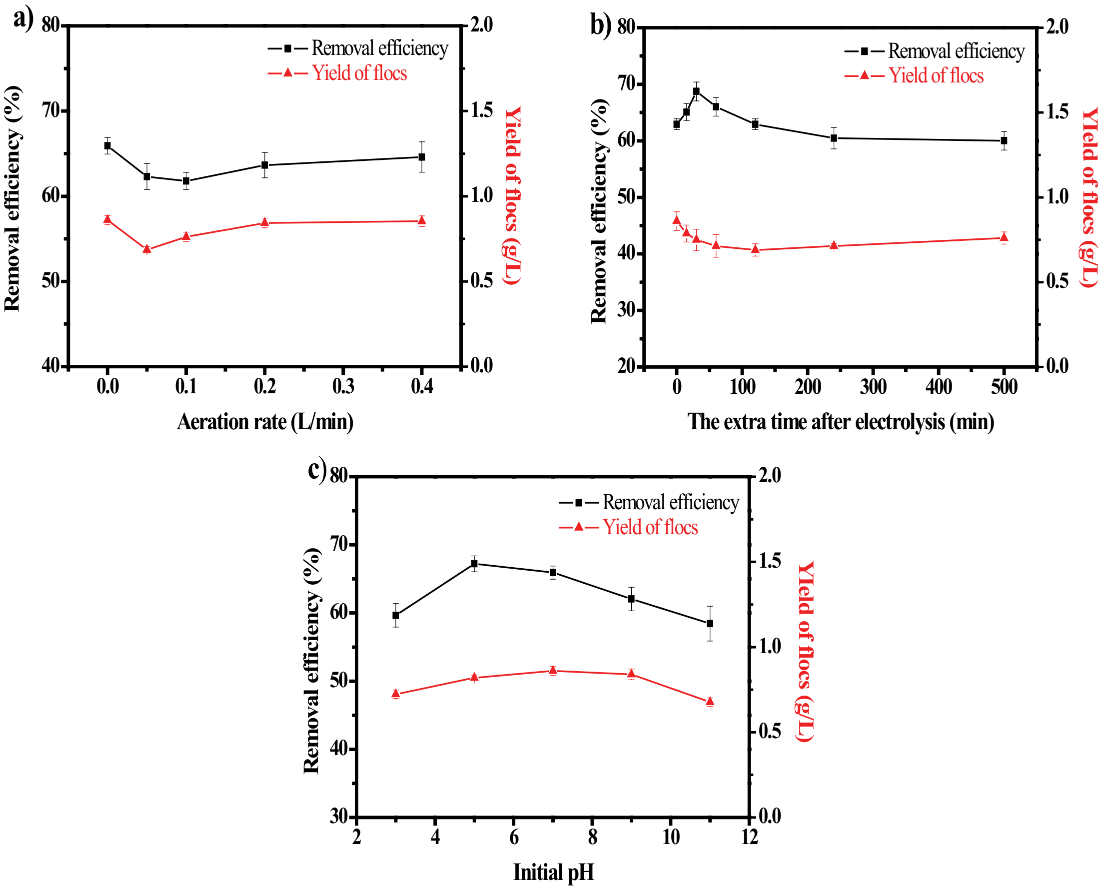


Fig. 6. Removal efficiency of fluorine wastewater under different operation conditions: (a) aeration rate = 0/0.05/0.1/0.2/0.4 L/min, extra time = 0 min, pH = 7; (b) extra time = 0/15/30/60/12/240/500 min, aeration rate = 0 L/min, pH = 7; (c) initial pH = 3/5/7/9/11, aeration rate = 0 L/min, extra time = 0 min. Conditions: $j = 10$ A/m^2, electrolysis time = 30 min, $r = 300$ rpm, electrolyte: 0.1 M NaCl + 0.2 M Na_2SO_4.

4. Conclusions

The wastewater contains a thousand kinds of pollutants. It is hard to investigate on the optimization of operating parameters for every kind of pollutant. This work proved the fact that the optimization of operation parameters of the EC process could be based on the maximization of flocs yield.

The flocs production generated during the EC process was studied. The flocs yield was proven to be dependent on some key operation conditions (aeration rate, extra time after electrolysis, and initial pH condition). The flocs yield reaches a maximum in the condition of no aeration, no extra time after electrolysis, and neutral initial pH.

The flocs role in the EC process for treating different typical kinds of pollutants was discussed. The variations and trends in removal efficiency were explained and analyzed with the consideration of flocs yield. The variations of removal efficiency of anions (F^-) and organics (MO) are consistent with the flocs yield, illustrating that improvement of anions and organics pollutants removal could be on account of maximization of in-situ electro-generated flocs yield. For heavy metal ions Ni^{2+}, the variation trend of removal efficiency over initial pH condition is not in accordance with that of flocs yield because both the flocs adsorption and (co-)precipitation contributed to the heavy metal ions removal.

Table 1
Optimized operation condition for different pollutant removal during the EC process

	Aeration rate (L/min)	Extra time (min)	Initial pH
Flocs yield	0	0	5~9
Ni^{2+}	0	30	11
MO	0	60	5~9
F^-	0	30	5~7

However, passivation on the electrodes decreases pollutant removal efficiency and increases power requirements, which is considered to be the crucial challenge of the development of EC. Different strategies have been proposed to avoid passivation such as aggressive ion addition, alternating current operation, mechanical cleaning of electrodes, and so on. Therefore, more work is ongoing to balance the relationship between optimized operation conditions and depassivation strategies.

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