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Removal of chloramphenicol by direct current and pulse current electrocoagulation: implications for energy consumption and sludge reduction

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ABSTRACT

The discharge of antibiotics in wastewater endangers human health. Electrocoagulation (EC) technology can effectively treat chloramphenicol (CAP) in wastewater, but its practical application is limited by issues such as plate passivation, high energy consumption, and a large sludge volume. This study compared the CAP removal performances of positive single pulse current electrocoagulation (PSPC-EC), alternating pulse current electrocoagulation (APC-EC), and conventional direct current electrocoagulation (DC-EC). Under optimal operating conditions, all three methods achieved similar CAP removal rates of >98%, although DC-EC was significantly faster. However, PSPC-EC and APC-EC reduced the sludge quality by 34.95% and 87.48%, respectively, compared with DC-EC and the energy consumption by 57.74% and 39.62%, respectively. PSPC-EC produced a slightly larger floc size than the other methods, which weakened the adsorption capacity. Energy-dispersive spectrometry demonstrated that APC-EC produced flocs with a higher carbon content, which indicates greater adsorption capacity. Fourier transform infrared spectroscopy showed that the flocs produced by the three methods had absorption peaks with similar intensities at the same characteristic wavelengths. The results confirmed that pulse current EC may be a better choice than DC-EC for CAP removal and can effectively reduce operating costs and sludge production in actual wastewater treatment.

Keywords: Chloramphenicol; Pulse current electrocoagulation; Antibiotic water treatment technology; Sludge reduction analysis

1. Introduction

Water pollution is increasingly significant problem. In particular, antibiotics are considered persistent organic pollutants of concern [1,2]. Antibiotics are used to prevent and control animal diseases, increase the yield of animal husbandry, and improve the utilization rate of feeds. However, their discharge into the environment increases bacterial resistance and makes disease prevention and control more difficult, which endangers human health directly and indirectly [3,4]. Chloramphenicol (CAP) is a representative antibiotic for which excessive intake may lead to adverse outcomes in humans, including neurotoxicity, leukemia, bone marrow disease [5], and aplastic anemia [6,7]. The European Union and United States have banned the use of CAP because of its extremely strong negative effects

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on living organisms [8]. However, because CAP has poor degradability, conventional water treatment technologies are unable to achieve a high removal rate [9].

Electrochemical methods have received considerable attention because of their wide applicability and few secondary pollutants [10], as well as their effectiveness at removing pollutants from the environment [11,12]. Electrocoagulation (EC) is a simple and efficient technology for treating sewage that is polluted by refractory pollutants [13]. EC depends on electrochemistry principles to oxidize metals and form metal ion flocculants, which precipitate by the addition of chemical flocculants. The flocs are then removed by adsorption [14]. EC has been used to treat petroleum-contaminated groundwater [15], heavy metal–contaminated sewage [16], dye industry sewage [17], municipal catering sewage [18], and drinking water [19,20].

In the presence of an electric field, the charge is transferred, and the metal anode (usually Fe) oxidizes to form Fe^{2+} and Fe^{3+} ions [21,22]. Under the action of a current, the metal anode dissolves while OH^- and O_2 are generated at the cathode. Under mass transfer and mutual reactions in the solution, insoluble Fe forms are produced such as $Fe(OH)_2$, $Fe(OH)_3$, and FeOOH [23]:

$$\mathrm{Fe}^{n+}_{(\mathrm{aq})} + n\mathrm{OH}^- \rightarrow \mathrm{Fe}\left(\mathrm{OH}\right)_n \quad (1)$$

$$\mathrm{Fe}\left(\mathrm{OH}\right)_3 \rightarrow \mathrm{FeOOH} + \mathrm{H_2O} \quad (2)$$

The electrodes add Cl^- ions to the reaction system that generate active substances such as ClO^-, Cl radicals, and other substances with oxidizing effects [24]. These result in the following possible reactions [25]:

$$\mathrm{Cl}^- - e^- \rightarrow \mathrm{Cl} \quad (3)$$

$$2\mathrm{Cl}^- - e^- \rightarrow {}^{\bullet}\mathrm{Cl}_2 \quad (4)$$

EC has important practical applications owing to its high removal rate, and it is the subject of active research because of its simple operation, low cost, and wide applicability [26]. However, its development faces certain challenges such as plate passivation, mass production of sludge, and the inhomogeneous medium in the reaction tank.

Conventional direct current electrocoagulation (DC-EC) has demonstrates considerable potential for some industrial applications, but it still has certain limitations, such as the formation of a passivation layer on the electrode surface during long-term operation. This passivation layer increases both the voltage across the electrode and the energy consumption and reduces the concentration of metal ions in the solution feed [27]. The passivation problem is typically solved by cycling a pulse current between on and off states. Relevant studies on using EC for pollutant removal have demonstrated that periodically reversing the direct current reduced the voltage at both ends of the electrode plate and effectively mitigated concentration polarization, which is a phenomenon that increases operating costs [28]. In addition, the use of an alternating current for the electrochemical biodegradation of pollutants significantly improved the activity of catalysts [29,30]. Thus, electrochemical technology using alternating current could be a promising avenue for water treatment [31]. However, previous studies have primarily focused on DC-EC and alternating pulse current EC (APC-EC). Few studies have explored the effectiveness of positive single pulse current electrocoagulation (PSPC-EC). Thus, research on the antibiotic removal mechanism of pulse current EC and DC-EC and on the influence of water quality and operating parameters are still in the early stages.

In this study, the CAP removal performances of three types of EC were compared: DC-EC, PSPC-EC, and APC-EC. The effects of water quality conditions and operating parameters on the CAP removal rate, energy consumption, and sludge production were evaluated. The objective was to characterize the CAP removal mechanisms of EC in general and APC-EC in particular. This study contributes to the literature by improving the economic efficiency of EC to improve its viability for actual wastewater treatment, and it provides a theoretical basis and technical support for the large-scale practical application of pulse EC.

2. Materials and methods

2.1. Chemicals, reagents, and equipment

All solutions were prepared by using ultrapure water and analytical grade reagents. The CAP standard was obtained from Alfa Aesar (Shanghai, China). The pH was adjusted by using hydrochloric acid (HCl) and sodium hydroxide (NaOH) [32]. Here, 0.1 mol/L HCl was prepared by diluting 11.7 mol/L HCl. To simulate wastewater, CAP solutions were prepared at concentrations of 10–80 mol/L by dissolving CAP in ultrapure water. In addition, 0.5–2 g/L sodium chloride (NaCl) was added to the CAP solutions to adjust the conductivity. The properties of the simulated wastewater are presented in Table 1.

The power supply was an intelligent alternating pulse power supply (GKPD numerical control type) from Shenzhen Shicheng Electronic Technology Co., (Guangdong, China). The output frequency (*f*), adjustable duty cycle (*r*), average current (*I*), and peak voltage (*V*) ranges were 1–5,000 Hz, 0%–100%, 0–100 A, and 0–36 V, respectively. The number of positive and negative pulses was adjusted in the range of 0–10. The output waveform of the power supply included DC, PSPC, and APC. The reactor had a volume of 800 mL and dimensions of 100 mm³ × 100 mm³ × 80 mm³. The reactor was prepared from polymethacrylate that was custom-made by Plexiglas (Guangdong, China). The electrodes were two Fe plates with a purity of 99.5% and dimensions of 50 mm³ × 100 mm³ × 1 mm³ from Huabei Technology

Table 1
Simulated wastewater properties

Initial pH	8
NaCl concentration (g/L)	1
Initial CAP concentration (mg/L)	10–80
Solution volume (mL)	500

Metal Materials Co., (Beijing, China). Finally, 600-mesh Si–C sandpaper from Hubei Yuli Abrasive Belt Group Co., (Jiangsu, China) was used for grinding.

The generated flocs were examined by particle size analysis, scanning electron microscopy (SEM, Zeiss GeminiSEM5000), energy-dispersive X-ray spectroscopy (EDS Aztec UltimMax, Oxford), and Fourier-transform infrared spectroscopy (FTIR, is10, Thermo Electron Corporation, US). Moreover, the microstructure of the generated solid products that adsorbed CAP were characterized.

2.2. Experimental conditions

Each group of reaction experiments was performed in an 800 mL reactor. The two Fe plates were connected to the positive and negative electrodes of the power supply to serve as the anode and cathode, respectively. The effective area of a Fe plate when immersed in simulated wastewater was 45 cm^2 (45 mm × 100 mm × 1 mm). Before the experiments, the Fe plates were polished with the Si–C sandpaper and cleaned by ultrasonication for 5 min. The distance between the plates was adjusted within the range of 5–25 mm by using the grooves on the sidewalls of the reactor. The current density (CD), duty cycle (r), current frequency (f), and positive and negative pulse wavenumbers were adjusted by using the intelligent alternating pulse power supply. The experiments were performed at room temperature (25°C ± 2°C). A magnetic stirrer was used at a constant speed of 250 rpm during the experiments to improve the mass transfer efficiency of the flocculants and pollutants in a solution. A schematic of the EC reactor is shown in Fig. 1.

2.3. Analytical methods

2.3.1. Determination of CAP concentration

The pH of the simulated wastewater was measured by using a SX721 pH meter from Shanghai Sanxin Instrument Co. (Shanghai, China). The CAP concentration in the solution was measured by UV spectrophotometry (Evolution-220) from Thermo Fisher Scientific (Shanghai, China). The experiment was maintained at room temperature. The solution in the reactor was stirred at a constant speed of 250 rpm to improve the mass transfer efficiency of the metal ion flocculant and CAP. Samples were filtered by using a 0.45-μm organic filter from Tianjin Navigator Lab Instrument Co. (Tianjin, China) and diluted with 0.1 mol/L HCl prior to the determination of the CAP concentration. The concentration of each CAP solution was prepared as per the standard. The absorbance of each solution was measured at 277 nm to obtain a standard curve of the CAP concentration. Then, the sample was filtered through a 0.45-μm organic filter and diluted appropriately. The corresponding absorbance of the sample was measured to obtain the CAP concentration.

2.3.2. Data analysis

The CAP removal rate (R_{CAP}(%)) was calculated as follows:

$$R_{\text{CAP}}\left(\%\right)=\frac{C_0-C}{C_0}\times 100\% \tag{5}$$

where C_0 and C (mg/L) are the CAP concentrations before and after EC treatment, respectively. The CD (A/m) was calculated as follows:

$$\text{CD}=\frac{I}{2S} \tag{6}$$

where I is the average current and S is the effective surface area of a single Fe plate immersed in a solution. The energy consumption (kWh/mg_{CAP}) of DC-EC (E_{DC}) and pulse current EC (E_{pulse}) were calculated as follows:

$$E_{\text{DC}}\left(\text{kWhmg}_{\text{CAP}}^{-1}\right)=\frac{U\times\int_0^{\text{te}} Idt}{V\left(C_0-C\right)} \tag{7}$$

$$E_{\text{pulse}}\left(\text{kWhmg}_{\text{CAP}}^{-1}\right)=\frac{U_P\times\gamma^2\times\int_0^{\text{te}} Idt}{V\left(C_0-C\right)60} \tag{8}$$

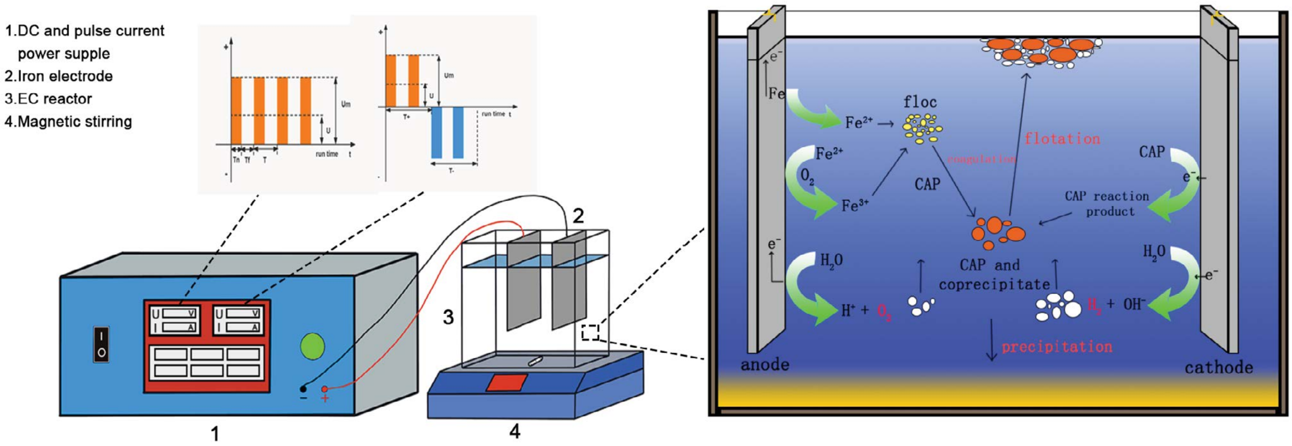


Fig. 1. Schematic of the EC reactor.

where U, t, V, I, U_p, and γ are the voltage applied across the electrode plate (V), treatment time (min), amount of simulated wastewater (m^3), DC intensity (A), peak pulse voltage intensity (V), and duty cycle (%), respectively.

2.3.3. Sludge volume analysis

The sludge volume produced by a sewage treatment process and the subsequent treatment of the sludge are important for evaluating the feasibility of the treatment technology. The organics removal to sludge ratio (ORSR) and sludge to iron ratio (SIR) are two important parameters [33] and are calculated as follows:

$$\text{ORSR} = \frac{\text{overall CAP removal}(\text{mg})}{\text{sludge quality}(\text{g})} \tag{9}$$

$$\text{SIR} = \frac{\text{sludge quality}(\text{g})}{\text{iron consumption}(\text{mole})} \tag{10}$$

where e is the elementary charge (i.e., 1.6022 × 10^{-19} C) and N_A is Avogadro's constant (i.e., 6.02214076 × 10^{23} mol^{-1}). A high ORSR value and low SIR value indicate the practicality of an EC process.

3. Results and discussion

3.1. Optimal reaction conditions

The optimal reaction conditions for DC-EC were determined. The effects of the pH, initial CAP concentration (C_0), plate spacing (PS), electrolyte concentration, and current density (CD) on the CAP removal rate were considered.

3.1.1. Effect of pH

The initial solution pH significantly influences the CAP removal rate of an EC treatment process [34]. Fig. 2a shows the effect of pH 2, 4, 6, 8, and 10 on the CAP removal rate. In the first 40 min, pH significantly affected the CAP removal rate. At 60 min, the CAP removal rates at pH 6, 8, and 10 reached 94.80%, 95.87%, and 98.81%, respectively. Moreover, the residual CAP concentrations were 1.01, 0.86, and 0.21 mg/L, respectively. These results can be explained by the large amount of OH$^-$ present under alkaline conditions, which reacts to produce additional substances during adsorption. However, under low pH conditions, the solubility of the dissolved oxygen decreases, which affects Fe-based hydroxide [35]. For practical application, the effects of the pH on the CAP removal rate as well as the cost of adjusting the pH should be considered. Thus, pH = 8 was determined most appropriate.

3.1.2. Effect of initial CAP concentration

Another factor that affects the CAP removal rate is the initial pollutant concentration in the wastewater. Experiments were performed at C_0 of 10–80 mg/L, and the results are shown in Fig. 2b. At a low C_0 = 10 mg/L, the CAP removal rate reached 80% after 20 min of treatment time. The CAP removal rate required less time to reach equilibrium at a low C_0 than at a high C_0. For the same reaction time of 40 min, C_0 of 10 and 80 mg/L resulted in CAP removal rates of 98.33% and 77.16%, respectively. In the later stages of the reaction, the CAP removal rate significantly decreased for the group with a high C_0. This is because, at the same CD, the amount of metal cations generated by the oxidation and dissolution of the Fe electrode is constant, so the adsorption amount of the generated flocs is constant. At high C_0, flocs are unable to adsorb all of the CAP, which reduces the CAP removal rate.

3.1.3. Effect of plate spacing

PS significantly influences the distributions of the electric field and flow field in an EC reactor. Fig. 2c shows the effect of PS (5–25 mm) on the CAP removal rate. Between 0 and 30 min, the CAP removal rate was high. After 30 min, the CAP removal rate slowly increased and then reached equilibrium. The final CAP removal rates at PS = 5, 10, 15, 20, and 25 mm were 99.02%, 95.93%, 99.86%, 91.25%, and 94.92%, respectively. Increasing PS increases the Ohmic drop between the plates and the electrolysis voltage, which increases the side reactions and decreases the CAP removal rate [36]. Furthermore, increasing the voltage across the plates increases the energy consumption. At very small PS, the ion diffusion rate between the plates is low, which results in poor contact between CAP and the generated flocs and thus decreases the CAP removal rate [37]. The optimal PS was determined to be 15 mm.

3.1.4. Effect of electrolyte concentration

The effect of the electrolyte concentration needs to be considered to reduce the energy consumption of EC. Previous studies have demonstrated that Cl$^-$ ions generate reactive chlorine species (RCS) during EC [38] such as ClO$^-$, which has a strong oxidizing ability and corrosive effect on metal plates. RCS react with metal electrodes to increase the amount of metal ion flocculants in the solution [39] and form a passivation layer on the electrodes. Fig. 2d shows the effect of the electrolyte concentration (i.e., NaCl concentration in this study) on the CAP removal rate. Within the initial 10 min, the NaCl concentration and CAP removal rate increased from 0.5 to 2 g/L and 16.87% to 39.66%, respectively. The increase in the NaCl concentration promoted the migration speed of the ions in the solution, which increased the transfer of electrons and the reaction rate. However, during the later stages of the reaction (after 45 min), the CAP removal rates at NaCl concentrations of 1.5 and 2 g/L were similar. At 60 min, the CAP removal rates at these NaCl concentrations were 99.82% and 99.85%, respectively. Increasing the NaCl concentration decreased the voltage applied across the solution, and the CD was 40 A/m^2. When the NaCl concentration was increased from 0.5 to 4 g/L, the EC voltage increased from 7.6 to 4.7 V, which reduced the energy consumption [40]. The electrolyte concentration should be optimized by considering both the CAP removal rate and cost of NaCl. Thus, the optimal NaCl concentration was determined to be 1 g/L.

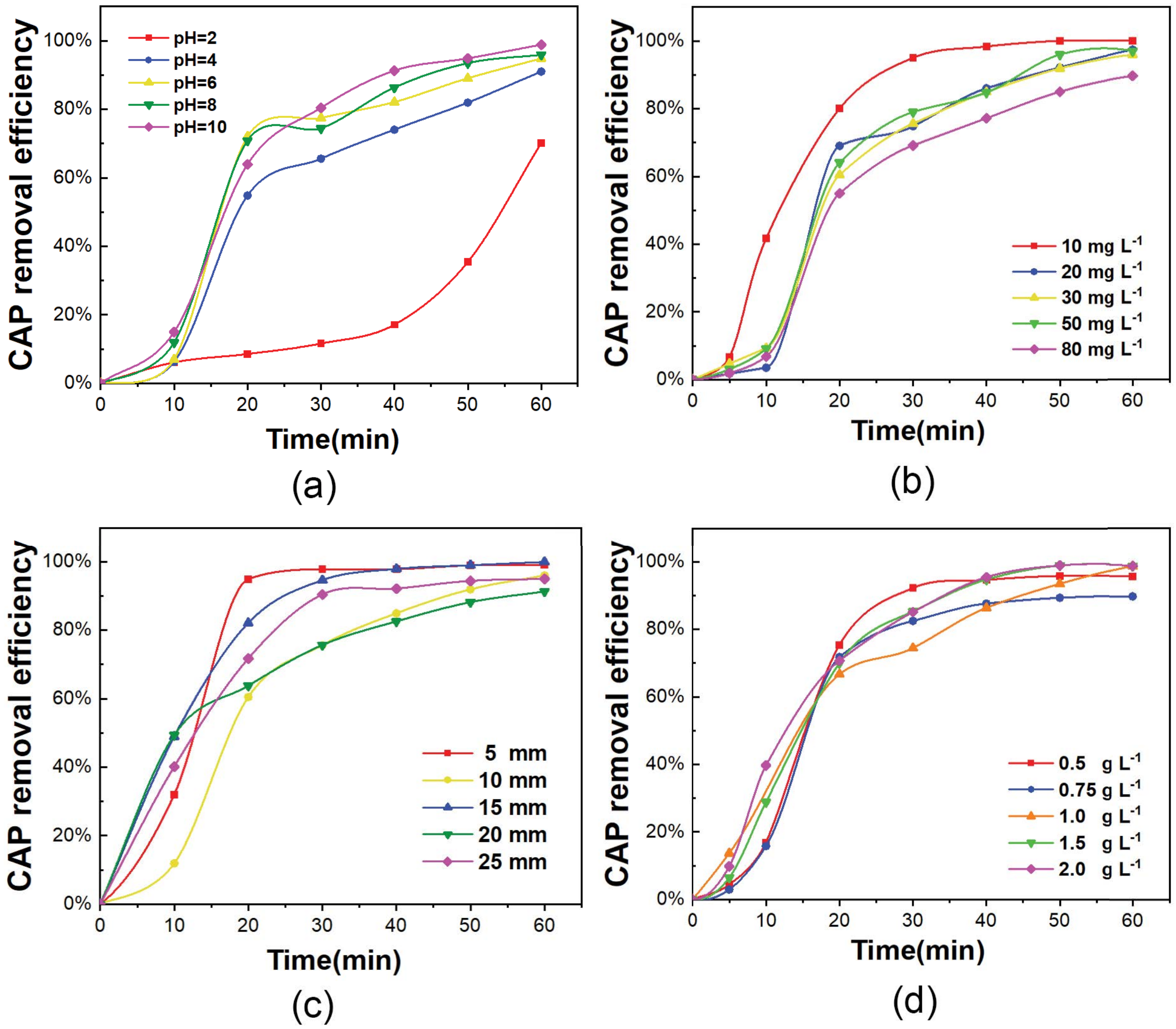


Fig. 2. Optimal reaction conditions for DC-EC: (a) Effect of pH at C_0 = 30 mg/L, CD = 40 A/m², NaCl concentration = 1 g/L, and PS = 10 mm. (b) Effect of C_0 at CD = 40 A/m², pH = 8, NaCl concentration = 1 g/L, and PS = 10 mm. (c) Effect of PS at CD = 40 A/m², pH = 8, and NaCl concentration = 1 g/L, respectively. (d) Effect of electrolyte concentration at CD = 40 A/m², pH = 8, and PS = 10 mm.

3.1.5. Effect of current density

The CD is considered the most important factor that affects the EC performance because it controls the floc generation efficiency as well as the generation of Fe^{3+} and OH^- ions [41]. It also affects the efficiency of hydrogen evolution at the cathode during EC [42]. Fig. 3 shows the relationship between the CD and CAP removal rate. At higher CD, less time was required to achieve a CAP removal rate of 90%. At the maximum CD of 70 A/m², a CAP removal rate of 90% was achieved in 25 min. A CAP removal rate of 98% was achieved in 45 min, and the residual CAP concentration was 0.52 mg/L. Higher CD increased the amount of dissolved Fe, which generated more Fe^{3+} and OH^- in the reactor and resulted in more flocs. However, the final CAP removal rate at 70 A/m² was not as good as at 40 and 50 A/m² because the flocs gradually dissolved when the CD was high. In other words, concentration polarization under high voltage and plate passivation reduced the EC efficiency. The EC performance should be evaluated in terms of both the CAP removal rate and energy consumption. Initially, increasing the CD increased the CAP removal rate. However, increasing the CD from 40 to 70 A/m² did not greatly improve the CAP removal rate. Thus, the optimal CD was determined as 40 A/m².

3.2. Influencing factors for PSPC-EC

In recent years, pulse current EC has become popular for sewage treatment. Compared with DC, a pulse current effectively solves the problems of plate passivation and concentration polarization. Moreover, a pulse current is

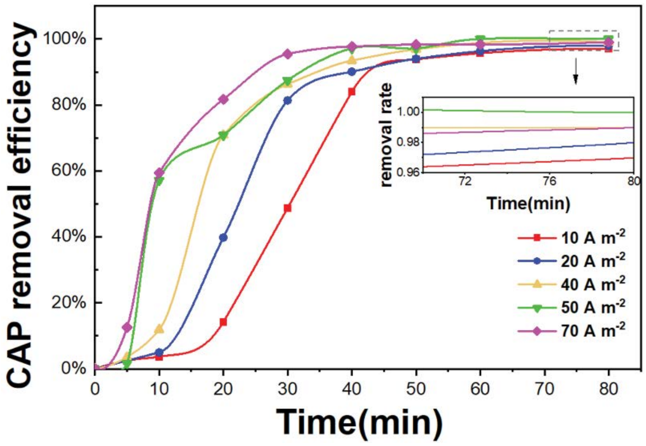


Fig. 3. Optimal reaction conditions for DC-EC: effect of CD on the CAP removal rate at pH = 8, NaCl concentration = 1 g/L, and PS = 10 mm.

advantageous in terms of energy consumption and sludge volume reduction [43]. Therefore, the influencing factors for the CAP removal rate by pulse current EC were evaluated. In particular, the effects of the current frequency (*f*), duty cycle (*r*), and peak voltage (*V*) on the CAP removal rate by PSPC-EC were evaluated based on previous studies that identified these factors as significant.

3.2.1. Pulse current frequency

The frequency (*f*) of a pulse current is an important property. Here, the experimental conditions were set to C_0 = 30 mg/L, CD = 40 A/m^2, pH 8, and electrolyte concentration of 2 g/L. Different *f* values were used to evaluate their effects on the CAP removal rate. The results are shown in Fig. 4. At *f* = 500–2,000 Hz, the CAP removal rate increased with increasing *f*. At 30 min, the CAP removal rate was 87.57%–94.15% for all samples. After 50 min, the CAP removal rate was 95.91%–99.19%. At *f* = 2,000 and 3,000 Hz, the CAP removal rate was 99.19%, which resulted in a residual CAP concentration of 0.261 mg/L. However, at *f* = 5,000 Hz (>2,000 Hz), the CAP removal rate was only 96.45% at 60 min. This suggests that the CAP removal rate decreased above a threshold *f*. This can be explained by the passivation mechanism of pulse current EC. A pulse current at a higher frequency shortens the current cycle, which effectively loosens the passivation layer and prevents the increased voltage and current caused by passivation of the Fe plate. The reduced efficiency results in more floc generation at the anode, which increases the CAP removal rate. Thus, the optimal *f* for PSPC-EC was determined as 2000 Hz.

3.2.2. Duty cycle

The duty cycle (*r*) is the ratio of the energization time to the total time in a complete pulse cycle. It directly affects the energization amount and thus the amount of floc generation by oxidation in the solution, hydrogen production at the cathode, and final energy consumption [44]. Different *r* values of 40%–80% for PSPC-EC were considered under the experimental conditions of C_0 = 30 mg/L, CD = 40 A/m^2, pH 8, electrolyte concentration of 2 g/L, and *f* = 2,000 Hz. The results are shown in Fig. 5. At *r* = 80%, the CAP removal rate reached 94.88%. At *r* = 40%, 50%, 60%, and 70%, the CAP removal rates were only 72.57%, 79.00%, 80.11%, and 84.83%, respectively. Fig. 5b shows that *r* = 40%, 60%, and 80% with the same CAP removal rate resulted in energy consumption s of 1.11775 × 10^{-5}, 4.00407 × 10^{-5}, and 8.63174 × 10^{-5} kWh/mg$_{\text{CAP}}$, respectively. A high *r* indicates a longer time in the on state and a higher energy consumption. A lower r indicates a shorter time in the on state. Plate passivation and concentration polarization decrease in the on state. Based on the CAP removal rate and energy consumption, the optimal *r* was determined as 60%.

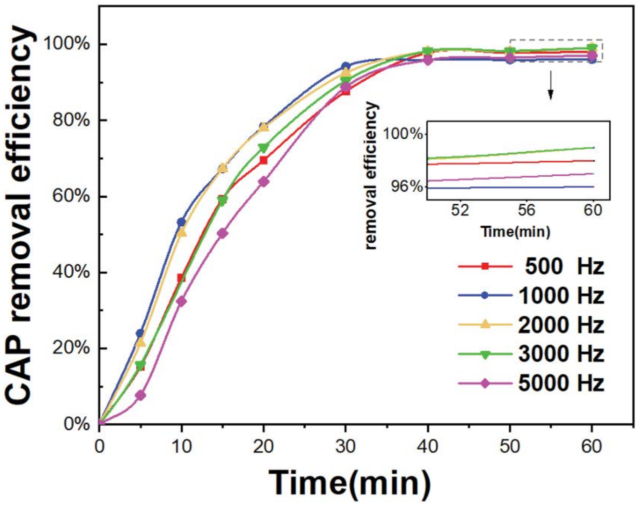


Fig. 4. Effect of the pulse current frequency on the CAP removal rate at CD = 40 A/m^2, pH = 8, NaCl concentration = 1 g/L, and PS = 10 mm.

3.2.3. Peak voltage

In pulse current EC, the peak voltage (*V*) and average current are positively correlated and accelerate the Fe dissolution rate at the anode. Fig. 6 shows the experimental results for the effect of *V* on the CAP removal rate. At high *V* (e.g., 4.8 and 5.5 V), the CAP removal rate quickly reached 20% in 5 min. In the first 10 min, the CAP removal rate increased with *V*, which was attributed to the increase in concentration of Fe^{2+} and Fe^{3+} ions in the solution, which increased the concentration of Fe-based hydroxides in the reactor. An increase in *V* has been demonstrated to reduce the saturation time for metal ion generation [45]. The increased floc generation increased the CAP removal rate. After 15 min, the CAP removal rate was lower at *V* = 5.5 V than at *V* = 4.8 V, which was attributed to an increase in side reactions with increasing *V*. Moreover, because of the enhanced electrical flotation, the flocs floated to the surface of the solution before making full contact with CAP in the solution, which reduced the CAP removal rate. Fig. 6b shows that *V* = 4.8 V resulted in an energy consumption of 2.479 × 10^{-5} kWh/mg$_{\text{CAP}}$ and CAP removal rate of 98.11%, which was the optimal performance.

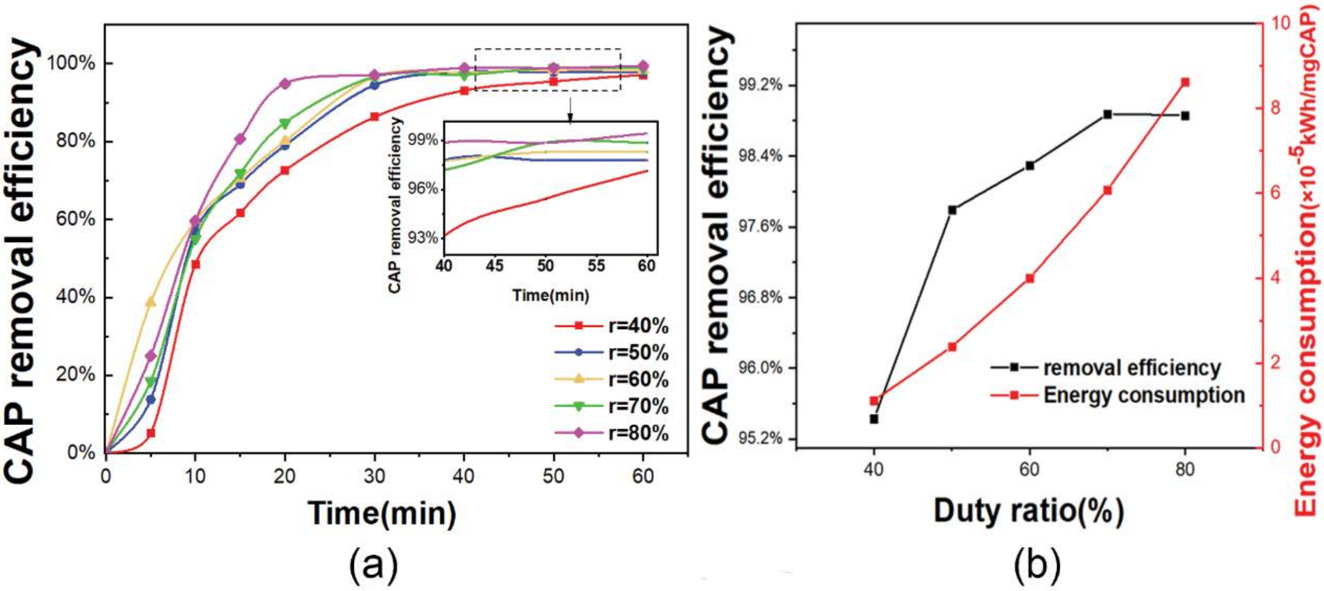


Fig. 5. (a) Effect of the duty cycle on the CAP removal rate of PSPC-EC at a current frequency of 2,000 Hz and peak voltage of 4.8 V. (b) Corresponding energy consumption at different duty cycles.

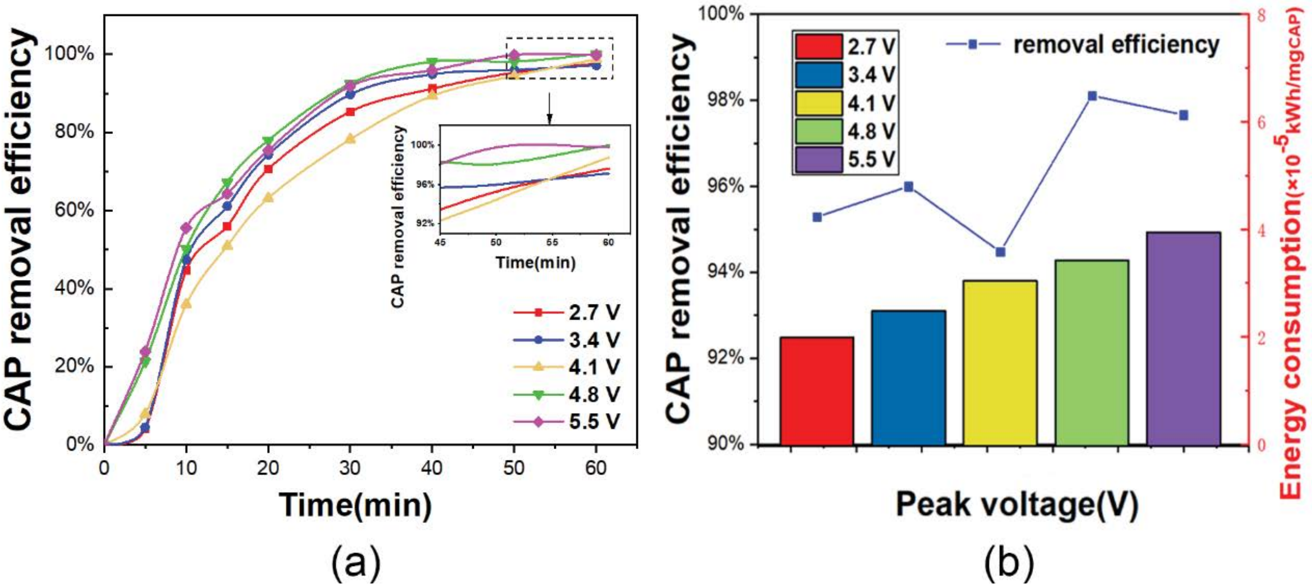


Fig. 6. (a) Effect of the peak voltage on the CAP removal efficiency of PSPC-EC at a current frequency of 2,000 Hz and duty cycle of 60%. (b) Corresponding energy consumption at different peak voltages.

3.3. Optimal reaction conditions for APC-EC

The optimal reaction conditions for APC-EC were determined. The effects of the current frequency (f), duty cycle (r), and current density (CD) on the CAP removal rate were investigated.

3.3.1. Effects of the current frequency, duty cycle, and current density

Fig. 7 shows that the CAP removal rate increased with f in the range of f = 500–3,000 Hz. At 90 min, the CAP removal rates at f = 2,000 and 3,000 Hz reached 97.30% and 96.82%, respectively.

Fig. 8 shows that r = 40%, 60%, and 80% with the same CAP removal rate corresponded to energy consumptions of 4.91×10^{-4}, 1.76×10^{-3}, and 3.79×10^{-3} kWh/mg$_{CAP}$, respectively. Thus, subsequent experiments used r = 60%.

For APC-EC, the peak voltage and average current do not typically show completely positive or negative correlation trends. Owing to the relatively low energy consumption and high CAP removal rate, the optimal CD was determined as 70 A/m^2 (Fig. 9).

3.3.2. Comparison between APC-EC and other EC processes

In wastewater treatment, the ultimate goal is to achieve a high removal rate at a relatively low cost. Moreover, energy consumption is an extremely important consideration for EC. The energy consumption of an EC process is calculated for a given CAP removal rate. Under optimal reaction conditions, the energy consumptions of DC-EC, PSPC-EC, and APC-EC were 9.475 × 10^{-5}, 2.387 × 10^{-5}, and 5.721 × 10^{-5} kWh/mg_{CAP}, respectively. Plate passivation involves the formation of a metal oxide film on the surface of the Fe electrode. A fraction of the energy consumption goes to generating oxygen, which reduces the process efficiency. Therefore, the efficiency of the EC process can be used as a convenient indicator of the degree of passivation [46]. Table 2 compares the CAP removal rates and energy consumptions of the three different EC processes. The lower energy consumptions of PSPC-EC and APC-EC indicate that they better protected against electrode passivation than DC-EC.

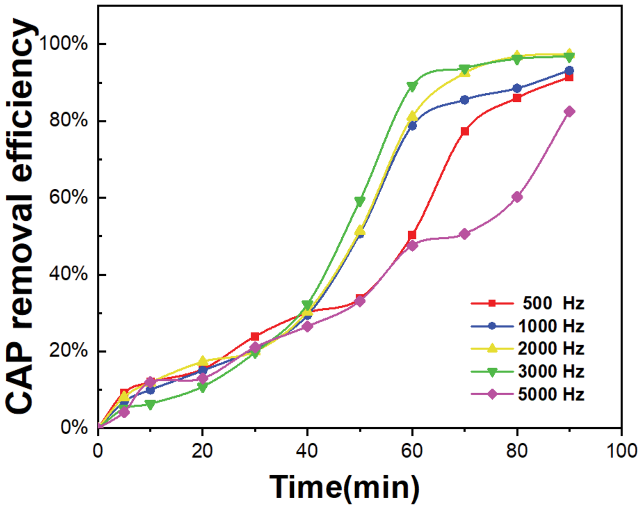


Fig. 7. Effect of the current frequency on the CAP removal rate. The duty cycle and CD were 60% and 70 A/m^2, respectively.

3.4. Characterization of floc properties

SEM-EDS and FTIR were used to characterize the flocs generated by the EC processes.

3.4.1. SEM-EDS results

Fig. 10 shows SEM images of the flocs at 50,000× magnification. The DC-EC flocs were uniformly shaped with a diameter of ~100 nm. The flocs had a large particle size with distinct edges. They had a compact structure in the

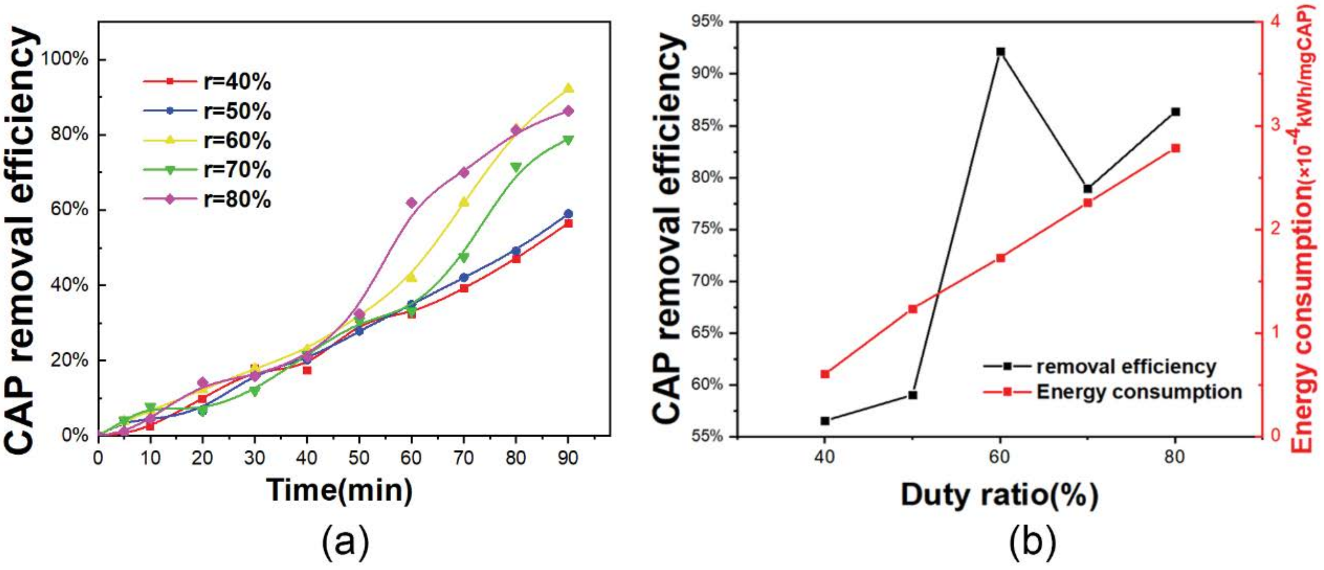
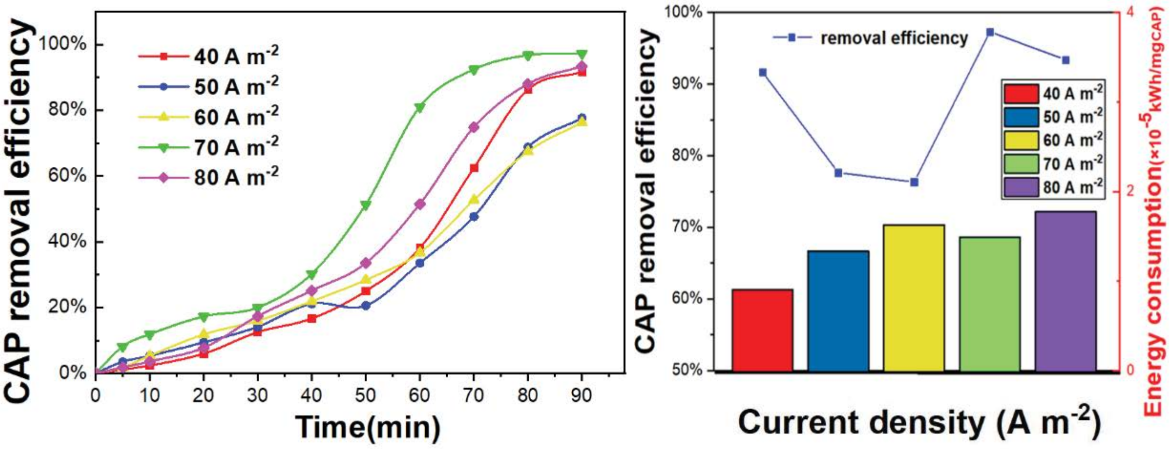


Fig. 8. (a) Effect of the duty cycle on the CAP removal rate of APC-EC at a current frequency of 3,000 Hz and CD of 70 A/m^2. (b) Corresponding energy consumptions at different duty cycles.

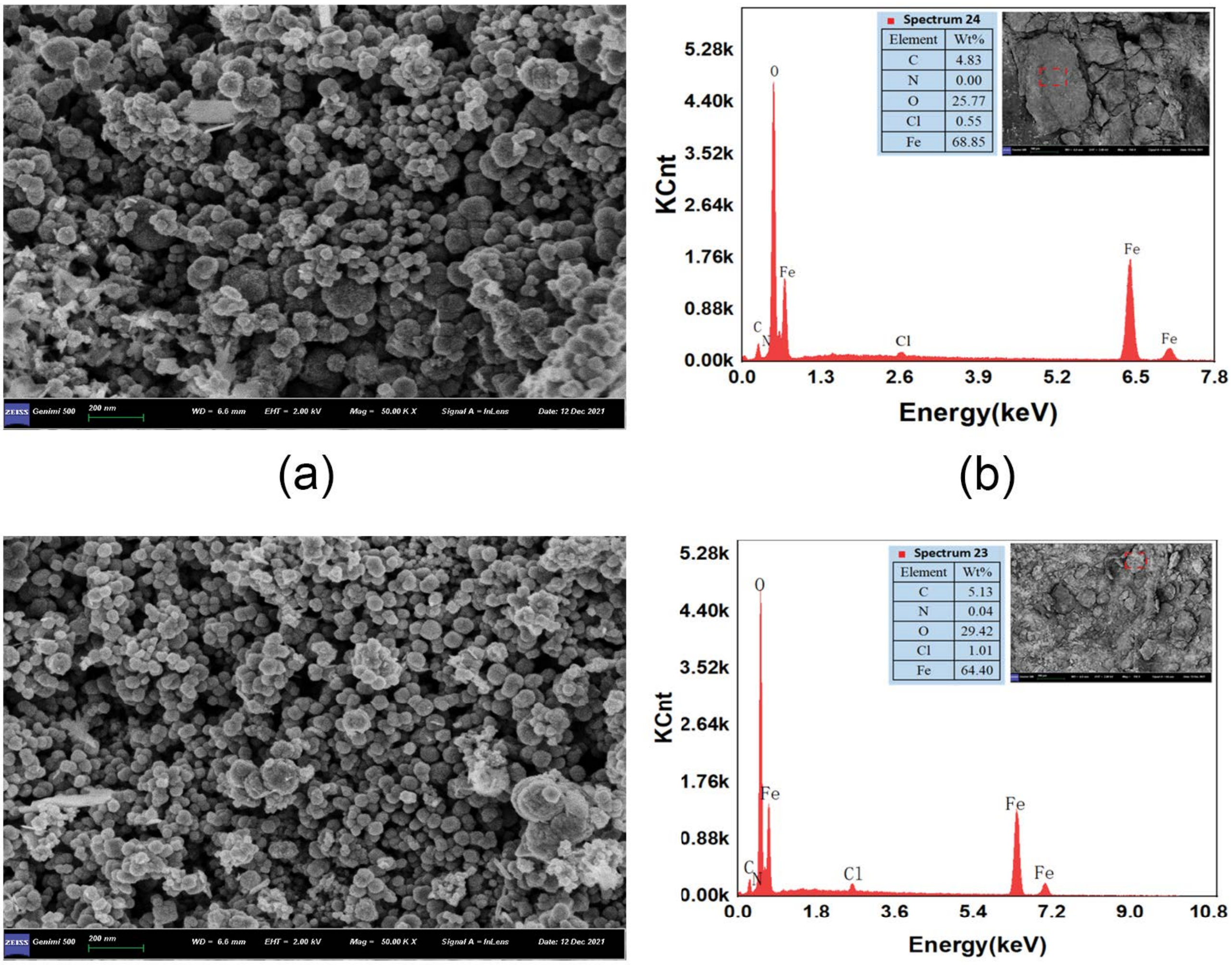
Table 2
CAP removal performances of the three EC processes

EC type	Time (min)	CD (A/m^2)	CAP removal rate (%)	Energy consumption (kWh/mg_{CAP})	Dry sludge (g/L)
DC-EC	30	70	98.28	9.475 × 10^{-5}	2.3640
PSPC-EC	35	70	98.85	4.004 × 10^{-5}	1.5378
APC-EC	90	70	98.36	5.721 × 10^{-5}	0.2960



(a) (b)

Fig. 9. (a) Influence of CD on the CAP removal rate at a current frequency of 3,000 Hz and duty cycle of 60%. (b) Corresponding energy consumptions at different current densities.



Spectrum 24

Element	Wt%
C	4.83
N	0.00
O	25.77
Cl	0.55
Fe	68.85

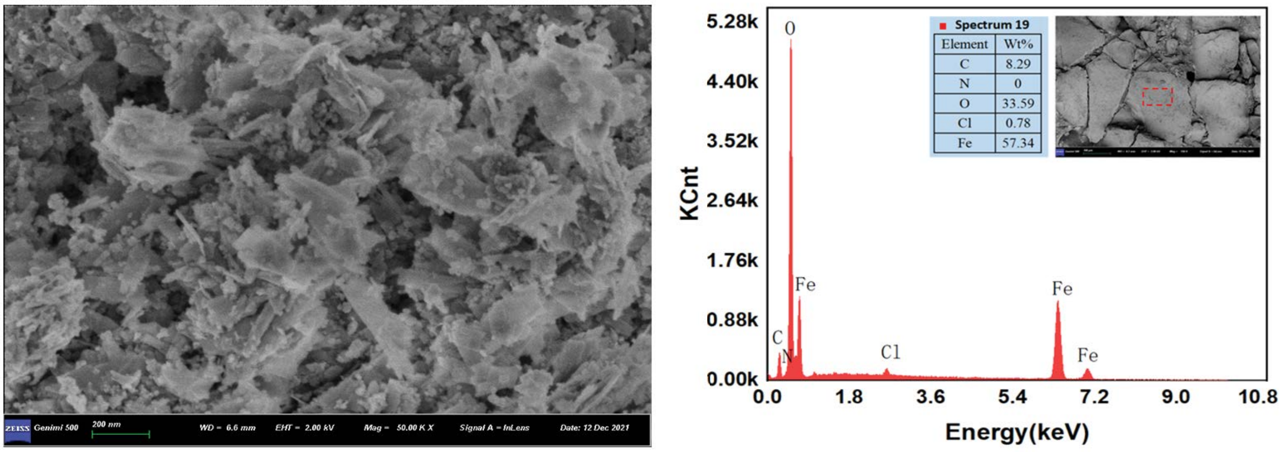
Spectrum 23

Element	Wt%
C	5.13
N	0.04
O	29.42
Cl	1.01
Fe	64.40

(a) (b)

(c) (d)

(Continued)



Element	Wt%
C	8.29
N	0
O	33.59
Cl	0.78
Fe	57.34

(e) (f)

Fig. 10. SEM and EDS analyses of flocs produced by different EC methods: (a, b) DC-EC, (c, d) PSPC-EC, and (e, f) APC-EC.

form of a closed sphere. The PSPC-EC flocs had a similar shape but different particle sizes, with diameters ranging from 50 to 200 nm. The APC-EC flocs were irregular spheres and flakes.

Fig. 10 also shows the EDS results on the elemental composition. The flocs mainly comprised C, N, O, Cl, and Fe. Fe had the highest atomic contents for the DC-EC, PSPC-EC, and APC-EC flocs of 68.85%, 64.40%, and 57.34%, respectively, followed by O at atomic contents of 25.77%, 29.42%, and 33.59%, respectively. The flocs underwent a series of side reactions in the solution. The C atomic contents were 4.83%, 5.13%, and 8.29%, respectively. In the reaction system, the only carbon source was CAP. Therefore, DC-EC and PSPC-EC had similar adsorption capacities. However, APC-EC had a much higher adsorption capacity. Thinner layers have a larger adsorption area than thicker layers. Thus, the greater adsorption capacity can be explained by the floc morphology.

3.4.2. FTIR characterization

Fig. 11 shows the FTIR spectra of CAP treated by the three EC methods. The absorbance and wavenumber are the ordinate and abscissa, respectively. The generated flocs showed characteristic absorption peaks at 544; 1,640; 3,118 and 3,443 cm^{-1}. The structures of the absorption peaks were similar for all three EC processes. The results indicated that CAP and iron hydroxide formed a co-precipitate that can remove effectively CAP from sewage. The absorption peak at 3,443 cm^{-1} can be attributed to the bending vibration of the H–O–H bond [47]. The peak at 3,118 cm^{-1} can be attributed to the stretching vibration of the O–H bond in $Fe(OH)_3$. The peak at 544 cm^{-1} can be attributed to the vibration of Fe–O bonds (Fe_2O_3, $Fe_{3-x}O_4$) [48,49].

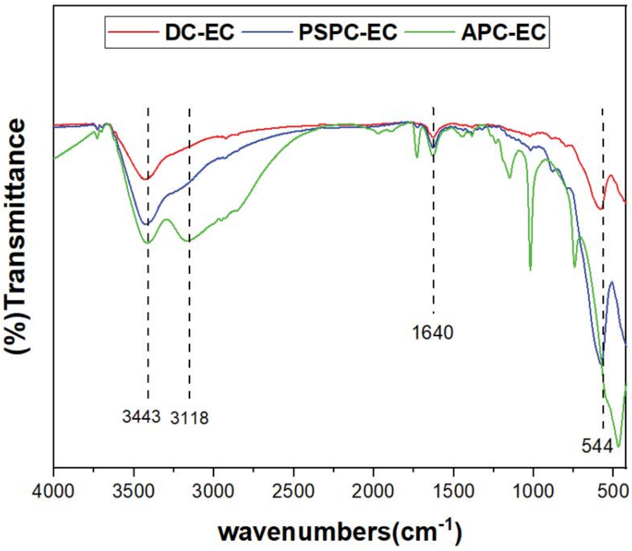


Fig. 11. FTIR analysis of flocs produced by different EC methods.

3.5. Sludge volume analysis

The CAP removal performances of the EC methods were evaluated in terms of the CAP removal rate, energy consumption, and sludge volume. The pulse current ECs required more time than DC-EC to achieve the same CAP removal rate but also produced less sludge. Because of the periodic switching of positive and negative currents, the diffusion rate of the cations dissolved in the anode to the solution increased, which suppressed the concentration polarization. Therefore, the pulse current ECs had a lower energy consumption than DC-EC. APC-EC had a higher energy consumption than PSPC-EC but produced much less sludge than both DC-EC and PSPC-EC.

In this study, APC-EC had an ORSR of 199.37 mg/g, which was much higher than those of PSPC-EC at 38.57 mg/g and DC-EC at 24.95 mg/g. APC-EC also had a lower SIR than the other two currents. Thus, APC-EC was more advantageous than the other two EC methods in terms of sludge production.

Table 3
Comparison of related studies on EC treatment of polluted wastewater

Method	Operating conditions	ORSR	SIR	Removal rate	References
APC-EC	pH = 8, PS = 10 mm, C_0 = 30 mg/L, 3,000 Hz, I = 0.35 A, r = 60%, t = 90 min	199.37 mg/g	4.40 g/mol	CAP: 98.36%	This experiment
PSPC-EC	pH = 8, PS = 10 mm, C_0 = 30 mg/L, 2,000 Hz, CD = 70 A/m^2, r = 60%, t = 35 min	38.57 mg/g	117.69 g/mol	CAP: 98.85%	This experiment
DC-EC	pH = 8, PS = 10 mm, C_0 = 30 mg/L, CD = 70 A/m^2, t = 30 min	24.95 mg/g	211.07 g/mol	CAP: 98.28%	This experiment
Persulfate enhanced EC	pH = 5, $C_{\text{persulfate}}$ = 5.6 g/L, j_a = 21 mA/cm, t = 35 min	11.1 g/L	2.7 L/moL	COD: 64%; CN: 98.1%	[50]
Fenton craft	pH = 6, $n_{[\text{H2O2}]}/n_{[\text{Fe2+}]}$ = 20, $n_{[\text{Fe2+}]}$ = 170 mM, t = 35 min	16.7 g/L	2.75 L/moL	COD: 64.2%	[51]
Fenton craft	pH = 6, $n_{[\text{H2O2}]}/n_{[\text{Fe2+}]}$ = 20, $n_{[\text{Fe2+}]}$ = 200 mM, COD$_0$ = 18, 725 mg/L	3.36 g/L	13.0 L/moL	COD: 55.8%	[52]

Table 3 compares related studies on the treatment of polluted wastewater by EC methods. Guvenc et al. [50] used persulfate enhanced EC treatment to remove pollutants from wastewater of the paint production industry at an initial pH of 5. The persulfate concentration and electrical current density were 5.6 g/L and 21 mA/cm, respectively. The ORSR and SIR values were 2.7 L/moL and 11.1 g/L, respectively, at a CD and reaction time of 21 mA/cm and 35 min, respectively. Biglarijoo et al. [51] used the Fenton oxidation method to remove chemical oxygen demand (COD) from a landfill leachate and calculated ORSR and SIR values of 2.75 L/moL and 16.7 g/L, respectively. They found that the Fe^{2+} content had a significant effect on ORSR and SIR.

4. Conclusion

This study investigated the optimal conditions for DC-EC, PSPC-EC, and APC-EC. For DC-EC, the optimal operating conditions were pH 8, C_0 = 30 mg/L, PS = 15 mm, electrode concentration of 1 g/L, and CD = 50 A/m^2, which resulted in a CAP removal rate of 98.28% in 30 min. For PSPC-EC, the optimal operating conditions were f = 2,000 Hz, r = 60%, and V = 4.8 V, which resulted in a CAP removal rate of 98.85% in 40 min. For APC-EC, the optimal operating conditions were f = 3,000 Hz, r = 60%, and CD = 70 A/m^2, respectively, which resulted in a CAP removal rate of 98.36% in 90 min. For a given CAP removal rate, PSPC-EC achieved a lower sludge production and energy consumption than DC-EC. EDS analysis showed that APC-EC produced flocs with a greater CAP adsorption than the other two EC methods. The FTIR results indicated that the three EC methods generate flocs with similar structures and facilitate CAP adsorption in sewage.

Future research directions for pulse current EC are described below:

- The CAP removal mechanism in the EC process should be modeled, which can provide a theoretical basis for CAP removal.
- The structure of the flocs produced by EC should be further studied. The flocs comprise various components, and the contribution of each component to CAP removal should be investigated.
- Current research on pulse current EC has mainly been on a laboratory scale, and it has not been applied to actual wastewater. Pulse current EC should be applied to actual wastewater containing CAP to evaluate the treatment effectiveness. This will lay a foundation for the practical application of pulse current EC to actual industrial wastewater containing antibiotics.

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Symbols

I — Current, A
S — Plate surface area, m^2
E_{DC} — Energy consumption of DC electrocoagulation, kWh/mg$_{\text{CAP}}$
E_{pulse} — Energy consumption of pulse current electrocoagulation, kWh/mg$_{\text{CAP}}$
t — Time, min
V — Volume, mL
γ — Duty cycle, %
C_0 — Initial CAP concentration, mg/L
C_t — CAP concentration at time t, mg/L
ORSR — Organics removal to sludge ratio, mg/g
SIR — Sludge to iron ratio, g/mol

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