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# Treatment of high strength methyl orange wastewater by electrocoagulation with periodic reversal of electrodes: Effect of voltage variation

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## ABSTRACT

The electrocoagulation process with periodic reversal of the electrodes was used to treat high strength synthetic methyl orange wastewater. The Al-Fe electrodes were considered as the optimal electrodes compared with Al-Al and Fe-Fe electrodes. Effect of voltage variation on color and COD removal efficiency, energy consumption, electrode consumption, sludge production and sludge density was investigated and discussed. 20 V and 50 min were considered the optimal applied voltage and treatment time in treating the wastewater. The effects of oxidation and reduction were enhanced continuously with increasing voltage during the electro coagulation process. However, adsorption and flocculation was still the main methyl orange removal pathway at different voltages.

*Keywords:* Electro coagulation; Periodic reversal of the electrodes; Methyl orange wastewater; Voltage variation; Running time.

## 1. Introduction

Dye wastewater has the characteristics of strong colors, low biodegradability and high chemical oxygen demand (COD), which is one of the most important component of industrial wastewater [1,2]. Between 1% and 15% of dye is released into the wastewater during dyeing process, which is very harmful for human and environment without being well treated [3–5]. Different kinds of technologies have been employed for the removal of dyes from wastewater. But low biodegradability, high cost and secondary pollution indicate that dye wastewater is not treated effectively by most biological processes as well as advanced oxidation processes [6,7].

Electro coagulation (EC) process takes electrons as intermediates to generate related metal hydroxide as coagulation to remove pollutant, which is an effective and innovative method to treat dye wastewater [8].

The EC process is a complex technology with physical and chemical processes. Fe or Al is dissolved from anode into aqueous solution, and generates corresponding metal ions, $Al^{3+}$ and $Fe^{3+}$ subsequently. Then the metal ions immediately react with the hydroxide to produce the corresponding metal hydroxide or poly-hydroxide as coagulations [6]. The effective metal hydroxide removes pollutants through adsorption and precipitation. Pollutants can be removed by adsorption, precipitation, chemical reaction and electrolytic flotation. The oxidation and reduction dissociation of water on electrode surface can produce oxygen in anode and hydrogen in cathode. The generation of bubble increases the turbulence of wastewater and enhances mass transport rate. The main reaction of EC is summarized as follows:

Anode:

$$M \rightarrow M^{n+} + ne^- \qquad (1)$$

(there M-Fe or Al, n-3)

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (2)$$

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Cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{3}$$

In the wastewater:

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3\ (gel) \tag{4}$$

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3\ (gel) \tag{5}$$

The advantages of EC process include easy operation, positive removal of pollutant, energy efficiency, environmentally friendly and cost effectiveness [9–11]. In addition, the rapid development of hydro power industry in China will cut down the operating cost and provide a favorable environment for EC process in wastewater treatment. The concentration polarization and metal oxide passivation layer, formed on electrodes, are two serious disadvantages of EC process, which can impede the dissolution of the metal plates into wastewater. The EC process with periodic reversal of the electrodes (PREC) has been reported to solve the problems of traditional EC process [12]. PREC enhances the transfer rate of metal ions and dissolves the passivation on the electrode surface, which can maintain a poorer degree of passivation on the surface of electrodes and obtain a more active removal efficiency of dye.

Traditional studies have focused on the optimization of control parameters of EC process, such as electrode material, applied voltage, initial pH, initial methyl orange concentration and inter-electrode distance, in order to maximize the efficiency of dye removal. The optimal dye concentrations in synthetic wastewater are less than 200 mg/L for the EC process [13–17]. Dye removal in the EC process would be affected obviously in treating high strength dye wastewater. The applied voltage is one of the most critical parameters of EC process [18,19]. The increase in voltage makes higher current and more metal ion dissolved into the wastewater, which would enhance dye removal and shorten reaction time, especially in treating high strength dye wastewater. However, limited information on the effect of voltage variation in a wide range on dye removal in EC process, especially in PREC is available. Moreover, the concentration of dye is always higher than 200 mg/L in practical dye wastewater. Hence, this paper focused on treatment of synthetic methyl orange waste water containing 500 mg/L methyl orange by PREC. The aim of this paper was to investigate the specific effect of voltage variation on performance of the PREC. The performance of the PREC was evaluated by color and COD removal efficiency (CR and CODR), energy consumption (ENC), pH, conductivity, sludge production (SP), sludge density (SD), and electrode consumption (ELC). Moreover, different electrodes including Al-Al, Fe-Fe and Al-Fe electrodes on the wastewater treatment were compared. Special attention was given to the effect of voltage variation on the removal mechanism of methyl orange by PREC.

## 2. Materials and methods

### *2.1. Experimental devices*

Structure of the PREC is shown in Fig. 1. The power supply connected to the PREC reactor can adjust the voltage from 0 to 100 V and transform the direction of electrode from 1 s to 99 h. Al and Fe were used as electrode materials. Magnetic stirrer was employed at the bottom of the electrolytic cell.

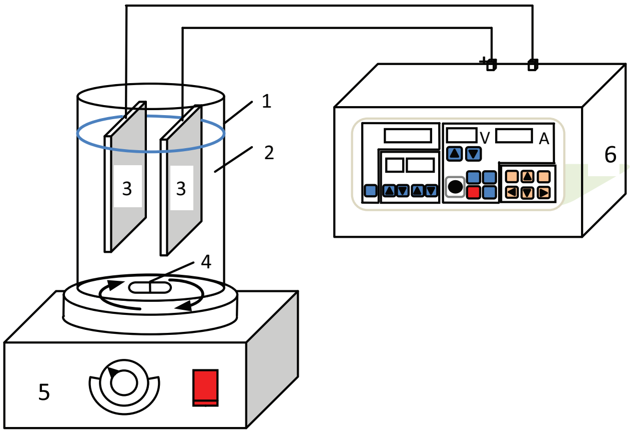


Fig. 1. Schematic diagram of the PREC system. 1. Electrolytic cell. 2. Synthetic methyl orange wastewater. 3. Electrodes (iron or aluminum). 4. Magnetic bar. 5. Magnetic stirrer. 6. Power supply (U-volt meter; I-ampere meter; t-the time for periodical reversal of electrodes).

The cycle of reversal time was 15 s for the first part and was 5 min for the second part of this experiment. Total area of the electrode was 24 cm² (6 cm × 4 cm). The electrodes were positioned vertically and parallel to each other with an inner gap of 2.5 cm. A beaker with volume of 500 mL was used as the electrolytic cell.

### *2.2. Experimental procedure*

The electrodes were polished by sandpaper before each experiment and were immersed in 15% HCl for 2 min, and then were rinsed with distilled water. Finally, the electrodes were dried and weighed ($m_1$). The electrodes were rinsed thoroughly with distilled water after each experiment, and then were dried and weighed again ($m_2$).

Fresh synthetic wastewater with methyl orange concentration of 500 mg/L was placed into the beaker each run. 1 g/L NaCl was added into the wastewater as electrolyte. The experiment was done under voltages of 5, 10, 15, 20, 25, 30 and 35 V. Each experiment was carried out for 60 min. Samples were taken out of the cell each 10 min. Color, COD and pH were measured after being filtrated by 0.45 μm filter paper. After each reaction, the solution was settled for 2 h, and then the volume ratio of the sludge to the total wastewater was measured. All experiments were repeated thrice. All chemicals and reagents used in this study were of analytical grade.

### *2.3. Analytical methods*

The methyl orange concentration was measured by a UV/V is spectrophotometer (Jinghua UV 2100, China) at a wavelength of 463 nm, the maximum absorbance of the methyl orange. COD, the sludge yield and consumption of electrode plate were measured according to standard methods [20]. The variation of pH was monitored by a pH meter (Leici PHS-25, China). The main calculations in this work are listed below:

$$CR(\%) = \frac{A_0 - A_t}{A_0} \times 100\% \tag{6}$$

*CR*—removal efficiency of color; $A_0$—absorbance values of methyl orange before treatment; $A_i$—absorbance values of methyl orange after treatment for t min.

$$CODR(\%) = \frac{COD_0 - COD_t}{COD_0} \times 100\% \tag{7}$$

*CODR*—removal efficiency of *COD; $COD_0$—COD* concentration before reaction; $COD_i$—*COD* concentration after treatment for *t* min.

$$ENC\left(kWhkg(MOr)^{-1}\right) = \frac{UIt}{1000\Delta MOr \times 0.5} \tag{8}$$

*ENC*—energy consumption; *U*—Voltage, *V*; *I*—Current, *A; t*—running time, *h*; ΔMOr—change in methyl orange concentration before and after treatment, mg/L; 0.5—volume of wastewater, 0.5 L.

$$SP\left(kg(sludge)kg(MOr)^{-1}\right) = \frac{(m_4 - m_2) - (m_3 - m_1)}{1000\Delta MOr \times 0.03} \tag{9}$$

$m_1$, $m_2$—mass of the crucible ready to initial methyl orange solution and effluent respectively, g; $m_3$, $m_4$—mass of the crucible containing 30 ml initial methyl orange solution and effluent after 2 h of drying respectively, g; ΔMOr—change in methyl orange concentration before and after treatment, mg/L; 0.03—volume of wastewater, 0.03 L.

$$SD\left(g\,L^{-1}\right) = \frac{(m_4 - m_2) - (m_3 - m_1)}{0.03 \times R} \tag{10}$$

*R*—volume ratio of sludge to methyl orange solution after treatment.

$$ELC\left(kgAl\ kg(MOr)^{-1}\right) = \frac{m_{Al1} - m_{Al2}}{\Delta MOr} \tag{11}$$

$$or\ ELC\left(kgAl\ kg(MOr)^{-1}\right) = \frac{m_{Al1} - m_{Al2}}{\Delta COD} \tag{12}$$

$$or\ ELC\left(kgFe\ kg(MOr)^{-1}\right) = \frac{m_{Fe1} - m_{Fe2}}{\Delta MOr} \tag{13}$$

$$or\ ELC\left(kgFe\ kg(MOr)^{-1}\right) = \frac{m_{Fe1} - m_{Fe2}}{\Delta COD} \tag{14}$$

*ELC*—electrode consumption; $M_{Al1}$—mass of Al electrode before treatment; $M_{Al2}$—mass of Al electrode after treatment; $M_{Fe1}$—mass of Fe electrode before treatment; $M_{Fe2}$—mass of Fe electrode after treatment; Δ*COD*—mass of removal of COD, kg; Δ*MOr*—mass of removal of methyl orange, kg.

In order to study the effect of voltage variation on methyl orange removal mechanism, the samples were taken out of the electrolytic cell after reaction at different voltages. The samples were extracted by organic solvents and subjected to GC–MS analysis using a 7890/5975 GC–MS system (Agilent, USA) to identify the by-products. Then the amount of dissolved metal ions in solution was measured by inductively coupled plasma mass spectrometry (ICP-MS) (NexION 300X; Perkin Elmer).The difference between consumption of electrodes and the amount of dissolved metal ions in solution was the amount of dissolved metal ions in flocs.

## 3. Results and discussion

### 3.1. Electrode material

Fe and Al were the most common electrodes used for EC process. Al-Al, Fe-Fe and Al-Fe were used as electrodes of the PREC to treat the synthetic methyl orange wastewater, respectively. Take CR and CODR as indices for assessing wastewater treatment performance, which are shown in Fig. 2. The experimental errors of CR and CODR were less than 4%. The PREC with Fe-Fe and Fe-Al electrodes achieved similar CR. Al-Fe electrodes got more positive CODR than others. To take 20 V as a case, CODR of 42.6%, 98.8% and 97%, and CR of 57%, 59.7% and 78% were achieved by Al-Al, Fe-Fe, Al-Fe electrodes, respectively. Al-Al electrodes got the poorest CR and CODR. The results would be explained by the fact that the iron ions had stronger enmeshment effect than aluminum ions and the synergistic effect of iron and aluminum ions [21].

Treatment of methyl orange wastewater by electro coagulation with Al-Al electrodes was reported and achieved 97% color removal under optimal conditions [16]. This result showed that the Al-Al electrodes also achieve a desired color removal under optimization conditions for 125 mg/L of methyl orange. Previous study has observed that the Al anode was superior to the Fe anode for removing disperse dye, and the Fe anode can get a greater removal efficiency than Al anode for the treatment of reactive dye [22]. Electro coagulation with Al-Fe electrodes has been proven as an efficient way to treat textile waste waters containing a variety of textile dyes and Reactive Brilliant Blue X-BR [23,24]. Al-Fe electrodes achieved better methyl orange and color removal efficiencies than Al-Al and Fe-Fe electrodes in this study. The possible reason was that the complexity formed by iron and aluminum got better methyl orange removal performance by adsorption and flocculation than separate iron-and aluminum. In summary, Al-Fe electrodes were considered as the optimum electrode material and were used in the following experiments.

It was worth noting that CODR with Fe-Fe electrodes increased to 52.1% for the first 30 min, and decreased to 14.8% at 60 min with voltage of 20 V. The color of wastewater disappeared gradually for the first 30 min and was deeper for another 30 min using Fe-Fe electrodes. The phenomenon was in accord with previous study, and the colloidal ferric hydroxide gave yellow-brown color into solution after EC treatment [13,18]. In Fig. 3, we observed that a new substance was produced when Fe-Fe was taken as electrodes. The peak of the new substance increased with enhancing voltage. The peak of the new substance increased with enhancing voltage. According to the results of GC-MS, the main new substance is N,N-dimethyl-1,4-Benzenedi-

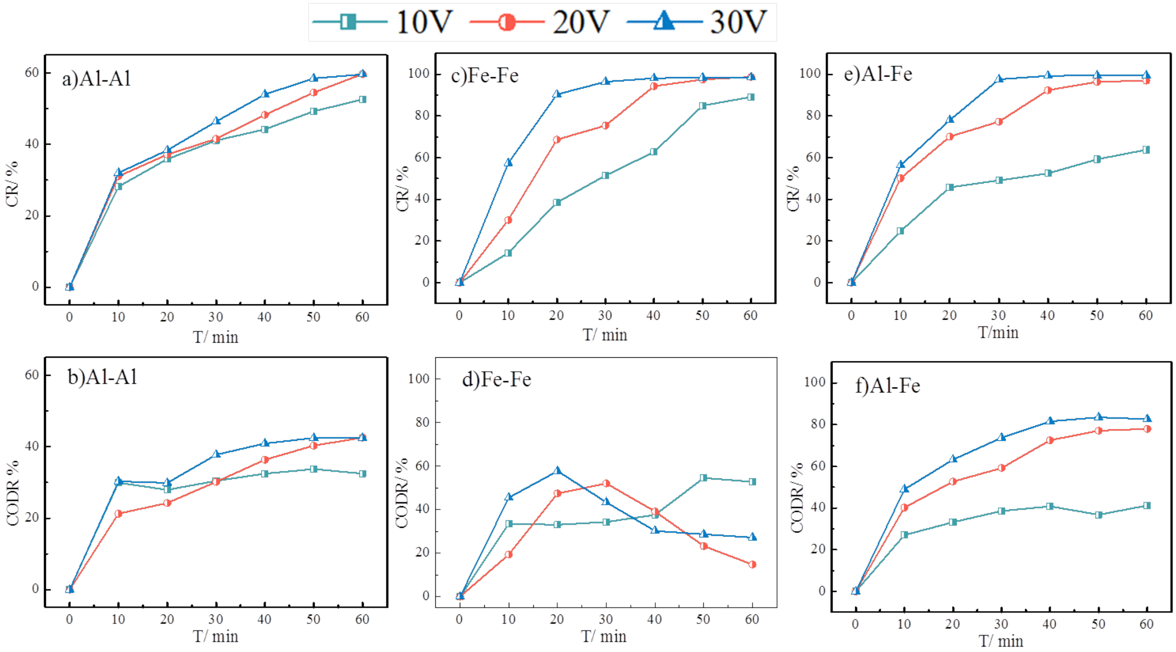


Fig. 2. Change of CR and CODR using Al-Al, Fe-Fe and Al-Fe as electrodes under different applied voltages.

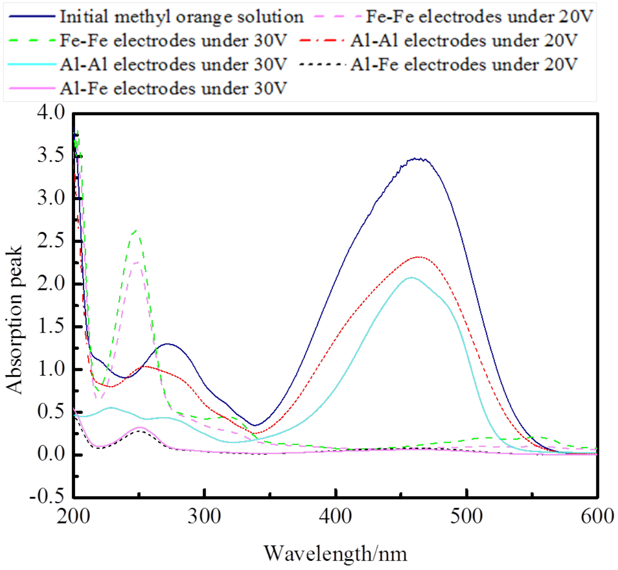


Fig. 3. Spectroscopic analysis after 1h of treatment using different electrodes.

amine. The results demonstrated that the Fe electrode is beneficial to the oxidation of methyl orange and the -N=N- was cleaved during oxidation. This result was similar to the previous studies [25,26]. So color of the wastewater disappeared gradually in the first 30 min for Fe-Fe electrodes. Moreover, the dissolved ferrous ions increased with enhancing voltage, resulting in an increase in the formation of intermediates. Previous study reported that the coagulation was the main pathway for COD removal and the oxidation process was the next [17]. Flocculation was the main method to remove methyl orange in the early stage of reaction for Fe-Fe electrodes. The reduction of iron ions was enhanced with the increase of voltage and running time, resulting in an increased production of the new substance. On the contrary, flocculation was gradually weakened during this period, which led to the analysis of organic matter and achieved a poor CODR.

### 3.2. Color and COD removal

Variations of CR and CODR with the increase of voltage are shown in Fig. 4. CR and CODR were improved continuously with increasing voltage. The removal efficiency of color was better than that of COD in all cases. The approximately complete removal of color was achieved when the voltage was higher than 20 V within 50 min, but only 82% of CODR was obtained in this case. Azo groups were the main reason that methyl orange generated color in the wastewater. The results indicated the existence of oxidation during EC process, which converted methyl orange to some simple organic compounds.

The new ecological hydrogen produced by the cathode and electronic have a high activity. Methyl orange can be reduced directly [Eq. (15)], and the new ecological hydrogen was capable of reacting with dye using $Fe^0$ as catalyst [25]. From results of electrode material, the metal ions dissolved in the Fe electrode can also help to break the -N=N-. Previous studies have demonstrated the presence of hypochlorous acid and chlorine using sodium chloride as an electrolyte and adding sodium chloride helped to improve pollutant removal rate [27–29]. The main reaction of sodium chloride was summarized as Eqs. (16), (17) and (18) [30]. The oxidation and reduction of dyes occurred with chemical structure fragmentation of dyes (Azo groups breaking) [31].

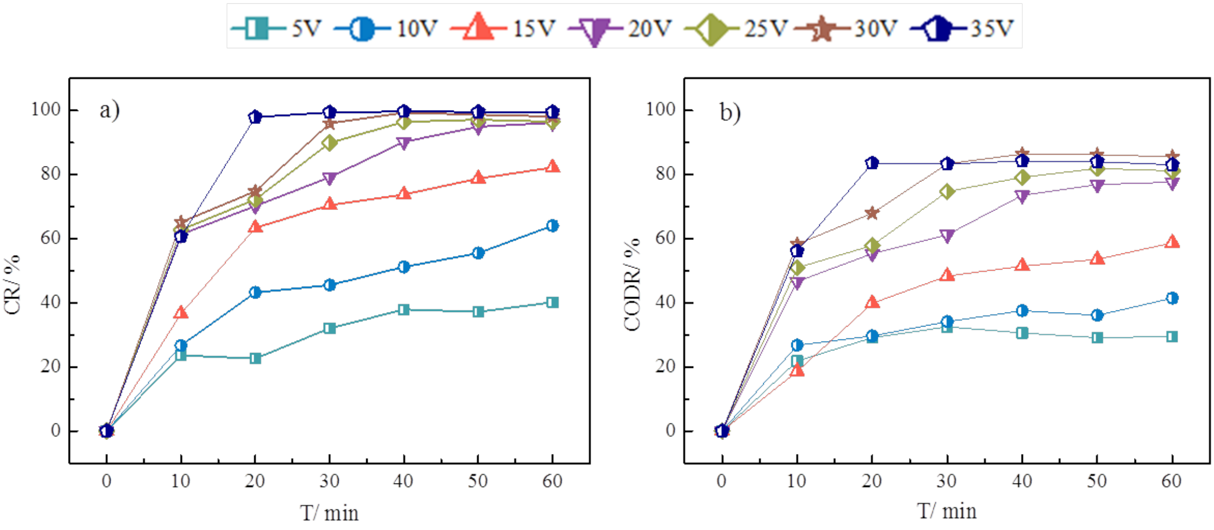
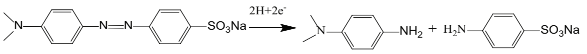


Fig. 4. Change of CR(a) and CODR(b) with processing time under different applied voltage.

 (15)

$$Cl^- - 2e \rightarrow Cl \quad (16)$$

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^- \quad (17)$$

$$HClO \rightarrow ClO^- + H^+ \quad (18)$$

Significant increase of dye removal efficiency was observed when voltage rose from 5 V to 15 V. In the case of 5 V, the current density was approximate zero, which meant that there was few metal ions dissolved in the wastewater and little flocculation formed. In previous literature, 97% of CR was achieved only at 4.4 V of voltage [16]. The reason was that the experiment in the literature was carried at a conductivity of 9.9 ms/cm, which was far greater than the conductivity of 2.05 ms/cm in this study. The optimal methyl orange concentration in previous study was 125 mg/L, which was only one quarter of this study. In this study, more than 97% of CR and 78% of CODR was obtained when the voltage exceeded 20 V after 1 h. Therefore, the PREC operated under high voltage was more suitable for the treatment of high strength methyl orange wastewater comparing with low voltage value, especially under low conductivity condition. There was slight increase of CR when the voltage was higher than 20 V and the running time was longer than 50 min. CODR did not change significantly when the voltage was higher than 20 V and the running time was longer than 40 min. This phenomenon can be explained by the super saturation of intermediates such as metal ions when the voltage was greater than 20 V. The metal ions dissolved in the anode continuously reacted with the hydroxide to form flocs during the EC process. However, the amount of metal ions and metal flocs would be excessive when the voltage was greater than a certain value. Therefore, there were little increase of flocs with further improving the ions dissolved from the anode [25].

There was a small change in the difference between CR and CODR when the voltage was changed. This meant that there was a certain degree of oxidation, which was affected by increasing voltage. However, the difference between CR and CODR was almost the same when the voltage was higher than 20 V. Adsorption and coagulation were the primary ways to remove methyl orange directly under higher voltage, leading to the same increments of CR and CODR. $Fe^{2+}$, ·OH and $ClO^-$ produced from $Cl^-$ were the main substances oxidizing or reducing methyl orange in the PREC system. A higher voltage should produce more $Fe^{2+}$, ·OH and $ClO^-$, but the excess accumulation of metal ions and coagulations on the surface of the electrode under higher voltage resulted in weakening oxidation and reduction performance.

### 3.3. Energy consumption

Energy consumption (ENC) was a major factor affecting the use of EC process. The lower voltage was consistent with the less energy consumption generally. ENC was a critical index for assessing the economic benefits of the PREC in treating the methyl orange. The ENC with the change of voltage is shown in Fig. 5. The ENC increased with the enhancement of applied voltage and running time. The increase rate of ENC at a higher voltage was faster than that at a lower voltage. The ENC was relatively slow when the voltage was lower than 20 V. The ENC of PREC was 22.7 kWh/kg (MOr) and 39.7 kWh/kg (MOr) after 1 h at 20 V and 25 V, respectively. The increase rate of ENC in the first 30 min was relatively slower than the later 30 min when voltage was greater than 25 V, especially with voltage of 35 V. The CR, CODR and ENC increased from 99.2%, 83% and 41.3 kWh/kg (MOr) to 99.6%, 83.3% and 83 kWh/ kg (MOr) at 35 V when the running time lasted from 30 min to 60 min, respectively. There were slight increase of CR and CODR in the later 30 min, but the ENC was doubled. The results meant that the utilization efficiency of current was lower at a higher voltage. It should be noted that temperature of the wastewater rose with the running time in the PREC process. The excess energy was dissipated as heat energy partially [16].

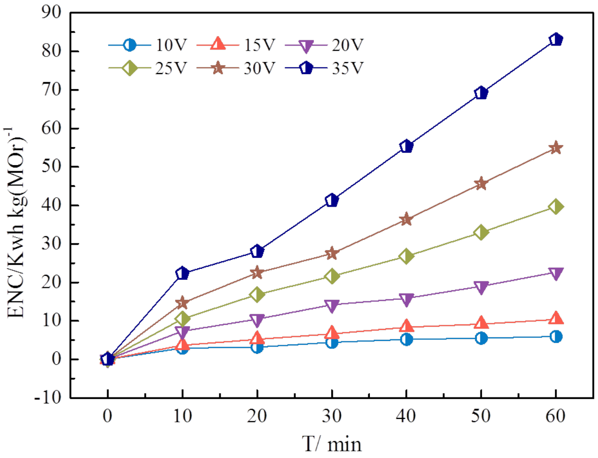


Fig. 5. Change of ENC under different applied voltages.

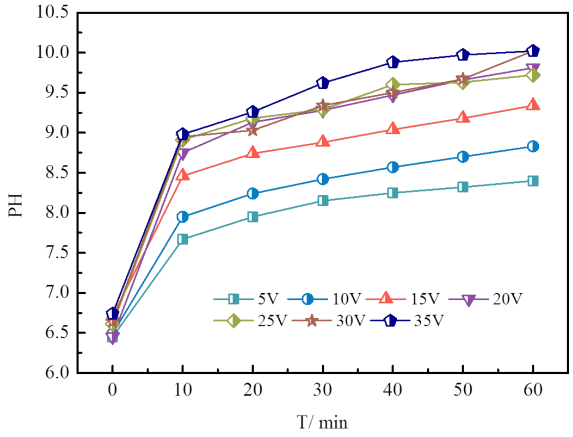


Fig. 6. The pH variation of the wastewater with running time under different applied voltages.

The CR and ENC were 97 ± 2% and 44 ± 3kWh/ kg (MOr) under optimal condition using conventional EC process [16]. The minimum ENC required to achieve 97% CR was 28 kWh/kg (MOr) in this study. Therefore, removal of the same mass of methyl orange required more energy consumption in conventional EC process. In addition, the low conductivity meant the small current density and the slow flocculation rate, which would be overcome by adopting relative high voltage value. Also it was cost-effective to use PREC to treat high strength methyl orange wastewater compared with conventional EC process.

### *3.4. The pH variations*

The pH value played a vital role in EC process by controlling the speciation of metal ions occurring in the PREC cell. The electrolysis of wastewater in the PREC produced hydroxide to raise the pH value. Fig. 6 shows the change of pH during PREC process under different voltages.

The pH value of the wastewater increased gradually with the proceeding of experiments and improved faster at higher voltage. The pH increased from 6.5 to 8.4 at a voltage of 5 V and from 6.4 to 10 at a voltage of 35 V after treatment of 1 h. The experimental errors of pH were less than 5%. The concentration of $OH^-$ was enhanced with the dissolution of metal ions and electrolysis of wastewater, lending to increase of pH value in EC process, especially under a higher voltage. More positive CR meant a greater change of pH value. The increase in the amount of hydroxide produced more metal hydroxide and flocculation to improve methyl orange removal [32,33].

Al and Fe hydroxides were different at different pH values. $Al(OH)_3$ with large surface area had a strong ability to absorb organic compounds, and has been considered to be the main substance in EC process [16]. $Fe(OH)_3$ was the dominant substance to remove organic matter [34]. The optimal pH of EC process with Al or Fe as electrode was different in treating dye wastewater. Previous paper has reported that optimal pH range was from 5 to 7 for both Fe and Al electrodes [18]. While being operated at extreme pH values, lower than 3 or higher than 10, color and COD removal performance of the EC process would be affected obviously. The aluminum irons were dissolved from Al electrode and produced $Al^{3+}$ and $Al(OH)_2^+$ within the pH range of 2–3. $Al^{3+}$ and $Al(OH)_2^+$ were transformed into $Al(OH)_3$ at pH values ranging from 4 to 9. The ratio of $Al(OH)_4^-$ was increased when pH higher than 10 [28]. Also different Fe hydroxides were produced in various pH values. The $Fe(OH)_2^+$ and $Fe(OH)^{2+}$ were dominant species in acidic solution which were transformed into $Fe(OH)_3$ spontaneously in the pH of 6–9.5. Finally, $Fe(OH)_4^-$ was generated when pH was higher than 9.5 [35]. From Fig. 4, we observed that the main COD and coloration were removed at the first 20 min. The pH value increased from 6.6 to 9.3 for the first 20 min. $Fe(OH)_3$ and $Al(OH)_3$ were mainstreams at this range of pH value. CR and CODR did not change significantly when running time was longer than 40 min. The pH was heightened from 9.7 to 10 for the last 20 min, and the main form of Fe hydroxide was $Fe(OH)_4^-$ in this range of pH value. $Fe(OH)_4^-$ did not play a crucial role in removing COD and color.

### *3.5. Sludge production, density and electrode consumption*

Sludge was generated during EC process. Most of the methyl orange was removed through the precipitation and enmeshment of metal flocculation forming sludge [36]. The better removal efficiencies of color and COD usually corresponded to more SP [37]. Fig. 7 shows the change of SP and SD with increase of applied voltage. The SP was improved continuously with increasing voltage. Small increase of SP was observed when the voltage increased from 5 V to 15 V. There was slight decrease on SP, from 1.96 kg (sludge)/kg(MOr) to 1.95 kg (sludge)/kg(MOr), when the voltage was enhanced from 15 V to 20 V. A significant increase of SP was observed when the voltage rose from 20 V to 25 V. A Higher voltage indicated more dissolved metal ions and more sludge generation. When the voltage was higher than a certain level, the excess of metal hydroxide, not being used to precipitate methyl orange completely, was produced. Therefore, SP increased steeply with enhancing voltage when the voltage was greater than 20 V. In previous literature, SP was 17.2 ± 0.9 kg (sludge) kg $(MOr)^{-1}$ under the optimal condition, which was much larger than the SP

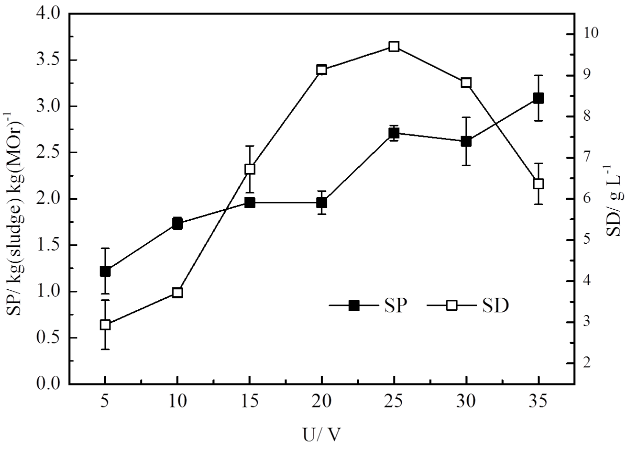


Fig. 7. Change of sludge production (SP) and sludge density (SD) with increasing applied voltage.

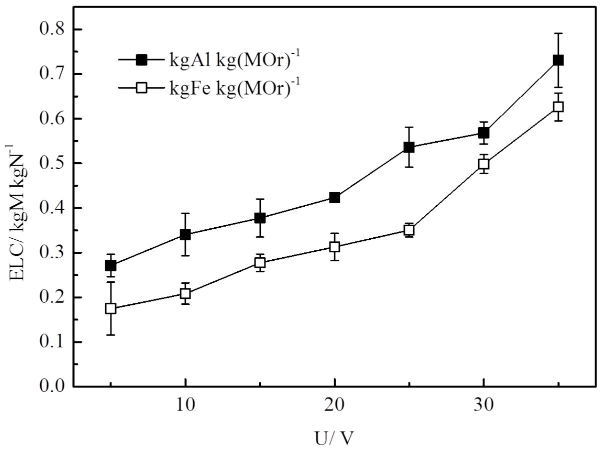


Fig. 8. Change of electrode consumption (ELC) with increasing applied voltage.

in this study [16]. The reason was that the concentration of methyl orange was higher and the current density was smaller in this study than previous study.

The SD was raised when the voltage increased from 5 V to 25 V, and then decreased with further improving the voltage. The maximum sludge density of 9.7 g/L was obtained at 25 V. The consumption of aluminum electrode was more than the iron electrode, and $Al(OH)_3$ occupied larger volume than $Fe(OH)_3$ at the same mass. The ratio of aluminum to iron consumption determined the SP, which was reduced from 2.8 to 1.1 when the voltage was raised from 5 V to 35 V. Therefore, the SD increased when the voltage increased from 5 V to 25 V. Simultaneously, more bubbles would be produced at a higher voltage, which induced the decline of SD when the voltage was higher than 25 V.

The electrode was an indispensable part in the EC system. The ELC was one of the most important indices for assessing performance of EC process. Fig. 8 shows the change of ELC with the enhancement of voltage. The higher the voltage was, the faster the electrodes were dissolved according to Faraday's law [38]. The ELC, both Al electrode and Fe electrode, kept increasing with the rise of voltage. The consumption of iron electrode was much smaller than that of aluminum electrode. This led to a small amount of $Fe^{2+}$ produced and a small chance of oxidation and reduction. This result was similar to the reports in previous study [22]. It can be attributed to the Fe electrode was more likely to form a passivation layer than the Al electrode in the same operation condition. The passivation layer would be overcome under a higher voltage, which promoted the dissolution of Fe electrode.

The desired removal efficiency, more than 96% of CR and 75% of CODR, was achieved at voltages of 20 V, 25 V, 30 V and 35 V when running time was 50 min, 40 min, 30 min and 20 min, respectively. There were slight increase on CR and CODR when the voltage or running time continued increasing. The corresponding SP and ELC were similar in those cases, but greater SD was observed at a higher voltage. More than 1.55 times of ENC was required to achieve the satisfactory CR and CODR at 35 V compared to 15 V. Comparing the various indicators in different situations and from the perspective of economic efficiency, 20 V and 50 min were considered as the optimal applied voltage and running time in present study.

### 3.6. Mechanism of methyl orange removal

Common flocculation, oxidation and reduction were two main routes for PREC to reduce coloration and remove COD. The insoluble $Fe(OH)_3$ or $Al(OH)_3$ was the major flocs to remove organic matter and dyes [34]. $Fe(OH)_3$ and $Al(OH)_3$ were converted into $Fe^{2+}$, $Fe^{3+}$ and $Al^{3+}$ at pH of 2, which did not have capacity to flocculate and remove methyl orange. Therefore, the methyl orange removed by flocculation was released into the solution at pH of 2 leading to increase of methyl orange concentration. The difference between the total removed methyl orange and the methyl orange removed by flocculation was the one removed by oxidation and reduction. As an indicator, methyl orange would undergo structural change when the pH value was adjusted to 2. The related reaction is shown in Fig. 9a and the methyl orange at pH of 2 showed peak at 510 nm.

In order to study the proportion of methyl orange removed by flocculation, the effluent at pH of 2 after treatment of 1 h under different voltages was analyzed by ultraviolet spectrophotometry. Spectroscopic analysis of the samples under different voltages at peak of 510 nm is shown in Fig. 10. About 3.3%, 17.8% and 17.3% of methyl orange was removed by oxidation and reduction and 77.2%, 80.2%, 82.3% of methyl orange was reduced though flocculation under 10 V, 20 V and 30 V, respectively. The degree of oxidation and reduction for color reduction at 20 V was similar to that at 30 V, but COD removal at 30 V was more than 20 V. The results confirmed that more intermediate was removed by oxidation and reduction at 30 V than at 20 V. These results indicated that a higher voltage would increase the ratio of oxidation and reduction, but flocculation was the main way to remove methyl orange.

The intermediate product in solution during the PREC process was measured by GC-MS. From the results of GC-MS, more than 95% of intermediate was $C_8H_{11}N$ under voltage of 10 V, 20 V and 30 V after reaction for 1 h. The structure of $C_8H_{11}N$ is presented in Fig. 9b. It demonstrated

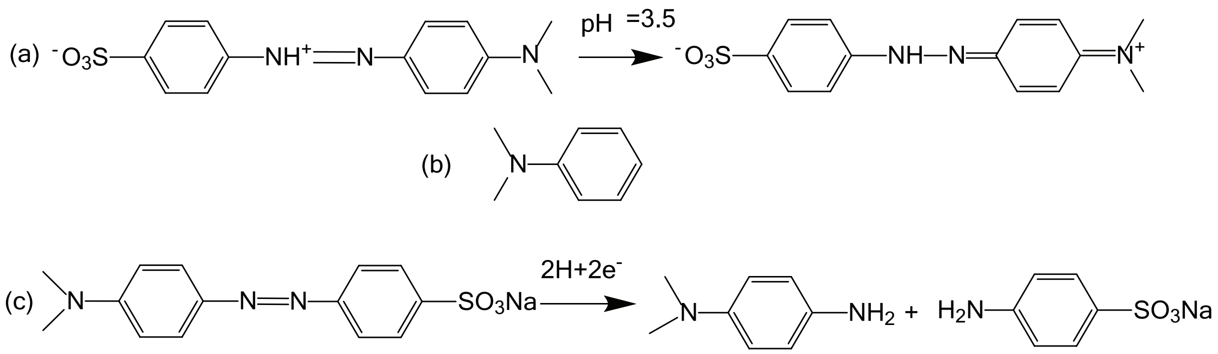


Fig. 9. Conversion of methyl orange in acidic solution (a), the chemical formula of C8H11N (b) and hydrogenation reduction reaction of methyl orange (c).

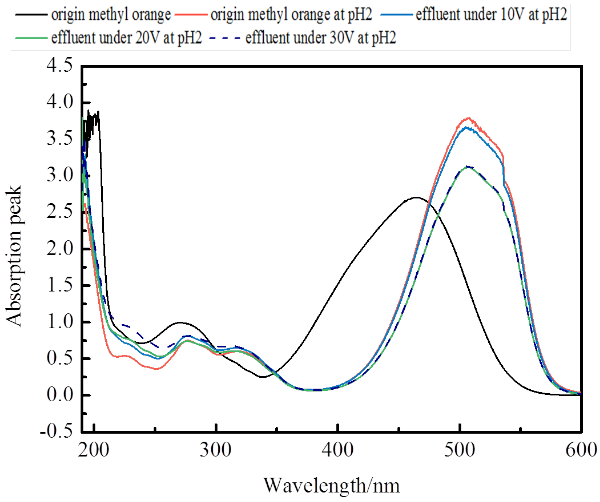


Fig. 10. Spectroscopic analysis of original methyl orange and effluent after treatment of 1 h at pH of 2 under different voltages.

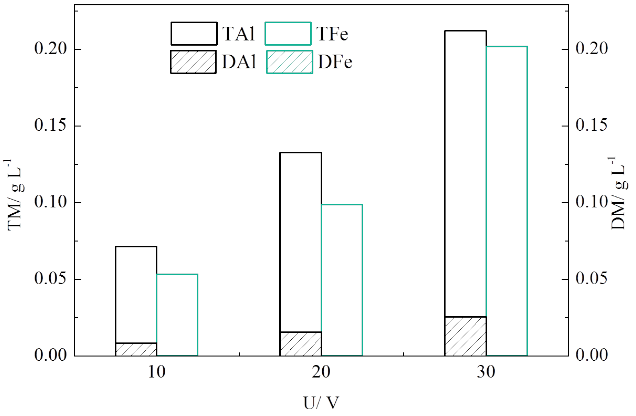


Fig. 11. Dissolved and precipitated metal ions at different voltages. TM - total dissolved metal ions; DM - dissolved metal ions after reaction of 1 h; SM - metal ions in the sludge after reaction of 1 h; M-Al or Fe.

the cleavage of the Azo bond in the methyl orange during treatment of PREC. The result was in accord with previous study [39,40]. The direct hydrogenation reduction of methyl orange is shown in Fig. 9c. The proportion of $C_8H_{11}N$ in the intermediate increased with the enhancement of voltage, 95.1% for 10 V, 96.5% for 20 V and 98.4% for 30 V. The results indicated that the oxidation and reduction were strengthened with the increase of voltage. However, proportion of oxidation and reduction in the PREC process was low, so the intensity of reinforcement was relatively small. More than 2.5% of intermediate was long-chain hydrocarbons, which proved the existence of ·OH and $ClO^-$ during EC process. A previous study has reported that chlorinated salts were broken down to produce highly oxidative reagent from chloride ions at the anode surface [41]. The ·OH and $ClO^-$ led to the formation of long-chain hydrocarbons by breaking the benzene ring of methyl orange. The total amount of intermediates increased when the voltage increased from 10 V to 20 V, then decreased with further improving the voltage. The low current density corresponded to the small amount of oxidizing material such as electronics and ·OH, leading to less intermediates. The oxidizing material increased with improving voltage, so the number of intermediates increased when the voltage was improved from 10 V to 20 V. Only around 2% of methyl orange remained in the effluent at 20 V, but flocculation, oxidation and reduction were enhanced continuously with increasing voltage further. Therefore, there was a decrease in the intermediates when the applied voltage changed from 20 V to 30 V.

The specific presence of metal ions after reaction of 1 h is shown in Fig. 11. Almost all dissolved iron and about 88% of the dissolved aluminum were used to eliminate methyl orange at each voltage. Total amount of dissolved iron and aluminum increased with heightening voltage, which was the reason why the higher methyl orange removal efficiency and greater SP were achieved at a higher voltage. In Fig. 2, the PREC with Al-Al electrodes got around 60% of CR and 40% of CODR only. In summary, the capability of iron and iron-aluminum hydroxides for removing color and COD was greater than aluminum hydroxides. The result was in accord with previous studies that reactive dyes were characterized by Azo bonds (N=N) and were removed by the Fe anode superior than Al anode [42,43].

The variation of voltage affected methyl orange removal to some extent. However, the shorter cycle of periodic elec-

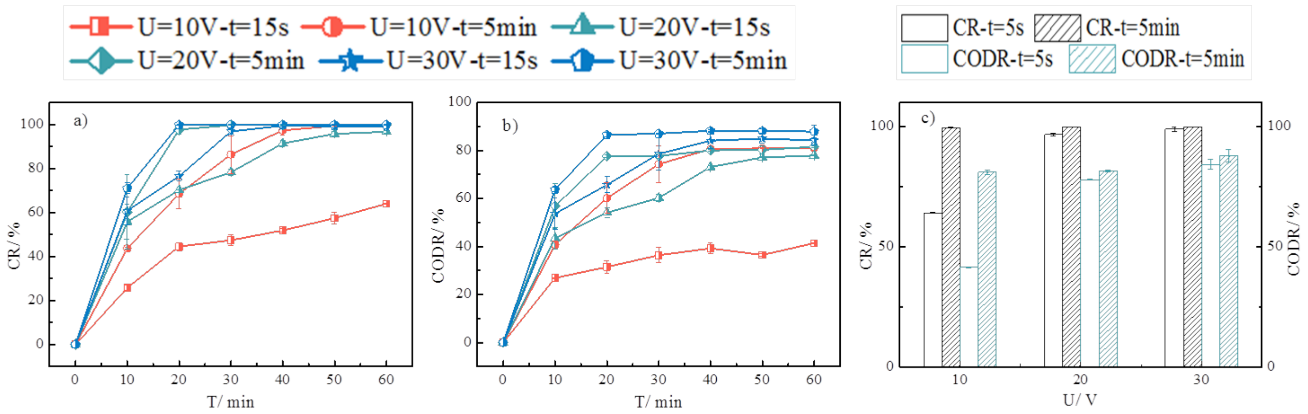


Fig. 12. Change of CR (a) and CODR (b) with running time under different applied voltages and the variation of removal efficiency with increasing voltage (c).

trode reversal time meant more time was consumed by the reversal process, leading to less useful time for removing dye [16]. 15 s of the cycle of periodic electrode reversal might limit the influence of the voltage variation on methyl orange removal performance. Therefore, the PREC with the reversal time of 5 min was employed to treat the methyl orange wastewater at 10 V, 20 V and 30 V, and the results are shown in Fig. 12.

The PREC with reversal time of 5 min achieved the desired CR and CODR in shorter operating time than that of 15s. CR and CODR using the PREC with reversal time of 5 min reached stabilization within 20 min at 20 V, and the CR and CODR were 97.6% and 77.5%. In addition, the CODR of PREC with reversal time of 5 min after 1 h of treatment was greater than that of 15 s. These results indicated that the PREC was a time-saving way to treat methyl orange wastewater by optimizing the operating parameters. More than 99.6% CR was achieved by PREC with reversal time of 5 min after 1 h of treatment in the three voltages. Greater CODR was achieved by PREC with cycle of reversal time of 5 min at higher voltage. The result verified that the voltage did have an impact on pathway to eliminate methyl orange.

## 4. Conclusions

PREC was employed in treating synthetic high strength methyl orange wastewater to investigate the specific effect of voltage variation on CR and CODR performance. The PREC operated under high voltage was a suitable way to treat high strength methyl orange wastewater, especially under low conductivity condition. Higher voltage achieved desired CR and CODR in shorter time. To obtain the similar methyl orange removal performance, the ENC was lower than previous studies because of the mode of PREC. The change of pH also gave an explanation to the phenomenon that CR and CODR increased slightly when voltage was greater than 20 V and running time was longer than 50 min. 20 V and 50 min were optimal operation conditions by considering the CR, CODR, ENC, SP and SD. High voltage would enhance the degree of oxidation and reduction for methyl orange removal, but flocculation was the main way to remove methyl orange.

## Abbreviations

EC — Electro coagulation
PREC — Electro coagulation with periodic reversal of the electrodes
CR — Color removal
CODR — Chemical oxygen demand removal
ENC — Energy consumption
ELC — Electrode consumption
SP — Sludge production
SD — Sludge density
MOr — Methyl orange
U — Voltage

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## References

[1] Z. Zaroual, M. Azzi, N. Saib, E. Chainet, Contribution to the study of electro coagulation mechanism in basic textile effluent, J. Hazard. Mater., 131 (2006) 73–78.
[2] A. Aouni, C. Fersi, M.B.S. Ali, M. Dhahbi, Treatment of textile wastewater by a hybrid electro coagulation/nanofiltration process, J. Hazard. Mater., 168 (2009) 868–874.
[3] A. Haririan, O. Fagoaga, H. Daneshvar, K. Morawski, D.H. Sillix, J.M. El-Amm, M.S. West, J. Garnick, S.D. Migdal, S.A. Gruber, S. Nehlsen-Cannarella, Predictive value of human leucocyte antigen epitope matching using HLA Match maker for graft outcomes in a predominantly African-American renal transplant cohort, Clin. Transplant., 20 (2006) 226–233.
[4] R.S.Y. Yavuz, Anodic oxidation of reactive black 5 dye using boron doped diamond anodes in a bipolar trickle tower reactor, Separ. Purif. Technol., 85 (2012) 130–136.

[5] J.H.B. Rocha, A.M.S. Solano, N.S. Fernandes, D.R. da Silva, J.M. Peralta-Hernandez, C.A. Martínez-Huitle, Electrochemical degradation of remazol red BR and novacron blue C-D dyes using diamond electrode, Electro catalysis, 3 (2011) 1–12.

[6] M.Y. Mollah, P. Morkovsky, J.A. Gomes, M. Kesmez, J. Parga, D.L. Cocke, Fundamentals, present and future perspectives of electro coagulation, J. Hazard. Mater., 114 (2004) 199–210.

[7] E. do Vale-Junior, D.R. da Silva, A.S. Fajardo, C.A. Martinez-Huitle, Treatment of an azo dye effluent by peroxi-coagulation and its comparison to traditional electrochemical advanced processes, Chemosphere, 204 (2018) 548–555.

[8] Y. Zhang, Y. Cong, Q. Wang, Electro coagulation-$TiO_2$ photo-assisted combined system applied to methyl orange wastewater removal, Environ. Eng. Manage. J., 12 (2013) 517–526.

[9] M.Y.A. Mollah, R. Schennach, J.R. Parga, D.L. Cocke, Electro coagulation (EC) — science and applications, J. Hazard. Mater., B84 (2001) 29–41.

[10] M. Kobya, M. Bayramoglu, M. Eyvaz, Techno-economical evaluation of electro coagulation for the textile wastewater using different electrode connections, J. Hazard. Mater., 148 (2007) 311–318.

[11] M.M. Emamjomeh, M. Sivakumar, Review of pollutants removed by electro coagulation and electro coagulation/flotation processes, J. Environ. Manage., 90 (2009) 1663–1679.

[12] K.W. Pi, L.X. Gao, Z. Li, M. Wang, L. Huang, PAC with high content of Al13 polymer prepared by electrolysis with periodical reversal of electrodes, Colloids Surfaces A: Physico chem. Eng. Asp., 387 (2011) 113–117.

[13] I.A. Sengil, M. Ozacar, The decolorization of C.I. Reactive Black 5 in aqueous solution by electro coagulation using sacrificial iron electrodes, J. Hazard. Mater., 161 (2009) 1369–1376.

[14] J. Vidal, L. Villegas, J.M. Peralta-Hernandez, R. Salazar Gonzalez, Removal of acid black 194 dye from water by electro coagulation with aluminum anode, J. Environ. Sci. Health. Part A, Toxic/Hazard. Subst. Environ. Eng., 51 (2016) 289–296.

[15] Q.P. Nguyen, Z.N. Sun, X.M. Hu, Decolorization of direct yellow R dye from aqueous solution by aluminum anode electrochemical, Adv. Mater. Res., 581–582 (2012) 58–63.

[16] K.-W. Pi, Q. Xiao, H.-Q. Zhang, M. Xia, A.R. Gerson, Decolorization of synthetic methyl orange wastewater by electro coagulation with periodic reversal of electrodes and optimization by RSM, Process Safe. Environ. Protect., 92 (2014) 796–806.

[17] Z. Yi, C. Yanqing, S. Peide, Experiment and kinetic model for methyl orange wastewater removal by electro coagulation, Chem. Ind. Eng. Soc. China, 60 (2009) 2339–2345.

[18] S.Y. Lee, G.A. Gagnon, Review of the factors relevant to the design and operation of an electro coagulation system for wastewater treatment, NRC Res. Press, 22 (2014) 421–429.

[19] F. Ozyonar, B. Karagozoglu, Treatment of pretreated coke wastewater by electro coagulation and electrochemical per-oxidation processes, Separ. Purif. Technol., 150 (2015) 268–277.

[20] S.E.P.A.o. China, Monitoring and analytic methods of water and wastewater, 4th ed., Environmental Science Press of China, Beijing, China, 2002.

[21] C.C. Barrera-Díaz, G. Roa-Morales, P. Balderas Hernández, C.M. Fernandez-Marchante, M.A. Rodrigo, Enhanced electro coagulation: New approaches to improve the electrochemical process, J. Electro chem. Sci. Eng., 4 (2014) 285–296.

[22] A. Singh, T. Saraswathy, Ramesh, S. Thanga, New trends in electro coagulation for the removal of dyes from wastewater: a review, Environ. Eng. Sci., 30 (2013) 333–349.

[23] A.K. Verma, Treatment of textile waste waters by electro coagulation employing Fe-Al composite electrode, J. Water Process Eng., 20 (2017) 168–172.

[24] Z. Fu, Treatment of reactive brilliant blue X-BR synthetic wastewater by asynchronous periodic reversal electro coagulation and its strengthening mechanism, Water Air Soil Pollut., 229 (2018) 69.

[25] Z.-n. Sun, Study on electro-coagulation treating dyeing and pharmaceutacal wastewater with Al/Fe periodically reversing, in, Northeastern University, 2013.

[26] S. Irki, D. Ghernaout, M.W. Naceur, Decolourization of methyl orange (MO) by electro coagulation (EC) using iron electrodes under a magnetic field (MF), Desal. Water Treat., 79 (2017) 368–377 (2017) 368–377.

[27] A.K. Golder, N. Hridaya, A.N. Samanta, S. Ray, Electro coagulation of methylene blue and eosin yellowish using mild steel electrodes, J. Hazard. Mater., B127 (2005) 134–140.

[28] S. Aoudj, A. Khelifa, N. Drouiche, M. Hecini, H. Hamitouche, Electro coagulation process applied to wastewater containing dyes from textile industry, Chem. Eng. Process., 49 (2010) 1176–1182.

[29] M. Kobya, H. Hiz, E. Senturk, C. Aydiner, E. Demirbas, Treatment of potato chips manufacturing wastewater by electro coagulation, Desalination, 190 (2006) 201–211.

[30] X. Chen, G. Chen, P.L. Yue, Separation of pollutants from restaurant wastewater by electro coagulation, Separ. Purif. Technol., 19 (2000) 65–76.

[31] S. HuiXiu, L. Guyuan, Studies on the treatment to dye wastewater from thread factory by electrical chemistry, Chong Qing Environ. Sci., 11 (1989) 36–41.

[32] M.-C. Wei, K.-S. Wang, C.-L. Huang, C.-W. Chiang, T.-J. Chang, S.-S. Lee, S.-H. Chang, Improvement of textile dye removal by electro coagulation with low-cost steel wool cathode reactor, Chem. Eng. J., 192 (2012) 37–44.

[33] A.R. Amani-Ghadim, S. Aber, A. Olad, H. Ashassi-Sorkhabi, Optimization of electro coagulation process for removal of an azo dye using response surface methodology and investigation on the occurrence of destructive side reactions, Chem. Eng. Process. Process Intensif., 64 (2013) 68–78.

[34] W.T. Mook, M.A. Ajeel, M.K. Aroua, M. Szlachta, The application of iron mesh double layer as anode for the electrochemical treatment of Reactive Black 5 dye, Environ. Sci., 54 (2017) 184–195.

[35] W.T. Mook, M.K. Aroua, M. Szlachta, C.S. Lee, Optimisation of reactive black 5 dye removal by electro coagulation process using response surface methodology, Water Sci. Technol., 75 (2017) 952–962.

[36] F. Ozyonar, Treatment of train industry oily wastewater by electro coagulation with hybrid electrode pairs and different electrode connection modes, Int. J. Electro. chem. Sci., 11 (2016) 1456–1471.

[37] S. Zodi, B. Merzouk, O. Potier, F. Lapicque, J.-P. Leclerc, Direct red 81 dye removal by a continuous flow electro coagulation/flotation reactor, Separ. Purif. Technol., 108 (2013) 215–222.

[38] T. Yang, B. Qiao, G.-C. Li, Q.-Y. Yang, Improving performance of dynamic membrane assisted by electro coagulation for treatment of oily wastewater: Effect of electrolytic conditions, Desalination, 363 (2015) 134–143.

[39] N. Daneshvar, A. Oladegaragoze, N. Djafarzadeh, Decolorization of basic dye solutions by electro coagulation: an investigation of the effect of operational parameters, J. Hazard. Mater., 129 (2006) 116–122.

[40] N. Daneshvar, H. Ashassi-Sorkhabi, A. Tizpar, Decolorization of orange II by electro coagulation method, Separ. Purif. Technol., 31 (2003) 153–162.

[41] R. Khosravi, S. Hazrati, M. Fazlzadeh, Decolorization of AR18 dye solution by electro coagulation: sludge production and electrode loss in different current densities, Desal. Water Treat., 57 (2015) 14656–14664.

[42] Z. Shen, W. Wang, J. Jia, J. Ye, X. Feng, A. Peng, Degradation of dye solution by an activated carbon fiber electrode electrolysis system, J. Hazard. Mater., 84 (2001) 107–116.

[43] J.-S. Do, C.-P. Chen, In situ oxidative degradation of formaldehyde with hydrogen peroxide electro generated on the modified graphites, Appl. Electro. chem., 24 (1993) 936–942.