



Impacts of operating parameters on oxidation–reduction potential and COD removal during the electrochemical removal of 2-chlorophenol

Yu Mei^{a,b}, Yin Lu^b, Zhiping Ye^a, Dongmei Xu^b, Hua Pan^b, Jiade Wang^{a,*}

^aCollege of Environment, Zhejiang University of Technology, Hangzhou, Zhejiang 310032, China, Tel. +86 057188320915; email: jdwang@zjut.edu.cn (J. Wang), Tel. +86 057188296322; email: imy1220@zjut.edu.cn (Y. Mei), Tel. +86 15858281394; email: Zhipingye@zjut.edu.cn (Z. Ye)

^bCollege of Biological and Environmental Engineering, Zhejiang Shuren University, Hangzhou, Zhejiang 310005, China, Tel. +86 057188297100; email: luyin_zjsru@aliyun.com (Y. Lu), Tel. +86 057188285802; email: dm25xu@163.com (D. Xu), Tel. +86 057188296322; email: panhua@xjtu.edu.cn (H. Pan)

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ABSTRACT

Oxidation–reduction potential (ORP) can be used as a parameter for monitoring the electrochemical removal of pollutants in wastewater. In this study, ORP online monitor was applied for the electro-oxidation treatment of 2-CP. The influences of current density, pH and supporting electrolyte (Na_2SO_4) concentration on ORP were investigated, and the linear relationships between ΔORP and COD removal efficiency were established based on these parameters. All of the R^2 value of the regression lines were greater than 0.86. Meanwhile, a multi-parameter linear equation involving ORP, current density, original pH, Na_2SO_4 concentration, reaction time and COD removal efficiency was established with R^2 of 0.89, which suggested ORP monitoring had the potential to influence 2-CP wastewater treatment.

Keywords: Electrochemical; 2-Chlorophenol; Oxidation–reduction potential; COD removal efficiency

1. Introduction

Chlorophenols (CPs) have been widely used in manufacturing industries, such as insecticides, herbicides, fungicides and dyes [1–3]. 2-Chlorophenol (2-CP) is listed as the priority pollutant by the United States Environmental Protection Agency, which is toxicity, resistance to biodegradation and a threat to both the aquatic ecosystem and human health [4].

Conventional methods are well-established technologies, such as coagulation and sorption [5], are extensively used for CPs removal, whereas it is difficult to obtain complete removals of CPs. Biologic methods are difficult to completely mineralize 2-CP because it is poisonous to microorganisms [6]. Advanced oxidation processes such as Fenton, ozonation and photocatalysis [7,8] are not economically feasible since they need much more extra reagents. Electrochemical

oxidation process is considered as a promising alternative for the treatment of CPs due to its total oxidation ability, fast reaction rate, high energy and environmental compatibility [9]. Many conventional anode materials, such as SnO_2 [10], platinum [11] and BDD [12], have been tested for the electro-oxidation of chlorophenols. The PbO_2/Ti will be served as the experimental electrode due to its long service life, low cost, easy preparation and stability [1].

It is noteworthy that electrochemical oxidation process still has the problem of excessive energy cost that restricts its wide application in wastewater advanced treatment. Many studies have carried out and found that optimizing electrode materials and developing new reactors can improve the current efficiency. However, the related on-line monitoring and control techniques of electrochemical oxidation process are rarely discussed in the literature.

* Corresponding author.

The ORP is applied as an indicator of the oxidizing or reducing properties of solutions [13]. ORP reflects the solution's tendency to accept or donate electrons and provides insight into the state of the reaction system [14,15]. ORP has been used as a monitoring or controlling parameter for many wastewater treatment systems, such as chlorination [16], biological nutrient removal [17–19], sulfide oxidizing [14], hydrogen production by fermentation [20], photocatalysis [21], the Fenton series process [22,23] and hydrometallurgy process [15]. Among the various strategies for the measure of COD removal, ORP is one of the promising techniques for monitoring the chemical processes. Moreover, the relationship between ORP value and COD removal efficiency has been demonstrated via models. Cheng et al. [24] developed a model reflecting the variant of ORP value in function of soluble chemical oxygen demand (SCOD) in the hydrolysis of the waste activated sludge process. Experimental results indicated that a linear relationship was established between ΔORP and SCOD under the proper NaOH concentration. Kim et al. [25] studied the relationship among ORP value, Fenton's reagent concentration and COD removal, and suggested that ORP could be used to control COD removal during the Fenton oxidize process. Wu and Wang [23] investigated the impacts of Fenton process operating parameters on ORP and pretreatment efficiency. And the multiple regression equations were established among ORP, operating parameters and treatment efficacy was established.

In the present study, ORP was used as a monitoring parameter during the removal of 2-chlorophenol. The effects of operating parameters including current density, initial pH and Na_2SO_4 concentration on ORP were discussed. In addition, the relationship between the change of ORP value and COD removal efficiency under these operating parameters was developed. Meanwhile, an equation including ORP, current density, original pH, Na_2SO_4 concentration, reaction time and COD removal efficiency was developed. These results provide useful information about the utilization of ORP in situ monitoring and controlling of electrochemical process.

2. Materials and methods

2.1. Experiments

The concentration of 2-CP was 150 mg L^{-1} and Na_2SO_4 was used as the supporting electrolyte. A laboratory-scale plate reactor with an effective volume of 3 L was built as shown in Fig. 1. The reactor consisted of a direct current (DC) power supply (MPS 601, Tradex, United States), titanium-based lead dioxide (PbO_2/Ti) anode, and titanium mesh-plates cathode. The effective surface of both electrodes was 5 cm in width and 10 cm in length, while the gap between the electrodes was 3 cm. A peristaltic pump (BT100-2J, Longer, China) at a flow rate of 266 mL min^{-1} was used between the reactor and the circulating tank for a good mass transfer in electrolyte. An ORP (SX-630, Sanxin, China) and a pH (SX711, Sanxin, China) probe were installed in the electrolysis bath for online monitoring ORP/pH during the electro-oxidation. Both probes were connected to a computer, and the software of MATLAB was utilized for acquiring data. The experiment ran for 120 min while the wastewater was sampled from the circulating tank every 5 min. The sampling volume was 6.0 mL each time.

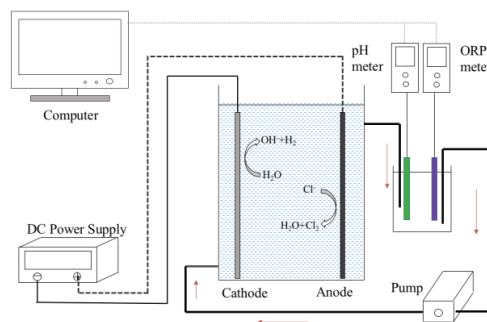


Fig. 1. Electrochemical experimental facility.

2.2. Analysis

COD was determined according to Chinese standard HJ/T 399-2007 with slight modifications. The solution was measured at a wavelength of 440 nm using a UV-visible spectrophotometer (UV-2910, Hitachi, Japan).

The COD removal efficiency was calculated by Eq. (1):

$$\text{COD removal efficiency} = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \cdot 100\% \quad (1)$$

where COD_0 and COD_t are the COD values of samples at electrolytic time 0 and t (g L^{-1}). The instantaneous current efficiency (ICE, %) was calculated by Eq. (2):

$$\text{ICE} = \frac{\text{COD}_t - \text{COD}_{t+\Delta t}}{8 \cdot I \cdot \Delta t} \cdot F \cdot V \cdot 100\% \quad (2)$$

where COD_t , $\text{COD}_{t+\Delta t}$ are the COD (g L^{-1}) values at time t and $t + \Delta t$ (s), respectively; F is the Faraday constant ($96,487 \text{ C mol}^{-1}$); V is the volume of the electrolyte (L^{-1}) and I is the current (A).

3. Results and discussion

3.1. Effect of operating parameters

3.1.1. Effect of current density

Under 2-CP concentration of 150 mg L^{-1} , pH 6.5, Na_2SO_4 concentration of 0.10 mol L^{-1} and electro-oxidation time of 120 min, COD removal efficiencies and ICE at different current density are presented in Figs. 2(a) and (b). With the increase of current density, the COD removal efficiency was improved. The ICE decreased gradually with the reaction time, and it was suggested that the intermediates became more difficult to be oxidized with the proceeding of degradation. ICE was also observed to drop when the density of current increased. Since part of current energy was consumed by the secondary oxygen evolution reaction under high current density, higher ICE could be obtained with a low current density [26]. However, the COD removal efficiency increased significantly when the current density increased from 8 to 15 mA cm^{-2} . Considering to the relatively high ICE could also be obtained at the current density of 15 mA cm^{-2} . Hence, the following current density would be 15 mA cm^{-2} .

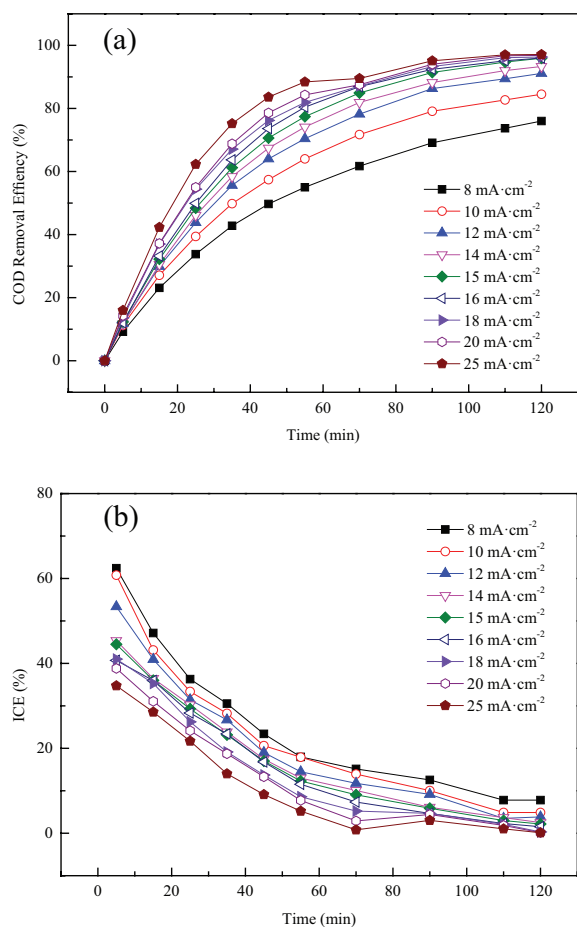


Fig. 2. Effect of current density on (a) COD removal efficiency, (b) instantaneous current efficiency (2-CP concentration: 150 mg L^{-1} ; initial pH 6.5; Na_2SO_4 concentration: 0.10 mol L^{-1}).

The effect of current density on ORP is shown in Fig. 3. The ORP was strongly influenced by both current density and oxidation time. At an early stage, ORP value sharply decreased in 5 min. In the second stage, the ORP increased and remained elevated for some time. In the final stage, the ORP tended to be stable. The initial ORP of the solution was $200 \pm 10 \text{ mV}$. At the current density of 8 mA cm^{-2} , the ORP value dropped sharply, from 209 to 12 mV in 5 min, and then the ORP gradually increased to 125 mV in following 120 min. At the current density of 15 mA cm^{-2} , the ORP value dropped from 210 to 80 mV in 5 min, and then increased slowly to 215 mV in the following 120 min. Meanwhile, the pH was increased remarkably. For example, at the current density of 8 mA cm^{-2} , the pH value increased from 6.52 to 10.50 in 5 min; while at the current density of 15 mA cm^{-2} , the pH value changed from 6.50 to 9.81 in 5 min. The trend of ORP value was opposite to that of pH value. The dramatic changes in pH led to changes in ORP [24]. The Cl^- in the solution reacted as the following reactions:

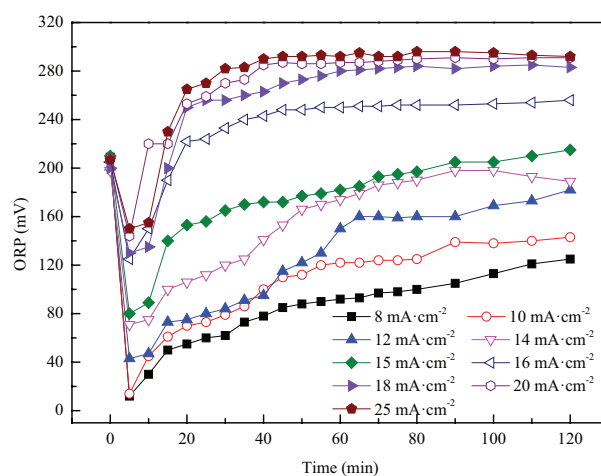
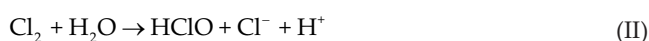


Fig. 3. Effect of current density on ORP (2-CP concentration: 150 mg L^{-1} ; initial pH 6.5; Na_2SO_4 concentration: 0.10 mol L^{-1}).



But under alkaline condition, Reaction (III) occurred easily, resulting in more hypochlorite ion. The hypochlorite ion was less oxidant than hypochlorite, so the oxidation capacity of the electrochemical system was reduced and the ORP value declined. This phenomenon also be observed in the water disinfection process. pH affected the equilibrium relationship of HClO/OCl^- strongly with the addition of sodium hypochlorite. The equilibrium of HClO/OCl^- influenced the oxidation reaction, thus causing the oxidation ability declining, as well as the ORP value [27]. At the current density of 8, 10, 12 and 14 mA cm^{-2} , the highest ORP values were 125, 143, 182 and 189 mV, respectively. This meant that oxidants had not accumulated under these conditions. At the current density of 15, 16, 18, 20 and 25 mA cm^{-2} , the highest ORP values were 215, 256, 283, 291 and 292 mV, respectively. The oxidative species such as hydroxyl radicals increased, the ORP increased and gradually tends to be stable. When current density increased from 8 to 15 mA cm^{-2} , the peak of ORP value increased from 125 to 215 mV and the increment reached about 90 mV. But when current density increased from 16 to 25 mA cm^{-2} , the peak ORP increased from 256 to 292 mV and conversely the increment was only 36 mV.

3.1.2. Effect of pH

Under 2-CP concentration of 150 mg L^{-1} , current density of 15 mA cm^{-2} , Na_2SO_4 concentration of 0.10 mg L^{-1} and electro-oxidation time of 120 min, COD removal efficiencies and ICE at different pH values were shown in Figs. 4(a) and (b), respectively. The results showed that the COD removal efficiency and ICE decreased with the increase of initial pH value. Obviously the electrochemical degradation of 2-CP favored the acid medium [27]. The higher the pH value was, the lower COD removal efficiency was, which showed that the possibility of acid-favored was attributed to the difficulty of total oxidation in alkaline condition [28].

ORP of solution at different pH values was exhibited in Fig. 5. The initial ORP values under the condition of pH 3, 4, 5,

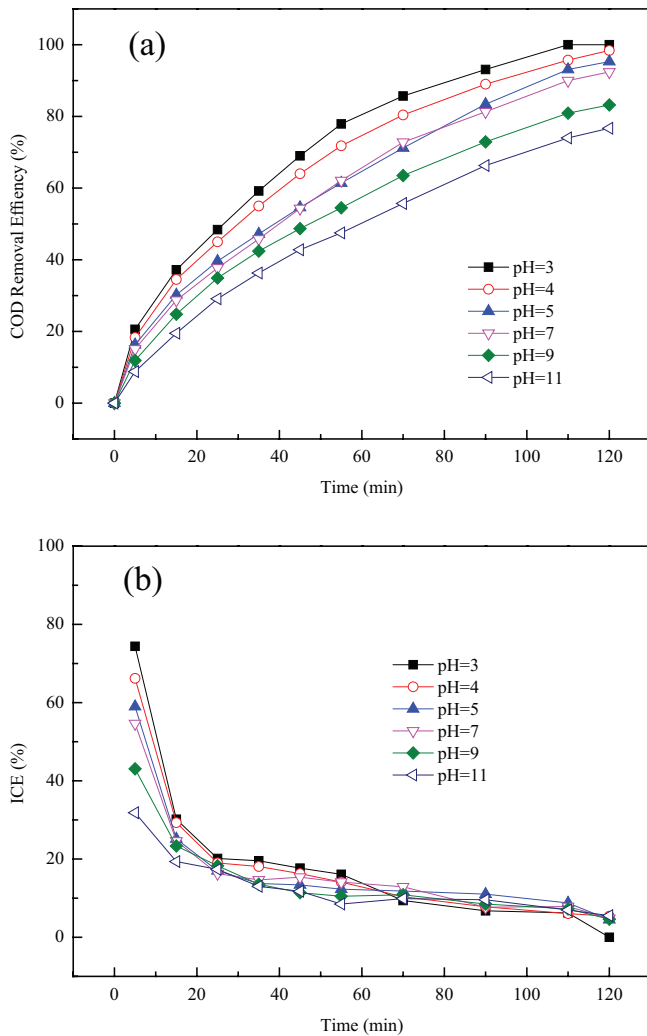


Fig. 4. Effect of pH on (a) COD removal efficiency (b) instantaneous current efficiency (2-CP concentration: 150 mg L^{-1} ; current density 15 mA cm^{-2} ; Na_2SO_4 concentration: 0.10 mol L^{-1}).

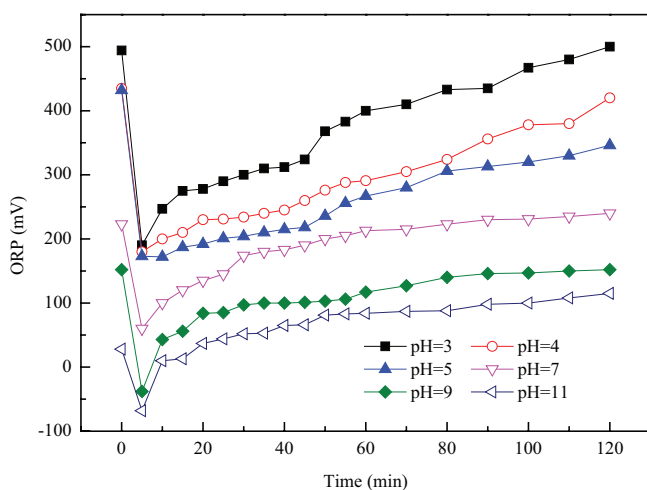


Fig. 5. Effect of pH on ORP (2-CP concentration: 150 mg L^{-1} ; current density: 15 mA cm^{-2} ; Na_2SO_4 concentration: 0.10 mol L^{-1}).

7, 9 and 11 were 494, 435, 432, 223, 152 and 28 mV, respectively. The dramatic changes in pH led to the changes in ORP [24]. A great linear correlation between the initial pH level and the ORP value was observed at the beginning of electrochemical process in Fig. 6. The R^2 value of the regression lines was 0.97. This could be deduced from the Nernst equation [24]. Sun et al. [26] found that a significant linear correlation between ORP and the initial pH at the beginning of Fenton oxidation. As seen in Fig. 5, the ORP was initially around 494 mV, and then it declined to 190 mV after 5 min at the initial pH of 3 due to the change of pH and the consumption of hydroxyl radical by the reductants in the wastewater. The ORP then increased gradually to 500 mV in the following 120 min, which can be explained by the generation of hydroxyl radicals in the reactor. Under the acid conditions, the system showed an oxidation tendency compared with the neutral or alkalinity one. The higher the initial pH value was, the lower the ORP value was achieved. The peak of ORP was 500, 420, 346, 240, 152 and 115 mV in responding to the initial pH of 3, 4, 5, 7, 9 and 11.

3.1.3. Effect of supporting electrolyte

Under 2-CP concentration of 150 mg L^{-1} , current density of 15 mA cm^{-2} , pH of 3 and electro-oxidation of 120 min, COD removal efficiencies and ICE at different concentrations of Na_2SO_4 are shown in Figs. 7(a) and (b). As presented in Fig. 7(a), COD removal efficiency increased first with the increase of Na_2SO_4 concentration, and then decreased to a lower value when Na_2SO_4 concentration was 0.12 mol L^{-1} . Fig. 7(b) shows that the highest ICE of 2-CP degradation (75.0%) was obtained at Na_2SO_4 concentration of 0.10 mol L^{-1} , which was 1.1 times higher than that obtained at Na_2SO_4 concentration of 0.12 mol L^{-1} . High concentration of Na_2SO_4 led to the high persulphate ions, reacting with 2-CP and thus increasing COD removal efficiencies [29].

ORP of solution at different Na_2SO_4 concentration are shown in Fig. 8. The curves of ORP value and Na_2SO_4 concentration at different reaction times were similar. Apparently, ORP value in solution increased with the concentration of Na_2SO_4 increasing from 0.05 to 0.10 mol L^{-1} , and then it declined. For example, the peak of ORP value was maximal

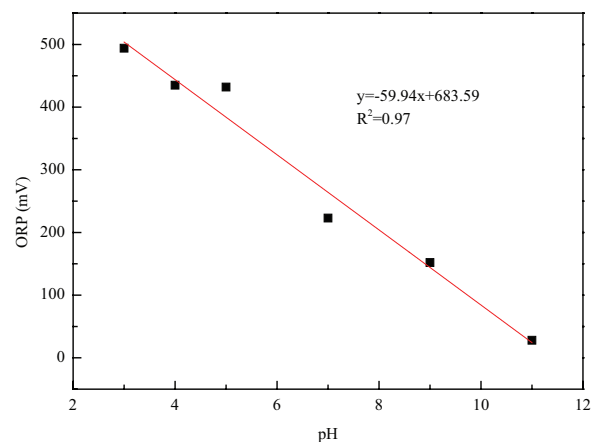


Fig. 6. Relationship between the initial pH level and the ORP values (data obtained from Fig. 5).

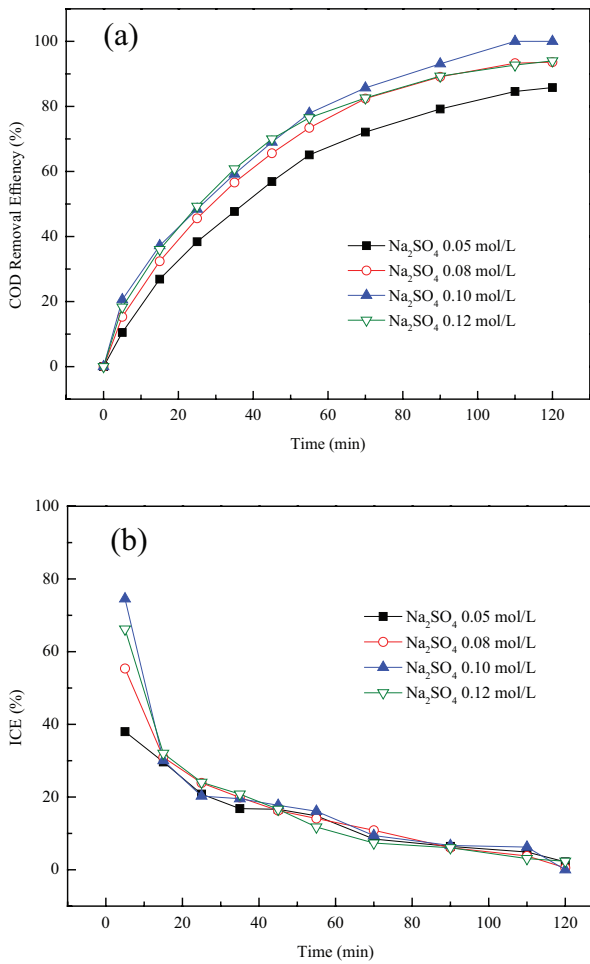


Fig. 7. Effect of Na₂SO₄ concentration on (a) COD removal efficiency (b) instantaneous current efficiency (2-CP concentration: 150 mg L⁻¹; current density 15 mA cm⁻²; pH 3).

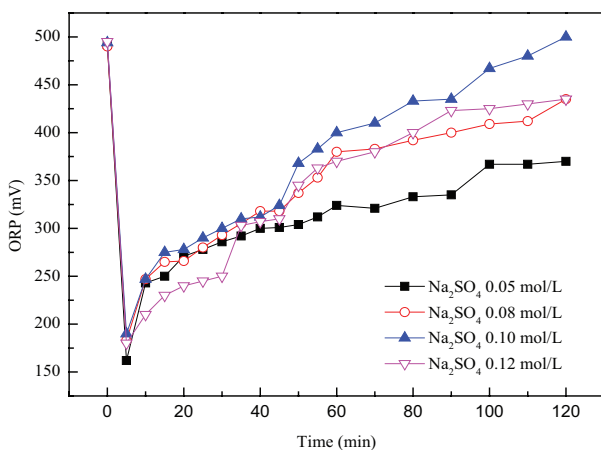


Fig. 8. Effect of Na₂SO₄ concentration on ORP (2-CP concentration: 150 mg L⁻¹; current density 15 mA cm⁻²; pH 3).

(500 mV) at Na₂SO₄ concentration of 0.10 mol L⁻¹, and then decreased to 435 mV with much more Na₂SO₄. The possible reason might be a high concentration of sulfate leading to the increase of reducibility of the solution.

3.2. Relationship between ΔORP and COD removal efficiency in various current densities, pH and supporting electrolyte concentration

A relationship between ΔORP and COD in function of current density, pH and supporting electrolyte concentration was developed. The ΔORP is defined by the following equation:

$$\Delta\text{ORP} = [\text{ORP}]_t - [\text{ORP}]_{5\text{min}} \quad (3)$$

where [ORP]_t = ORP value being measured at time *t*; and [ORP]_{5min} = ORP value being measured at 5 min.

Fig. 9(a) presents the correlations between the ΔORP values and COD removal efficiencies at different reaction time and current density. COD removal efficiency increased with the increase of ΔORP values. For example, when the current density was 12 mA cm⁻², the COD removal efficiency increased from 11.8 to 91.1% in 130 min so as the increase of ΔORP from 0 to 139 mV. When the ΔORP was higher, the decomposition of organic compounds took place at a higher oxidation level, resulting in a higher COD removal efficiency. The equations of ΔORP and COD removal efficiency are listed in Table 1. The R² values of the regression lines were 0.98, 0.97, 0.95, 0.97, 0.95, 0.87, 0.90, 0.89 and 0.90 in current density of 8, 10, 12, 14, 15, 18, 20 and 25 mA cm⁻², respectively. According to these results, all lines have positive correlation coefficients.

Fig. 9(b) shows the correlations between the ΔORP values and COD removal efficiencies at different reaction time and initial pH values. For example, at pH of 11, the COD removal efficiency was 76.7% at ΔORP value of 183 mV at 120 min; at pH of 7, the COD removal efficiency was 92.4% at ΔORP value of 180 mV at 120 min; at pH of 3, the COD removal efficiency was 100.0% at ΔORP value of 310 mV at 120 min. Equations of these regression lines are listed in Table 2. The R² value of the regression lines were greater than 0.86. In acid solution, the ORP values were higher and the ΔORP values were larger than in alkalinity solution, indicating that the solution oxidation ability was helpful for the removal of COD.

Fig. 9(c) shows the correlations between the ΔORP values and COD removal efficiencies at different reaction time and Na₂SO₄ concentration. It could be seen that different concentrations of Na₂SO₄ affected the ΔORP and COD removal efficiency. For example, when Na₂SO₄ concentration was 0.08 mol L⁻¹, the COD removal efficiency was 93.6% at ΔORP value of 252 mV at 120 min; when Na₂SO₄ concentration was 0.10 mol L⁻¹, the COD removal efficiency was 100.0% at ΔORP value of 310 mV at 120 min; when Na₂SO₄ concentration was 0.12 mol L⁻¹, the COD removal efficiency was 94.0% at ΔORP value of 255 mV at 120 min. The data are listed in Table 3. As can be seen, for the four regression linear equations, R² values were 0.93, 0.97, 0.96 and 0.97 at Na₂SO₄ concentration of 0.05, 0.08, 0.10 and 0.12 mol L⁻¹, respectively. The simulated lines are well matched the relations between ΔORP and COD in various concentrations of Na₂SO₄. The R² value of the regression lines was greater than 0.93. When the concentration of Na₂SO₄ was higher than 0.1 mol L⁻¹, the oxidation ability of the solution was reduced and the ΔORP was low. That might result from reduction of the overdose SO₄²⁻ ions. These good

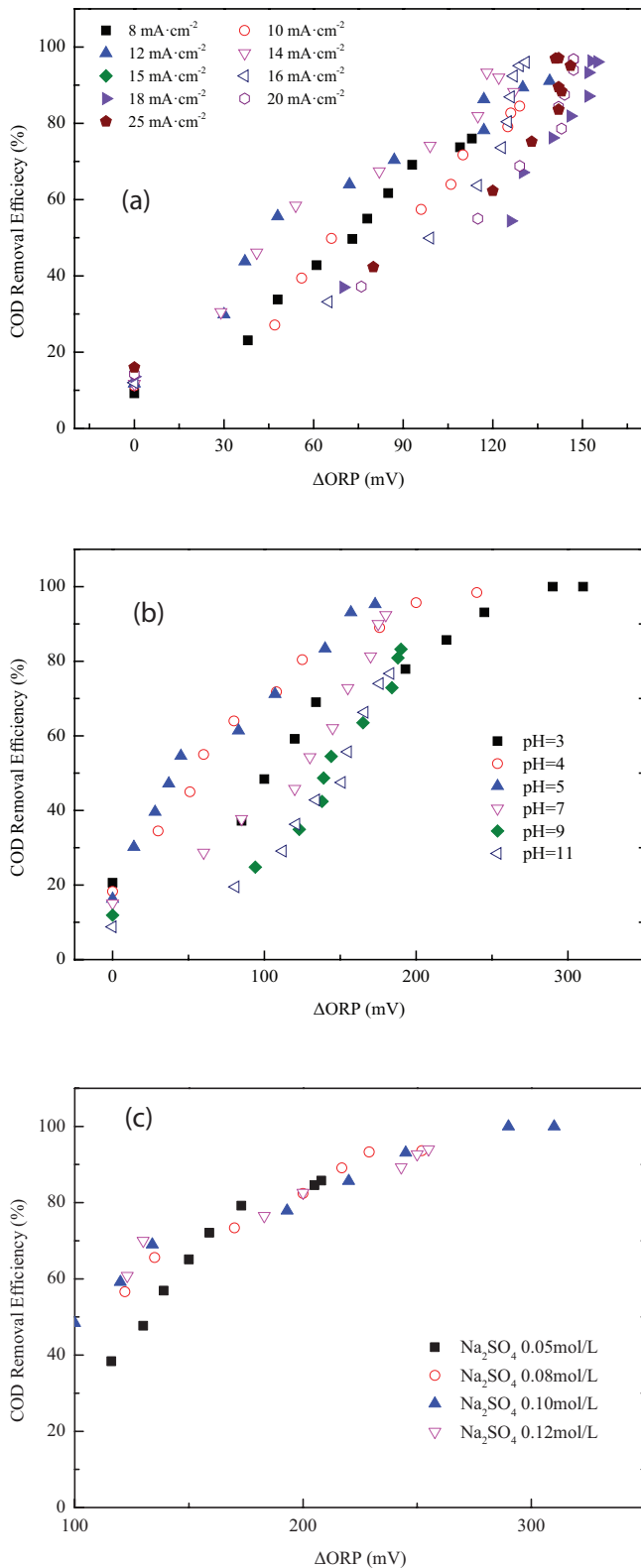


Fig. 9. (a) Correlations between the Δ ORP and COD removal efficiencies at the different reaction time for different current density. (b) Correlations between the ORP and COD removal efficiencies at the different reaction time for different pH. (c) Correlations between the ORP and COD removal efficiencies at the different reaction time for different Na_2SO_4 concentration.

Table 1

Summary of regression lines between Δ ORP and COD removal efficiency developed for various current densities

Current density (mA cm^{-2})	Regression line	R^2 value
8	$\text{COD}\% = 0.6395 \times \Delta\text{ORP} + 4.7757$	0.98
10	$\text{COD}\% = 0.5747 \times \Delta\text{ORP} + 7.2077$	0.97
12	$\text{COD}\% = 0.5486 \times \Delta\text{ORP} + 19.564$	0.95
14	$\text{COD}\% = 0.6044 \times \Delta\text{ORP} + 16.794$	0.97
15	$\text{COD}\% = 0.6843 \times \Delta\text{ORP} + 3.9448$	0.95
16	$\text{COD}\% = 0.6390 \times \Delta\text{ORP} + 1.8635$	0.87
18	$\text{COD}\% = 0.5262 \times \Delta\text{ORP} + 5.8915$	0.90
20	$\text{COD}\% = 0.5557 \times \Delta\text{ORP} + 5.1922$	0.89
25	$\text{COD}\% = 0.5543 \times \Delta\text{ORP} + 8.7378$	0.90

Table 2

Summary of regression lines between Δ ORP and COD removal efficiency developed for various pH

pH	Regression line	R^2 value
3	$\text{COD}\% = 0.2717 \times \Delta\text{ORP} + 22.995$	0.96
4	$\text{COD}\% = 0.3317 \times \Delta\text{ORP} + 29.723$	0.92
5	$\text{COD}\% = 0.4167 \times \Delta\text{ORP} + 26.491$	0.96
7	$\text{COD}\% = 0.4358 \times \Delta\text{ORP} + 4.8472$	0.92
9	$\text{COD}\% = 0.3873 \times \Delta\text{ORP} - 1.0916$	0.86
11	$\text{COD}\% = 0.3876 \times \Delta\text{ORP} - 3.7834$	0.86

Table 3

Summary of regression lines between Δ ORP and COD removal efficiency developed for various Na_2SO_4 concentration

Na_2SO_4 concentration (mol L^{-1})	Regression line	R^2 value
0.05	$\text{COD}\% = 0.4044 \times \Delta\text{ORP} + 1.3932$	0.93
0.08	$\text{COD}\% = 0.3408 \times \Delta\text{ORP} + 13.48$	0.97
0.10	$\text{COD}\% = 0.2717 \times \Delta\text{ORP} + 22.995$	0.96
0.12	$\text{COD}\% = 0.2778 \times \Delta\text{ORP} + 25.309$	0.97

linear relationships suggested that the Δ ORP values were related to the removal of COD. The optimum Na_2SO_4 concentration was 0.10 mol L^{-1} .

3.3. Relationship among ORP, current density, original pH, sodium sulphate concentration, reaction time and COD removal efficiency

In order to find out the relationship among ORP, current density, original pH, Na_2SO_4 concentration, reaction time and COD removal efficiency, a typical multiple regression equation was established using Origin 7.0. A total of 190 runs of data sets from the electrochemical process for 2-CP removal were used to develop the model. Table 4 lists the linear regression equation, with R^2 greater than 0.88. This good linear relationship suggested that ORP could be used to monitor the electrochemical process.

Table 4
Details of the regression model

Model	Input parameter	Output parameter	R ²	Regression equation
Regression model	Current density, original pH, sodium sulphate concentration, reaction time and ORP	COD removal efficiency	0.8878	COD removal efficiency = $-0.16276+0.00281$ (current density)+ 0.01709 (original pH)+ 1.5595 (sodium sulphate concentration)+ 0.00495 (reaction time)+ $9.766624E-4$ (ORP)

4. Conclusions

Electro-oxidant process of 2-CP was carried out to evaluate the impacts of operating parameters on ORP value and COD removal efficiency. The results showed that the operating parameters such as current density, original pH, supporting electrolyte concentration and reaction time had great influences on ORP and COD removal efficiency. The optimal operating parameters were current density of 15 mA cm⁻², original pH of 3 and Na₂SO₄ concentration of 0.10 mol L⁻¹ at 120 min. The regression equation among ORP, current density, original pH, sodium sulphate concentration, reaction time and COD removal efficiency was established with the R² of 0.89. These good linear relationships showed that the ORP values were related to the removal of COD, which could be monitored and used for electrochemical control.

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