

## Application of Three-dimensional Electrolysis in the Study of Crystal Violet Wastewater

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Three-dimensional electrolysis treatment of wastewater has unique advantages in cleanliness and efficiency. This work was aimed at investigating the application of three-dimensional electrolysis in treatment of Crystal Violet (CV) wastewater. Firstly, the five single factors which consist of applied voltage, electrolysis time, electrolyte concentration, pH value in the system and the aeration rate for the impact on reduction efficiency of COD were systematically studied. The influence of these factors on COD degradation and the optimum operation conditions of electrolysis were found. The orthogonal test was carried out to determine the interaction effect of five single factors: electrolysis time > pH > external voltage > electrolyte concentration > aeration rate. The optimal experimental electrolysis conditions were determined: the pH was 5, the voltage was 14 V, aeration rate was 50 L/h, Na<sub>2</sub>SO<sub>4</sub> electrolyte concentration was 0.15 mol/L, and the electrolysis time was 120 min. Since CV wastewater is common in printing and dyeing industry, this study highlights the potential of the three-dimensional treatment in wastewater treatment. This method has great advantages in both energy saving and high efficiency.

### 1. Introduction

With the development of the chemical industry, resource shortage and pollution problems have brought wide concern (Zhu, 2018). Dyes are excessively used in various industries with a lot of wastewater. It is vitally important to control the discharge of dyes wastewater into the environment. CV is a kind of typical triphenylmethane dye, which is widely applied in textile, paper, leather, veterinary medicine and food industry (Rahmat et al., 2019). Conventional treatment methods for wastewater contain adsorption, electrolysis, photocatalytic oxidation, electrocoagulation, biological methods etc. During which, three-dimensional electrodes system shows unique advantages in higher efficiency, no secondary pollution, lower energy cost, and higher mass transfer efficiency, but it has more complicated operating conditions compared to two-dimensional electrodes (Wang et al., 2014). Different from two-dimensional electrodes, three-dimensional electrodes system consists of a two-dimensional electrode with additional fillers in the middle (Yavuz and Shahbazi, 2012). Three-dimensional electrodes system has a larger reaction surface area due to these fillers. The fillers can act as a catalyst too, which accelerate the reaction (Zhang et al., 2020). Three-dimensional electrodes system has been already successfully used in many effluent systems, such as coking wastewater (Liu et al., 2020), Acid Orange 7 (Zhao et al., 2010) and landfill leachate (Nageswara Rao et al., 2009) etc. But only a few studies (Yin et al., 2015) investigated the application of three-dimensional electrolysis in the treatment of dyes wastewater. There are many studies on three-dimensional electrolysis treatment wastewater, but few studies on triphenylmethane dyes and industrialization. This paper used three-dimensional electrolysis to treat CV wastewater. In order to investigate the effects of various operating conditions on the electrolytic process and removal of COD, this experiment listed some factors such as external voltage, electrolyte concentration, electrolysis time, pH and aeration. Finally, the magnitude of the impact on the five factors was determined by orthogonal experiments.

## 2. Experimental section

Electrolysis reactor with dimensions of 10×8×8 cm was used in this experiment. The surface area of the electrode is 8×8 cm, and the distance between the plates is 8 cm. The Ti-IrO<sub>2</sub>/RuO<sub>2</sub>-IrO<sub>2</sub> electrodes (DSA) was selected as an anode, while the graphite plate as the cathode. And the coconut shell activated carbon was used as the filling material.

To avoid affecting the results, activated carbon was prepared before experiments. First, activated carbon was soaked in 200 mg/L crystal violet solution. After the solution faded, the activated carbon was filtered out. Then the new solution was added into the activated carbon again and the procedure was repeated several times until the colour of the solution is no longer changing within an hour. It is considered that the adsorption has reached saturation and the effect of the adsorption can be ignored during this period.

Potassium hydrogen phthalate was used as a solute and deionized water as a solvent to prepare solutions with COD concentrations of 0, 10, 50, 100 and 150 mg/L. The prepared potassium hydrogen phthalate solution was used as a benchmark, silver sulfate-sulfuric acid solution was used as a catalyst and potassium dichromate solution was used as digestion reagent. After digestion, light transmittance was measured by spectrophotometer under the condition of 445 nm. The standard curve is shown in Figure 1.

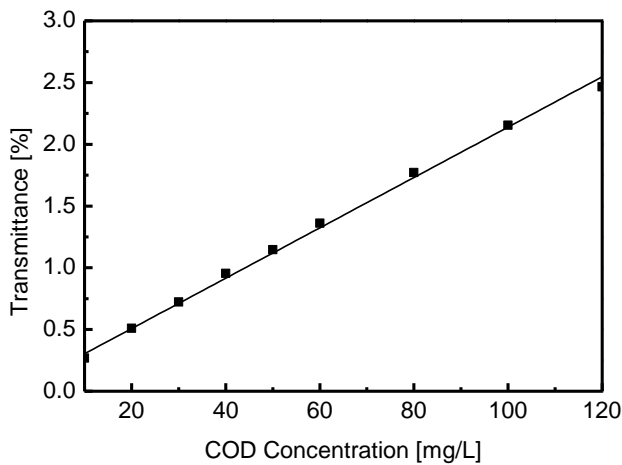


Figure 1: Standard curve of COD

Through linear fitting of transmittance data, the linear equation is obtained using Eq(1).

$$y = 0.0204x + 0.0995 \quad (1)$$

Curve fitting variance:  $R^2 = 0.9966$ . This equation is used to calculate the COD concentration of the system in the experiment.

The simulated crystal violet wastewater is treated with an initial concentration of 200 mg/L and a volume of 250 ml. During the single-factor electrolysis experiment, the standard operating conditions were set as follows: the aeration rate was 50 L/h, the electrolysis time was 120 min, the concentration of Na<sub>2</sub>SO<sub>4</sub> was 0.1 mol/L, the pH value was 6, and the electrolysis voltage was 11 V.

To study the interaction of these factors, an orthogonal experiment was carried out. The orthogonal experiment factors and levels are set as Table 1.

Table 1: Orthogonal experiment factors and levels

pH	Voltage [V]	Electrolysis time [min]	Electrolyte concentration [mol/L]	Aeration rate [L/h]
3	5	60	0.05	0
4	8	90	0.10	20
5	11	120	0.15	50
6	14	150	0.20	100

### 3. Results and discussion

#### 3.1 Effect of electrolysis voltage

Electrolysis voltage not only affects the polarization behaviour of particle electrodes but also affects energy consumption. As shown in Figure 2, both the COD degradation and current increase with the increase in voltage. Degradation of COD increases rapidly first and then gradually becomes stable. This is because the voltage is the driving force for the reaction, with the increase of voltage, the conditions on the reaction reach the limit (Zhang et al., 2013). The current increases slowly first and then rapidly since the acceleration of the conductive particles. The side reactions are explosively generated when the voltage is above 14 V. The current increase means excess energy consumption. Considering the degradation of COD and energy consumption, electrolysis voltage is selected to be 11 V.

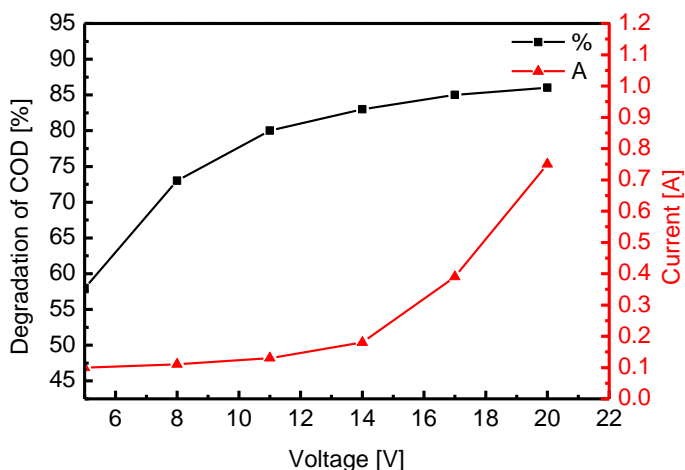


Figure 2: Effects of electrolysis voltage on the removal of COD

#### 3.2 Effect of electrolyte concentration

Different concentration of electrolyte affects the ability to generate free radicals, and free radicals can degrade organic pollutants (Yu et al., 2020). Figure 3 shows that the electrolyte concentration affects the degradation of COD and the current. At first, the current and degradation of COD increase quickly because early addition of electrolyte improves mass transfer efficiency and accelerates the reaction. With the continuous growth of electrolyte concentration, both the degradation of COD and the current increases slowly. Since the concentration of the electrolyte has less impetus to the mass transfer, the subsequent increase of concentration has little effect on the reaction. Considering the cost, the concentration of  $\text{Na}_2\text{SO}_4$  is chosen to be 0.1 mol/L.

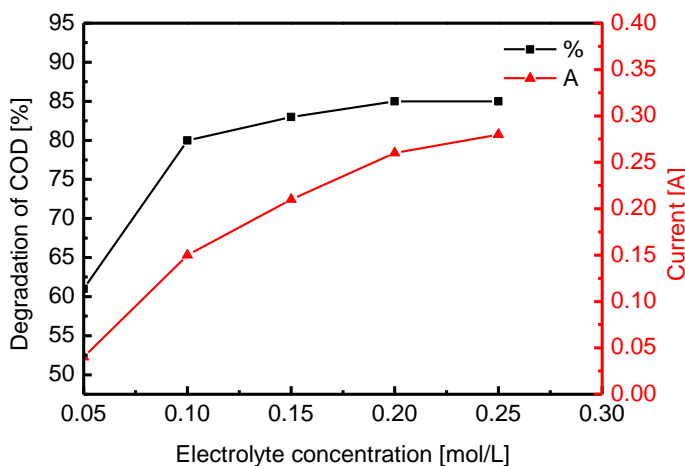


Figure 3: Effects of electrolyte concentration on the COD degradation

### 3.3 Effect of electrolysis time

As we all know, the longer electrolysis time, the higher COD degradation degree. Longer electrolysis time will cost a lot of energy. Figure 4 displays the effect of electrolysis time on COD degradation. Originally, the removal speed is the fastest. When the electrolysis reacts for 30 min, the COD degradation reaches 52 %. As electrolysis time increases from 30 min to 180 min, the degradation of COD increases from 52 % to 83 %. The COD degradation almost remains the same after 120 min. This is because the dye concentration is very low and the reaction rate is very slow. Considering the degradation of COD and economy, the electrolysis time is confirmed as 120 min.

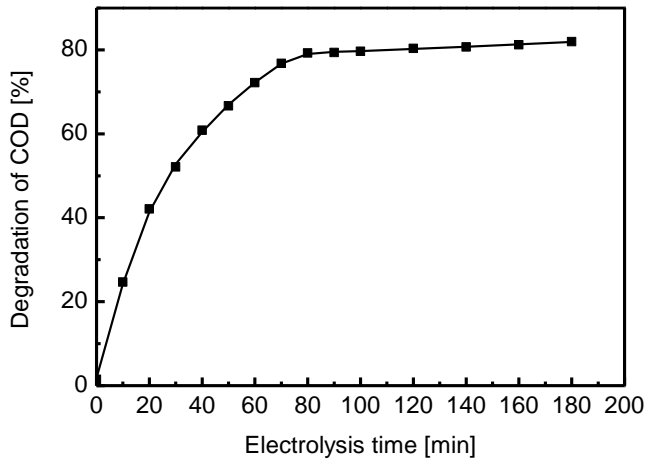


Figure 4: Effects of electrolysis time on the degradation of COD

### 3.4 Effect of pH

When the system is under acidic conditions, the degradation of the compound is higher. The removal rate tends to be decreasing gradually (Sun et al., 2019). The high acidity of the system will affect the service life of the electrode (DSA electrode contains metal). As shown in Figure 5, when the pH value is between 3 ~ 6, the COD degradation are similar, about 85 %. When the pH of the system gradually changes to neutral or alkaline, the degradation of the COD decreases significantly. This is because the increase of the pH value of the solution is not conducive to the release of oxidizing groups in the electrolytic reaction (Uğurlu et al., 2019). Considering the service life of the electrode, the pH value is selected to be 5.

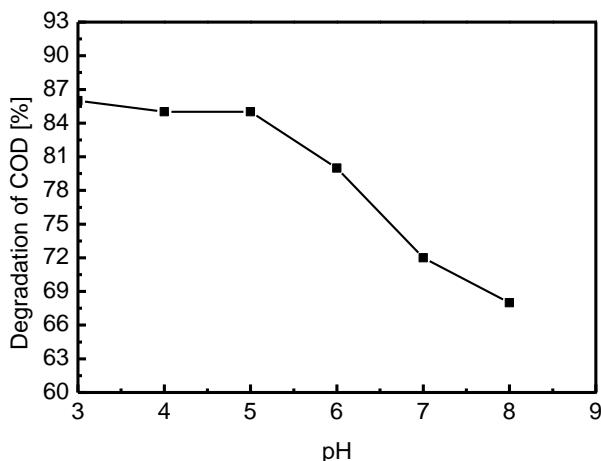


Figure 5: Effects of pH on the COD degradation

### 3.5 Effect of aeration

Aeration rate affects not only the mass transfer efficiency but also the short-circuiting of the fluid. As shown in Figure 6, the COD removal efficiency rises with the increase of aeration rate before 50 L/h. Because the increase

of the aeration rate improves the mass transfer efficiency. The degradation of COD reaches to the maximum value of 81 %. The degradation of COD decreases with the increase of the aeration rate when it is more than 50 L/h. This is because the continuing increase of the aeration rate leads to the short-circuiting. So, 50 L/h is the optimal choice.

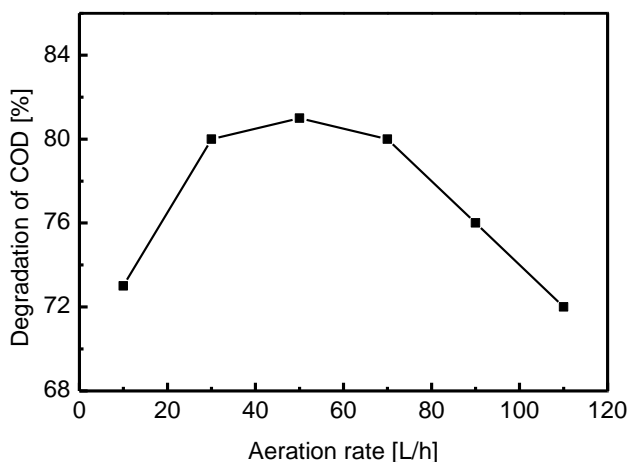


Figure 6: Effects of aeration intensity on the removal of COD

### 3.6 Orthogonal test

An orthogonal experiment was designed to study the effects of those above factors. As shown in Table 2, the magnitude of the impact on the five factors is as follows: electrolysis time > the value of pH > voltage > electrolyte concentration > aeration rate. Take the results and energy consumption into account, the optimal operating conditions are finally determined: the voltage is 14 V, pH = 5, aeration rate is 50 L/h, electrolyte concentration is 0.15 mol/L, and the electrolysis time is 120 min. The COD degradation achieved 88 % under this condition.

Table 2: Orthogonal test and results

Factors	pH	Voltage [V]	Electrolyte concentration [mol/L]	Time [min]	Aeration [L/h]	COD degradation
1	3.0	5	0.05	60	0	56
2	3.0	8	0.10	90	20	77
3	3.0	11	0.15	120	50	90
4	3.0	14	0.20	150	100	89
5	4.0	5	0.15	150	20	83
6	4.0	8	0.20	120	0	88
7	4.0	11	0.05	90	100	76
8	4.0	14	0.10	60	50	74
9	5.0	5	0.20	90	0	73
10	5.0	8	0.10	60	100	65
11	5.0	14	0.15	150	50	92
12	5.0	11	0.05	120	20	76
13	6.0	5	0.10	120	100	63
14	6.0	8	0.05	150	50	77
15	6.0	11	0.20	60	20	68
16	6.0	14	0.15	90	0	73
Avr.1 value 1	81.5	69.5	71.5	66.7	75.5	—
Avr.2	82.8	76.3	73.7	74.7	76.5	—
Avr.3	75.0	77.3	76.8	79.2	75.8	—
Avr.4	72.2	78.5	79.7	81.5	71.0	—
Range	10.310	9.61	8.81	15.4	4.70	—

#### 4. Conclusions

Nowadays, more and more CV wastewater is discharged into the environment, so it is urgent to find an appropriate method to treat. Three-dimensional electrolysis treatment on CV wastewater has unique advantages in efficiency and cleanliness, so it is a great method. In this work, the system values of pH, voltage, electrolyte concentration, electrolysis time, and the aeration rate were systematically investigated by single-factor experiments to find regular impacts on the three-dimensional electrolysis. The optimal operating condition for each single factor experiment was determined. The orthogonal test was designed to research the influence degree of these parameters and comprehensive optimum conditions. Combined experiment results with energy consumption, the optimal operating conditions were determined as follows: the voltage is 14 V, pH = 5, aeration rate is 50 L/h, electrolyte concentration is 0.15 mol/L and the electrolysis time is 120 min. COD degradation reaches 88 % under this experiment condition. Three-dimensional electrolysis saved lots of energy and time compared to two-dimensional electrolysis. In this work, the COD degradation was relatively high, it provided an effective method to reduce the discharge of crystal violet wastewater. In order to meet the requirements of energy conservation and efficiency at the same time, future studies should pay more attention to the electrolysis time, pH and the voltage factors when carrying out three-dimensional electrolysis experiments. Three-dimensional electrolytic wastewater is the most promising way of industrial treatment, it is beneficial to environmental protection and sustainable development. In particular, the appropriate choice of fillers can not only improve the reaction rate but also reduce the cost. Later researches will be focused on the field of filling particles, especially in the field of practical manoeuvrability.

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