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Study on the Application of Three-dimensional Electrolysis in Treatment of Malachite Green Dye Waste Water

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Abstract

This paper focused on the application of three-dimensional electrolysis in treatment of Malachite Green (MG) dye waste water. Regular influence on the reduction of COD by the pH value of the system, the impressed voltage, the type and concentration of electrolyte, the aeration and the electrolysis time was investigated in the experimental part. As a result, the optimal technological conditions of the degradation process were determined. Furthermore, to explore interaction of the parameters, the experiment selected five factors including voltage, electrolyte concentration, time for orthogonal test. For another, based on the analysis results of the intermediates in the electrolysis process by Ultraviolet (Uv) light scanning method, the degradation process of MG could be divided into three stages inferentially described as follows: the side chains on the benzene fell off; then the ring structure of the benzene cracked in the electric field; ultimately carbonaceous organic matters with small molecules were oxidized into carbon dioxide. The exploratory studies provide fundamental data for the three-dimensional electrolysis of dye wastewater treatment.

Keywords: wastewater treatment, three-dimensional electrolysis, Malachite Green, COD reduction, degradation mechanism

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INTRODUCTION

With the rapid development of production industry bringing out large amounts of waste water, water pollution for its adverse effects both on human beings and the environment has become one of the most urgent issues to be dealt with timely and appropriately (Wang and Yang 2016, Wang and Yi 2016). Many industries such as textile, paper, cosmetic, etc. take the widely used synthetic dyes as staining agent. These dyes are highly harmful for the health of living species (Baghdadi et al. 2017, Chen et al. 2002, Fang-Bai et al. 1999, Yang et al. 2006). As a type of antibacterial and antiprotozoal synthetic dyes, Malachite green (MG) has been extensively used for coloring of leather, wool, cotton, jute and silk resulting the by-produce of dye waste water inescapably. Due to its physical and chemical properties, MG shows out to be very persistent in the environment, non-biodegradable, toxic to mammalian cells and carcinogenic in nature (Baghdadi et al. 2017, Beak et al. 2009, Buvaneswari and Kannan 2008, Man et al. 2012). Therefore, exploring an efficient and stable method for the removal of dye effluents is of great significance.

In recent years, various of physical, chemical or biological methods have been investigated academically for the removal of dyes from the waste water, such as adsorption, electrolysis, photo-catalytic oxidation, activated sludge and so on. Among all the method explored, electrolysis especially the three-dimensional electrolysis is one of the most promising approaches for its advantage of high efficiency, low investment cost, and less secondary pollution (Wang et al. 2013, Yin and Zhao 2015, Zhang et al. 2007). Different to the two-dimensional electrodes, the three-dimensional method fills the electrodes with the particle electrodes, and each particle becomes an independent electrode (the third electrode), which greatly increases the reaction area of the reactor. Electrochemical reaction not only occurs on the geometric surface of the electrode, and in the entire three-dimensional space. The material mass transfer efficiency has been greatly improved, and further improved the reaction efficiency (Ban et al. 2016, Wu et al. 2016). However, the efficiency, energy consumption

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and operating life of the three-dimensional electrolysis in treating organic wastewater are affected by many conditions (Chai et al. 2010, Liang et al. 2017). This work is aiming to investigate the effect of different parameters such as pH, voltage on the efficiency of three-dimensional electrolysis in the treatment of MG dyes waste water.

EXPERIMENTS AND METHODS

Three-dimensional Electrolytic Reactor

Considering the impact of three-dimensional electrolytic reactor on the degradation of MG, the reactor was designed as follows. The cell volume was designed as: 10 cm × 8 cm × 8 cm. The distance between the two electrodes is 8 cm. The surface of the electrode was 8 cm × 8 cm.

Electrode material: graphite plate was used as cathode; DSA electrode (RuO2 / Ti and IrO2 / Ti) as anode; coconut shell activated carbon as filler.

Pretreatment: Activated carbon particles were soaked with 200 mg / L malachite green solution until the solution faded, filtered, and then the new malachite green solution was re-added to the activated carbon until the color faded and then filtered. Repeat the operation, until the addition of new malachite green solution activated carbon, the solution within 1 hour without color and concentration changes, which means the activated carbon adsorption has been saturated and the impact of adsorption in the electrolysis experiments can be ignored.

Experimental Reagents

Malachite green (MG, molecular formula: $C_{23}H_{25}ClN_2$, molecular weight: 364.92 g/mol) was supplied by Zhongtian experimental instrument co. LTD (Zhengzhou, China). Stock solution of MG with the needed concentration was prepared by dissolving the required amount of the MG in deionized water. Sodium sulfate (Na_2SO_4) obtained from Aibi Chemical Reagent Co., Ltd (Shanghai, China) was configured to different concentrations of solution for the electrolysis process. Sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) provided from Tianzheng Fine Chemical Reagent Factory (Tianjin, China) were used to perform the pH of electrolytic solution. The supply of the other reagents used in the experiment was summarized as followes: Potassium hydrogen phthalate ($C_8H_5KO_4$, Aibi Chemical Reagent Co., Ltd provided), silver sulfate (Ag_2SO_4, Meisco Tianjin Chemical Co., Ltd. provided), potassium dichromate ($K_2Cr_2O_7$, Aibi Chemical Reagent Co., Ltd provided).

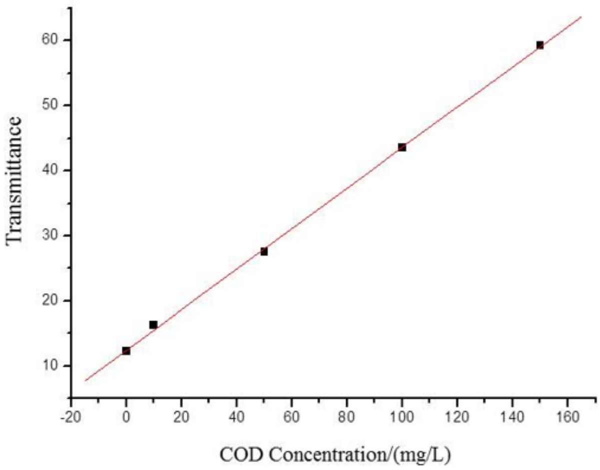

Fig. 1. Standard curve of COD

Experimental Set-up

Calibration curves

With potassium hydrogen phthalate as solute and deionized water as solvent, a solution with COD concentrations of 0.0, 10, 50, 100 and 150 mg / L respectively was prepared. The potassium hydrogen phthalate solution prepared was used as a benchmark, silver sulfate - sulfuric acid solution as a catalyst, potassium dichromate solution as a digestion reagent, and the transmittance was measured at 445nm. The standard curve is shown in **Fig. 1**.

The fitting equation of the curve is as follows:

$$y = 0.0698x + 0.0349$$

Where coefficient of determination: R^2=0.9981.

This equation was used to calculate the COD concentration.

Methods

The degradation efficiency of COD in waste water system by three-dimensional electrolysis is affected by various parameters (Cui et al. 2009, Liang et al. 2017, Xu et al. 2008). In this study, electrolysis voltage, concentration of the conductive medium, degradation time or pH was taken as the operating variables in a set of experiments and the other parameters not as operating variables were kept as stable conditions. The operating variables and stable conditions in each set of experiment were show in **Table 1**. The initial concentration of malachite green simulated wastewater is 200 mg / L.

Table 1. Operating variables and stable conditions

Experiment	Parameters:				
	Voltage/v	Electrolyte concentration/(mol / L)	Time/min	pH	Airflow/(L/h)
1	√	0.1	120	6	50
2	8	√	120	6	50
3	8	0.1	√	6	50
4	8	0.1	120	√	50
5	8	0.1	120	6	√
√ : **Taken as a variable**					

Table 2. Factors and levels of orthogonal experimental

pH	Voltage/v	Airflow/(L/h)	Electrolyte concentration/(mol / L)	time/min
4	5	0	0.05	60
6	8	20	0.10	90
8	11	50	0.15	120
10	14	100	0.20	150

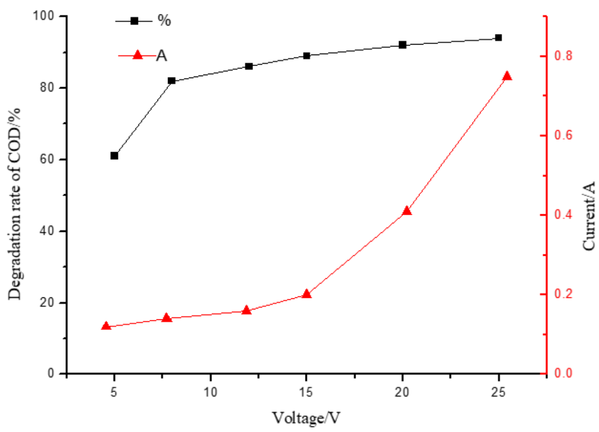

Fig. 2. Effects of electrolysis voltage on the removal of COD

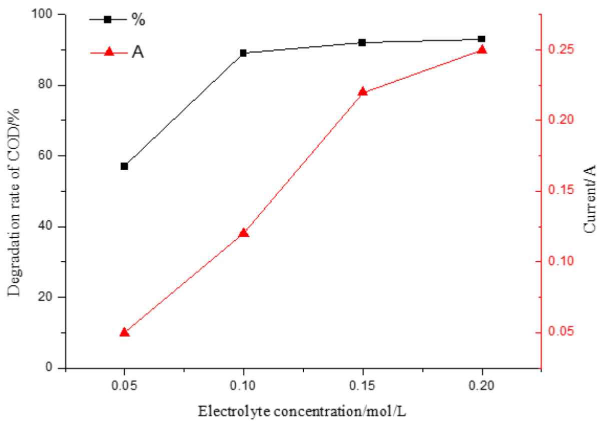

Fig. 3. Electrolyte concentration relationships with COD degradation rate

Furthermore, to explore interaction of the parameters, the experiment selected five factors including voltage, electrolyte concentration, electrolysis time for orthogonal test. **Table 2** shows the experimental conditions.

The degradation of COD was monitored under the different experimental conditions by means of spectrophotometry.

RESULTS AND DISCUSSION

Effect of Cell Voltage

The electrochemical reaction is electron reaction actually. As the electric potential of the applied electric field is increased by 1v, the activation energy of the reaction is reduced by 41.8-54.5v and the electrolysis reaction rate is accelerated by about 107-109 times (Wu et al. 2016). Electrolysis voltage is of great importance for the efficiency of electrolysis. **Fig 2** shows the effects of electrolysis voltage on the removal of COD.

As can be seen from **Fig. 2**, both the COD degradation rate of the wastewater and the current of the system increase with the increase of the voltage, but the increase rate is different. When the electrolysis voltage is 8v, COD removal waste water reaches more than 80%. When the voltage exceeds 8v, although the COD has increased, but the increasing trend is very smooth, in the contrast, the current change is significantly increased. The current means increased energy consumption, so considering the energy consumption and processing efficiency the electrolysis voltage was set at 8v.

Effect of Electrolyte Concentration

Organic wastewater solution usually contains few ions and the current in the system may be tiny without any substance that increases its conductivity. To increase the conductivity of the solution, inorganic salts should be added to improve the conductivity. With more electrolyte, the solution conductivity increases, which could accelerate the electrochemical reaction, meanwhile the probability of side effects also increased (Sun et al. 2012). **Fig 3** shows Electrolyte concentration relationships with COD degradation rate.

As can be seen from **Fig. 3**, when the concentration of Na_2SO_4 increases, COD degradation rate of

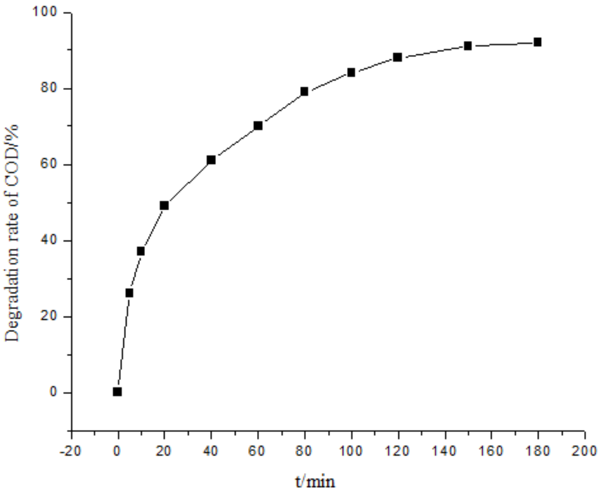

Fig. 4. Electrolysis time and the degradation rate of COD

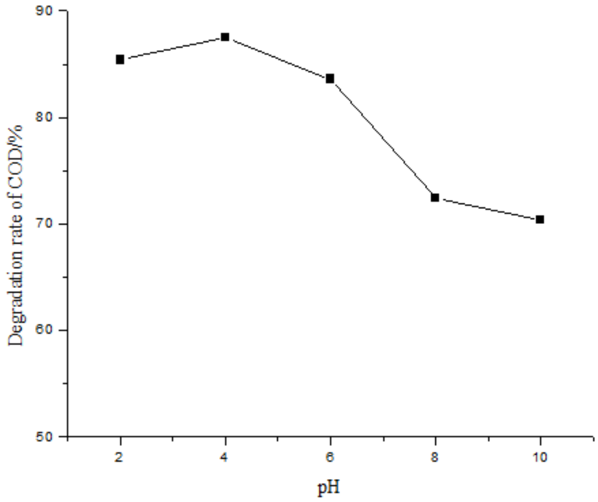

Fig. 5. pH relationships with COD degradation rate

wastewater increased significantly, but the increasing trend is different. The maximum COD degradation rate is only 40% without Na_2SO_4 added. This is due to the water conductivity is relatively low and the system reaction current is relatively small. When the concentration of Na_2SO_4 added in the system gradually increasing, the conductivity of the solution and the current also increased. The increased current accelerates the reaction speed of each ion or group in the solution and the removal rate is remarkably improved. When the electrolyte dosage is greater than 1mol / L, then the reaction current increases, but the current efficiency will be greatly reduced. In addition, with the concentration of Na_2SO_4 increasing, the interaction between ions and the association effect increase. The high electrolyte concentration will affect the normal degradation of organic compounds. Under the experimental conditions, the recommended dosage of Na_2SO_4 is 0.10 mol / L.

Effect of Electrolysis Time

In the electrolysis process, the time not only influences the electrolysis efficiency, but also is the most important aspect of the energy utilization (Xiong et al. 2003). Therefore, the appropriate reaction time can not only help COD get better degradation, but also control the power consumption in the lowest range. **Fig 4** shows Electrolysis time and the degradation rate of COD.

As **Fig. 4** showed, the degradation rate of COD increased with electrolysis time. From the slope of the curve, the rate of the electrolytic reaction has been decreasing from the start of the reaction until 180 min. The first 20 minutes of the reaction rate is the fastest, and the COD concentration of wastewater decreased rapidly, but later the rate has been slowing down. As the concentration of organic matter in the system is getting lower and lower, the diffusion rate also became slower, the reaction driving force decreased, so the reaction rate also slowed down. After 100 min of electrolysis, the removal rate of COD was not obvious. Therefore taking the issue of reducing operating costs into account, the electrolysis time was set 120 min.

Effect of pH

The pH of the system influenced the production of groups with strong oxidizing ability in the electrolysis. As described in the preceding electrolysis mechanism, the presence of H^+ can promote the formation of oxidation groups such as·OH and H_2O_2 in the system, thereby accelerating the progress of the electrolysis reaction. On the other hand, the pH of the system also affects the service life of the electrode, especially when metal electrodes or metal oxide electrodes are present in the electrolytic reactor, such electrodes can be corroded under acidic conditions, resulting in Shortened service life (Xiong et al. 2001, Zheng et al. 2016). **Fig. 5** shows pH relationships with COD degradation rate.

As is clear from **Fig. 5**, when the system was in acidic conditions, the degradation efficiency was higher than the alkaline conditions. Especially when the pH value is equal to 4, the COD degradation rate is the highest at 87.5% followed by 85.4%. When pH was 6, the COD degradation rate reached 83.6%. The electrodes used in this experiment were DSA electrodes and graphite electrodes. DSA electrode surface coated with a layer of metal oxide, the substrate is also made of titanium metal, so the pH value of the experiment should not be too low, the final selection of the pH was 6.

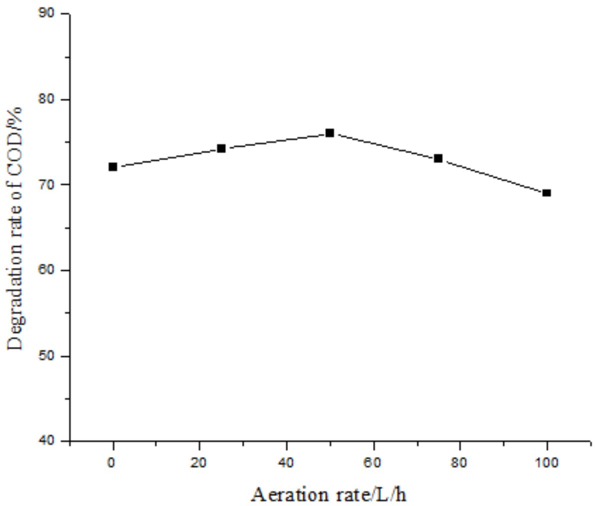

Fig. 6. The influence of aeration intensity on the removal rate of COD

Effect of Aeration

The essence of three-dimensional electrode method is heterogeneous reaction, the process involves gas-solid-liquid multi-phase. The main role of aeration is to increase the concentration of oxygen in the water, thereby promoting the reaction. On the other hand, aeration at the same time make the system of particle packing activated carbon in suspension, which can reduce the short-circuit current, thereby enhancing the current efficiency (Li et al. 2010). **Fig. 6** shows The influence of aeration intensity on the removal rate of COD.

As can be seen from **Fig. 6**, the optimal aeration rate is 50 L / h. The COD degradation rate under this condition is 76.2%. Whether it is to increase or decrease the amount of aeration, degradation will be some degree of decline, the decline is not very obvious. Without considering other conditions, the experiment can choose 50 L / h as the aeration.

Orthogonal Experiment

The efficiency of organic wastewater and COD degradation in waste water system in three-dimensional electrolysis is affected by various parameters. The previous study on the voltage, the concentration of conductive medium, degradation time, pH of aeration has been performed respectively. Orthogonal test is one of the most effective method to explore the interaction between the various parameters (Shi et al. 2014). In this experiment, voltage, electrolyte concentration and reaction time were selected for orthogonal test to explore the mutual influence between these factors. **Table 3** shows the orthogonal test and test results.

According to the range in the **Table 3**, the impact of various factors was order as follows in electrolytic test: electrolysis time> pH> voltage> electrolyte concentration> aeration. It can also be concluded that the optimal combination of these five factors is pH 6, voltage 14 v, aeration 50 L / h, electrolyte concentration 0.2 mol / L and electrolysis time 150 min. Combined with the results of single factor experiments, considering the influence of aeration on the test is not too large, and the energy saving, the final selected electrolysis conditions: pH 6, voltage 8 v, no aeration, electrolyte concentration 0.1 mol / L, electrolysis time is 120 min. Under these experimental conditions, the COD degradation rate was 86%.

Table 3. Orthogonal test and test results

Factors	pH	Voltage/v	Aeration/L/h	Electrolyte concentration/moL/L	Time/min	COD degradation
1	4	5	0	0.05	60	58%
2	4	8	20	0.1	90	76%
3	4	11	50	0.15	120	85%
4	4	14	100	0.2	150	87%
5	6	5	20	0.15	150	83%
6	6	8	0	0.2	120	90%
7	6	11	100	0.05	90	76%
8	6	14	50	0.1	60	75%
9	8	5	50	0.2	90	73%
10	8	8	100	0.15	60	65%
11	8	11	0	0.1	150	80%
12	8	14	20	0.05	120	78%
13	10	5	100	0.1	120	64%
14	10	8	50	0.05	150	74%
15	10	11	20	0.2	60	69%
16	10	14	0	0.15	90	74%
Avr.1 value 1	76.500	69.500	75.500	71.500	66.750	
Avr.2	81.000	76.250	76.500	73.750	74.750	
Avr.3	74.000	77.500	76.750	76.750	79.250	
Avr.4	70.250	78.500	73.000	79.750	81.000	
Range	10.750	9.000	3.750	8.250	14.250	

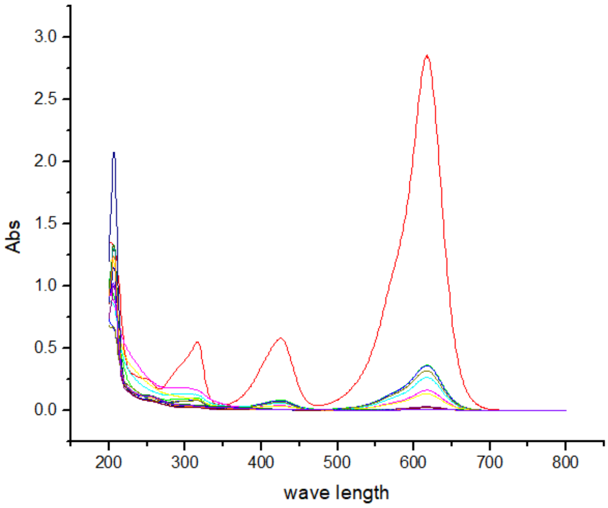

Fig. 7. The result of Uv-vis scanning

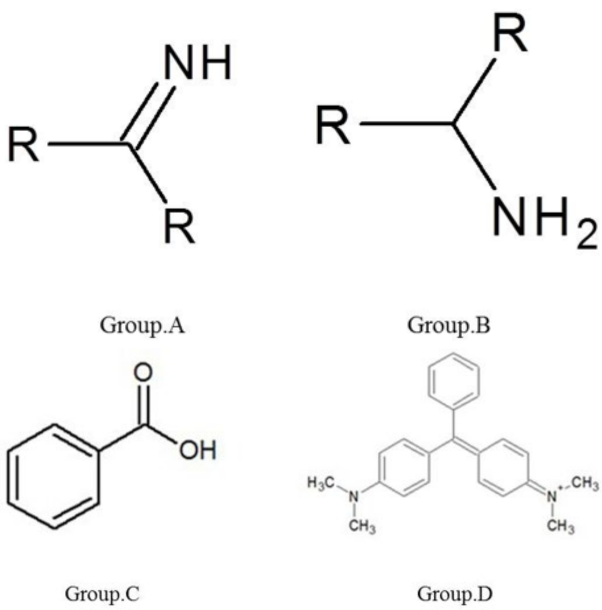

Fig. 8. Four groups in the water sample

EXPLORATION ON DEGRADATION MECHANISM

Generally, intermediate products would be produced in the degradation of organics (Chen et al. 2002b, He et al. 2004, Xie et al. 2016). In order to explore the intermediate product in the electrolysis, the sample was scanned by the ultraviolet-visible (Uv-vis) in the range of 200 nm-800 nm. The wavelength and absorbance curve was made as shown in **Fig. 7**.

It can be seen from the **Fig. 7** that MG with its decomposition products in the Uv - vis region had four distinct absorption bands and the four absorption peak wavelengths were relatively concentrated. Significant characteristic absorption peaks appeared at 617 nm, indicating a sharp change in the structure of MG. It is estimated by analysis that the water sample contains the following four groups in **Fig. 8**.

It can be speculated that the degradation process was following the steps below. Firstly, the side chain of MG fell off, then the tricyclic separated and the middle of the oxidation of C to carboxylic acid, lastly the carbon ring opened up, and gradually the small molecules decomposed into CO_2 and nitrogen oxides. The detailed degradation process was described as follows in **Fig. 9**.

CONCLUSION

In view of this study, Malachite green, as a kind of typical triphenylmethane dyes is degraded by a three-dimensional electrode reactor with DAS electrode as anode, graphite plate as cathode and activated carbon as particle electrode. Because of the adsorption of activated carbon, before each experiment, activated carbon should be saturated with wastewater, to reduce its influence to the experimental results. Several influence factors are studied on the degradation experiments,

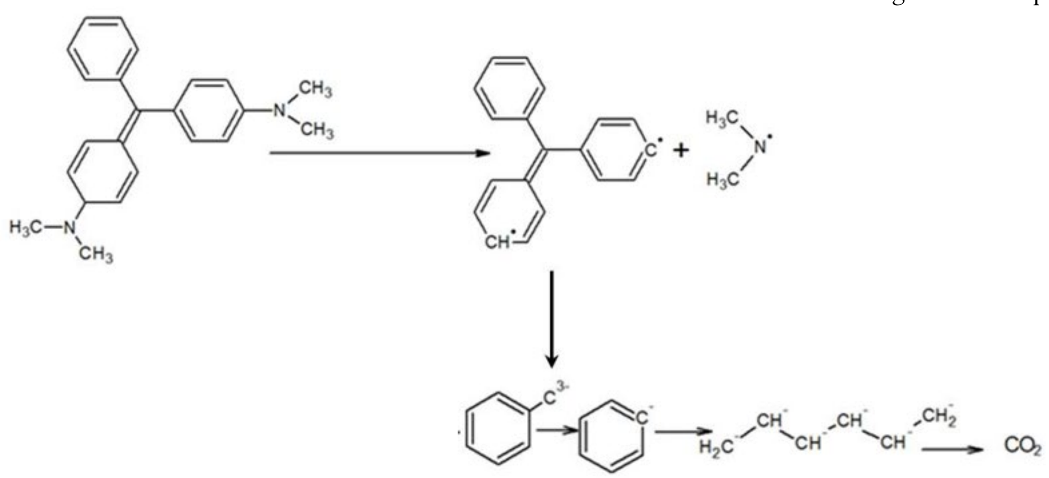

Fig. 9. The degradation process of MG

including the pH value of the system, the voltage, the type and concentration of electrolyte, the aeration and the electrolysis time. The optimum reaction conditions and parameters are selected by orthogonal test. The influence of various parameters on the test order from big to small as follows: electrolytic time > electrode voltage > system pH > value of electrolyte concentration > aeration. The final electrolysis conditions are determined to 8V for electrode voltage, 6 for initial pH value, 0 for aeration quantity, 0.1 mol/L for electrolyte (Na_2SO_4) concentration and 120 min for electrolysis time. In the reaction condition, the final COD degradation rate is 86%. By reducing the sampling interval, increasing the number of sampling, measuring MG concentration and COD concentration of the sample, and then being scanned by means of UV-Vis, initially explore the mechanism of degradation reactions of formulas. The degradation process was following the steps below. Firstly, the side chain of MG fell off, then the tricyclic separated and the middle of the oxidation of C to carboxylic acid, lastly the carbon ring opened up, and gradually the small molecules decomposed into CO2 and nitrogen oxides. It is hoped that these researches will be helpful for the application of three-dimensional electrolysis in the treatment of dye waste.

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