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Decoloration of alizarin red S in aqueous solution by glow discharge electrolysis

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Abstract

The oxidation of alizarin red S by hydroxyl radicals, which were generated from glow discharge electrolysis, was investigated. Various influencing factors such as the applied voltage, the initial pH, the catalytic action of Fe^{2+} ion and the distance between cathode and anode were examined. Chemical oxygen demand (COD), ultraviolet (UV) absorption spectra, atomic force microscopy (AFM) and gas chromatogram–mass spectrum (GC–MS) were used to monitor the decoloration process. The results show that alizarin red S rapidly underwent decoloration and was eventually mineralized into carbon dioxide, water, and inorganic ions. It was confirmed that phthalic acid and carboxylic acids were produced in the decoloration process. The probable mechanism for the decoloration of alizarin red S induced by hydroxyl radical was also discussed.

Keywords: Glow discharge electrolysis; Alizarin red S; Hydroxyl radical; Oxidation; Decoloration

1. Introduction

Glow discharge electrolysis (GDE) is a novel electrochemical process in which active species occurred between an electrode and electrolyte [1]. If the platinum wire anode comparing with cathode were thin enough, then non-Faraday electrolysis would be observed. With an increase in applied voltage, at first, conventional electrolysis takes place that obeys Faraday's law. When the voltage reaches a critical value, a glow discharge phenomenon appears around the anode and conventional electrolysis is destroyed. At this time, the process does not obey Faraday's law and it is termed ‘‘glow discharge electrolysis’’ (GDE) [2,3]. In GDE, various active species are produced, including hydroxyl radicals, hydrogen peroxide and aqueous electrons, as well as other energetic species. These highly reactive species can be introduced into solution by diffusion and thereby oxidize pollutants in that solution. The important reactive species involved in the degradation of organic contaminants is hydroxyl radical [4,5].

Some aromatic compounds can cause cancer, malformation, nephritis and other diseases and so much attention has been paid to their potential harmful effects on the environment. Recently, plasma treatment of wastewater has attracted a great deal of attention from environmental chemists because of its amenability to automation, its high efficiency and environmental compatibility. Anodic glow discharge electrolysis was regarded as a promising technology because it did not need a special power supply or an evacuating system. Earlier studies have shown that contaminants such as phenol [6], chlorophenols [7], α-naphthol [8], chloroanilines [9], and acredine orange [10] can be degraded by GDE. Major intermediates, including oxalic acid, formic acid, and other carboxylic acids were detected and this suggested that GDE was an effective process for the degradation of toxic substances. In this paper, we examine the decoloration of alizarin red S as a model

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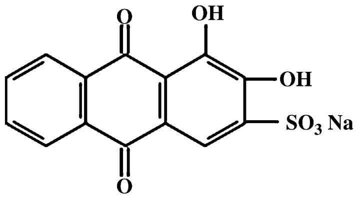


Scheme 1. Chemical structure of alizarin red S.

pollutant in wastewater. The chemical structure of alizarin red S is shown in Scheme 1.

2. Experimental

The experimental apparatus used comprised a high voltage power supply and a reactor. The power supply was a DH 1722-6 d.c. power unit providing voltages of 0–1000 V and a current range of 0–0.3 A. In this experiment, the optimum voltage used was 600 V and the current changed from 120 to 150 mA. The reactor contained a needle-to-plate electrode geometry system as shown in Fig. 1. A pointed platinum anode of diameter 0.5 mm was sealed in a glass tube to generate glow discharge in aqueous solution. The cathode was a graphite plate (diameter: 70 mm) suspended above the anode at a distance of about 10 mm. The discharge reactor was coated with an outer water jacket to keep the solution at a constant temperature. There was a magnetic stirring bar at the bottom of reactor to keep the solution mixed. During the experiments, certain amounts of the reaction solution were periodically sampled from the sampling port for analysis. The experiments are performed under the following conditions as listed in Table 1 unless otherwise remarked.

UV absorption spectra of the reaction solution were recorded using an UV-3400 Spectrometer (Hitachi, Japan) at intervals. In addition, the chemical oxygen demand (COD) measurement was carried out using a COD analyzer (Lanzhou, China). The pH of solutions was adjusted with NaOH or H_2SO_4 solution. pH measurements were carried out using a combined glass electrode standardized with pH buffer solutions (HORIBA).

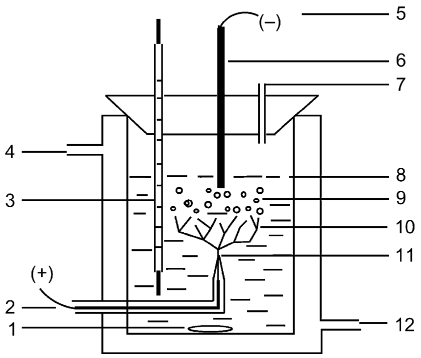


Fig. 1. Experimental setup of the glow discharge electrolysis. 1, stirring bar; 2, anode; 3, thermometer; 4, cooling water outlet; 5, cathode; 6, graphite; 7, gas outlet; 8, solution level; 9, gas bubbles; 10, glow discharge area; 11, platinum wire; 12, cooling water inlet.

Table 1
Experimental conditions

Parameter	Value
Voltage (V)	600
The range of current (mA)	120–150
Distance between electrodes (mm)	10
Diameter of discharge electrode (mm)	0.5
Aqueous Na_2SO_4 (mg/L)	2
Alizarin red S (mg/L)	30
Initial pH	6.78
Volume (mL)	250

The particle size and shape of samples were measured by a Seiko SPI-3800N atomic force microscopy (AFM). GC–MS analysis was performed on a gas chromatography–mass spectrometry (Atrlent, USA) equipped with a DB-5 column (30 m × 0.25 mm ID, 0.25 μm film thickness, J&W, USA). Electron impact (EI) was used as ionization technique with electron energy 70 eV with *m*/*z* ranging from 20 to 300. Ion source temperature was 230 °C. The injector and detector temperatures were set at 250 °C. Helium served as carrier gas at a constant flow of 1.2 mL/min (He, 99.999%).

3. Results and discussion

3.1. Optimum condition for decoloration

3.1.1. Typical current–voltage relationship

Fig. 2 shows the typical current–voltage characteristics of the decoloration process, which can be divided into several sections. There is a linear section below 200 V, which is conventional electrolysis. When the voltage was raised to 200 V, small gases left the wire anode; between 200 V and 380 V, the readings of both current and voltage fluctuated widely and a small spark could be seen around the anode. From 380 V to 520 V, the current stabilized and a smooth pale sheath of vapor appeared. Above 520 V of applied voltage, a continuous reddish spark appeared. If the applied voltage was too high, the anode would be easily destroyed. Hence, in our experiment, the applied voltage was kept at 600 V.

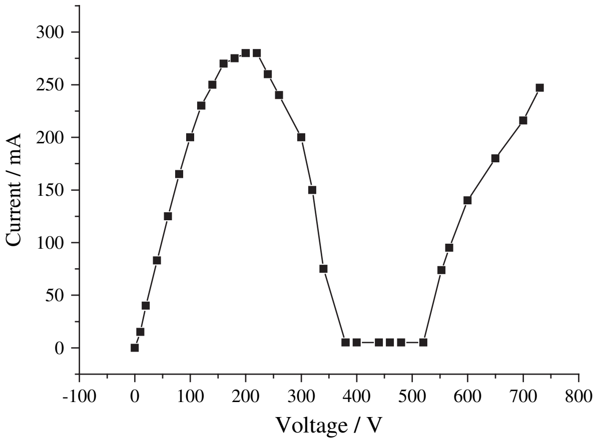


Fig. 2. The current–voltage characteristics in GDE.

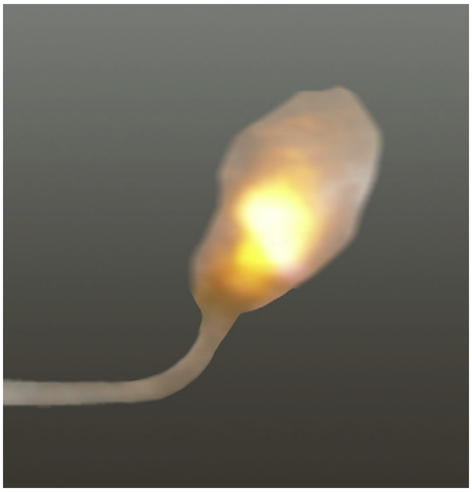


Fig. 3. Photograph of glow discharges in aqueous solution.

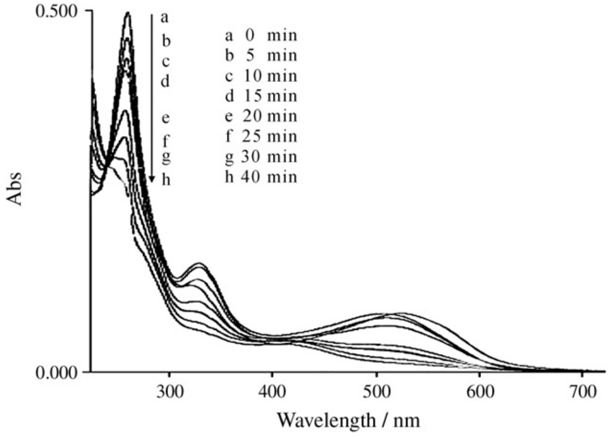


Fig. 4. The UV spectra of alizarin red S solution.

Although it is known that shortening the distance between the anode and cathode would increase the intensity of glow discharge, if the distance is less than 10 mm, the anode would be also destroyed; thus, in this study, a 10 mm gap was employed. A photograph of glow discharges in aqueous solution is shown in Fig. 3.

3.1.2. Effect of pH

The higher pH of the solution benefited the deprotonation of alizarin red S; the ionic species of alizarin red S is easily destroyed by the highly reactive species present. The results in Table 2 show that with increasing pH from 3.0 to 12.0 the decoloration rate increased. Above pH 12, the decoloration rate decreased, owing to the formation of ferric hydroxide to decrease the effect of Fe^{2+} ion as the Fe^{2+} ion is a catalyst in this study.

3.2. Decoloration of alizarin red S

3.2.1. UV absorption spectra of alizarin red S

Spectrophotometric analysis is a convenient method to examine the decoloration process. Fig. 4 shows the absorption spectra of alizarin red S at different reaction times. The observed reduction in absorbance at 255 nm implies that the anthracene ring was gradually destroyed as a result of the process.

3.2.2. pH changes of the solution

The results of the changes of pH in decoloration process of alizarin red S are given in Fig. 5. It can be seen that the pH of reaction solution decreased at first, then increased and remained approximately unchanged for a while, finally increased again. Early studies proved [6,8,11] that the degradation of macrocyclic compounds undergo the following steps: hydroxylation, opening ring, forming smaller organic acids, and mineralizing to form carbon dioxide and water. In this study, the decrease of pH may be caused by forming some of the organic acids at first; after mineralizing the escape of carbon dioxide caused the raise of pH.

Table 2
Decoloration rate of different pH of initial solution

pH	3.65	4.15	6.80	7.65	9.11	10.99	12.32
Decoloration rate (%)	33.33	39.74	65.91	62.33	65.67	73.47	63.33

3.2.3. Atomic force microscopy observations of alizarin red S on mica

Atomic force microscopy (AFM) was used for observing the surface erosion of alizarin red S in decoloration process. Fig. 6a–d shows the AFM images of the alizarin red S on the mica surface under different decoloration times. There are a plenty of alizarin red S cluster particles, which were accumulated on mica surface tightly (Fig. 6a). The tight cluster particles were weakened clearly after reaction time from 20 to 40 min, that is, the aromatic ring was attacked by •OH radical (Fig. 6b and c) to form smaller molecules. The reaction lasted for 70 min, during which the cluster particles on the mica surface almost disappearing, and a lot of inorganic salts (e.g. sodium carbonate and sodium sulfate) appeared (Fig. 6d).

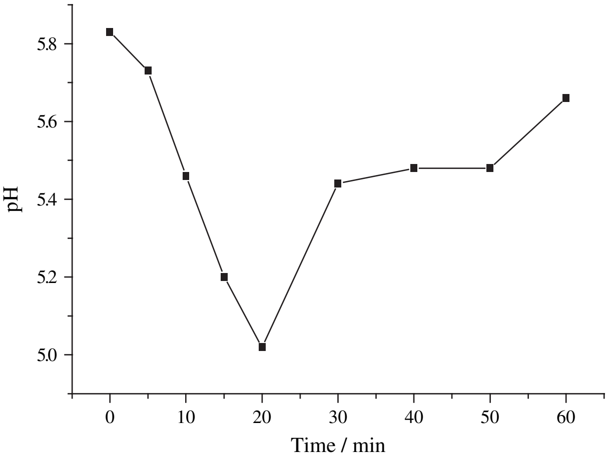


Fig. 5. pH changes of the solution alizarin red S.

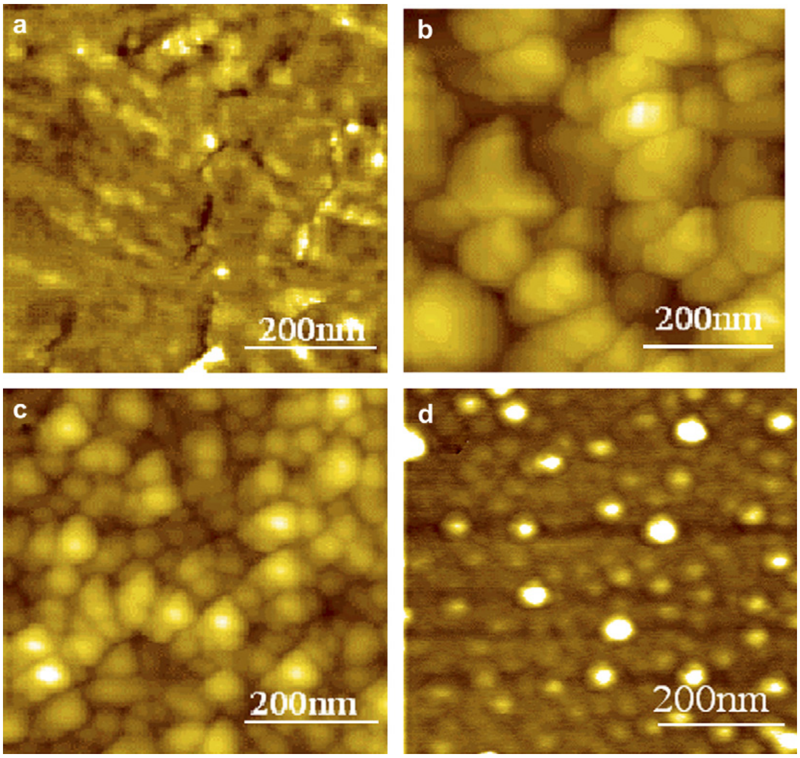


Fig. 6. AFM images of alizarin red S on mica treated at different decoloration time (30 mg/L): (a) 0 min; (b) 20 min; (c) 40 min; (d) 70 min.

3.2.4. Intermediate products examined by GC–MS and the possible decoloration mechanism for alizarin red S

To understand the decoloration mechanism, a GC–MS analyzer was used to monitor the intermediate products. Under the glow discharge electrolysis, alizarin red S was degraded gradually to give the phthalic acid and benzoic acid at the beginning, and then, they were further oxidized to form some of carboxylic acids with smaller molecular weight. The final products would be inorganic ions, $CO_2^{m/z}$, and water. Just like mentioned in Section 3.2.2, the changing trends of pH have also proved the formation and/or decomposition of intermediate products in decoloration process. Of course, the intermediate products would be changed with reaction time. As an example, we only showed here two results in Fig. 7a and b.

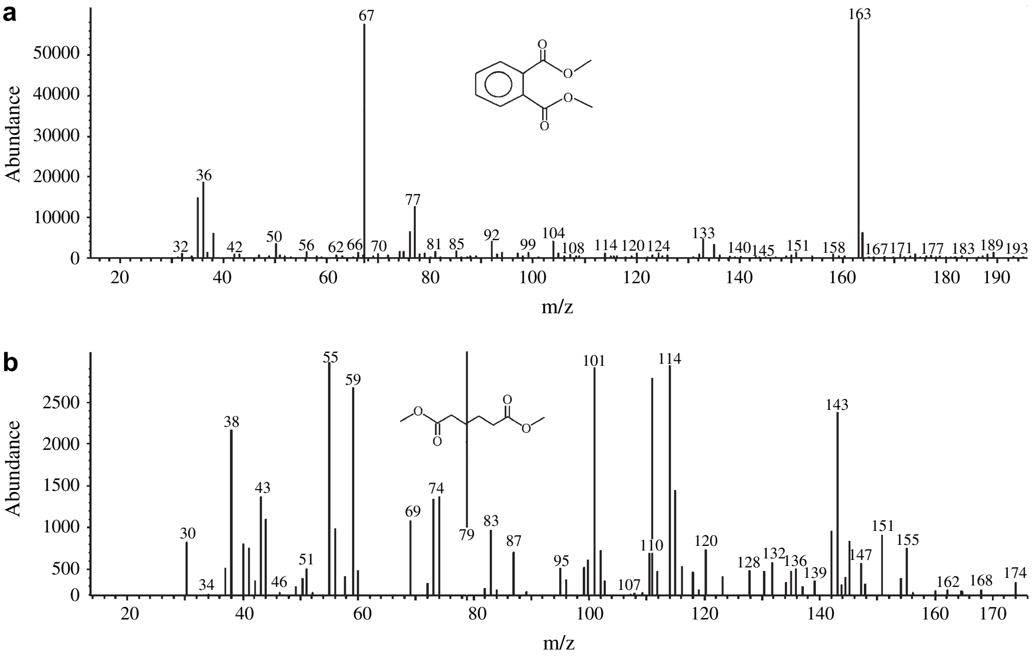
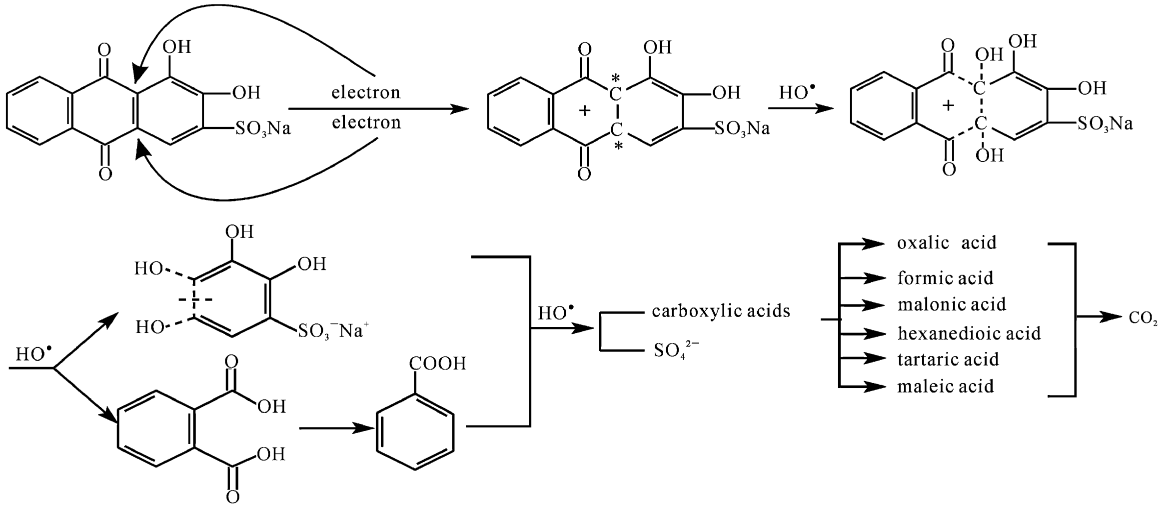


Fig. 7. Mass spectra of the main intermediate products in decoloration process of alizarin red S.



Scheme 2. The reaction path of alizarin red S.

Based on the analysis results above, a possible degradation mechanism is given in brief in Scheme 2.

3.2.5. Effect of Fe^{2+} ion

All the above mentioned studies were carried out in the absence of Fe^{2+} ion.

In the experiment, the COD value of alizarin red S solution (initial concentration: 30 mg/L) was determined and is shown in Fig. 8. Of course, in the determination, the blank solution must have the same amount of Fe^{2+} ion to deduct the effect from the absorbance. The COD was rising at first and then decreased with the lasting time of decoloration in the absence of Fe^{2+} ion; this is due to a lot of OH radicals attacking the alizarin red S and gradually producing lots of small molecules of organic acid after opening the ring. However, if the Fe^{2+} ion solution (2.0×10^{-4} mol/L) was added into the alizarin red S solution, the COD value would be decreased very quickly and 80% of decoloration rate could be gained within 10 min. The reason is that the Fe^{2+} ion combined with H_2O_2 produced in the glow discharge process just acts as the Fenton's reagent [12,13].

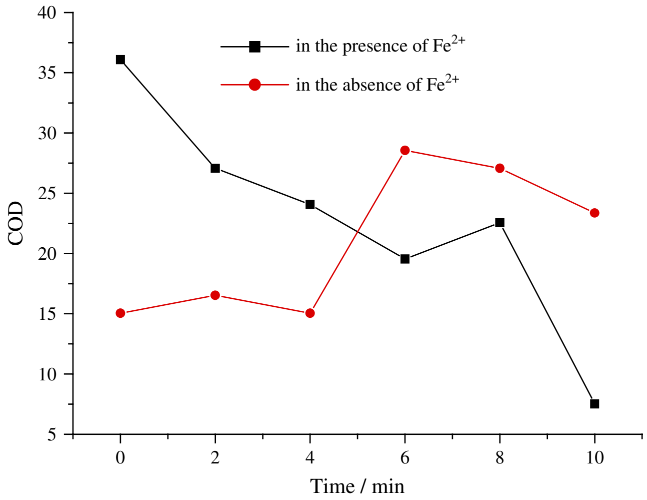


Fig. 8. The COD values of alizarin red S.

4. Conclusion

It may be concluded that the glow discharge electrolysis (GDE) is potential technique for treating dye wastewater. Because it can provide a lot of highly energetic species during the glow discharge electrolysis, many organic compounds, for example, alizarin red S, were destroyed and mineralized finally to form carbon dioxide and water. Generally speaking, the energetic species, for example, highly energetic electron and hydroxyl radical, play an important role in decoloration process. Moreover, the presence of Fe^{+} ion combined with H_2O_2 produced in the glow discharge process just acts as the Fenton's reagent to raise the efficacy of decoloration. In this study, 250 mL of alizarin red S solution (30 mg/L) would be removed within 10 min in the presence of Fe^{+} ion by glow discharge electrolysis.

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