



## De-colorization of Reactive Brilliant Orange X-GN by a novel rotating electrochemical disc process

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### Abstract

A novel electrochemical setup for wastewater treatment—rotating electrochemical disc process (RECDP) was developed in this article. The anode and cathode are distributed alternatively and evenly on a flat round disc, which was designed to improve mass transfer of organics from bulk solution to electrode surface, while at the same time increasing oxygen transfer from air to the liquid to benefit the organics oxidization. The color removal of dye Reactive Brilliant Orange X-GN (RBO) was experimentally investigated using the setup. The results show that the RECDP could efficiently remove the color by 99.5% after 60-min electrolysis. The influence of factors such as the disc rotating speed, current intensity, pH, and treating time was also explored, and the de-colorization mechanism was studied with electron paramagnetic resonance (EPR), UV-Vis, and IR. It has been confirmed that the free radicals oxidization leads to the dye de-coloration.

**Key words:** electrochemistry; de-colorization; dye; wastewater; rotating electrochemical disc process (RECDP)

### Introduction

The electrochemical technology is well known as a green advanced oxidation process for wastewater treatment. It does not add extra chemicals during the treatment and thus does not pose potential pollution to the environment. Compared to other technologies, electrochemical method is economical, efficient, and its space requirement is usually much lower (Chen, 2004). Successful applications of electrochemical technology to various wastewater, have been reported world wide (Min *et al.*, 2004; Rao *et al.*, 2001; Szpyrkowicz *et al.*, 2005), such as dyeing wastewater (Wang *et al.*, 2006; Shen *et al.*, 2001; Lin and Chen, 1997; Xiong *et al.*, 2001), the wastewater containing nitrobenzene compounds (Xu *et al.*, 2006), *p*-nonylphenol (Kuramitza *et al.*, 2002), or cyanide (Lanza and Berlazzoil, 2002), landfill leachate (Thaveemaitree *et al.*, 2003), phenolic wastewater (Korbahti and Tanyolac, 2003), coffee curing wastewater (Bejankiwar *et al.*, 2003), and tannery wastewater. To increase reactor efficiency and decrease side reactions, many new electrode materials and reactors were developed recently (Subbiah *et al.*, 2003; Polcaro *et al.*, 2004; Zanta *et al.*, 2003; Zollinger *et al.*, 2004; Rodriguez and Martinez, 2005; Xiong *et al.*, 2002).

However, the mass transfer of organics and oxygen from bulk solution to electrode surface always hinders

the overall treatment efficiency for traditional electrochemical reactor. Moreover, high organic concentration in the wastewater led to the lacking of dissolved oxygen for anode oxidation, resulting in a longer treating time. Rotating electrochemical disc process (RECDP) has been developed in this study and employed for wastewater treatment. The anodes and cathodes are distributed alternatively and evenly on a round electrochemical disc, and are connected with conducting wire respectively. By rotating the disc, the thickness of static liquid film on the electrodes surface could be decreased significantly and thus increases the mass transfer of organics to and from the electrode surface. At the same time, because there are always 50% of anodes and cathodes rotating out of the bulk solution, there is enough opportunity for the thin liquid film to be re-oxygenated. Granular activated carbon, which can be polarized at high gradient electric field, was filled on the disc between the anodes and the cathodes in this developed reactor. During the treatment, a micro-electrolytic cell could be formed around each granular activated carbon particle (Zhou and Zhou, 1994). Therefore, the effective electrode area of this reactor is increased, and the transfer distance of the reactant is shortened (Jia *et al.*, 1999).

Dyes have been widely applied in the fabrics, home interiors decoration materials, leather accessories, plastics, automobile, and paper industries. Dye industries are one of the major ones responsible for water pollution (Subbiah *et al.*, 2003). It is rather difficult to treat dye wastewater

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because hot and strongly colored textile-dyeing wastewater is notoriously known to contain a large amount of suspended solids, with high COD concentration and a highly fluctuating pH (Jia *et al.*, 1999).

A typical reactive dye, Reactive Brilliant Orange X-GN (RBO), is widely used for dyeing cotton, silk, and viscose fiber, and is difficult to be coagulated or to be degraded using traditional biological methods. In present article, the effectiveness of the developed RECDP reactor was examined by treating simulated RBO wastewater. The color removal of the wastewater was employed as an index and the optimum working conditions of the RECDP reactor were studied. Also, the preliminary mechanism of this treatment process was proposed with EPR, UV, and IR.

## 1 Materials and methods

### 1.1 Materials

The molecular structure of RBO is shown in Fig.1. Commercial RBO was purchased from Shanghai Jiaying Chemical Co. Ltd., China. The dye was diluted by distilled water to a constant initial concentration of 100 mg/L (with initial pH around 7.2). Real wastewater samples usually contain high concentration of salts and thus Na<sub>2</sub>SO<sub>4</sub> (Shanghai Chemical Reagent Co. Ltd., China) with a dosage of 100 mg/L was added into the solution to simulate the ionic strength in actual situation and to ensure conductivity. Granular activated carbon and graphite were purchased from Shanghai Tansu Co. Ltd., China and 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was purchased from Aldrich, USA. HCl and NaOH were also obtained from Shanghai Chemical Reagent Co. Ltd., China. All the chemicals used were certified grade or better.

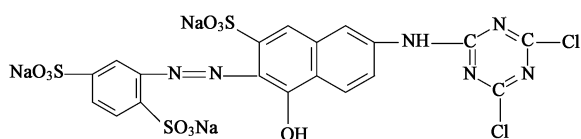


Fig. 1 Chemical structure of Reactive Brilliant Orange X-GN (RBO).

### 1.2 Analytical method

The samples were taken periodically and filtered qualitative filter paper to remove large particles. Ultraviolet and visible absorption of the samples were determined by UV-2102PCS (Unico Inc., USA), pH was determined by PHS-3B (Shanghai Rex Instrument Factory, China). Electron Paramagnetic Resonance (EPR) spectrum was determined by EPR EMX-8 (Bruker, Germany) (operated at X-band, using 100 kHz field modulation frequency). The spin trapping agent was DMPO. The sample solution after electrolysis at color removal more than 80% was added into surplus BaCl<sub>2</sub> depositing the SO<sub>4</sub><sup>2-</sup>. Then the filtrate was condensed and air-dried to a constant weight for IR analysis (IR Prestige-21, Shimadzu, Japan).

### 1.3 Experimental apparatus

The experimental apparatus is the batch arc cell with a rotating electrochemical disc (Fig.2). The rotating electrochemical disc was an acryl glass disc with 18 cm diameter, 3.6 mm thickness. The cathodes was made of copper, with 6 cm in length, 1.2 cm in width, and 0.8 mm in thickness. The anodes was made of graphite, with 6 cm in length, 1.2 cm in width, 2.7 mm in thickness. The granular activated carbon was filled between the anodes and the cathodes, in the shape of a trapezoid (upper base: 0.8 cm, lower base: 1.66 cm, hypotenuse: 6 cm, thickness: 4 mm). The mean grain size of the granular activated carbon is 1.0 mm.

The anodes and cathodes were connected with the positive and negative post adapters of the direct current power supply respectively, with a carbon electric brush. The rotating speed of the disc was controlled by an electromotor (Shanghai Biaozhun Moxing Factory, China).

### 1.4 Electrochemical method

A 0.4-L of sample solution of certain concentration was put into a batch reactor shown in Fig.2 for each experimental run.

## 2 Results and discussion

### 2.1 Operating conditions

#### 2.1.1 Rotating speed

The rotation of the electrochemical disc plays two roles in the reactor. One is to stir the solution and thus enhancing the mass transfer from the bulk solution to the stationary thin liquid film on the electrode surface, speeding up the adsorption and de-sorption of organics on and off the electrode surface. The other role is to form liquid film which guarantees the electrolysis to proceed when part of the disc is exposed to the air, where accelerates the oxygen

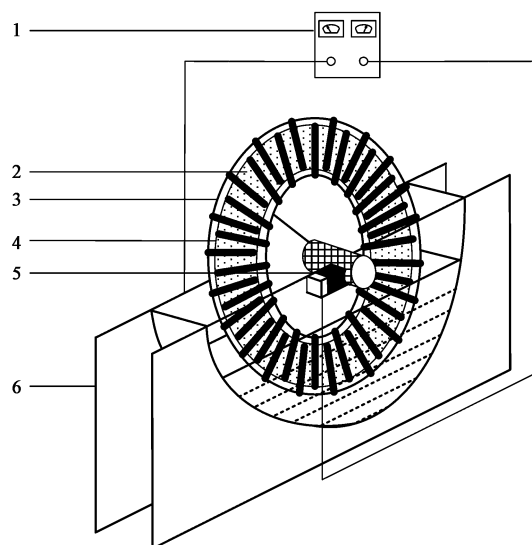


Fig. 2 Experimental apparatus. (1) electrical supply; (2) granular activated carbon; (3) conducting wire; (4) rotating electrochemical disc; (5) carbon brush; (6) electrolytic cell.

exchange between the liquid film and air.

The following equation can be derived from the two film theory and was used to calculate the overall mass transfer coefficient (Yang *et al.*, 2003),  $K_{1,i}a_V$  ( $s^{-1}$ ), for each compound  $i$ :

$$K_{1,i}a_V = K_1a_{O_2} \left( \frac{D_{1,i}}{D_{1,O_2}} \right)^{0.5} \left( 1 + \frac{1}{H_i \left( \frac{k_{g,i}}{k_{l,i}} \right)} \right)^{-1} \quad (1)$$

where,  $K_{1,i}a_V$  ( $s^{-1}$ ), is overall mass transfer coefficient between gas and liquid phase for compound  $i$ ,  $K_1a_{O_2}$  ( $s^{-1}$ ) is determined as shown below,  $D_{1,i}$  ( $cm^2 \cdot s$ ) is liquid diffusivity of compound  $i$ ,  $D_{1,O_2}$  ( $cm^2 \cdot s$ ) is liquid phase diffusion coefficient of oxygen,  $H_i$  is the Henry's law constant of compound  $i$  (dimensionless), and  $k_{g,i}/k_{l,i}$  is the ratio of gas phase mass transfer coefficient to liquid phase mass transfer coefficient for compound  $i$  (dimensionless). The correlation proposed by Alexander and Shah (1976) was used to calculate the overall mass transfer of oxygen,  $K_1a_{O_2}$  ( $s^{-1}$ ) from the gas-phase to the liquid-phase:

$$K_1a_{O_2} = 0.06371 \times (V'_l)^{0.3014} \times (V'_g)^{0.4484} \quad (2)$$

where,  $V'_l$  ( $(kg \cdot m^2)/s$ ) is liquid-phase superficial mass velocity and  $V'_g$  ( $(kg \cdot m^2)/s$ ) is gas-phase superficial mass velocity. From Eqs.(1) and (2), it could be learned that as the rotating speed increases,  $V'_g$  goes up which leads to higher  $K_1a_{O_2}$ , and increases the overall mass transfer coefficient  $K_{1,i}a_V$ . This is confirmed in Fig.3a, that the color removal increases with the rotating speed of the disc.

However, when the rotating speed exceeds 70 r/min, the color removal stays relatively stable. This might be

explained that the thickness of the stationary film on the surface of the electrode could not be decreased by high rotating speed. The mass transfer of organics and oxygen might not be positively affected by the enhanced rotating speed and thus the overall removal does not increase significantly. In addition, the solution will be splashed out of the cell by the electrochemical disc if the rotating speed is too high. Therefore, it is important to keep a suitable rotating speed (70 r/min) during the treatment.

### 2.1.2 Current intensity

Electrolysis current is a critical factor in electrochemical reactor. Once the voltage is set, increasing the current usually removes more organics. Fig.3b shows the relationship between current intensity and dye removal. Color removal increased with current intensity from 0.5 to 1.5 A as expected. However, as the current continued to increase, the color removal did not go significantly high. In general, electricity cost is always a consideration in electrochemical reactor, besides overall removal, proper current intensity should be carefully selected to compromise the cost. In addition, large current could cause a high chance of wasting energy in heating up the water.

### 2.1.3 pH

For this experiment, the current was kept around 1.5 A. The results are presented in Fig.3c. Although the optimum pH for color removal is at neutral pH value or a slightly acid, the reactor is not very sensitive to pH and has surprisingly stable performance within the pH range of 2.25–11.83, which enlightens the possibility of treating real wastewater without adjusting pH.

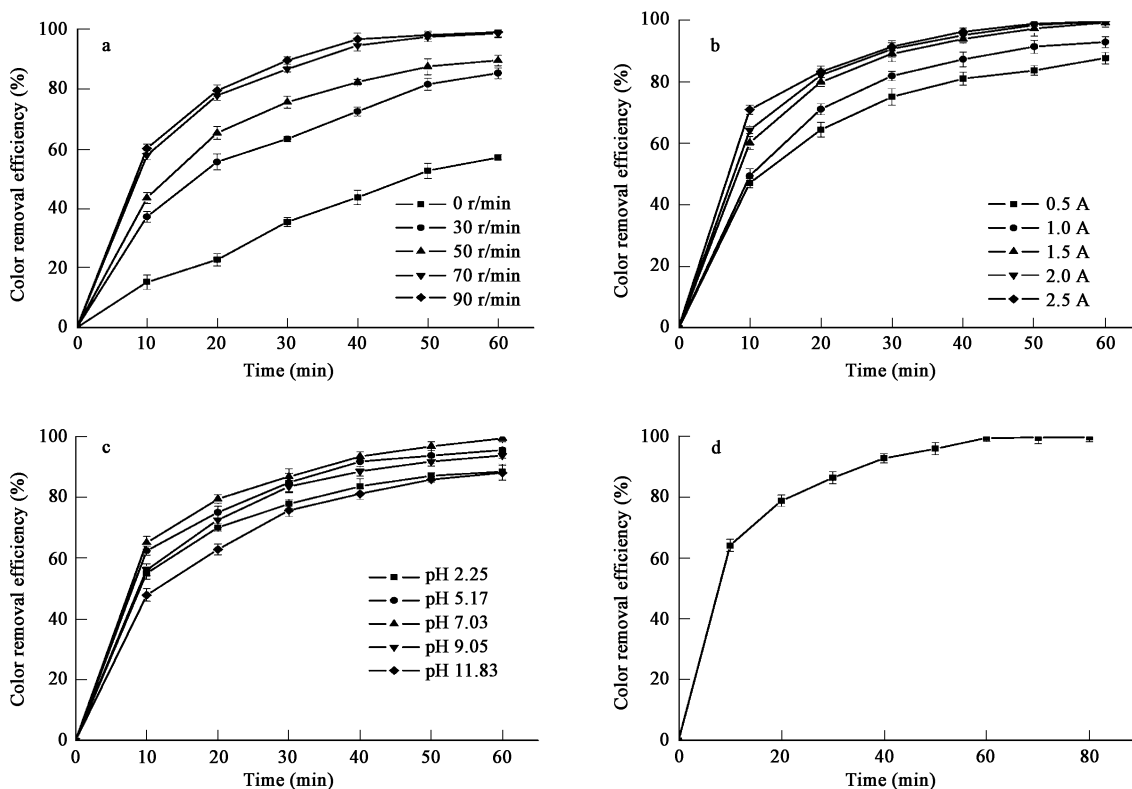


Fig. 3 Effect of electrolysis operating factors on the color removal efficiency. (a) rotating speed; (b) current density; (c) pH; (d) treating time.

### 2.1.4 Treating time

For this experiment, the current was kept around 1.5 A and pH was kept around 7.2. These results show as expected, that the color degree of the solution is being decreased gradually with increasing electrolysis time, whereas total energy consumption increases with time. From Fig.3d, it could be seen that the color removal increase rapidly during the first 20 min, then the slope became flat. It is also noticed that when the treating time is 40 min, the dye removal is already over 95%, which indicates that further electrolysis might not be necessary.

## 2.2 Mechanisms

Usually, the mechanisms of electrochemical treatment process involved in treatment of organic wastewater are electro-floatation, electro-coagulation, and electro-oxidation at the anode (Rajeshwar *et al.*, 1994; Simonsson, 1997). Previous work showed that the mechanism of organics removal from solution using ACF electrodes was proposed as follows: adsorption of dissolved organics on ACF electrode surface → electrochemical aggregation of organics to form large aggregates → de-sorption of the large aggregates from ACF electrodes surface → coagulation of the large aggregates by  $\text{Fe}(\text{OH})_x$  (Barthand Flippen, 1995; Yang *et al.*, 2004). It is believed that electrochemical treatment always involving free radicals and free radical reaction is the key for organics oxidation (Han *et al.*, 1998; Ku *et al.*, 2005; Zimbron and Reardon, 2005). To verify the assumption, the experiments (current 1.5 A; pH 7.2) were performed to determine the existence of free radicals.

The EPR spectroscopy is a technique to detect the presence of unpaired electrons in environmental samples. It has distinct advantages in many applications, especially for the direct measurement of free radicals which hold unpaired electrons (Han *et al.*, 1998). Free radicals play an important role in many physiological and pathophysiological pathways (Bonventre, 1993; Maessen, 1993). However, the detection of organic free radicals is difficult because of their low concentration and exceptionally short half-life. Furthermore, in many practical cases, it is common that more than one kind of free radical are involved in the EPR detection, and hence the detected signal may be composed of a number of overlapping spectra, which gives rise to difficulty in quantitative analysis of the signal (Prisner *et al.*, 2001; Kirste *et al.*, 1992). As free radicals are highly reactive to detect directly, the spin trapping technique has been developed since late 1960s (Chalfont *et al.*, 1968; Janzen and Blackburn, 1968), and has made remarkable contributions to identify various free radicals over decades of development (Ren *et al.*, 2004). The combination of EPR and spin-trapping method is a sensitive and selective technique to detect unstable radicals such as hydroxyl radicals (Han *et al.*, 1998). Radical in water could be trapped with DMPO as a stable radical. For this experiment, the simulated dye wastewater was treated in the RECDP reactor for 10 min, then 5 ml DMPO was added into the solution with stirring. The EPR spectrum was measured for this prepared sample at room temperature and the result is shown in Fig.4. It could be learned that

there is a strong evidence of free radical formation during the electrochemical treatment (Han *et al.*, 1998), which proves that free radicals do exist in this reactor, combined with previous research (Shen *et al.*, 2001; Jia *et al.*, 1999; Yang *et al.*, 2004).

Color removal is of prime importance for the textile industries. The changes in absorbance characteristics of the dye RBO solution were investigated over a large wavelength interval (from 200 to 800 nm) during the electrochemical de-colorization process, and the results are shown in Fig.5. The spectra show that there is a maximum absorbance at 498 nm (which is the characteristic absorption of the RBO) in the visible region. This peak disappears gradually during the electrochemical treatment process. There are also two peaks observed at 265 and 385 nm, respectively, in the UV region which become less intense as the electrolysis progresses. The decrease of absorption peaks of RBO at  $\lambda_{\text{max.}} = 498$  nm indicated a rapid destruction the molecular structure and quick removal of RBO.

Figure 6 shows a typical IR spectrum of dye and/or organic compounds remaining in the solution when color removal was higher than 80% (with the same initial concentrations). The sample was not taken at color removal close to 100% since total mineralization may occur and

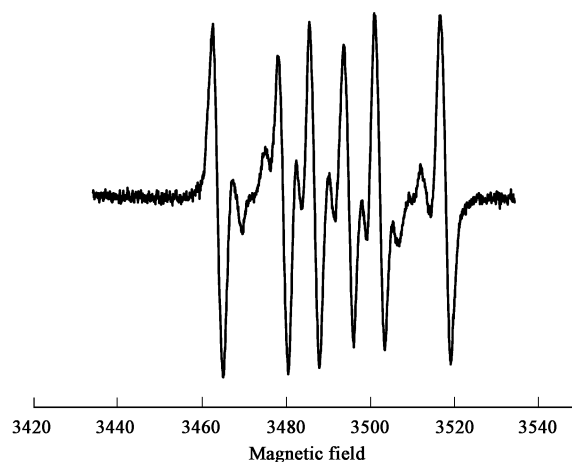


Fig. 4 Electron Paramagnetic Resonance (EPR) spectra of RBO.

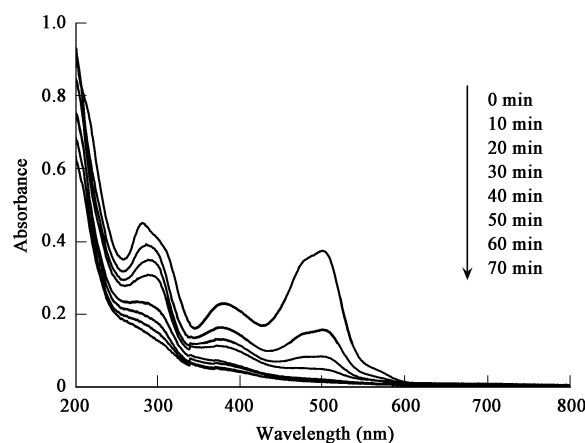


Fig. 5 UV-Vis spectra of RBO.

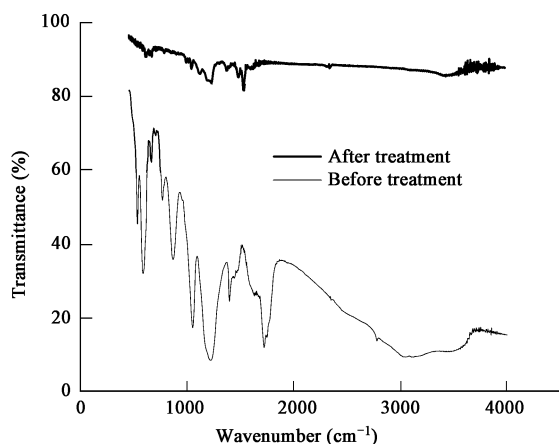


Fig. 6 Typical IR spectrum of RBO and organic compounds remaining in the solution, color removal 80%.

it would be difficult to observe the intermediates. The solution was added with surplus  $\text{BaCl}_2$  to deposit  $\text{SO}_4^{2-}$ , then was condensed and air-dried to constant weight. It can be seen that some structural changes might have occurred during the electrochemical process. It is obvious in Fig.6 that there are peaks at 1359, 1315, and 752  $\text{cm}^{-1}$  emerging while peaks of 1502, 1473, 1277, and 694  $\text{cm}^{-1}$  disappearing. The O–H and C=O stretching vibrations have become broader and larger due to the production of many small molecular acids. The peaks at 1045 and 1186  $\text{cm}^{-1}$  become smaller, which belong to  $\text{R-SO}_3^-$  (Shen *et al.*, 2002, 2005). The peaks at 1359, 1315, and 752  $\text{cm}^{-1}$  are considered as an expression of  $-\text{NO}_2$ , and the peaks at 1502, 1473, 1277, and 694  $\text{cm}^{-1}$  as an expression of naphthyl or  $-\text{N}=\text{N}-$ . Thus it can be concluded that the  $-\text{N}=\text{N}-$  and naphthyl must be attacked by an OH radical or other oxidants to form  $\text{N}^-$  and  $\text{N}^-$  then oxidized to  $-\text{NO}_2$  (Shen *et al.*, 2002, 2005).

### 3 Conclusions

This work developed a new electrochemical method RECDP to increase the mass transfer of organics and oxygen for the reactor. Simulated RBO wastewater was used as an index for treatment results. Based on the experimental results the following conclusions are drawn.

The RECDP can be used to efficiently remove color from simulated dyeing. The efficiency of color removal reached as high as 99.5% after 60-min electrolysis (rotate speed 70 r/min, current intensity 0.15 A, and pH 7.2).

The results of the UV-Vis experiments indicated a rapid decrease of RBO during the treatment. The EPR experiment showed the evidence of the free radical formation. Former work speculated that free radical reaction caused the organics oxidation and combined with previous research. It is proved that free radical reaction plays an important role in organics removal. The IR experiment showed the oxidation of the dye in the RECDP is successfully realized.

The operating conditions of this reactor were also studied. Color removal increases with the rotating speed of the disc with current intensity from 0.5 to 1.5 A. Although the

optimum pH for color removal is at neutral pH value or a slightly acid, the reactor is not very sensitive to pH and has surprisingly stable performance within the pH range of 2.25–11.83. At different treating time, the color removal increase rapidly during the first 20 min, then the slope was not that sharp and became flat after 60 min treatment.

### Acknowledgements

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