Indirect anodic oxidation applied for treatment of simulated wastewater containing Cationic Red X-GRL and Disperse Red 3B
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ABSTRACT
The treatment of simulated wastewater containing Cationic Red X-GRL (X-GRL) or Disperse Red 3B (DR-3B) dye was carried out by indirect anodic oxidation, using Ti/SnO2 electrodes as the anode. The influences of pH value, voltage, electrolysis time and sodium chloride dosage on the degradation performance were studied by single factor experiment. Furthermore the nitrogen states and UV-Vis spectra in dyes degradation were analyzed. The results showed that under the optimum condition ($\text{pH} = 3$, voltage $= 20 \text{ V}$, NaCl $= 2.5 \text{ g/L}$), the decolorization and chemical oxygen demand removal of X-GRL were 98% and 67%, respectively; and those of DR-3B were 51% and 61%, respectively. The azo double bond conjugated system in X-GRL is much more easily destroyed than the anthraquinone conjugated system in DR-3B; the aryl ring structures of them can be partially degraded.

INTRODUCTION
Dyeing wastewater which is a typical refractory wastewater is always derived from the dye application process. It has complex elements and high chemical oxygen demand (COD), while its biochemical oxygen demand is rather lower (Suwanruji & Freeman 2006). The treatment of industrial dyeing wastewater is an urgent problem that should be solved (Nadafi et al. 2011; Silveira et al. 2011). Meanwhile, many treatment methods have been studied, such as the adsorption method (Mare et al. 2007), membrane separation methods (Koyuncu 2002; Ince & Tezcanli 2004; Lopes & Petrus 2005; Jian et al. 2007), and biological treatment (Patel & Gupte 2013). However, with the increasing environmental requirement, the traditional treatment methods for dyeing wastewater such as the biochemical process (Baêta et al. 2012; Murali et al. 2013) hardly meet the emission standard. So it is critical to improve the previous treatment method of wastewater in the dye industry (Panizza et al. 2000a, 2000b).

Electrochemical treatment is a new advanced oxidation technology (Jia et al. 1999; Wang et al. 2012). The electrochemical oxidation process can be divided into two categories, direct oxidation and indirect oxidation methods (Rajkumar & Muthukumar 2012). Kirk et al. (1985) used the method of direct oxidation to deal with aniline dyes, the results showed that the percentage of aniline dyes conversion was 97%, and 72.5% of them converted into CO2. Chang et al. (1995) studied the process of direct oxidation and they found that the pollutant was absorbed on the surface of the anode at first, and then it was removed by transferring of the anodic electron. The research of Correa-Lozano et al. (1996) showed that the higher the current density was, the greatly higher current efficiency and organic oxidation degree were. In Panizza et al. (2000a, 2000b), the authors found that the chlorination in the electrolyte could remove...
organic matter through the indirect process. Dávila-Jiménez et al. (2000) and Vlyssides et al. (1999) used the anode electrolysis to deal with the actual dye wastewater and got a satisfactory treatment effect. In recent years, new ways to deal with dye-containing wastewater have been identified, including new methods (Verma et al. 2012; Abdessamad et al. 2014) and new materials (Ozdes et al. 2014).

The dyes of Direct Dark Brown M (DDB-M) and Reactive Brilliant Blue KNR (RBB-KNR) have been studied thoroughly by our group (Yang et al. 2012), and the result was better than our expectation. In order to study the degradation performance of Cationic Red X-GRL (X-GRL) and Disperse Red 3B (DR-3B) by indirect anodic oxidation with Ti/SnO2 as the anode, we have discussed the influences of factors, nitrogen states and UV-Vis spectra.

**EXPERIMENTAL**

**Reactor**

The experimental facility of this study is the same as our previous research (Yang et al. 2012). A 250 mL beaker was used for the container, and the cathode and anode were graphite and Ti-SnO2, respectively, and the distance between those electrodes was 3 cm. The superficial areas of the two electrodes both were 20 square centimetres (cm²), and their length and width were 10 centimetres and 2 centimetres, respectively. The length of the electrodes that were immersed below the liquid level was 6 centimetres, and the effective area of the electrode was 24 cm² (both sides). The electrolyte used in the reactor was a sodium chloride system.

**Reagents**

X-GRL and DR-3B were obtained from a company. All other reagents were of analytical grade and used without any purification.

**Analytical procedure**

The treatment effect of the dye-containing wastewater was measured by the indicators of the percentage of decolorization and COD removal. The decolorization effect of the dyes solutions was determined by the drop of their absorbance at the maximum visible wavelength ($\lambda_{\text{max}}$). The percentage of decolorization ($\eta_{\text{color}}$) was calculated by Equation (1) (Brillas & Martínez-Huitle 2015):

$$\eta_{\text{color}}(\%) = \frac{A_0 - A_t}{A_0} \times 100$$

where $A_0$ and $A_t$ are the absorbance values at $\lambda_{\text{max}}$ before treatment and after a treatment time $t$, respectively.

The COD was tested in accordance with the international standard method (ISO 6060:1989), and the percentage of COD removal ($\eta_{\text{COD}}$) was calculated by Equation (2):

$$\eta_{\text{COD}}(\%) = \frac{COD_0 - COD_t}{COD_0} \times 100$$

where $COD_0$ and $COD_t$ are the experimental values measured by the above method before treatment and after treatment time $t$, respectively.

All the indicators of the nitrite nitrogen, nitrate nitrogen, ammonia nitrogen and the total nitrogen were measured by the standard International Organization for Standardization (ISO) methods (ISO 5665:1984; ISO 6777 1984; ISO 7150-1 1984; ISO 7890-3 1988).

**RESULTS AND DISCUSSION**

**Effects of operating parameters**

**Effect of initial pH**

The pH of the solution can influence the charged state of small molecular pollutants in wastewater, so pH is one of the important factors affecting organics degradation. In this study, the decolorization and COD removal were studied with different pH values under certain conditions (electrolysis time of 60 min, applied cell voltage of 20 V and sodium chloride (NaCl) concentration of 2.5 g/L), and the results are shown in Figure 1.

As can be seen from Figure 1, the decolorization and COD removal of X-GRL and DR-3B were both reduced with initial pH values ranging from 1 to 9. The decolorization effect of X-GRL was significantly better than DR-3B, since the electro-reduction of azo groups of X-GRL is an irreversible one-step and four-electrons reduction in acid media.
With the electrolysis of NaCl solution, the active chlorine such as chlorine (Cl₂), hypochloric acid (HClO), and hypochlorite (ClO⁻/Cl⁻) was formed (shown as Equation (3) to Equation (5)). The adsorption of chloride ions is related to the acidity, and it also determines the efficiency of dye degradation.

\[ 2Cl^- \rightarrow Cl_2 + 2e^- \]  
\[ Cl_2 + H_2O \rightarrow HClO + HCl \]  
\[ HClO \rightleftharpoons H^+ + ClO^- \]  

Increasing hydrogen concentration is beneficial to the generation of HClO as shown in Equation (5). The oxidizability of HClO is stronger than ClO⁻, so the pH values have a significant effect on the degradation of dyes.

The acidic reaction condition was the optimal as shown in Figure 1, and the optimum pH condition was identified as 3 after considering the cost.

**Effect of voltage**

To test the effect of voltage on the oxidation of dyes, experiments were conducted at voltages from 5 to 25 V. The decolorization and COD removal under different voltages are shown as Figure 2(a) and 2(b), respectively.

The increase of voltage is beneficial for decolorization and COD removal as shown in Figure 2. When the voltage reached 20 V, the decolorization of X-GRL came to an ideal effect while that of DR-3B was only about 50%; the COD removal of X-GRL and DR-3B reached above 60%.

With the increase of voltage, the electrochemical reaction was accelerated and the concentration of active chlorine increased, which can improve the decolorization and COD removal of dyes. The hydrogen generated by electrolytic reaction attacked chromogenic azo bonds in X-GRL at first, and the intermediates were generated. Then, the triazole heterocyclic was degraded to small molecules, and the N-methylbenzylamine as intermediates decomposed into...
benzyl alcohol and methylamine. The hydrogen increased with increasing voltage, and the reactions were accelerated, thus X-GRL was decolorized significantly. The decolorization efficiency of DR-3B is relatively lower, since DR-3B exists in low solubility and has a stable chromophore structure. When the voltage reached about 17.5 V, the ring structure of X-GRL began to be broken, and then was degraded, the COD removal was significantly increased; the condensed ring anthraquinone structure of DR-3B is difficult to degrade, therefore the COD removal increased slowly.

However, as the voltage rises, the reaction cost increases; in addition, the side effects aggravate. After taking into account both the energy consumption and the electrode life, we selected 20 V as the optimum reaction voltage.

Effect of electrolysis time

The decolorization and COD removal were measured for the time from 2 to 100 min, to study the influence of reaction time on the degradation of dyes. The results are shown in Figure 3.

As time went on, the oxidative electricity increased and the degradation of dyes improved significantly (shown in Figure 3). The decolorization of X-GRL was better than DR-3B, while the COD removals of those two dyes were almost the same.

The COD removal of dyes had obviously improved within 60 min; the decolorization of X-GRL was close to the maximum at 30 min and that of DR-3B continuously increased within 100 min. Since some intermediate product of DR-3B appears a darker color, the DR-3B decolorized slower than the X-GRL.

The decolorization improves with time since oxidative electricity increases. However, the degradation of dyes improves slowly after 60 min, so we defined the best electrolytic time was 60 min.

Effect of sodium chloride

In order to study the influence of NaCl on the degradation of dyes, different quantities of NaCl were added to several reactive systems. The NaCl initial concentration was from 1.0 to 3.5 g/L. The decolorization and COD removal of dyes changed with NaCl dosage, as shown in Figure 4.

As is shown in Figure 4, NaCl dosage has more effect on the COD removal than decolorization. Both the decolorization and COD removal improved significantly when NaCl dosage was increased. Besides, the X-GRL had much a better decolorization effect than DR-3B.

NaCl has a significant influence on the degradation of dyes, since it generates active chlorine, such as ClO\(^{-}\). Active chlorine makes the homogeneous reactions occur in the reaction system and results in dye decolorization.

The formation of reactive chlorine and its catalytic reaction are shown as Equations (3), (4) and (6).

\[
\text{Dye} + \text{HClO} (\text{Cl}_2, \text{ClO}^-) \rightarrow \text{Intermediate Product} + \text{Cl}^-
\]  

(6)

After the NaCl concentration reached 2.5 g/L, the decolorization and COD removal were not obviously improved with further increase of NaCl. Therefore, the optimal concentration of NaCl is 2.5 g/L.

Under optimum conditions, the decolorization of X-GRL came up to 98% while that of DR-3B was only 51%; meanwhile, the COD removal of X-GRL and DR-3B were 67% and 61%, respectively. The degradation effects
of X-GRL were considerably better than that of most research reported in the literature. Li et al. (2016) studied the degradation of X-GRL by electrochemical oxidation on a PbO₂ anode modified by Ce, the results showed that the decolorization and total organic carbon (TOC) removal of X-GRL reached 93.45% and 48.23%, respectively. Zhou & He (2008) used a modified PbO₂ electrode for degradation of X-GRL by the electrochemical oxidation method, and the decolorization and COD removal were 63.6 and 21.6%.

**Degradation law analysis**

In order to study the degradation law of the two dyes (X-GRL, DR-3B), the changes of various state nitrogen content and UV-Vis spectrum over time were analyzed under the optimal conditions.

**Nitrogen states analysis**

Under the optimal condition, the concentrations of total nitrogen, nitrite nitrogen, nitrate nitrogen and ammonia nitrogen in the dye solution were measured for the time from 2 to 60 min, the result is shown as Figure 5.

As is shown in Figure 5, the total nitrogen content in the solution reduced rapidly and the ammonia nitrogen content increased at the initial stage. Most nitrogen existed in the solution as ammonia nitrogen. Then, the ammonia nitrogen content decreased gradually, while the total content of nitrite nitrogen and nitrate nitrogen increased gradually. Finally, there was a small amount of ammonia nitrogen and nitrite nitrogen in the solution.

As the electrolysis started, the active substances began to react with X-GRL, the azo bond of the molecules was broken and nitrogen gas was released. At the acidic condition, the nitrogen atom that connected with methylene can be converted into ammonia nitrogen. Some of that is oxidized by active chlorine to nitrite and nitrate nitrogen; the others are converted to nitrogen gas. Meanwhile, triazole groups react with active chlorine and evolve as nitrogen gas.

For anthraquinone dye, the alpha amino groups are converted to ammonia at first. Then almost all of the ammonia...
nitrogen is oxidized to nitrate nitrogen. As the solubility of DR-3B is low and the concentration of active chlorine is relatively high, nearly all the nitrite nitrogen is oxidized to nitrate nitrogen.

UV-Vis spectrum analysis

In order to investigate the electrolytic process of dyes, the UV-Vis spectrum was analyzed. The changes of UV-Vis absorption spectra for the electrolytic solution of dyes at different times were observed, shown as Figure 6.

From Figure 6(a), we can speculate that the absorption peak of the conjugated system formed by the azo double bond of X-GRL is located in the visible region at 512 nm, and the benzene has a characteristic absorption peak in the ultraviolet region at 288 nm.

At 2 min, the absorption peak in visible light significantly decreased, due to the azo double bond conjugated systems, as the chromophore in X-GRL dye molecules, decomposing. After 60 min, the absorption peaks in visible light were weakened remarkably, which represents the azo double bond being almost broken; the absorbance in the ultraviolet region also declined obviously, that indicates the phenyl ring structure was partly degraded. After 100 min, there was no obvious absorption peak, which indicates that most X-GRL was degraded.

According to the above analysis, we can infer that the unsaturated azo double bond is first destroyed, which results in the initial red color fading. The phenyl ring structure is increasingly degraded as the reaction continues.

As can be seen in Figure 6(b), three absorption peaks of DR-3B are located, in the visible region at 590 nm and 540 nm, and the ultraviolet region at 282 nm, respectively. The absorption peaks at 590 and 540 nm represent chromophoric groups in the conjugated system of anthraquinone dye. According to the spectral theory, the absorption peak at 282 nm is a result of the phenyl structure.

At 2 min, the absorption peak in visible light decreased, this indicates that the anthraquinone conjugated system in DR-3B dye molecules was destroyed and the anthraquinone was partly degraded. After 100 min, absorption peaks both in the ultraviolet region and visible region still existed, which indicates DR-3B was degraded partly and the aryl ring of DR-3B was not degraded thoroughly.

Based on the above, we can speculate that the anthraquinone conjugated system was destroyed and the color faded. The anthraquinone structure can be partially degraded and is present in some intermediate products and inorganic salts.

Comparison of four dyes

As we can see, the optimum conditions of DDB-M and RBB-KNR are the same as X-GRL and DR-3B. The degradation effects for these four dyes are summarized in Table 1.

As shown in Table 1, the percentage of decolorization for DR-3B is the lowest, and that of others is rather high. DR-3B exists as the nonionic state which has low solubility, so it is difficult to react with the active chlorine. The ether bond of the beta site, at the junction of the aryl group in DR-3B, is broken.

The alpha amino group was substituted by the free radical, and that created a new darker color. So the decolorization efficiency of DR-3B is rather low. In addition, the chromophoric group of DR-3B is the anthraquinone ring
which is difficult to degrade. So its COD removal is low, especially much lower than that of RBB-KNR.

**CONCLUSION**

The effect of the indirect electrolytic method for X-GRL degradation is ideal. Under optimal conditions (pH of 3, electrolysis time of 60 min, applied cell voltage of 20 V and sodium chloride concentration of 2.5 g/L), the decolorization and COD removal of X-GRL are 98% and 67%, respectively, while the degradation effect of DR-3B is not satisfied. Under the same conditions, the decolorization and COD removal of DR-3B are 51% and 61%, respectively.

During the degradation of the dyes, the nitrogen states and UV-Vis spectra were analyzed. In the electrolysis process, the azo double bond conjugated system of X-GRL is destroyed rapidly and nitrogen-containing intermediates or nitrogen gas are released. Then, intermediates are oxidized to ammonia, nitrite, nitrate, and nitrogen gas. Meanwhile, the azo double bond conjugated system is almost broken and the phenyl ring structure of the X-GRL is partly degraded. For DR-3B dyes, the conjugated systems of DR-3B are broken and the alpha amino groups are converted to ammonia at first. Ammonia is oxidized to nitrate gradually, and a small amount of nitrite nitrogen exists in the solution; some other structures are destroyed. Hence, eventually the DR-3B is partly degraded.

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**REFERENCES**

Comparative anodic oxidation on boron-doped diamond electrode of two different dyes: separately and mixed. *Desalination and Water Treatment* 52 (7–9), 1735–1744.


Brillas, E. & Martínez-Huitle, C. A. 2015
Decontamination of wastewaters containing synthetic organic dyes by...


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