Improved electrochemical oxidative degradation of Reactive Red 24 dye by BDD anodes coupled with nitrate: operating parameters, kinetics, and degradation pathways

Yining Tang

Hunan University

Deliang He (✉ lab223@163.com)

Hunan University <https://orcid.org/0000-0001-6928-0686>

Yanni Guo

Hunan University

Jun Shang

Hunan University

Lei Zhou

Hunan University

Rong Pan

Hunan University

Wei Dong

Hunan University

Mengli Liu

Hunan University

Research Article

Keywords: EAOP, EO, Nitrate, Azo dye wastewater, RR24, BDD electrode

Posted Date: July 29th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-761055/v1>

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Improved electrochemical oxidative degradation of Reactive Red 24 dye by BDD anodes coupled with nitrate: operating parameters, kinetics, and degradation pathways

Abstract: The electrochemical oxidation (EO) process coupled with BDD anode and nitrate was used to improve Reactive Red 24 (RR24) removal efficiency in wastewater treatment. The effects of operating parameters on the decolorization efficiency of RR24 were discussed, and the optimal operating parameters were obtained as follows: 45 mA cm⁻², 100 mM SO₄²⁻, 7 mM NO₃⁻, 60°C, pH 5.88, and 100 mg L⁻¹ RR24 initial concentration. The energy consumption for 100% decolorization within 15 min is 0.92 kWh m⁻³, and the total organic carbon (TOC) reaches 51.35% within 90 min. Through the effect of quenchers on RR24 decolorization efficiency, various active species in the EO process were studied. It was found that •OH was closely related to the decolorization degradation of RR24, reaching a contribution rate of 99.47%. Finally, we propose the degradation pathways of RR24 by UV-Vis spectrum and LC-MS test. In summary, the proposed treatment process could be applied to treat RR24 dyes as an efficient method.

Keywords: EAOP; EO; Nitrate; Azo dye wastewater; RR24; BDD electrode.

1 Introduction

There are many kinds of dyes, allowing for a colorful world in people's lives and producing huge economic benefits. At the same time, a large amount of dye wastewater is discharged into the environmental water, reducing the transparency and oxygen content of the water body and affecting the growth of aquatic organisms and microorganisms. Azo dyes are primary used in the printing and dyeing industries, accounting for more than 70% of the dyes. Azo dyes are aromatic compounds containing azo groups (- N = N -). Some dyes and their

degradation products are toxic and threaten human and animal health (Nidheesh et al., 2018). As a typical azo dye, Reactive Red 24 (RR24) is widely used in the printing and dyeing industries because of its strong chromaticity stability and easy production. Unfortunately, RR24 is difficult to degrade, remains in the water for a long time, and has a greater hidden danger of environmental pollution (Brillas and Martinez-Huitle, 2015). Therefore, an environmentally friendly way for RR24 treatment is necessary.

In recent years, traditional physicochemical and biological treatment methods have been adopted in dye wastewater treatment. However, these technologies have some unavoidable disadvantages (Brillas and Martinez-Huitle, 2015). For example, physical adsorption produces a lot of sludge, which brings secondary pollution; although biodegradation has good prospects, the degradation of macromolecules is more complex, the retention time is extended, and the decolorization efficiency is low (Moussa et al., 2017). Thus, the electrochemical advanced oxidation process (EAOP) can be used as an auxiliary or alternative to traditional methods due to its many advantages (Wu et al., 2012). EAOP can oxidize organic pollutants directly by electron transfer and indirectly oxidize organic pollutants on the anode surface by electrochemical active substances (such as $\bullet\text{OH}$) and improves oxidation efficiency (Florenza et al., 2014; He et al., 2015). Therefore, a suitable anode material in the EAOP is critical.

Among the currently known materials, boron-doped diamond (BDD) film is an ideal material for indirect electrochemical oxidation of organic pollutants (Beck et al., 2000; Gandini et al., 2000; Panizza and Cerisola, 2005; Siedlecka et al., 2018). This is because the BDD electrode has incomparable advantages over other electrodes (graphite, Pt, and DSA), such as wide electrochemical window, corrosion resistance, low adsorption, and it can produce a large number of $\bullet\text{OH}$ that indirectly oxidate azo dyes instead of releasing oxygen (reactions (1)-(3)) (Wang et al., 2000; Panakoulis et al., 2010; Wachter et al., 2015; Soni et al., 2017). Previous research has shown that the BDD electrode's influence on the $\bullet\text{OH}$ of an electrocatalytic system depends on the operating

parameters, such as current density, supporting electrolyte and concentration, solution pH, temperature, and pollutant concentration (Kuchtova et al., 2020). However, to improve the degradation efficiency of single electrochemical oxidation (EO), high current density and extended electrolysis time are usually adopted, which limiting its promotion and application in the industry, as shown in Table 1.

Table 1 Examples on the EO degradation treatment of organic wastewater by BDD electrodes

Pollutants	Anodes	Operational parameters	Color removal (%)	Energy Consumption	Ref.
Acid Violet 7 dye	Nb/BDD	j_{app} : 60 mA cm ⁻² C_0 : 200 mg L ⁻¹ C_e : 0.05 M Na ₂ SO ₄ V: 1 L t: 1.5 h	100	12.85 kW ₃ h kg ⁻¹ m ⁻³	(Brito et al., 2018)
Orange II	Si/BDD	j_{app} : 100 mA cm ⁻² C_0 : 100 ppm C_e : 0.1 M Na ₂ SO ₄ V: 1 L t: 3 h	72.3	—	(Luo et al., 2018)
Reactive Blue 19 dye	Nb/BDD	j_{app} : 41 mA cm ⁻² C_0 : 100 mg L ⁻¹ C_e : 0.04 M Na ₂ SO ₄ pH: 5 t: 2 h	52.7	—	(Li et al., 2020)
diazo dye	BDD	j_{app} : 20 mA cm ⁻² C_0 : 180 mg L ⁻¹ C_e : 0.05 M Na ₂ SO ₄ pH: 3 V: 0.5 L t: 1 h	80	>0.065 kWh (g COD) ⁻¹	(Medrano-Rodríguez et al., 2020)
Brown HT treatment	BDD	j_{app} : 71 mA cm ⁻² C_0 : 80 mg L ⁻¹ C_e : 0.05 M Na ₂ SO ₄ pH: 3 V: 0.16 L t: 1 h	100	2.25 kWh (g COD) ⁻¹	(Corona-Bautista et al., 2021)

Recently, some researchers have adopted a combined oxidation technology to overcome the shortcomings of the single EO method. (He et al., 2019; Vasconcelos et al., 2019). However, ozone and PDS directly impact human health, and hydrogen peroxide's transportation and storage costs are high. It is necessary to find an efficient and environmentally friendly combined oxidation technology to degrade dye wastewater. NO₃⁻ has attracted our attention because it is an oxidative oxyacid salt with specific oxidizing properties, and NO₃[•] can also react with ionic compounds to form secondary free radicals, such as SO₄^{•-} (Umschlag et al., 2002; Wang

and Qu, 2006). Moreover, there is still no work on adding NO_3^- as a catalyst to the SO_4^{2-} solution for EO synergistic treatment to improve the degradation effect of simulated wastewater RR24. Therefore, NO_3^- was considered adding to the EO system.

In this study, NO_3^- was added an EO- SO_4^{2-} system with Ti/BDD as the anode to improve the electrochemical decolorization and mineralization of simulated wastewater RR24. To obtain the best operating parameters, the effect of operating parameters on the decolorization efficiency of RR24 is discussed. Furthermore, the influence and contribution of active substances are discussed through free radical scavenging experiments. Finally, to propose the possible degradation mechanism and route of RR24, the degradation intermediates of RR24 were identified by high-performance liquid chromatography-mass spectrometry (LC-MS). We hope the proposed treatment process could be used to treat RR24 dyes as an efficient method.

2 Materials and methods

2.1 Materials and chemicals

RR24 (molecular formula $\text{C}_{26}\text{H}_{17}\text{ClN}_7\text{Na}_3\text{O}_{10}\text{S}_3$, more information is listed in Table SM-1), Potassium ferricyanide ($\text{K}_3[\text{Fe}(\text{CN})_6]$), Sodium persulfate (PS), Methanol (MeOH), Phenol, and Tert-butanol (TBA), Coumarin, 7-hydroxycoumarin (7OHC), sodium perchlorate (NaClO_4), sulfuric acid (H_2SO_4) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd., Anhydrous sodium sulfate (Na_2SO_4), potassium chloride (KCl), sodium nitrate (NaNO_3), and sodium hydroxide (NaOH) were purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd. All water is ultra-pure water ($<0.1 \mu\text{S/cm}$), and all above reagents are

analytical grade. The Ti/BDD electrode was purchased from Dual Frontier Co-creation Science & Technology Co., Ltd.

2.2 Experiment setup and operation steps

The electrochemical degradation RR24 simulated wastewater experimental device uses a 150 mL beaker as an electrolytic cell, with Pt as the cathode and Ti/BDD as the anode. DC stabilized power supply (WLS-05, Sangli, China) controlled the current density. A magnetic stirrer controlled the stirring speed. The electrode area is 2 cm², and the distance between the electrodes is 2 cm. It adopts intermittent measurement and uses NaOH and H₂SO₄ to adjust the pH (pH-3C, Shanghai, China).

Cyclic voltammetry (CV) test used an electrochemical workstation (CHI660E, Shanghai, China) with a three-electrode system (Ti/BDD as a working electrode, saturated calomel electrode (SCE) as the reference electrode, and Pt served as a counter electrode).

2.3 Experimental analysis method

The concentration of RR24 was obtained by UV-Vis spectrophotometer (Shimadzu UV-2600, Japan) (Text SM-1, Fig. SM-1).

The color removal is calculated via the following Eq. (4) (Miao et al., 2020):

$$\text{Color removal} = \frac{A_0 - A_t}{A_0} \times 100\% \quad (4)$$

where A_0 and A_t are the absorbances at time 0 and t respectively.

The free radical quencher MeOH, TBA, and phenol were added to RR24 simulated wastewater to study free radicals' influence and contribution rate.

The energy consumption in the degradation process of RR24 is estimated by following Eq. (5) (Uranga-

Flores et al., 2015):

$$E_c = \frac{U I t}{1000V} \quad (5)$$

where U is mean voltage (V) during the electrolysis; I is current (A); t represents the electrolysis time (h); V represents the volume of wastewater being treated (m^3).

Whether the electrochemical degradation process of RR24 satisfies the pseudo-first-order kinetics can be judged by Eq. (6) (Palma-Goyes et al., 2010):

$$\ln(A_0 / A_t) = k \times t \quad (6)$$

where A_0 and A_t are the absorbances at time 0 and t respectively, and k represents the apparent rate constant.

The concentration of $\bullet OH$ in the $EO-NO_3^-/SO_4^{2-}$ the system is evaluated using coumarin as a fluorescent probe (Lout et al., 2005). The $\bullet OH$ can react with coumarin in a ratio of 1:1 to form highly fluorescent 7-hydroxycoumarin (7OHC). A fluorescence spectrophotometer (F-7000, China) was used to obtain a standard curve of the concentration and fluorescence intensity of 7OHC, at an emission wavelength of 456 nm and an excitation wavelength of 346 nm (Xiang et al., 2011). Then take samples at the same time interval to detect the fluorescence intensity of 7OHC, and finally calculate the concentration of $\bullet OH$.

The intermediate products of RR24 were obtained by LC-MS (Agilent 1290 UPLC/6550 Q-TOF, USA) (Li et al., 2019). A Waters C18 column (2.1 mm $\times$ 50 mm) was applied to LC analysis. The sample injection volume is 20 μ L through the auto-sampler. Gradient elution was carried out with 0.1% formic acid aqueous solution and MA solution at a flow rate of 0.3 mL min⁻¹. The mass spectrometer was operated in electrospray positive ionization mode (4000V). The scanning range of the mass spectrometer was the first level, 50-1000m/z.

3 Results and discussion

3.1 Morphology and electrochemical properties of the BDD anode

Fig. 1. SEM image of the BDD (a, b); CV curves of the BDD electrode at different scan rate (v) (c), the

relationship curve between I_p and $v^{1/2}$, in 0.5 M KCl +4 mM $K_4Fe(CN)_6$ solution (d); The CV curves of the BDD in RR24 simulated wastewater at 150 mv s⁻¹, the oxidation peak of RR24 (e); Variation curve of $\bullet OH$ concentration on the surface of the BDD electrode with electrolysis time (f), conditions: ([COU] = 1 mM; j = 20 mA cm⁻²; [NaNO₃] = 7 Mm; [Na₂SO₄] = 100 mM; 20 °C).

Fig. 1a and 1b show that the BDD film's crystal shape is large and clear, and the crystal morphology is relatively complete. In other words, BDD film is of good quality. We knew that the BDD electrode has excellent physical properties and excellent electrochemical properties. As the scan rate (v) increases, the oxidation peak current (I_p) increases, and there is a good linear relationship between $v^{1/2}$ and I_p (Fig. 1c, and 1d), which means the diffusion process is the control step of the EO reaction. Moreover, the electrochemical window is an important indicator to measure the electrocatalytic performance of electrode material. As Fig. 1e shown that the electrochemical window of the Ti/BDD electrode is 3.50 V, which is much larger than that of Pt or DSA electrode (El-Ghenymy et al., 2015; He et al., 2015; Soni et al., 2017). The prominent oxidation peak of RR24 near 1.34V of the CV curve proves an electron transfer reaction in the electrocatalytic process of RR24 on the BDD surface. This is evidence of the direct electrochemical oxidation of RR24. Moreover, the BDD electrode's high catalytic activity positively correlates with the $\bullet OH$ produced on the surface (Panizza et al., 2001; Panizza and Cerisola, 2005). As shown in Fig.1f, the generation rate of $\bullet OH$ is 1.05275 $\mu M \text{ min}^{-1}$, indicating that the BDD electrode represents a high electrocatalytic oxidation performance for RR24 (Tang et al., 2020).

3.2 Determination of degradation system

Fig. 2 The relationship curve between RR24 decolorization rate and time under different degradation system

(a); Function principle of the EO-NO₃⁻/SO₄²⁻ system (b), conditions: ([RR24] = 50 mg L⁻¹; V=50 mL; j = 50

mA cm⁻²; [Na₂SO₄] = 50 mM; [PS] = 5 mM; [NaClO₄] = 50 mM [NaNO₃] = 50 mM, as supporting electrolyte;

[NaNO₃] = 5 mM, adding to other supporting electrolyte; 20°C)

A supporting electrolyte is added to the electrochemical degradation system to transfer electrons; generally,

one of sulfate (SO_4^{2-}), nitrate (NO_3^-), and chloride (with side effects, generally not used) are used as the supporting electrolyte (Uranga-Flores et al., 2015). Fig. 2 shows that the decolorization effect of RR24 is different from the electrolysis system of different supporting electrolytes. At 30 min, the decolorization efficiency from low to high list as follows: EO-NO_3^- (37.33%) < EO-SO_4^{2-} (66.73%) < $\text{EO-NO}_3^-/\text{ClO}_4^-$ (73.76%) < $\text{EO-NO}_3^-/\text{SO}_4^{2-}$ (100%), among which $\text{EO-NO}_3^-/\text{SO}_4^{2-}$ decolorization efficiency is the most significant, so $\text{EO-NO}_3^-/\text{SO}_4^{2-}$ system was used to degrade RR24. It is shown that NO_3^- plays a catalytic role, greatly improving the production rate of $\cdot\text{OH}$ radicals, thereby accelerating the degradation and decolorization of RR24 (Garcia-Segura et al., 2018). Furthermore, the related chain reaction of NO_3^- and SO_4^{2-} can produce more $\cdot\text{OH}$, reactions (7)-(8) (Buck et al., 2018). As shown in Fig. 2b, it can well explain the functional principle that $\text{EO-NO}_3^-/\text{SO}_4^{2-}$ system can efficiently degrade RR24 simulated dyes.

3.3 The effect of operating parameters

3.3.1 The effect of current density

Fig. 3 Effect of current density on decolorization rate (a), conditions: ($[\text{RR24}] = 50 \text{ mg L}^{-1}$; $[\text{Na}_2\text{SO}_4] = 50 \text{ mM}$; $[\text{NaNO}_3] = 5 \text{ mM}$; original pH; 20°C); Effect of SO_4^{2-} concentration on decolorization rate (b), conditions: ($[\text{RR24}] = 50 \text{ mg L}^{-1}$; $j = 45 \text{ mA cm}^{-2}$; $[\text{NaNO}_3] = 5 \text{ mM}$; original pH; 20°C); Effect of NO_3^- concentrations on decolorization rate (c); conditions: ($[\text{RR24}] = 50 \text{ mg L}^{-1}$; $j = 45 \text{ mA cm}^{-2}$; $[\text{Na}_2\text{SO}_4] = 100 \text{ mM}$; original pH; 20°C)

As shown in Fig. 3a, the current density has a profound impact on the degradation of RR24. At 15 min, under the current density of 30, 40, 45, and 50 mA cm^{-2} , the decolorization rates of RR24 were 54.36%, 79.20%, 93.49%, and 98.43%, respectively, achieving good decolorization in a relatively short time. At 45 and 50 mA cm^{-2} , the RR24 decolorization rate improves significantly, reaching almost 100% at 25 min. In the electrolysis

process, $\ln(A_0/A_t) - t$ accords with the pseudo-first-order kinetic relationship, and the apparent kinetic constants k are 0.064 min^{-1} , 0.12 min^{-1} , 0.22 min^{-1} , 0.36 min^{-1} (R^2 , 0.96), respectively, which means the decolorization rate of RR24 is mainly controlled by current density. A high current density accelerates the electron transport rate; therefore, the direct oxidation rate will be accelerated. (He et al., 2015). At the same time, the $\bullet\text{OH}$ concentration will continue to increase, speeding up the oxidation of organic matter, which accelerates the breaking of $-\text{N}=\text{N}-$ in RR24 molecular, leading to decolorization. The current efficiency decreases as the current increases. A lower current density is more conducive to reducing energy consumption and increasing current efficiency and the degradation time. In terms of energy consumption, 45 mA cm^{-2} is appropriate.

3.3.2 The effect of SO_4^{2-} concentration

The addition of supporting electrolytes can significantly change the electrochemical reaction process and increase the degradation efficiency. As Fig. 3b shown that the decolorization rate of RR 24 in the electrochemical system when the SO_4^{2-} concentration is 25, 50, 75, 100 mM at 15 min is 83.15%, 94.77%, 97.61%, 98.76%, respectively. As the SO_4^{2-} concentration increases, the decolorization rate of RR 24 has been greatly improved. This is because the increase in SO_4^{2-} concentration increases the conductivity of the solution; that is to say, it promotes the transfer rate of electrons in the electrolyte, which is beneficial to greatly increase the generation rate of $\bullet\text{OH}$ (Li et al., 2020; Santos et al., 2020). Moreover, under the same current density, the increase in conductivity reduces the cell pressure, thereby reducing energy consumption. Considering comprehensively, the SO_4^{2-} concentration is selected as 100 mM.

3.3.3 The effect of NO_3^- concentration

The addition of NO_3^- has a significant effect on the decolorization rate of RR24 (Fig. 3c). The

decolorization rate of RR24 increased with the increase of NO_3^- concentration, and the effect of 7mM and 9mM was similar. At 20 min, the corresponding decolorization rates of 1, 3, 5, 7, 9 mM are 28.46%, 86.87%, 96.44%, 99.00%, and 99.96%, respectively. The addition of a small amount of NO_3^- can greatly improve the decolorization efficiency of the EO process. Moreover, $\ln(A_0/A_t) - t$ accords with the pseudo-first-order kinetic relationship in the electrolysis process. The ratio of the apparent kinetic constant is about 1:4:5:8:8 when NO_3^- concentration is 1, 3, 5, 7, 9 mM. It shows that NO_3^- can enhance $\bullet\text{OH}$ generation rate, thereby increasing the apparent kinetic constant of decolorization during the degradation process (Li et al., 2019; Ding et al., 2020). Therefore, NO_3^- concentration is 7mM.

3.3.4 The effect of different temperatures

Fig. 4 Effect of temperatures on color removal rate (a), conditions: ([RR24] = 50 mg L⁻¹; j = 45 mA cm⁻²;

[Na₂SO₄] = 100 mM; [NaNO₃] = 7 mM; original pH); Effect of initial pH on color removal rate (b),

conditions: ([RR24] = 100 mg L⁻¹; j = 45 mA cm⁻²; [Na₂SO₄] = 100 mM; [NaNO₃] = 7 mM; 20°C); Effect of

initial concentrations of RR24 on color removal rate (c), conditions: (j = 45 mA cm⁻²; [Na₂SO₄] = 100 mM;

[NaNO₃] = 7 mM; original pH; 20°C); The color removal and TOC removal of RR24 varies with degradation

time under optimal operating parameters (d), conditions: ([RR24] = 100 mg L⁻¹; j = 45 mA cm⁻²; [Na₂SO₄] =

100 mM; [NaNO₃] = 7 mM; original pH; 60°C).

Fig. 4a shows that the color removal rate of RR24 is 22.87%, 41.68%, 72.45%, and 79.67% under the conditions of 20, 30, 40, and 60°C at 2.5 min. In other words, the temperature has a large influence on the decolorization rate of RR24, which increases with the increase of temperature. At 40°C and 60°C, due to the higher temperature, the dye molecules are more reactive and easier to react with •OH, resulting in higher degradation efficiency. Moreover, RR24 dyeing generally adopts a high temperature (80-90°C) dyeing process, and the discharge temperature of wastewater is close to 60°C. Therefore, 60°C is selected in the degradation process, which is convenient and energy-saving.

3.3.5 The effects of different initial pH

The effect of pH on the decolorization of RR24 was studied. As shown in Fig.4b, at 20 min, under the conditions of pH 3, 5.88 (original value), 9, and 11, the decolorization rates of RR24 are 72.77%, 99.12%, 99.76%, and 99.80%, respectively. Acidic conditions have an inhibitory influence on the electrochemical electrolysis of RR24, but under neutral and alkaline conditions, the color removal rate of RR24 increases slightly with the increase of pH, but it is not obvious (Ammar et al., 2006). using Si/BDD as the anode to degrade the indigo carmine solution, their results showed that the dye solution faded to colorless at pH 10.0 faster than at pH 3.0, which consistent with our research results. Based on these results, the electroactive substances dyes present in the solution can be used to explain the anodizing behavior of RR24 dyes under acidic and alkaline conditions using BDD. Because dyes in alkaline media are more susceptible to oxidation than those in acid media (Liang et al., 2007), the pH of the simulated dye wastewater was not adjusted in this experiment.

3.3.6 Effect of the initial concentration of RR24

Fig.4c shows the different initial concentrations of 50-200 mg L⁻¹ of RR24 on the decolorization efficiency. At 15 min, the decolorization efficiency of RR24 was 99.91%, 98.94%, and 97.98%, respectively, which decreased with the increase of its initial concentration, but the overall decolorization efficiency was excellent. In the electrolysis process, $\ln(A_0/A_t) - t$ satisfies the pseudo-first-order kinetic relationship; At 50 mg L⁻¹ and 100 mg L⁻¹, the apparent kinetic constants are close, 0.52 min⁻¹ and 0.50 min⁻¹, respectively. Under the same other conditions, the amount of •OH produced on the electrode surface is certain; As the initial concentration increases, the concentration of radicals is diluted, and the probability of collision with dye molecules decreases, and the entire electrochemical oxidation process turns into diffusion control, which reduces the decolorization

rate. Within a certain range, the amount of $\bullet\text{OH}$ on the surface of BDD is constant. The higher the initial concentration of RR24, the more the number of $-\text{N}=\text{N}-$ fractured simultaneously, the subsequent accumulation of intermediate products will inevitably require more free radical which prolonged degradation time increased energy consumption. Therefore, the initial concentration is 100 mg L^{-1} .

3.37 Energy consumption and Mineralization

The best operating parameters are current density 45 mA cm^{-2} , supporting electrolyte concentration 100 mM , NO_3^- concentration 7 mM , temperature 60°C , initial pH is not adjusted, initial dye concentration 100 mg L^{-1} . The energy consumption for 100% decolorization within 15 min is 0.92 kWh m^{-3} , and the TOC reaches 51.35% within 90 min (Fig. 4d). The energy consumption is low, and the mineralization rate is good. The selected treatment method has greater advantages compared with other methods, as shown in Table 2.

Table 2 Different treatment technologies on RR24

Technology	Means	Degradation parameter			Removal/%		Other parameter	Ref.
		C_0 (mg L^{-1})	Time (min)	C_e	Color	Organic		
Photocatalysis	0.75 g L^{-1} TiO_2	10	60	—	88.69	TOC = 17.78	—	(Zhu et al., 2013)
Photocatalysis	1.0 g L^{-1} ZrW_{11}Sn	8	240	—	45.1	—	—	(Feng, 2015)
Electrocoagulation	Al electrodes	100	35	2.5 g L^{-1} NaCl	97.9	COD = 83.8	—	(Abu Ghalwa et al., 2015)
Adsorption	1.0 g L^{-1} SBB-ZnO3	250	60	—	42.1	—	$q_{\max} = 105.2$ mg g^{-1}	(Van et al., 2021)
EO- $\text{NO}_3^-/\text{SO}_4^{2-}$	Ti/BDD	100	90	100 mM Na_2SO_4	100	TOC = 51.35	$E_c = 0.92$ kWh m^{-3}	In this paper

C_0 is dye's initial concentration, and C_e is concentration of the supporting electrolyte.

3.4. The relative contribution of different active species

TBA and MeOH are used as scavengers for $\bullet\text{OH}$ and $\text{SO}_4\bullet^-$ (Zhang et al., 2013). Methanol can remove $\bullet\text{OH}$ and $\text{SO}_4\bullet^-$ very quickly, but TBA is relatively inert to $\text{SO}_4\bullet^-$ (Kamagate et al., 2018). Similarly, phenol can also remove $\bullet\text{OH}$, $\text{SO}_4\bullet^-$ and $\text{NO}_3\bullet$. As shown in Fig. 5a, 5b, and 5c, TBA, MeOH, and phenol all have a great inhibitory effect on the decolorization efficiency of RR24, showing that $\bullet\text{OH}$ is the main active substance in the degradation and decolorization of RR24, while the direct effect of $\text{NO}_3\bullet$ and $\text{SO}_4\bullet^-$ is negligible, the system mainly relies on the oxidation of $\bullet\text{OH}$. The addition of phenol almost directly oxidizes RR24 at the electrode, showing that direct electron transfer (DET) contribution in this system is minimal. By analyzing the apparent kinetic constants, the relative contribution of different active species to the decolorization of RR24 can be estimated. After processing the data with pseudo-first-order kinetics (Fig. 5d. and Table 3), results show that the contribution rate of $\bullet\text{OH}$ reached 99.47%. In other words, the addition of NO_3^- , act as a catalytic agent, greatly improves the production of $\bullet\text{OH}$ in the $\text{EO-NO}_3^-/\text{SO}_4^{2-}$.

Fig.5. Different free radical quenchers to RR24 decolorization rate curve with time: TBA (a), MeOH (b), phenol (c) and its $\ln(A_0/A_i) - t$ relationship (d); ([RR24] = 100 mg L⁻¹; $j = 45 \text{ mA cm}^{-2}$; [Na₂SO₄] = 100 mM; [NaNO₃] = 7 mM; original pH; 60°C

Table 3 Rate constants and contribution rates of different active species

	Active species	k	R^2	Contribution rate
none	DET+ $\bullet\text{OH}$ + $\text{SO}_4^{\bullet-}$ + $\text{NO}_3^{\bullet}$	0.6596	0.99	100%
TBA	DET+ $\text{SO}_4^{\bullet-}$ + $\text{NO}_3^{\bullet}$	0.0035	0.99	
MeOH	DET+ $\text{NO}_3^{\bullet}$	0.0033	0.97	
phenol	DET	0.0017	0.97	0.26%
	$\bullet\text{OH}$	0.6561		99.47%
	$\text{NO}_3^{\bullet}$	0.0016		0.24%
	$\text{SO}_4^{\bullet-}$	0.0002		0.03%

3.5. RR24 degradation pathway

Fig. 6. RR24 UV-Vis full spectrum under different degradation time conditions (a), the color of RR24 under different degradation time (b), conditions: ($[\text{RR24}] = 100 \text{ mg L}^{-1}$; $j = 45 \text{ mA cm}^{-2}$; $[\text{Na}_2\text{SO}_4] = 100 \text{ mM}$; $[\text{NaNO}_3] = 7 \text{ mM}$; original pH; 60°C)

The UV-Vis spectra at different electrolysis times (Fig. 6a) shows that after 2.5 min of reaction, the absorption peaks at 510 nm and 534 nm are significantly reduced, the naphthalene ring absorption peaks at 370 nm are reduced, and the benzene ring absorption peaks at 238 nm and 287 nm are dropping slightly. After 10 min, the characteristic absorption peaks at 510 nm and 534 nm disappeared completely, and the conjugated chromonic system containing azo bonds in the RR24 molecule was destroyed and decolorized. In the ultraviolet region, the benzene ring absorption peak at 287 nm and the naphthalene ring absorption peak at 370 nm disappeared, leaving only the benzene ring absorption peak at 238 nm. The results show that in a short reaction time, EAOP can rapidly degrade the azo group and naphthalene ring in the dye wastewater into benzene ring products, and finally be oxidized to CO_2 and H_2O .

amide and the amide group and the naphthalene or triazine rings (Xikui Wang et al., 2011). The triazine compound is oxidized further to 6-chloro-1,3,5-triazine-2,4-diol, 4-amino-6-chloro-1,3,5-triazin-2-ol and the amino converted to a hydroxyl group. Aniline compounds are turned into phenolic compounds, oxidized to benzoquinone, and finally oxidized to CO_2 and H_2O (Ruiz et al., 2011; Asghar et al., 2015). Naphthalene compounds are converted into 2, 4-(benzodiazepine) phthalic acid, and 1-isocyanate naphthalene; forming sulfate ions through the sulfonic acid group cut from the naphthalene ring, and finally the nitrogen in the RR24 molecule is oxidized to nitrate ion (Thiam et al., 2016).

4 Conclusion

First, for high-efficiency decolorization and degradation, the $\text{NO}_3^- + \text{SO}_4^{2-}$ system is determined to be a suitable electrochemical system for RR24 degradation by comparing the oxidative degradation systems of different electrolytes. Secondly, the effect of several operating parameters on RR24 decolorization is discussed. Among them, the current density and NO_3^- concentration have the greatest impact. The best operating process parameters for RR24 electrochemical degradation are obtained: current density 45 mA cm^{-2} , 100 mM support electrolyte, 7 mM NO_3^- , at 60°C , initial pH is not adjusted, and RR24 initial concentration 100 mg L^{-1} . Under this condition, the energy consumption for 100% decolorization within 15 min was 0.92 kWh m^{-3} , and the TOC reached 51.35% within 90 min. The quencher on the decolorization of RR24 electrochemical decolorization was also studied. It was found that $\bullet\text{OH}$ was closely related to the decolorization degradation of RR24, reaching a contribution rate of 99.47%. Finally, the samples were scanned by UV-Vis at different electrolysis times, and LC-MS tested the samples after 40 min of electrolysis to deduce the possible degradation route of RR4 by analyzing the intermediate products in the degradation process. To achieve higher dye wastewater treatment efficiency, the $\text{EO}/\text{NO}_3^- + \text{SO}_4^{2-}$ system can perform advanced treatment on the effluent after biological treatment

and return to the biological treatment system through the system or secondary biological treatment with carbon source added.

Declarations

Ethics approval and consent to participate

Not applicable

Competing interests

The authors declare that they have no competing interests.

Funding

The authors declare that they have no known competing financial interests.

Author Agreement

The specific work of each author in this study was as follows:

Yining Tang: Writing- Reviewing and Editing, Deliang He: Supervision, Yanni Guo: Supervision, Jun Shang: Conceptualization, Methodology, Lei Zhou: Data curation, Rong Pan: Investigation, Wei Dong: Data curation, Liu Mengli: Investigation.

All the authors confirmed that they have reviewed the manuscript entitled ‘ Electrochemical oxidative decolorization of Reactive Red 24 dye by BDD anodes: operating parameters, kinetics, and degradation pathways’ and approved its submission to the journal of ‘Environmental Science and Pollution Research’.

Acknowledgements

The authors would like to thank Zhou yuan from Shiyanjia Lab (www.shiyanjia.com) for the HPLC-MS analysis.

Availability of data and materials’ statement

All data generated or analysed during this study are included in this published article and its supplementary

information files.

References

- Abu Ghalwa, M., N., Saqer, A.M., 2015. Removal of Reactive Red 24 Dye by Clean Electrocoagulation Process Using Iron and Aluminum Electrodes. *J. Chem. Eng. Process Technol.* 07. <http://doi.org/10.4172/2157-7048.1000269>
- Ammar, S., Abdelhedi, R., Flox, C., Arias, C., Brillas, E., 2006. Electrochemical degradation of the dye indigo carmine at boron-doped diamond anode for wastewaters remediation. *Environ. Chem. Lett.* 4, 229-233. <http://doi.org/10.1007/s10311-006-0053-2>
- Asghar, A., Raman, A.A.A., Daud, W.M.A.W., 2015. Advanced oxidation processes for in-situ production of hydrogen peroxide/hydroxyl radical for textile wastewater treatment: a review. *J. Cleaner Prod.* 87, 826-838. <http://doi.org/10.1016/j.jclepro.2014.09.010>
- Beck, F., Kaiser, W., Krohn, H., 2000. Boron doped diamond (BDD)-layers on titanium substrates as electrodes in applied electrochemistry. *Electrochim. Acta.* 45, 4691-4695. [http://doi.org/10.1016/s0013-4686\(00\)00621-6](http://doi.org/10.1016/s0013-4686(00)00621-6)
- Brillas, E., Martinez-Huitle, C.A., 2015. Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review. *Appl. Catal. B: Environ.* 166, 603-643. <http://doi.org/10.1016/j.apcatb.2014.11.016>
- Brito, C.N., Ferreira, M.B., de O. Marcionilio, S.M.L., de Moura Santos, E.C.M., Léon, J.J.L., Ganiyu, S.O., Martínez-Huitle, C.A., 2018. Electrochemical Oxidation of Acid Violet 7 Dye by Using Si/BDD and Nb/BDD Electrodes. *J. Electrochem. Soc.* 165, E250-E255. <http://doi.org/10.1149/2.1111805jes>
- Buck, C., Skillen, N., Robertson, J., Robertson, P.K.J., 2018. Photocatalytic OH radical formation and quantification over TiO₂ P25: Producing a robust and optimised screening method. *Chinese Chem Lett* 29, 773-777. <http://doi.org/10.1016/j.cclet.2018.04.022>

Corona-Bautista, M., Picos-Benitez, A., Villasenor-Basulto, D., Bandala, E., Peralta-Hernandez, J.M., 2021. Discoloration of azo dye Brown HT using different advanced oxidation processes. *Chemosphere*. 267, 129234. <http://doi.org/10.1016/j.chemosphere.2020.129234>

Ding, J., Bu, L., Zhao, Q., Kabutey, F.T., Wei, L., Dionysiou, D.D., 2020. Electrochemical activation of persulfate on BDD and DSA anodes: Electrolyte influence, kinetics and mechanisms in the degradation of bisphenol A. *J. Hazard. Mater.* 388, 121789. <http://doi.org/10.1016/j.jhazmat.2019.121789>

El-Ghenymy, A., Centellas, F., Rodríguez, R.M., Cabot, P.L., Garrido, J.A., Sirés, I., Brillas, E., 2015. Comparative use of anodic oxidation, electro-Fenton and photoelectro-Fenton with Pt or boron-doped diamond anode to decolorize and mineralize Malachite Green oxalate dye. *Electrochim. Acta*. 182, 247-256. <http://doi.org/10.1016/j.electacta.2015.09.078>

Feng, S., 2015. Photocatalytic Degradation of Simulated Dye Wastewater with Polyoxometalate/Titanium Dioxide Composite. School of environmental and chemical engineering. Dalian Jiaotong University

Florenza, X., Solano, A.M.S., Centellas, F., Martinez-Huitle, C.A., Brillas, E., Garcia-Segura, S., 2014. Degradation of the azo dye Acid Red 1 by anodic oxidation and indirect electrochemical processes based on Fenton's reaction chemistry. Relationship between decolorization, mineralization and products. *Electrochim. Acta*. 142, 276-288. <http://doi.org/10.1016/j.electacta.2014.07.117>

Gandini, D., Mahe, E., Michaud, P.A., Haenni, W., Perret, A., Comninellis, C., 2000. Oxidation of carboxylic acids at boron-doped diamond electrodes for wastewater treatment. *J. Appl. Electrochem.* 30, 1345-1350. <http://doi.org/10.1023/a:1026526729357>

Garcia-Segura, S., Lanzarini-Lopes, M., Hristovski, K., Westerhoff, P., 2018. Electrocatalytic reduction of nitrate: Fundamentals to full-scale water treatment applications. *Appl. Catal. B: Environ.* 236, 546-568. <http://doi.org/10.1016/j.apcatb.2018.05.041>

389 He, Y., Huang, W., Chen, R., Zhang, W., Lin, H., Li, H., 2015. Anodic oxidation of aspirin on PbO₂, BDD and porous
390 Ti/BDD electrodes: Mechanism, kinetics and utilization rate. Sep. Purif. Technol. 156, 124-131.
391 <http://doi.org/10.1016/j.seppur.2015.09.036>

392 He, Y., Lin, H., Guo, Z., Zhang, W., Li, H., Huang, W., 2019. Recent developments and advances in boron-doped
393 diamond electrodes for electrochemical oxidation of organic pollutants. Sep. Purif. Technol. 212, 802-821.
394 <http://doi.org/10.1016/j.seppur.2018.11.056>

395 Kamagate, M., Amin Assadi, A., Kone, T., Coulibaly, L., Hanna, K., 2018. Activation of persulfate by irradiated
396 laterite for removal of fluoroquinolones in multi-component systems. J. Hazard. Mater. 346, 159-166.
397 <http://doi.org/10.1016/j.jhazmat.2017.12.011>

398 Kuchtova, G., Chylkova, J., Vana, J., Vojs, M., Dusek, L., 2020. Electro-oxidative decolorization and treatment of
399 model wastewater containing Acid Blue 80 on boron doped diamond and platinum anodes. J. Electroanal. Chem.
400 863. <http://doi.org/10.1016/j.jelechem.2020.114036>

401 Li, W., Liu, G., Miao, D., Li, Z., Chen, Y., Gao, X., Liu, T., Wei, Q., Ma, L., Zhou, K., Yu, Z., 2020. Electrochemical
402 oxidation of Reactive Blue 19 on boron-doped diamond anode with different supporting electrolyte. J. Environ.
403 Chem. Eng. 8. <http://doi.org/10.1016/j.jece.2020.103997>

404 Li, X., Tang, S., Yuan, D., Tang, J., Zhang, C., Li, N., Rao, Y., 2019. Improved degradation of anthraquinone dye by
405 electrochemical activation of PDS. Ecotoxicol. Environ. Saf. 177, 77-85.
406 <http://doi.org/10.1016/j.ecoenv.2019.04.015>

407 Liang, C., Wang, Z.S., Bruell, C.J., 2007. Influence of pH on persulfate oxidation of TCE at ambient temperatures.
408 Chemosphere. 66, 106-113. <http://doi.org/10.1016/j.chemosphere.2006.05.026>

409 Louit, G., Foley, S., Cabillic, J., Coffigny, H., Taran, F., Valleix, A., Renault, J.P., Pin, S., 2005. The reaction of
410 coumarin with the OH radical revisited: hydroxylation product analysis determined by fluorescence and

411 chromatography. Radiat. Phys. Chem. 72, 119-124. <http://doi.org/10.1016/j.radphyschem.2004.09.007>

412 Luo, D., Ma, D., Liangzhuan Wu, Zhi, J., 2018. A High-Performance Wastewater Treatment System for Orange II

413 Degradation Using a Boron-doped Diamond Electrode and Enhanced by Zeolite-TiO₂ Photocatalyst. Int. J.

414 Electrochem. Sci., 5904-5922. <http://doi.org/10.20964/2018.06.45>

415 Medrano-Rodríguez, F., Picos-Benítez, A., Brillas, E., Bandala, E.R., Pérez, T., Peralta-Hernández, J.M., 2020.

416 Electrochemical advanced oxidation discoloration and removal of three brown diazo dyes used in the tannery

417 industry. J. Electroanal. Chem. 873. <http://doi.org/10.1016/j.jelechem.2020.114360>

418 Miao, D., Liu, G., Wei, Q., Hu, N., Zheng, K., Zhu, C., Liu, T., Zhou, K., Yu, Z., Ma, L., 2020. Electro-activated

419 persulfate oxidation of malachite green by boron-doped diamond (BDD) anode: effect of degradation process

420 parameters. Water Sci. Technol. 81, 925-935. <http://doi.org/10.2166/wst.2020.176>

421 Moussa, D.T., El-Naas, M.H., Nasser, M., Al-Marri, M.J., 2017. A comprehensive review of electrocoagulation for

422 water treatment: Potentials and challenges. J. Environ. Manage. 186, 24-41.

423 <http://doi.org/10.1016/j.jenvman.2016.10.032>

424 Nidheesh, P.V., Zhou, M., Oturan, M.A., 2018. An overview on the removal of synthetic dyes from water by

425 electrochemical advanced oxidation processes. Chemosphere. 197, 210-227.

426 <http://doi.org/10.1016/j.chemosphere.2017.12.195>

427 Palma-Goyes, R.E., Guzman-Duque, F.L., Penuela, G., Gonzalez, I., Nava, J.L., Torres-Palma, R.A., 2010.

428 Electrochemical degradation of crystal violet with BDD electrodes: effect of electrochemical parameters and

429 identification of organic by-products. Chemosphere. 81, 26-32.

430 <http://doi.org/10.1016/j.chemosphere.2010.07.020>

431 Panakoulis, T., Kalatzis, P., Kalderis, D., Katsaounis, A., 2010. Electrochemical degradation of Reactive Red 120

432 using DSA and BDD anodes. J. Appl. Electrochem. 40, 1759-1765. <http://doi.org/10.1007/s10800-010-0138-2>

433 Panizza, M., Cerisola, G., 2005. Application of diamond electrodes to electrochemical processes. *Electrochim. Acta*.
 434 51, 191-199. <http://doi.org/10.1016/j.electacta.2005.04.023>
 435 Panizza, M., Michaud, P.A., Cerisola, G., Comninellis, C., 2001. Anodic oxidation of 2-naphthol at boron-doped
 436 diamond electrodes. *J. Electroanal. Chem.* 507, 206-214. [https://doi.org/10.1016/S0022-0728\(01\)00398-9](https://doi.org/10.1016/S0022-0728(01)00398-9)
 437 Ruiz, E.J., Arias, C., Brillas, E., Hernandez-Ramirez, A., Peralta-Hernandez, J.M., 2011. Mineralization of Acid
 438 Yellow 36 azo dye by electro-Fenton and solar photoelectro-Fenton processes with a boron-doped diamond
 439 anode. *Chemosphere.* 82, 495-501. <http://doi.org/10.1016/j.chemosphere.2010.11.013>
 440 Santos, G.O.S., Eguiluz, K.I.B., Salazar-Banda, G.R., Sáez, C., Rodrigo, M.A., 2020. Understanding the electrolytic
 441 generation of sulfate and chlorine oxidative species with different boron-doped diamond anodes. *J. Electroanal.*
 442 *Chem.* 857. <http://doi.org/10.1016/j.jelechem.2019.113756>
 443 Siedlecka, E.M., Ofiarska, A., Borzyszkowska, A.F., Bialk-Bielinska, A., Stepnowski, P., Pieczynska, A., 2018.
 444 Cytostatic drug removal using electrochemical oxidation with BDD electrode: Degradation pathway and toxicity.
 445 *Water Res* 144, 235-245. <http://doi.org/10.1016/j.watres.2018.07.035>
 446 Soni, B.D., Patel, U.D., Agrawal, A., Ruparelia, J.P., 2017. Application of BDD and DSA electrodes for the removal
 447 of RB 5 in batch and continuous operation. *J. water Process Eng.* 17, 11-21.
 448 <http://doi.org/10.1016/j.jwpe.2017.01.009>
 449 Tang, Y., He, D., Guo, Y., Qu, W., Shang, J., Zhou, L., Pan, R., Dong, W., 2020. Electrochemical oxidative degradation
 450 of X-6G dye by boron-doped diamond anodes: Effect of operating parameters. *Chemosphere.* 258.
 451 <http://doi.org/10.1016/j.chemosphere.2020.127368>
 452 Thiam, A., Brillas, E., Garrido, J.A., Rodríguez, R.M., Sirés, I., 2016. Routes for the electrochemical degradation of
 453 the artificial food azo-colour Ponceau 4R by advanced oxidation processes. *Appl. Catal. B: Environ.* 180, 227-
 454 236. <http://doi.org/10.1016/j.apcatb.2015.06.039>

455 Umschlag, T., Zellner, R., Herrmann, H., 2002. Laser-based studies of NO₃ radical reactions with selected aromatic
 456 compounds in aqueous solution. *Phys. Chem. Chem. Phys.* 4, 2975-2982. <http://doi.org/10.1039/B110263J>
 457 Uranga-Flores, A., de la Rosa-Juarez, C., Gutierrez-Granados, S., de Moura, D.C., Martinez-Huitile, C.A., Hernandez,
 458 J.M.P., 2015. Electrochemical promotion of strong oxidants to degrade Acid Red 211: Effect of supporting
 459 electrolytes. *J. Electroanal. Chem.* 738, 84-91. <http://doi.org/10.1016/j.jelechem.2014.11.030>
 460 Van, H.T., Nguyen, L.H., Dang, N.V., Chao, H.-P., Nguyen, Q.T., Nguyen, T.H., Nguyen, T.B.L., Thanh, D.V., Nguyen,
 461 H.D., Thang, P.Q., Thanh, P.T.H., Hoang, V.P., 2021. The enhancement of reactive red 24 adsorption from
 462 aqueous solution using agricultural waste-derived biochar modified with ZnO nanoparticles. *RSC Adv.* 11, 5801-
 463 5814. <http://doi.org/10.1039/d0ra09974k>
 464 Vasconcelos, V.M., Ponce - de - León, C., Rosiwal, S.M., Lanza, M.R.V., 2019. Electrochemical Degradation of
 465 Reactive Blue 19 Dye by Combining Boron - Doped Diamond and Reticulated Vitreous Carbon Electrodes.
 466 *ChemElectroChem.* 6, 3516-3524. <http://doi.org/10.1002/celec.201900563>
 467 Wachter, N., Pereira, G.F., Rocha-Filho, R.C., Bocchi, N., Biaggio, S.R., 2015. Comparative Electrochemical
 468 Degradation of the Acid Yellow 49 Dye Using Boron-Doped Diamond, beta-PbO₂, and DSA (R) Anodes in a
 469 Flow Reactor. *Int. J. Electrochem. Sci.* 10, 1361-1371. <http://doi.org/10.1088/2053-1591/ab66a0>
 470 Wang, J., Swain, G.M., Tachibana, T., Kobashi, K., 2000. Incorporation of Pt particles in boron-doped diamond thin
 471 films applications in electrocatalysis. *Electrochem. Solid-State Lett.* 3, 286-289.
 472 <http://doi.org/10.1149/1.1391126>
 473 Wang, Y., Qu, J., 2006. Electrocatalytic Reduction of Nitrate in Water with a Palladium-Modified Copper Electrode.
 474 *Water Environ. Res.* 78, 724-729. <https://doi.org/10.2175/106143006X110665>
 475 Wu, J., Zhang, H., Oturan, N., Wang, Y., Chen, L., Oturan, M.A., 2012. Application of response surface methodology
 476 to the removal of the antibiotic tetracycline by electrochemical process using carbon-felt cathode and DSA

(Ti/RuO₂-IrO₂) anode. Chemosphere. 87, 614-620. <http://doi.org/10.1016/j.chemosphere.2012.01.036>

Xiang, Q., Yu, J., Wong, P.K., 2011. Quantitative characterization of hydroxyl radicals produced by various photocatalysts. J Colloid Interface Sci 357, 163-167. <http://doi.org/10.1016/j.jcis.2011.01.093>

Xikui Wang , Yuechang Wei , Chen Wang , Weilin Guo , Jingang Wang, Jiang, J., 2011. Ultrasonic degradation of reactive brilliant red K-2BP in water with CCl₄enhancementPerformance optimization and degradation mechanism. Sep. Purif. Technol. 81, 69-76. <http://doi.org/10.1016/j.seppur.2011.07.003>

Zhang, J., Shao, X., Shi, C., Yang, S., 2013. Decolorization of Acid Orange 7 with peroxymonosulfate oxidation catalyzed by granular activated carbon. Chem. Eng. J. 232, 259-265. <http://doi.org/10.1016/j.cej.2013.07.108>

Zhu, X., Shi, F., Huang, C., Sheng, F., Guo, G., Mu, J., Wang, W., zhang, R., 2013. Photocatalytic Degradation of C.I. Reactive Red 24 Solution with Titanium Dioxide. Journal of Dalian Jiaotong University 034, 87-92. <http://doi.org/10.3969/j.issn.1673-9590.2013.02.021>

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