Studies on Decolorization of Brilliant Green, Kinetics and Intermediates by Electrochemical Oxidation

WANG Li [1, a*], WANG Junbo[2,] CHEN Long[2] and NIU Yujie[2]

[1]Zhejiang Shuren University, Hangzhou, Zhejiang province, PRC

[2]Huangshan University, Huangshan, Anhui province, PRC

[a]email: wlll36@163.com

Keywords: Brilliant Green; Electrochemical oxidation; Decolorization; Kinetics; Intermediates
Abstract. In this paper brilliant green (BG) was decolorized by electrochemical oxidation. Kinetics and Intermediates were also studied. The results showed that the decolorization of BG by electrochemical oxidation was fitted to pseudo first-order reactions. Activation energy was 34.9 kJ/mol. HPLC –MS results confirmed that the intermediates included polymerization, oxidative cracking reaction and N-demethylation.

Introduction

Brilliant green (BG) is a kind of dye ($C_{27}H_{34}N_2O_4S$, molecular weight:482.64 g/mol) which is widely used in staining and biological applications such as large intestine staining, skin staining, to color fibers, printed circuit boards, inks and also used in antiseptic preparation which is active against Gram-positive bacteria. BG will cause some degree of hypersensitivity reactions, carcinogenicity, microbial and fish toxicity [1]. At the same time, its release into environment can impart color to water and increase BOD value. Removal of the dye of brilliant green from wastewater has become a tough issue due to its stable character under harsh condition and biodegradation resistance [2].

Many methods have been applied to degrade BG. One promising technique for organic contaminants degradation is the electrochemical process, which offers several advantages, such as versatility, environmental compatibility and easy automation [3]. In this paper electrochemical oxidation was used to decolorize BG and test its decolorization kinetics and intermediates.

Experimental

All chemicals were of analytical grade unless otherwise stated. All were purchased from Shanghai Chemical Reagent Ltd.

A UV-Vis spectrophotometer (UV-2450) was employed to measure the concentration of BG solutions before and after electrolysis. The degeneration efficiency [4] was calculated using the following Eq. (1):

$$\%E = \frac{(A_i - A_f)}{A_f} \times 100$$

(1)

Cyclic voltammograms (CVs) experiments were performed with a conventional three-electrode cell using a CHI 660E electrochemical workstation (Shanghai Chenhua, China). The working electrode was Pt disc (Φ3 mm diameter), and the counter electrode was platinum foil (2 cm^2). A saturated calomel electrode (SCE) was placed in a separate compartment to serve as the reference electrode. RDEs were supplied by ATA-1B model instruments (Jiangyan Yinhe Ltd.), and a Pt disk electrode (RDE) to remove any complicating effects associated with the substrate–deposit interface. Before each test the Pt electrode surface was polished on suede using an aqueous alumina 0.5μm paste, rinsed thoroughly with Milli-Q water and then patted dry using a lint free tissue. The supporting electrolyte was KCl (C=50 g·L^{-1}).

All HPLC runs were performed using an UPLC-Qtof-MS (model: XeVO-G2-XS-qtof, Waters, USA). The column used in all experiments was a Agilent Zorbax-Phenyl stainless steel column of

250×4.6 mm i.d., 1.7 μm particle size (Santa Clara, CA, USA). The mobile phase for the reversed mode procedure, used in quantification analysis, was an isocratic mode that uses 0.005 M CH_3COONH_4 and CH_3CN at 30:70 v/v.

Results and discussion

A UV-Vis spectrophotometer (UV-2450) was employed to measure the characteristic absorption wavelength of BG, and it was 623 nm, shown in Fig. 1. At the same time, the standard absorption curve was tested and was shown in Fig. 2.
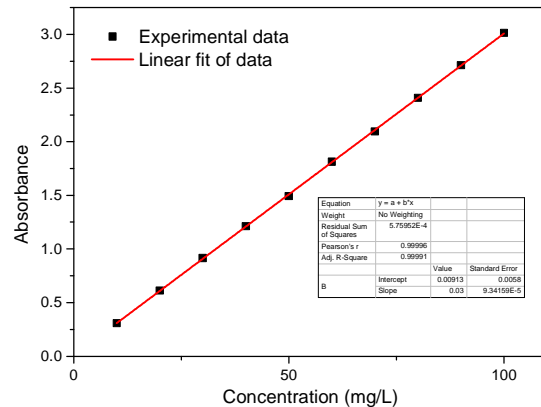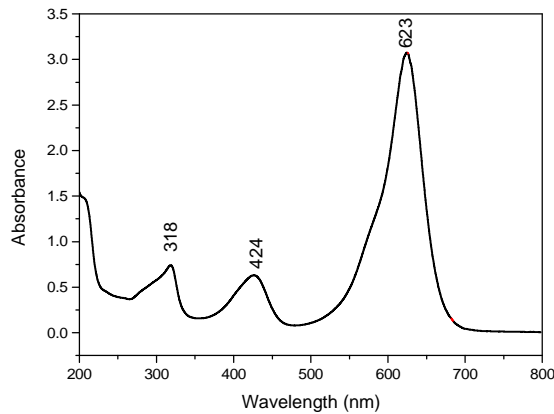

Fig. 1 characteristic absorption wavelength of BG,

Fig. 2 The standard absorption curve

According to the results of Fig. 1 and Fig. 2, the decolorization of BG was performed with the temperature changing from 298 to 338 K. The electrolysis potential was set at 1.20 V. The dependence of logarithm of BG concentration (lnC_0/C) on degradation time (t) at various temperatures was obtained. The results were shown in Fig. 3. The good linear relationships illustrated that the decolorization of BG by electrochemical oxidation was fitted to pseudo first-order reactions. The relationship between lnk and 1/T at different temperatures was illustrated in Fig. 4. The apparent rate constant k values in working electrode cell were calculated and the results were shown in table 1. From table 1 it could be deduced that temperature increasing was helpful for BG decolorization. According to Arrhenius equation [5] apparent activation energy was calculated as 34.9 kJ·mol^{-1}.
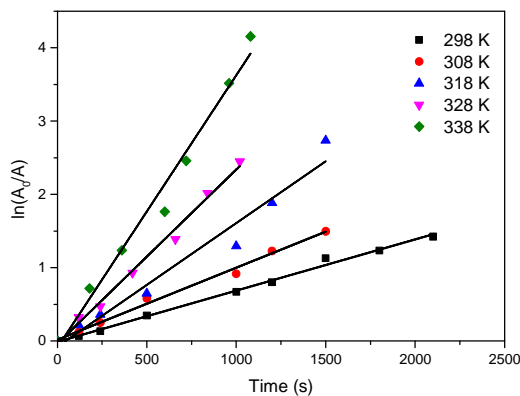

Fig. 3 The linear relationship between $ln(C_0/C)$ and time t   (C_0=100 mg/L)

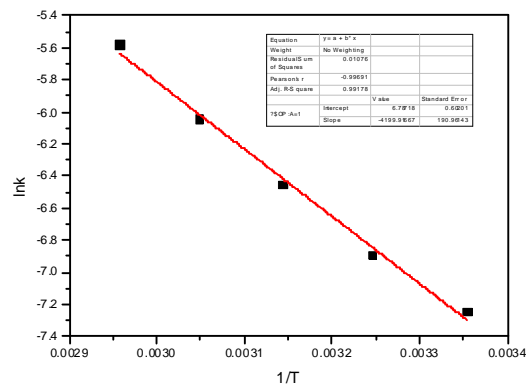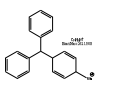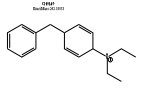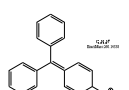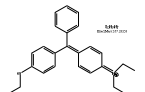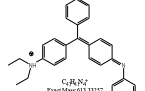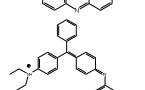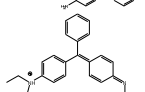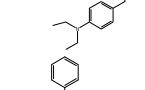**Fig.4** The linear relationship between lnk and 1/T.
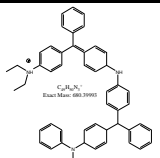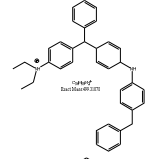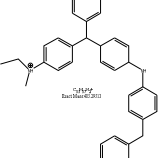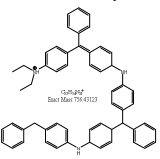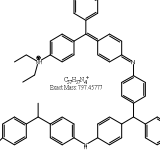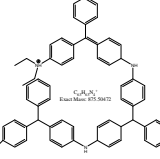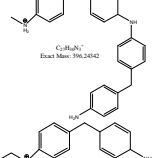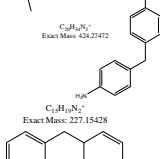
Table 1. Apparent rate constant k values at different temperatures.

T	298	308	318	328	338
1/T	0.00336	0.00325	0.00315	0.00305	0.00296
lnk	-7.2376	-6.8930	-6.4540	-6.0320	-5.5801
k	0.00072	0.0010	0.0016	0.0024	0.0038

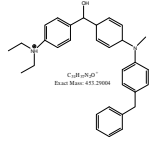The intermediates of electro-oxidation of BG could be suggested on the basis of HPLC. The results were shown in table 2. The schematic degeneration path of BG concluded by UPLC-QTOF-MS was shown in Fig. 5. It included polymerization, oxidative cracking reaction and N-demethylation.

Table 2 Intermediates of BG decolorization by electro-oxidation

Formula	Molecular structure	Molecular weight
$C_{14}H_{16}N_+$		198.1279
$C_{19}H_{20}N_+$		262.1593
$C_{17}H_{24}N^+$		242.1900
$C_{19}H_{18}N^+$		260.1429
$C_{25}H_{29}N_2^+$		357.23253
$C_{43}H_{41}N_4^+$		613.3326
$C_{42}H_{42}N_3^+$		588.3374
$C_{40}H_{44}N_3^+$		566.3531
$C_{48}H_{43}N_4^+$		675.3486

Formula	Structure	Exact Mass
$C_{49}H_{50}N_3^+$		680.3997
$C_{36}H_{39}N_2^+$		499.3103
$C_{35}H_{37}N_2^+$		485.2954
$C_{55}H_{54}N_3^+$		756.4314
$C_{57}H_{57}N_4^+$		797.4573
$C_{63}H_{63}N_4^+$		875.5047
$C_{31}H_{37}N_2O^+$		453.2903
$C_{27}H_{30}N_3^+$		396.2435
$C_{29}H_{34}N_3^+$		424.2744
$C_{15}H_{19}N_2^+$		227.1540

Conclusions

The decolorization of BG by electrochemical oxidation was fitted to pseudo first-order reactions. Activation energy was 34.9 kJ/mol. The intermediates detected by UPLC-QTOF-MS found that the main reactions included polymerization, oxidative cracking reaction and N-demethylation reaction.
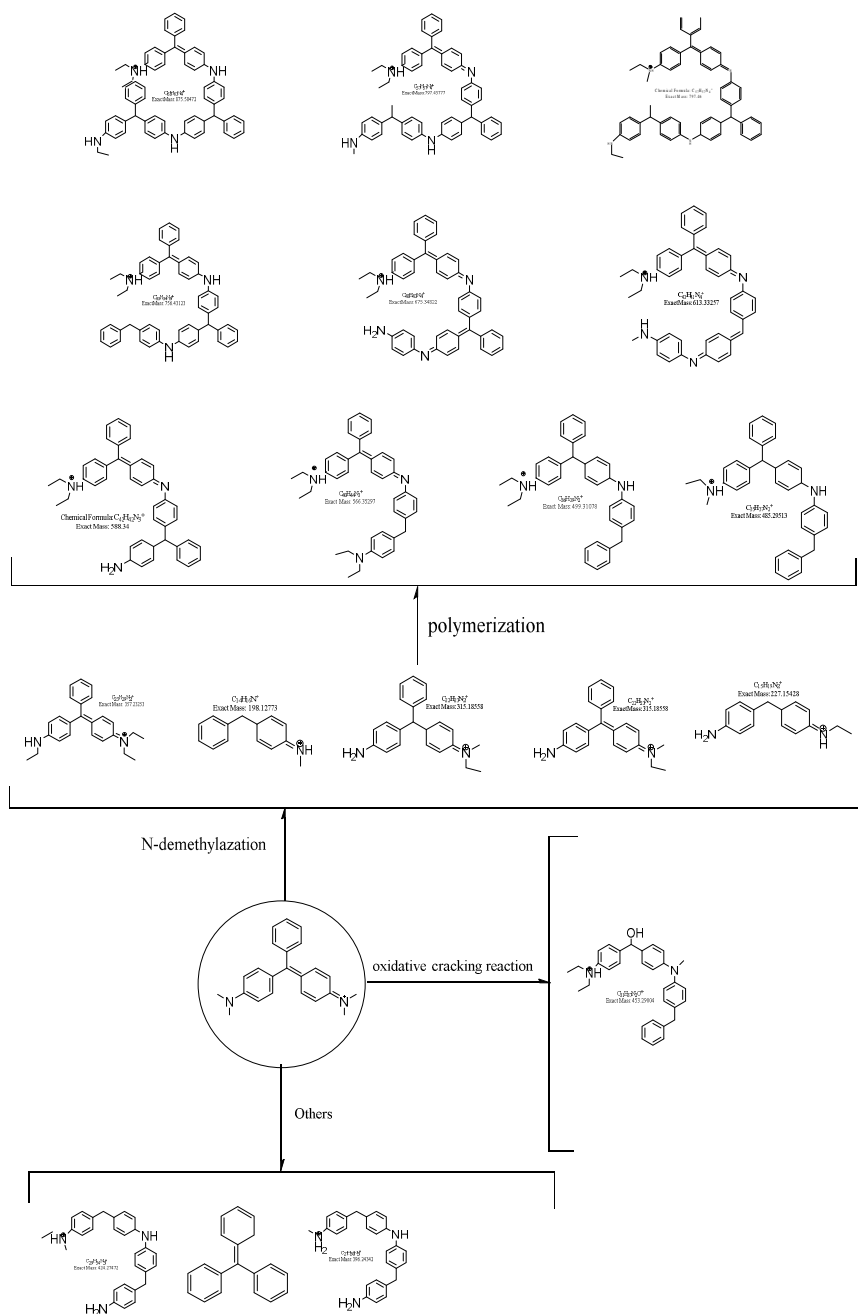.

Fig.5 The schematic degeneration path of BG concluded by UPLC-QTOF-MS.

References

[1] C.M. A. R Mohamed. J Alloy Compd.Vol. 509 (2011), p. 1648.

[2] S. R. Couto. J Hazard Mater. Vol.148, (2007), p. 768.

[3] C A Martìnez-Huitle, E Brillas. Appl Catal B Environ Vol. 87, (2009), p.105.

[4] G. Charrier, S. Lévy, J. Vigneron, A. Etcheberry, N. Simon. Diam Relat Mater Vol. 20 (2011), p. 944.

[5] L Du, J. Wu, C. W. Hu. Electrochim. Acta. Vol. 68, (2012), p. 69