

Decoloration of aqueous Brilliant Green by using glow discharge electrolysis

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Abstract

This paper described a plasma degradation of Brilliant Green (BG) by glow discharge electrolysis. Various influencing factors such as the voltage, the distance between cathode and anode were examined. Ultraviolet (UV) absorption spectra, gas chromatogram–mass spectrum (GC–MS), and chemical oxygen demand (COD) were used to monitor the degradation process and to identify the major oxidation intermediates. It was confirmed that benzoic acid, 1,2,3,4,5,6-cyclohexanehexaol, and carboxylic acids (e.g., oxalic acid, succinic acid and hydroxyacetic acid) were produced in the degradation process. The results showed that BG rapidly underwent degradation and eventually mineralized into CO₂ and H₂O.

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Keywords: Glow discharge electrolysis; Brilliant Green (BG); Hydroxyl radicals; Oxidation; Degradation intermediates

1. Introduction

In recent years, many papers focus on the advanced oxidation technologies (AOTs) for treating the wastewater, since there are a lot of highly active species, especially •OH radical, occurring in these processes. Some of these methods have reached the practical application stage [1]. However, the expensive equipment and the significant energy consumption are still a common problem. To search a green chemical process for removing the persistent organic pollutants from water has been an active topic. One of them is the glow discharge electrolysis plasma (GDE). In fact, as early as the 1950s, Hickling and coworkers [2,3] have reported the glow discharge electrolysis in aqueous. Then, Sengupta et al. [4,5] have also investigated the non-Faraday behavior of the contact glow discharge electrolysis (CGDE) in aqueous chemistry, especially, for the mechanism of producing •OH radical in detail. The progress of these methods has been summarized in a monograph [6] and two reviews [7,8]. There are a few of papers concerning the application of this method in treating wastewater

[9–17]. Recently, we put both anode and cathode completely in the solution to degrade the nitrophenols, a better result was obtained [18].

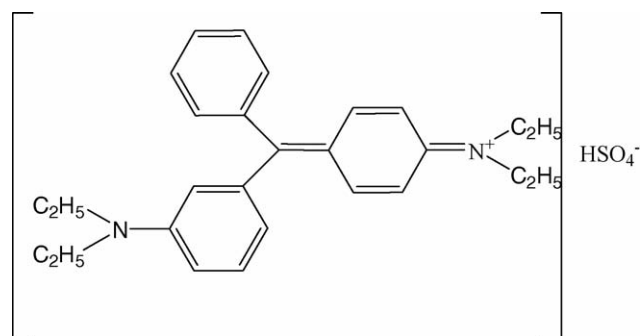
Brilliant Green (BG) is a dye (Scheme 1) used widely in modern textile industries. The dye-containing wastewater causes a serious consequence to health, especially, to the eyes of humans and animals [19]. We have reported [12,14] the degradation of some of dye-containing wastewater by the CGDE and obtained the satisfactory results. Now, in the present paper we will continue this study, focusing on the examination of degradation intermediates responsible for the color fading and on the understanding of the possible decoloration mechanism. The chemical structure of BG is shown in Scheme 1.

2. Experimental

The experimental apparatus consists of a high voltage power supply and a reactor. The power supply was a Model DH 1722-6 dc power unit (Shanghai, China) providing voltages of 0–1000 V and a current range of 0–0.3 A. In this experiment, the optimum voltage used was 600 V and the current was 120–150 mA. The reactor vessel contains a needle-to-plate electrode geometry system as shown in Fig. 1. A pointed platinum anode with a diameter

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Scheme 1. Chemical structure of BG.

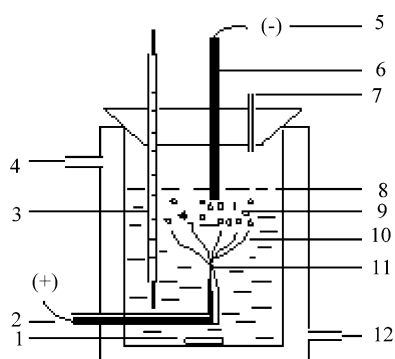


Fig. 1. Experimental setup of the glow discharge electrolysis. 1, Stirring bar; 2, anode; 3, thermometer; 4, cooling water outlet; 5, cathode; 6, graphite rod; 7, gas outlet; 8, solution level; 9, gas bubbles; 10, glow discharge area; 11, platinum wire; 12, cooling water inlet.

of 0.5 mm was sealed into a glass tube to generate glow discharge in aqueous solution. The cathode was a graphite rod (diameter: 70 mm) suspended above the anode at a distance of about 10 mm. The discharge glass reactor (19.7 cm height with external diameter 7.4 cm and internal 5.4 cm) was coated with an outer water jacket to keep the solution at a constant temperature. There was a magnetic stirring bar at the bottom of reactor to keep the solution mixed well. During the experiments, certain amounts of the solution were periodically sampled from the sampling port for analysis. BG was dissolved in sodium sulfate, where 2 g/L the sodium sulfate was as an electrolyte. The experiments are performed under the conditions as listed Table 1 unless mentioned otherwise.

The ultraviolet (UV) absorption spectra of reaction solutions were recorded by using a model UV-3400 Spectrometer

Table 1
Experimental conditions of glow discharge electrolysis

Parameter	Value
Voltage (V)	600
Current (mA)	120–150
Distance between electrodes (mm)	10
Diameter of discharge electrode (mm)	0.5
Aqueous Na ₂ SO ₄ (g/L)	2
Brilliant Green (mg/L)	30
Initial pH	6.72
Pressure (kPa)	101.325
Volume (mL)	250

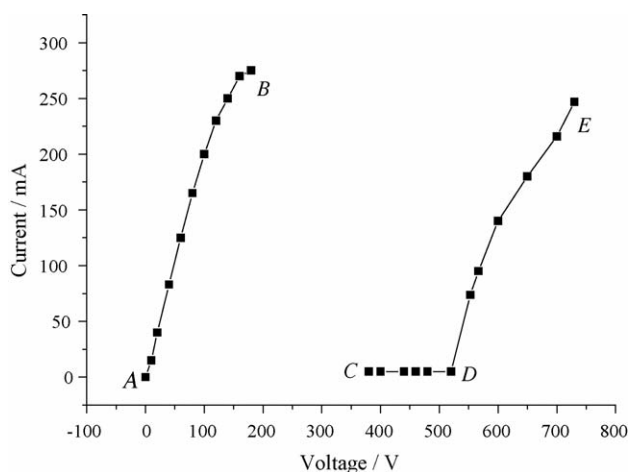


Fig. 2. The current–voltage characteristics of glow discharge electrolysis process.

(Hitachi, Japan) at intervals. In addition, the chemical oxygen demand (COD) measurement was carried out using a COD analyzer (BIYUE 5B-3, China). The pH of degradation solutions was adjusted with NaOH or H₂SO₄ solution.

GC–MS analysis was performed on an GC (6890N)/MS (5973N) system (Arlent, USA) equipped with a DB-5 column (30 m × 0.25 mm ID, 0.25 μm film thickness) (J&W, USA). Electron impact (EI) was used as ionization technique with electron energy 70 eV with *m/z* range from 20 to 300. Ion source temperature was 230 °C. The injector and detector temperatures were set at 250 °C. Helium served as carrier gas at a constant flow of 1.2 mL/min (He, 99.999%). After starting under isothermal conditions at 60 °C for 2 min, the temperature was linearly raised with 4 °C/min until 290 °C and then remain the temperature for 30 min. Mass spectral identification of the volatiles was carried out by comparing spectra with those in the NIST02L (National Institute of Standards and Technology, Gaithersburg, MD, USA) mass spectral library and those in the Wiley (New York, NY, USA) mass spectral library.

3. Results and discussions

3.1. The optimum degradation voltage

Fig. 2 shows a typical current–voltage characteristic in the degradation process, which can be divided into several sections. There is a linear section below 200 V (A → B), where the conventional electrolysis proceeded. When the voltage was raised up to 200 V (B), small gas bubbles were leaving the wire anode. Between 200 and 380 V (B → C), the readings of both current and voltage fluctuated widely so that the readings are less important for the drawing in Fig. 2. From 380 to 520 V (C → D), the current become stabilized, and a smooth pale sheath of vapor appeared and flashes of light were bigger. Over the voltage of 520 V (D → E), the continuous reddish spark was brought into view. At the same time, the intensity of light emission increased with increasing voltage, while the current was also increased. However, if the voltage was too high, it would consume energy and destroy the anode. Hence, in our experiment, the applied



Fig. 3. Photograph of glow discharges at 600 V in aqueous solution.

voltage was kept at 600 V and the current 150 mA. Photograph of brilliant glow discharge photography at 600 V is shown in Fig. 3.

3.2. The distance between cathode and anode

As we know, the distance between both electrodes is an important factor to the discharge possible. If keeping the other conditions constant in the study, the intensity of discharge observed was decreasing with increasing the distance between both electrodes at 600 V. That is, the discharge can only occur in a limited distance, for this work the optimum is 10 mm. If less than 10 mm, the pointed platinum anode was melted rapidly.

3.3. UV absorption spectra of Brilliant Green samples

The degradation process of BG (30 mg/L, 250 mL) was studied with an UV–vis spectrophotometer and the results in the first 10 min shown in Fig. 4. The change of absorption indicated that there is a rapid decrease of absorption bands at 627,

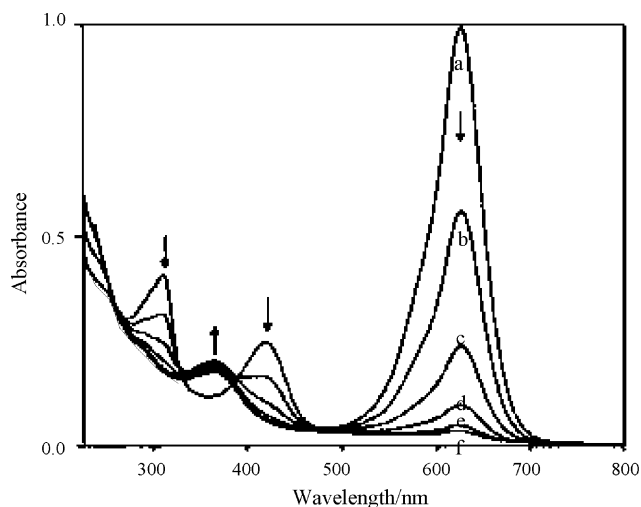


Fig. 4. The UV spectra of BG solution at different degradation time under GDE. a, Untreated BG solution; b, 2 min; c, 4 min; d, 6 min; e, 8 min; f, 10 min.

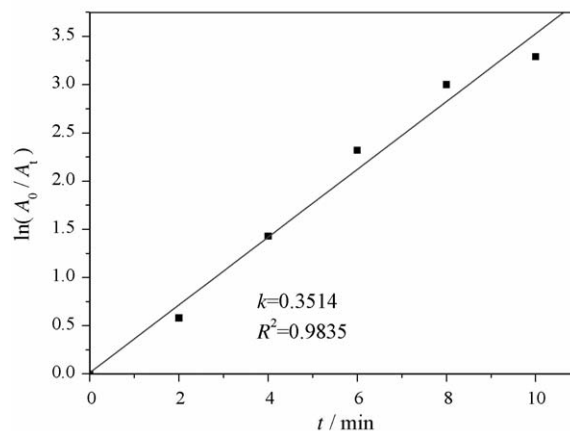


Fig. 5. Kinetic plot on the degradation of BG at 627 nm.

311 and 419 nm, respectively, demonstrating the destruction of BG and the formation of oxidation intermediates. The oxidation product shows a new absorption peak at 365 nm. These can be considered that the conjugated and double bond system of BG are destroyed to some degree firstly during the oxidation, leading to the production of intermediates [20]. The different rate of decrease at 627, 311 and 419 nm illustrated that the degradation of different groups in BG molecular was not carried out at the same speed. In the experiments, the decrease of absorbance peak at 627 nm was selected to study the degradation process of BG. After 10 min, the degradation rate BG at 627 nm is 95%.

3.4. Degradation rate

The decoloration of BG by GDE was observed to be a function of time at 627 nm. The experimental data on initial oxidation were fitted into the following equation [21]:

$$\ln(A_0/A_t) = kt$$

where A_0 and A_t are absorbance of the dyes at time 0 and at time t . k is the first order rate constant in min^{-1} and t is the time in min. When $\ln(A_0/A_t)$ was plotted against time (Fig. 5) a linear relationship with correlation coefficient $k = 0.3514$, $R^2 = 0.9835$ were obtained. The reaction may follow pseudo-first order kinetics [22].

3.5. pH changes of the solution

The results of the change of pH of degradation solution are given in Fig. 6. It can be seen that the pH of the BG solution decreased at first, and then remained unchanged and increased again for a while. The decrease of pH may be due to acidic intermediates produced during the degradation. The major degraded component in the oxidation of BG confirmed by GC–MS is a few of organic acid with small molecular weight such as oxalic acid, succinic acid and hydroxyacetic acid. The smaller molecular organic acids would be further oxidized into water and CO_2 to make the pH value slightly rising again.

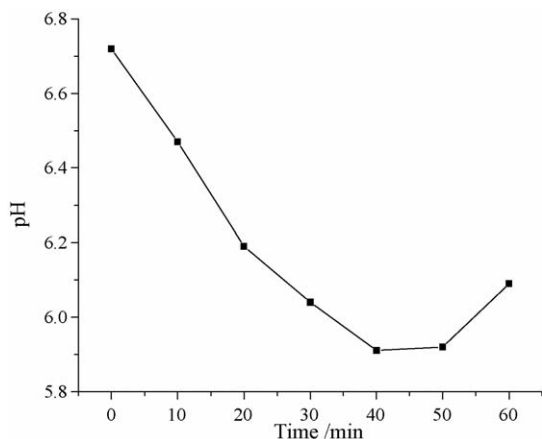


Fig. 6. pH changes of the Brilliant Green solution under GCE.

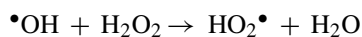
3.6. Degradation products of Brilliant Green analyzed by GC–MS

For more understanding the mechanism of degradation of Brilliant Green in aqueous solution, a GC–MS technique was used to determine the intermediates formed in the whole degradation process (Fig. 7). Most important intermediates identified by GC–MS spectroscopy were listed in Table 2. As has been already pointed out in Section 3.5, the decrease of pH values imply that some of organic acids were formed during the degradation, which agreed exactly with GC–MS. That is, the Brilliant Green molecule is cleaved into benzoic acid and 1,2,3,4,5,6-cyclohexanehexaol at first, and further producing lots of smaller molecule of organic acids after opening the ring. The finally main products are water and CO₂.

3.7. Effect of Fe²⁺

All of the above mentioned studies were carried out in the absence of Fe²⁺ ion.

Because in the previous works [12,14] it was found that the presence of Fe²⁺ ion could improve the degradation of dye-containing wastewater, thus, the following experiment was done in the presence of Fe²⁺ ion. About the action of Fe²⁺ ion in the contact flow discharge electrolysis, Hickling and coworkers [2,3] have proposed the mechanism as follows:



followed by

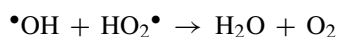
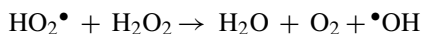
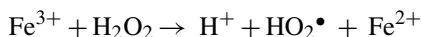
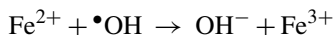


Table 2

Most important intermediates identified by GC–MS spectroscopy at 5 min

2-Hydroxypropanoic acid	
Hydroxyacetic acid	
4-Oxopentanoic acid	
Oxalic acid	
Succinic acid	
(1E,2E)-Ethanediol dioxime	
Glycerol	
Benzoic acid	
1,2,3,4,5,6-Cyclohexanehexaol	

Generally, only H₂O₂ was not easy to cause the degradation of pollutants in CGDE. In the presence of Fe²⁺, the following process should be added:



That is to say, in the presence of Fe²⁺, more •OH free radicals were produced due to the catalysis of Fe²⁺, which, in turn, accelerated the degradation reaction.

The value of COD is one of the parameters to examine the quality of water, hence, we use the COD change to observe the effect of Fe²⁺ ion. Of course, in the determination, the blank solution must be added the same amount of Fe²⁺ ion to deduct the effect from the absorbance. The results at the beginning were

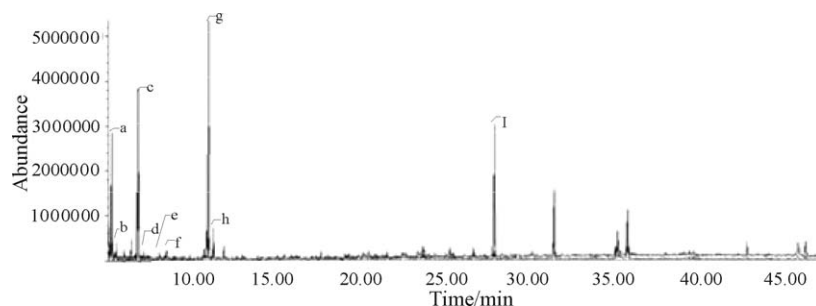


Fig. 7. GC-MS spectroscopy of the main intermediates of the BG degradation under GDE at 5 min.

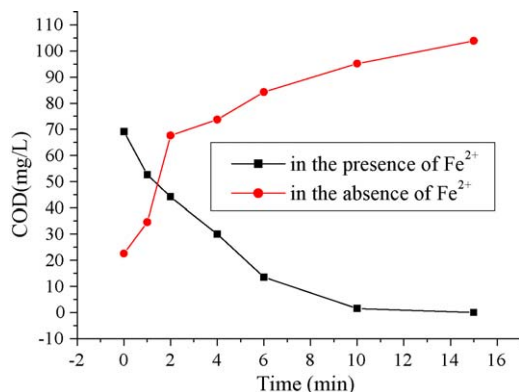


Fig. 8. The COD values of BG at different time by GDE.

given in Fig. 8. In the absence of Fe²⁺ ion, as the reaction progresses the COD was raising slowly, owing to the formation of intermediates to add the absorbance. However, if a drop of Fe²⁺ ion solution (2.0×10^{-4} mol/L) was added into the BG solution, the COD value of was decreased quickly and the removal of 100% is gained in 15 min. That is, a lot of intermediates were destroyed in a short time to form H₂O₂ and CO₂. In a sense, it may be considered a combination effect caused by Fe²⁺ ion and H₂O₂ [23–25].

4. Conclusion

Based on the experiments reported here, it may be concluded that in the glow discharge electrolysis the Brilliant Green molecule is, at first, cleaved into benzoic acid and 1,2,3,4,5,6-cyclohexanehexaol, and further being destroyed to form some lots of organic acids. The final main products are CO₂, water and a little of inorganic ion such as SO₄²⁻. For observing the intermediates and degradation mechanism, the study was performed in the absence of Fe²⁺ ion. However, if a trace amount of Fe²⁺ ion was added into the Brilliant Green solution (30 mg/L, 250 mL), 95% of degradation rate could be obtained within 10 min. The reason is that Fe²⁺ ion acts as a catalyst in the degradation processes.

Acknowledgements

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References

- [1] M.A. Malik, A. Ghaffar, S.A. Malik, Water purification by electrical discharges, *Plasma sources Sci. Technol.* 10 (2001) 82–91.
- [2] R.A. Davies, A. Hickling, Glow discharge electrolysis. Part I. The anodic formation of hydrogen peroxide in inert electrolytes, *J. Chem. Soc.* (1952) 3595–3602.
- [3] A.R. Denaro, A. Hickling, Glow discharge electrolysis in aqueous solutions, *J. Electrochem. Soc.* (1958) 265–270.
- [4] S.K. Sengupta, R. Singh, A.K. Srivastva, A study on the origin of nonFaradaic behavior of anodic contact glow discharge electrolysis, *J. Electrochem. Soc.* 145 (1998) 2209–2213.
- [5] S.K. Sengupta, R. Singh, A.K. Srivastva, A study on the nonFaradaic yields of anodic contact glow discharge electrolysis using cerous ion as the scavenger: an estimate of the primary yield of OH radicals, *Indian J. Chem.* 37A (1998) 558–560.
- [6] J.R. Chen, *Low-Temperature Plasma Chemistry & its Application*, Science Press, Beijing, 2001, pp. 20–114 (Chinese).
- [7] J.Z. Gao, X.Y. Wang, Z.A. Hu, J.G. Hou, Q.F. Lu, A review on chemical effects in aqueous solution induced by plasma with glow discharge electrolysis, *Plasma Sci. Technol.* 3 (3) (2001) 765–774.
- [8] J.Z. Gao, A novel technique for wastewater treatment by contact glow-discharge electrolysis, *Pakistan J. Biol. Sci.* 9 (2) (2006) 323–329.
- [9] M. Tezuka, M. Iwasaki, Oxidative degradation of phenols by contact glow discharge electrolysis, *Denkikagaku* 65 (12) (1997) 1057–1060.
- [10] M. Tezuka, M. Iwasaki, Plasma induced degradation of chlorophenols in aqueous solution, *Thin Solid Films* 316 (1998) 123–127.
- [11] M. Tezuka, M. Iwasaki, Liquid-phase reactions induced by gaseous plasma decomposition of benzoic acids in aqueous solution, *Plasma Ions* 1 (1999) 23–26.
- [12] J.Z. Gao, Z.A. Hu, X.Y. Wang, J.G. Hou, X.Q. Lu, J.W. Kang, Oxidative degradation of acridine oxange induced by plasma with contact glow discharge electrolysis, *Thin Solid Films* 390 (2001) 154–158.
- [13] J.Z. Gao, Y.J. Liu, W. Yang, L.M. Pu, J. Yu, Q.F. Lu, Oxidative degradation of phenol in aqueous induced by plasma from a direct glow discharge, *Plasma Sources Sci. Technol.* 12 (2003) 1–6.
- [14] J.Z. Gao, X.Y. Wang, Z.A. Hu, H.L. Deng, J.G. Hou, X.Q. Lu, J.W. Kang, Plasma degradation of dyes in water with contact glow discharge electrolysis, *Water Res.* 37 (2003) 267–272.
- [15] J.Z. Gao, W. Yang, Y.J. Liu, H.L. Deng, P. Chen, P.J. Na, Q.F. Lu, Oxidative degradation of *o*-chlorophenol with contact glow discharges in aqueous solution, *Plasma Sci. Technol.* 5 (1) (2003) 1609–1614.
- [16] J.Z. Gao, Z.A. Hu, Q.F. Lu, P.J. Na, P. Chen, Y.J. Liu, J. Yu, Degradation of chloroanilines in aqueous solution by contact glow discharge electrolysis, *Plasma Sci. Technol.* 5 (2) (2003) 1721–1727.
- [17] J.Z. Gao, K. Gai, Y.J. Dong, Plasma induced degradation of benzidine in an aqueous solution, *Plasma Sci. Technol.* 5 (5) (2003) 1983–1986.

- [18] J.Z. Gao, L.M. Pu, W. Yang, J. Yu, Y. Li, Oxidative degradation of nitrophenols in aqueous solution induced by plasma with submersed glow discharge electrolysis, *Plasma Process. Polym.* 1 (2004) 171–176.
- [19] G. Krishna, S. Bhattacharyya, Arunima, Adsorption characteristics of the dye, Brilliant Green, on neem leaf powder, *Dyes Pigments* 57 (2003) 211–222.
- [20] J.S. Chen, M.C. Liu, J.D. Zhang, Y.Z. Xian, L.T. Jin, Electrochemical degradation of bromopyrogallol red in presence of cobalt ions, *Chemosphere* 53 (2003) 1131–1136.
- [21] I.K. Konstantinou, T.A. Albanis, TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations. A review, *Appl. Catal. B: Environ.* 49 (2004) 1–14.
- [22] K. Swaminathan, S. Sandhya, A.C. Sophia, K. Pachhade, Y.V. Subrahmanyam, Decolorization and degradation of H-acid and other dyes using ferrous-hydrogen peroxide system, *Chemosphere* 50 (2003) 619–625.
- [23] Q.Q. Wang, A.T. Lemley, Oxidative degradation and detoxification of aqueous carbofuran by membrane anodic Fenton treatment, *J. Hazard. Mater. B* 98 (2003) 241–255.
- [24] E. Guivarch, N. Oturan, M.A. Oturan, Removal of organophosphorus pesticides from water by electrogenerated Fenton's reagent, *Environ. Chem. Lett.* 1 (2003) 165–168.
- [25] L. Lunar, D. Sicilia, S. Rubio, P.B. Dolores, U. Nickel, Identification of metal degradation products under Fenton's reagent treatment using liquid chromatography–mass spectrometry, *Water Res.* 34 (2000) 3400–3412.