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Study on Decolorization of Rhodamine B by SS304L, SS316 Stainless Steel and Titanium Cathode Electrode in Dual-Cell Electro-Fenton

Yi-Ta Wang*, Yi-Chi Hsieh**, You-Chen Lin** and Yu-Han Li**

Keywords：Electro-Fenton, stainless steel, titanium, Rhodamine B (Rh B), decolorization rate.

ABSTRACT

This paper aims at investigating the stainless steel 304L (SS304L), 316 (SS316) and titanium electrodes used as working electrode carrying out decolorization of Rhodamine B (Rh B) by Electro-Fenton method. In the dual-cell Electro-Fenton system, the decolorization of Rh B was compared by three different cathodes sequentially via the adjusted parameter of operating factors including working potential, initial pH, Fe^{2+} concentration, supporting electrolyte concentration. The results indicate that the decolorization rate of Rh B was greatest in the case of SS316 and the decolorization approached 64.7% under the suitable condition after 30 min.

INTRODUCTION

Wastewater treatment is worldwide issue, because water pollution related many industries such as textile and printing bring about serious environment and human health problem. In addition, chemically characteristic of dye wastewater causing effluent with bright color and pH variation are difficult to treatment and harmful to exterior of environment.

Rhodamine B (Rh B) is xanthene dye. It usually is used to textile, plastic, leather, paper, printing and dyeing ... and other industries (Cheng, 2017). In addition, it is used to metal analysis reagents, waterborne traceability reagents, herbicide … and color mark et al. Rh B dye is fluorescent dyes that have good stability and water solubility (Nidheesh, 2014). Fig.1 (Xu, 2013) shows the Rh B dye chemical structure. In recent years, reported that Rh B dyes have been shown to be carcinogenic, reproductive and develop toxic to humans or animals (Taziki, 2012). Therefrom, Rh B dye waste water must effective treatment. Otherwise, it has harmful to exterior of environment.

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* *Associate professor, Department of Mechanical and Electro-Mechanical Engineering, National ILan University, Yilan City, Yilan County 26041, Taiwan.*

** *Graduate student, Department of Mechanical and Electro-Mechanical Engineering, National ILan University, Yilan City, Yilan County 26041, Taiwan.*

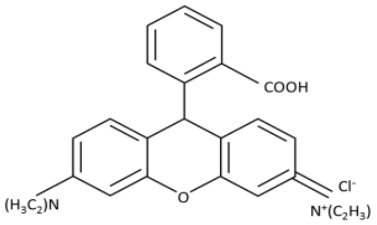

Fig. 1. Rh B dye chemical structure (Xu, 2013).

Fenton's reaction with tartaric acid in 1894 found that when hydrogen peroxide (H_2O_2) was added to ferrous ions (Fe^{2+}), it produced a very strong oxidative capacity (Babuponnusami, 2014).

In recent years, the application of electrochemical advanced oxidation processes (EAOPs) as advanced oxidation methods (AOPs) has been paid more and more attention by researchers, especially in the treatment of toxic pollutants that cannot be biodegradable.

Oturan (2000) designed the Electro-Fenton reaction system by the principle of electrochemical oxidation (EAOPs). The degradation principle is the decomposition of organic pollutants or dyes by indirect oxidation, and chemical reactions as shown in equation 1 to 3.

$$H_2O_2+Fe^{2+}+H^+ \rightarrow Fe^{3+}+H_2O+\bullet OH, \quad (1)$$

$$O_2+2H^++2e^- \rightarrow H_2O_2 \quad E^0=0.695\ V/NHE, \quad (2)$$

$$Fe^{3+}+e^- \leftrightarrows Fe^{2+} \quad E^0=0.77\ V/NHE, \quad (3)$$

Electro-Fenton which generates strong hydroxyl radicals (•OH) to decompose the target organic

pollutants. Among the advanced oxidation processes, Fenton method is the most effective way to decompose organic wastewater (Ai, 2008) and Electro-Fenton which is kind of Fenton can repair problem of iron sludge and promote processing time.

One of the electrode materials affect performance in Electro-Fenton system. Electrons provide in the anode. It has to steady materials. According to the literature (Nidheesh, 2012) indicate platinum (Pt) usually is used to anode. Its mechanical properties include good at conductivity and anticorrosion. Therefrom, Pt material is used to this study in anode.

The cathode material is mainly effective factor deciding the efficiency of the Electro-Fenton process (Yang, 2011). Chou et al. (1999) used that different materials oxidation of hexamine wastewater in Electro-Fenton system. It reported that stainless steel > titanium > graphite > lead in the $[Fe^{3+}] \rightarrow [Fe^{2+}]$ ability. Therefrom, in this study, SS304L, SS316 and titanium were selected as cathodes to compare with decolorization via suitable parameter determined by previous studies of our group.

Materials and methods

2.1 Experiment materials

In this study, SS304L, SS316 and Ti electrode was employed as cathode in Electro-Fenton system, and the Rh B decolorization rate were investigated in cathode chamber.

Fig. 2 shows that schematic diagram of the dual-cell system set up. The experimental were employed in three electrode electrochemical workstation at room temperature. The prepared three cathodes having same area during the experimental were selected as working electrode. Pure platinum sheet was employed as anode and the reference electrode was Ag/AgCl. The experiments were worked with constant aeration (50 sccm) and magnet stirring (700 rpm).

The SS304L, SS316 and Ti surface were cleaned by various grades of sandpaper used in 100, 240, 400, 600, 800, 1000, 1200 and 1500 grades sequentially. Then, the contaminations on electrodes were removed by ultrasound cleaning in acetone solution during 30 min.

2.2 Analytical method

We sampled a 200 mL electrolyte solution including iron (II) sulfate (Acros Organics, Belgium), potassium nitrate (Nihon Shiyaku Industries Ltd, Japan) and Rhodamine B (Sigma Aldrich Ltd, USA) and then measured absorbance from samples by

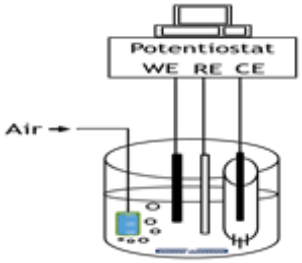

Fig. 2. Schematic diagram of Electro-Fenton experimental methods.

spectrophotometer (SH-U880, Shishin Technology Co., Ltd., Taiwan) during Electro-Fenton process.

To calculate the decolorization ratio (D), the decolorization (D) can be gained from the Equation (4):

$$D(\%) = \frac{A_0 - A_n}{A_0} \times 100\% , \quad (4)$$

Where A_0 is the initial absorbance value and A_n is the final absorbance value.

In order to go a step further analyzing the kinetics of Rh B decolorization, the kinetic model could be described and expressed by Equation (5):

$$\frac{dC}{dt} = -kC^m , \quad (5)$$

Where C is the concentration of Rh B, t is the reaction time, k is the reaction rate constant, m is the reaction order.

The above equation can be transformed into Equation (6) when the kinetic equation represents the variation of absorbance of Rh B along time. It can be written as pseudo-first order:

$$\ln(\frac{C}{C_0}) = -kt , \quad (6)$$

Where C is the concentration at time t and C_0 is the initial concentration. Constant k is the kinetic coefficient for first order reaction when the cathode fit well to a pseudo-first order equation.

Results and discussion

1. Working voltage effect

The working voltage will affect production of H_2O_2 and Fe^{2+}, and then influence the efficiency of Electro-Fenton reaction. Fig. 3 is the decolorization performance about suitable voltage of Ti, SS304L and SS316. It showed that the decolorization performance from the lowest to the highest are as follows SS304L, SS316, and Ti. Fig. 4 is analysis of pseudo-first order decolorization kinetics about suitable voltage of Ti, SS304L and SS316. All the correlation coefficients (R^2) values were higher than 0.95, displaying the good

linear fitting between experimental data and the pseudo-first order kinetic model. In Table 1, the Rh B decolorization shows that the maximal k arrives at 0.021 min^{-1} on the Ti cathode. It indicated that the rate of Rh B decay with Ti was 1.75 times faster than with SS316 and 2 times faster than with SS304L, respectively.

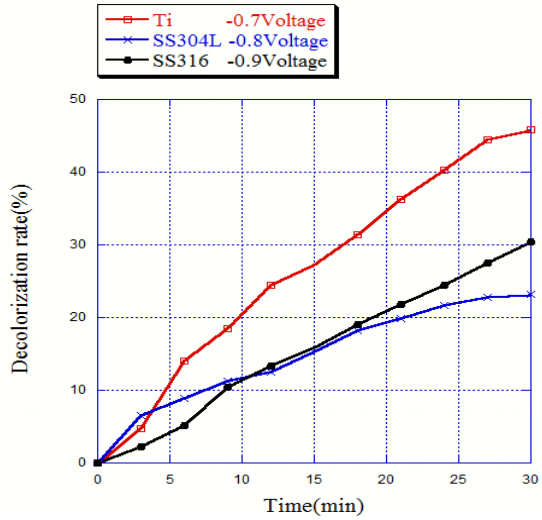

Fig. 3. Decolorization performance about suitable voltage of SS304L, SS316 and Ti.

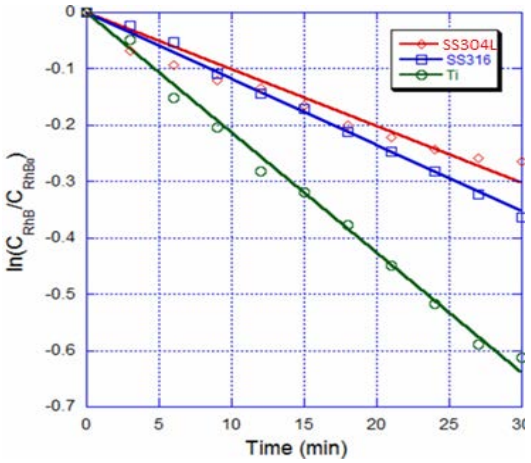

Fig. 4. Analysis of pseudo-first order decolorization kinetics about suitable voltage of SS304L, SS316, and Ti.

Table 1. Rate constant of SS304L, SS316 and Ti.

	SS304L	SS316	Ti
k(min^{-1})	0.012	0.010	0.021

2. pH effect

Nidheesh (2012) showed that, when pH value too low, Hydrogen ions may affect the possibility of the Electro-Fenton reaction; on the other hand, The hydroxide ion and iron combine to form a precipitate of ferric hydroxide, and inhibition of the Electro-Fenton reaction when pH value too high. These parts the pH value of each electrode was suitabled. Fig. 5 is the decolorization performance about suitable pH value of Ti, SS304L and SS316. It showed that the decolorization performance from the highest to the lowest are as follows SS316, Ti, and SS304L. It displayed that adjust the pH value make SS316 decolorizing ability beyond Ti electrode. Fig. 6 is analysis of pseudo-first order decolorization kinetics about suitable pH value of Ti, SS304L and SS316. All the R^2 were higher than 0.95, displaying the good linear fitting between experimental data and the pseudo-first order kinetic model. The slope after calculating the kinetic linear equation represents the electrochemical decolorization reaction rate of the system. The results showed that Electro-Fenton system performed Rh B decolorization reaction rate, SS316 and Ti electrode reaction rate close to and faster than SS304L electrode system, in which SS316 degradation rate is the fastest. The Rh B decolorization shows that the maximal k arrives at 0.022 min^{-1} on the SS316 cathode as seen from the Table 2. It indicated that the rate of Rh B decay with SS316 was 1.57 times faster than with SS304L and 1.05 times faster than with Ti, respectively.

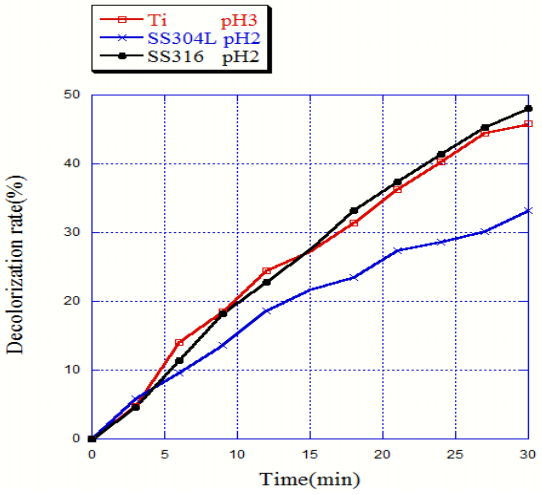

Fig. 5. Decolorization performance about suitable pH value of SS304L, SS316 and Ti.

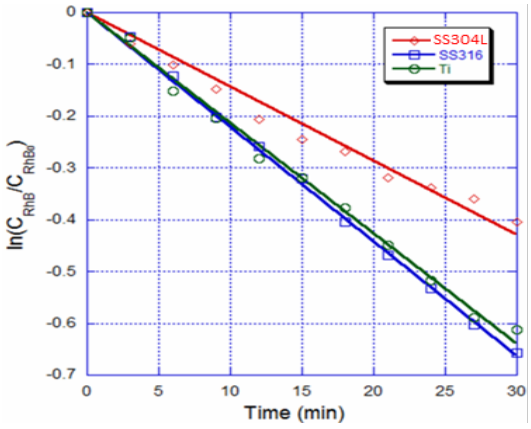

Fig. 6. Analysis of pseudo-first order decolorization kinetics about suitable pH value of SS304L,

SS316 and Ti.

Table 2. Rate constant of SS304L, SS316 and Ti.

	SS304L	SS316	Ti
k(min^{-1})	0.014	0.022	0.021

3. Electrolyte concentration effect

The effect of KNO_3 concentration on decolorization of Rh B with SS304L, SS316 and Ti cathode was evaluated by the Electro-Fenton system.

The suitable KNO_3 addition of employed electrodes had investigated through a series experimental. Fig. 7 demonstrates that the decolrization of Rh B is clear influenced by the KNO_3 concentration. For the SS316 electrode, the decolorization rate was higher than the other electrodes. After 30min of KNO_3 concentration experimental, the decolorization rate of Rh B on the SS316 electrode was arrived at 52%. However, the Ti and SS304L electrodes achieved on 45% and 42% during 30min.

To further investigate the influence of electro-Fenton with three different electrodes, the decolorization processes were fitted by psedo-firstorder model to analyze Rh B decolorization with SS304L, SS316 and Ti electrode.

All the correlation coefficients values were higher than 0.99, displaying good linear fitting between experimental data and kinetic model shown in the Fig. 8. The Rh B decolorization shows that the maximal k arrived at 0.025min^{-1} on the SS316 cathode as seen from the Table 3.

It indicated that the rate of Rh B decay with SS316 was 1.32 times faster than with SS304L and 1.81 times faster than with Ti. The SS316 electrode was fastest to decolor Rh B between three electrodes.

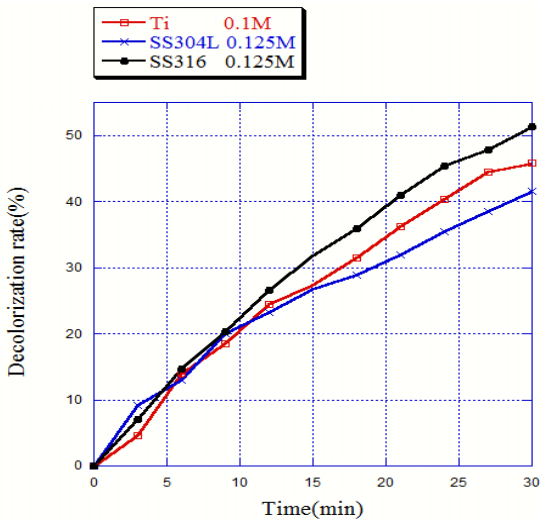

Fig. 7. Comparison of effect of KNO_3 concentration with SS304L, SS316 and Ti electrode on variation of decolorization rate of Rh B with time.

4. Fe^{2+} effect

The effect of Fe^{2+} concentration on decolorization of Rh B with SS304L, SS316 and Ti

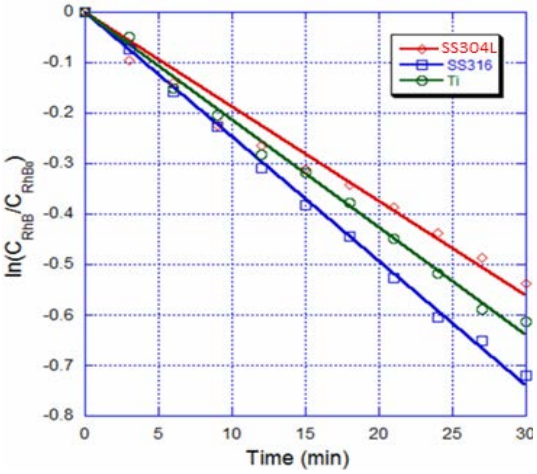

Fig. 8. Comparison of effect of KNO_3 concentration with SS304L, SS316 and Ti electrode on kinetic analysis for the pseudo-first order of Rh B declorization.

Table 3. Reaction rate constant of SS304L, SS316 and Ti.

	SS304L	SS316	Ti
k(min^{-1})	0.019	0.025	0.021

cathode was by the evaluated Electro-Fenton system.

The suitable Fe^{2+} addition of employed electrodes had investigated through a series experimental. Fig. 9 demonstrates that the decolrization of Rh B is clear influenced by the Fe^{2+} concentration. For the SS316 electrode, the decolorization rate was higher than the other electrodes. After 30min of Fe^{2+} concentration experimental, the decolorization rate of Rh B on the SS316 electrode was arrived at 65%. However, the Ti and SS304L electrodes achieved on 45% and 52% during 30min. The trends of three decolorization rate were on the whole the same within the 30min and declorization rate slowed down in the latter part, which can be ascribed to decreasing Fe^{2+} concentration during electro-Fenton process. It might allude to the poor effective regeneration of Fe^{2+} from Fe^{3+}.

To further investigate the influence of electro-Fenton with three different electrodes, the decolorization processes were fitted by pseudo-first order model to analyze Rh B decolorization with SS304L, SS316 and Ti electrode.

All the correlation coefficients values were higher than 0.99, displaying good linear fitting between experimental data and kinetic model shown in the Fig. 10. The Rh B decolorization shows that the maximal k arrived at 0.038min^{-1} on the SS316 cathode as seen from the Table 4.

It indicated that the rate of Rh B decay with SS316 was 1.52 times faster than with SS304L and

1.81 times faster than with Ti. The SS316 electrode was fastest to decolor Rh B among three electrodes and the Ti electrode was the slowest.

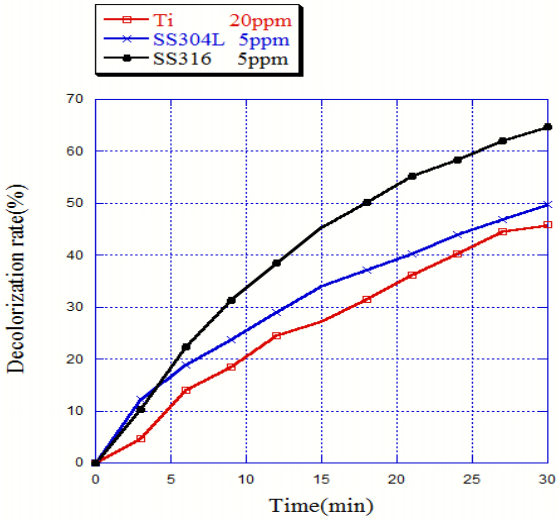

Fig. 9. Comparison of effect of Fe2+ concentration with SS304L, SS316 and Ti electrode on variation of decolorization rate of Rh B with time.

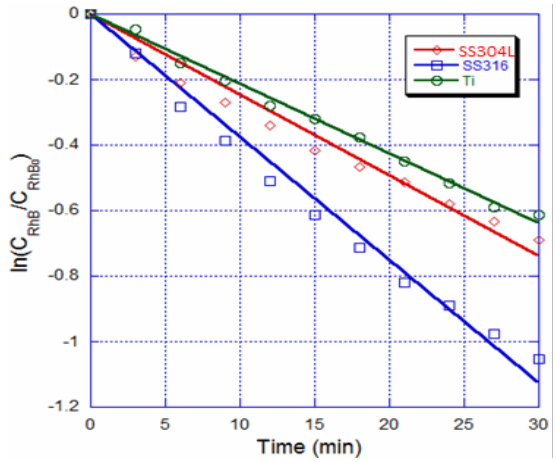

Fig. 10. Comparison of effect of Fe^{2+} concentration with SS304L, SS316 and Ti electrode on kinetic analysis for the pseudo-first-order of Rh B declorization.

Table 4. Reaction rate constant of SS304L, SS316 and Ti.

	SS304L	SS316	Ti
k(min^{-1})	0.025	0.038	0.021

Conclusions

In this research, stainless steel 304, 316 and titanium cathode electrode in dual-cell electro-Fenton compared decolorization in suitable parameter. The results indicate are as follows:

1. The SS304L, SS316 and Ti electrodes was employed as cathode in electro-Fenton process. Each influence factor of electro-Fenton process was compared under suitable parameter condition.
2. After the suitable experimental show that the decolorization rate SS316, SS304L and titanium were 64.7%, 49.7% and 45.8%, respectively. It obvious that SS316 have the best decolorization rate for electro-Fenton process.
3. During pseudo-first order kinetic model, SS316 had the fastest decay rate of reaction rate constant k=0.038 min^{-1}.
4. Therefore, this article provides helpful for the application of SS304L, SS316 and Ti electrode in electro-Fenton decolorization of dye pollutants.

Acknowledgments

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References

Ai, Z. H., Xiao, H. Y., Mei, T., Liu, J., Zhang, L. H., Deng, K. J. and Qiu, J. R., "Electro-Fenton Degradation of Rhodamine B Based on a Composite Cathode of Cu2O Nanocubes and Carbon Nanotubes," J. Phys. Chem. C., 112 (31), 11929-11935(2008).

Babuponnusami, A. and Muthukumar, K., "A review on Fenton and improvements to the Fenton process for wastewater treatment", Journal of Environmental Chemical Engineering, 2(1), 557-572(2014).

Cheng, Z.L., Li, Y.X. and Liu, Z., "Novel adsorption materials based on graphene oxide/Beta zeolite composite materials and their adsorption performance for rhodamine B", Journal of Alloys and Compounds, 708, 255-263(2017).

Chou, S., Huang, Y.H., Lee, S.N., Huang, G.H. and Huang, C., "Treatment of high strength hexamine-containing wastewater by electro-Fenton method", Water Research, 33(3), 751-759(1999).

Nidheesh, P.V. and Gandhimathi, R., "Comparative Removal of Rhodamine B from Aqueous Solution by Electro-Fenton and Electro-Fenton-Like Processes", CLEAN - Soil, Air, Water, 42(6), 779-784(2014).

Nidheesh, P.V. and Gandhimathi, R., "Trends in electro-Fenton process for water and wastewater treatment: An overview", Desalination, 299, 1-15(2012).

Oturan, M.A., "An ecologically effective water treatment technique using electrochemically generated hydroxyl radicals for in situ

destruction of organic pollutants: Application to herbicide 2,4-D", Journal of Applied Electrochemistry, 30(4), 475-482(2000).
Taziki, M., Shemirani, F., and Majidi, B., "Robust ionic liquid against high concentration of salt for preconcentration and determination of rhodamine B", Separation and Purification Technology, 97, 216-220(2012).
Xu, H.Y., Qi, S.Y., Li, Y., Zhao, Y. and Li, J.W., "Heterogeneous Fenton-like discoloration of Rhodamine B using natural schorl as catalyst: optimization by response surface methodology", Environ Sci Pollut Res Int, 20(8), 5764-72(2013).
Yang, C. W. and Wang, D., "A Comparative Study on the Different Cathodes of Electro-Fenton Process for the Decoloration of Methyl Orange Azo Dye in Water," Computer Science for Environmental Engineering and EcoInformatics, 158, 19-25(2011).

SS304L、SS316 不銹鋼和鈦電極於雙槽式電芬頓法進行 Rh B 染料脫色性能之研究

王宜達 謝毅基 林祐辰 李育漢
國立宜蘭大學機械與機電工程學系

摘 要

隨者科技不斷進步人類開發許多的商業染料，在使用染料過程常有大量有色廢水產生；因此，如何有效處理這些有色廢水為大家所關注之議題。本研究利用 304 不銹鋼(SS304L)、316 不銹鋼(SS316)和鈦(Ti)電極，應用電芬頓(Electro-Fenton)法觀察系統脫色 Rh B(Rhodamine B)染料之效能。實驗藉由電芬頓法進行參數調整，包含：工作電壓、酸鹼值(pH 值)、支持電解質濃度和亞鐵離子(Fe^{2+})濃度；觀察在這三種電極之電芬頓系統脫色 Rh B 染料之效益。結果顯示，SS316 不銹鋼電極的脫色性能為這三種電極中之最佳，其脫色效率在系統運行 30 分鐘後可達 64.7%。