Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.980328

57 (2016) 2073–2080
January

Taylor & Francis
Taylor & Francis Group

Electrochemical destruction of polyvinyl alcohol mediated by electrogenerated Ce(IV) in aqueous solution

Kai-Yu Huang[a], Wei-Lung Chou[b], Chih-Ta Wang[c,*], Chi-Min Shu[a]

[a]*Doctoral Program, Department of Safety Health and Environmental Engineering, National Yunlin University of Science and Technology, Yunlin 64002, Taiwan, Tel. +886 5 5342601, ext. 4499; emails: s81191@hotmail.com (K.-Y. Huang), shucm@yuntech.edu.tw (C.-M. Shu)*
[b]*Department of Safety, Health and Environmental Engineering, Hungkuang University, Taichung 433, Taiwan, Tel. +886 4 26318652, ext. 4005; Fax: +886 4 26319175; email: wlchou@sunrise.hk.edu.tw*
[c]*Department of Safety Health and Environmental Engineering, Chung Hwa University of Medical Technology, Tainan 717, Taiwan, Tel. +886 6 2671214, ext. 850; Fax: +886 6 2675049; email: ctwwang@gmail.com*

Received 18 March 2014; Accepted 17 October 2014

ABSTRACT

This study investigated the electrogeneration of Ce(IV) and its application on the destruction of polyvinyl alcohol (PVA) in an undivided electrochemical cell. The effects of electric current, concentration of nitric acid, and temperature on PVA destruction efficiency were investigated and the corresponding specific energy consumptions (SEC) were also evaluated. The experimental results indicate that the PVA destruction increased with increasing the applied current, the concentration of nitric acid, and decreasing the temperature. When considering the PVA destruction efficiency and the corresponding SEC simultaneously, the best operating condition was found by 92% at the optimal applied current 0.1 A, concentration of nitric acid 0.5 M, and temperature 323 K, respectively. A pseudo-first-order kinetic model provided a good fit to the experimental results at various temperatures. The activation energy was calculated to be 78.27 kJ mol^{-1}, based on pseudo-first-order rate constants from the Arrhenius equation.

Keywords: Mediated electrochemical oxidation (MEO); Polyvinyl alcohol (PVA); Specific energy consumption (SEC); Activation energy

1. Introduction

Various types of synthetic polymers have been used in industries including polyvinyl alcohol (PVA), polyvinyl chloride, and polypropylene (PP) for manufacturing products. However, the environmental problem resulting from the production needs to be solved. PVA is a water-soluble polymer, commonly used as a sizing agent in the textile and paper-coating industries [1], and also used as an ophthalmic lubricant in the pharmaceutical industry for products such as adhesives, emulsion paints, paper coatings, and detergent-based materials. However, the release of PVA from industries causes many ecological problems [2]. The wastewater containing PVA causes environmental issues due to its ability to mobilize heavy metals from sediments in lakes and water streams [3]. However, conventional biological technologies do not satisfactorily reduce PVA concentration in wastewaters because the PVA-degrading capacity of most microorganisms

---

*Corresponding author.

is extremely restricted and specific [4]. Therefore, an efficient method must develop for the destruction of PVA in wastewater. There have been several researches on the degradation of PVA, including microorganisms degradation [5–9], photochemically degradation [10–12], ultrasonic techniques [13], radiation-induced degradation [14], adsorption [15,16], chemical oxidation [17–19], and electrocoagulation [20–22]. However, to date, there is little research on the attempt of using mediated electrochemical oxidation (MEO) technology for the destruction of PVA.

Recently, electrochemical technology has been applied for treating pollutants from wastewater [23,24]. MEO is a novel technology for the destruction of organics. These advantages of the MEO process are that the oxidation reaction takes place at room temperatures and pressures, the oxidation products formed are usually carbon dioxide and water, and the oxidizing agent can conveniently be reused, minimizing the production of secondary wastes [25–29]. In the MEO process, the mediator ion is a transition metal, for example, cerium (IV), silver (II), and cobalt (III). These mediators are basically strong oxidizing agents and are suitable to destruct organic complexes. Chung et al. [27] reported their work on Ag (II)/Ag (I)–MEO system for the destruction of NO and NO_2 in nitric acid medium. Balaji et al. [28] studied the MEO process taking 1 M Ce(III) as the initial mediator in nitric acid medium for the destruction of phenol. Balazs et al. [29] reported on the bench scale system destruction of organics using the silver (II) MEO process through continuous CO_2 monitoring. Cerium ion has been selected as the redox mediator in this study because of its high redox potential of 1.61 V, fast electrochemical oxidation of Ce(III) to Ce(IV), easy recovering characteristic and negligible water oxidation rate.

In this study, the effects of various parameters such as the applied current, concentration of nitric acid, and temperature at a comparatively low Ce concentration on the PVA destruction rate were investigated. The specific energy consumptions (SEC) under different operation conditions was evaluated. In addition, the kinetic constants for the destruction of PVA were determined and the activation energy was also calculated using a pseudo-first-order kinetic model for the MEO process.

2. Materials and methods

2.1. Materials and reagents

Cerium (III) nitrate hexahydrate was obtained from Alfa Aesar (Great Britain, USA). PVA (molecular weight in the range of 13,000–23,000 g mol^{-1}) was purchased from Sigma-Aldrich (Saint Louis, MO 63103, USA) with a hydrolysis degree ranging from 98 to 99%. An aqueous solution containing PVA was prepared in deionized water at 363 K by stirring. The concentration of the supporting electrolyte in the aqueous solutions was adjusted by the addition of HNO_3 (Gato Prerez, Spain). Potassium iodide (KI) was obtained from Union Chemical Work Ltd (Hsin-Chu, Taiwan) and iodine was purchased from Toyobo Co. Ltd (Osaka, Japan). Boric acid (H_3BO_3) was purchased from Merck (Darmstadt, Germany). All chemical reagents were prepared by dilution with deionized water to the desired concentrations.

2.2. Apparatus

Fig. 1 shows the schematic diagram of the MEO system in this study. The electrolytic cell was a 1.0 dm^3 glass vessel equipped with a water jacket and a magnetic stirrer. The solution temperature was controlled by continuously circulating water through the water jacket from a constant temperature circulating bath (Model BL-720, Taiwan). A magnetic stirrer bar (Suntex, SH-301, Taiwan) was spun at the center of the bottom of the cell. The platinum anode (6 cm^2) and platinum cathode (1 cm^2) was immersed in the PVA aqueous solution at a depth of 5.5 cm with the electrodes approximately 4 cm apart. The assembly was connected to a direct current power source (Sourcemeter 2400 Series, Cleveland, OH, USA).

2.3. Experimental methods and analysis

For each run, 0.5 dm^3 of synthetic wastewater containing PVA was tested. The magnetic stirrer was turned on and set at 300 rpm. The stirring speed was high enough to provide good mixing in the electrolytic

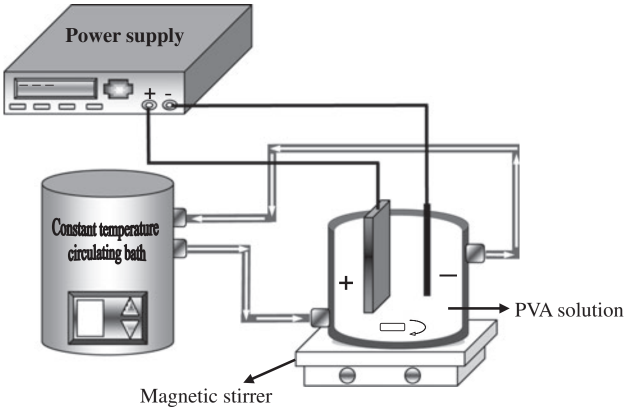

Fig. 1. Schematic diagram of the MEO equipment.

cell during the treatment process. A fixed amount of HNO_3, between 0.1 and 1 M, was added to the synthetic wastewater to increase the solution conductivity. The direct current power source was operated with a constant current of 0.05–0.4 A. A constant temperature of 303–343 K was maintained by circulating water from the temperature-controlled bath through the water jacket.

Ce(IV) concentration was quantitatively determined using ferrous ammonium sulfate dissolved in 0.005 M nitric acid [30]. The amount of Ce(IV) generated theoretically is dependent on the quantity of applied electricity. According to Faraday's laws of electrolysis, the theoretical production of Ce(IV) amount (m_t) at electrolysis time t can be calculated as below [31]:

$$m_t = \frac{MIt}{zF} \tag{1}$$

where M is molecular weight of Ce; I is the applied current; z is the electrons transferred per Ce(III) ion ($z = 1$ in $\text{Ce(III)} \rightarrow \text{Ce(IV)} + e^-$); F is Faraday's constant. The current efficiency is calculated using Eq. (2).

$$\text{Current efficiency (CE)} = \frac{m_e}{m_t} \times 100\% \tag{2}$$

where m_e is the Ce(IV) amount obtained experimentally.

Quantitative determination of PVA concentration was carried out using a UV–vis spectrophotometer (Hach, DR-2800, USA) after the addition of boric acid and iodine solutions, according to the procedure described by Finley [32]. A calibration curve was obtained by plotting the absorbance value at 680 nm against PVA concentration. The calculation of the PVA destruction efficiency after the MEO treatment was performed using the following formula:

$$DE\ (\%) = \frac{C_0V_0 - C_tV_t}{C_0V_0} \times 100 \tag{3}$$

where C_0 is the initial concentration in mg L^{-1}, C_t is the concentration value at time t in mg L^{-1}, V_0 is the initial volume of the treated wastewater in L, and V_t is the volume of the treated wastewater at time t in L.

3. Results and discussion

3.1. Effects of electric current and electrolysis time on Ce (III) oxidation

The MEO used electrochemically generated Ce(IV) from the initial Ce(III) to destroy PVA to carbon dioxide and water. The following reactions simultaneously take place in the electrochemical cell for this Ce(III)/Ce(IV) system [33].

At anode,

$$Ce^{3+} \rightarrow Ce^{4+} + e^- \tag{4}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{5}$$

At cathode,

$$Ce^{4+} + e^- \rightarrow Ce^{3+} \tag{6}$$

$$HNO_3 + 2H^+ + 2e^- \rightarrow HNO_2 + H_2O \tag{7}$$

In solution,

$$2HNO_2 + O_2 \rightarrow 2HNO_3 \tag{8}$$

The Ce(IV) is electrooxidized from Ce(III) at anode or electroreduced to Ce(III) at cathode (Eqs. (4) and (6)). For the undivided cell, the combination of Ce(III) oxidation at anode (Eq. (4)), and the reduction of Ce(IV) at cathode produced the net amount of Ce(IV) in the water. Nitric acid can be simultaneously reduced at cathode to nitrous acid (Eq. (7)). Nitric acid can be regenerated in solution by the chemical reaction of nitrous acid and oxygen (Eq. (8)).

Obviously, the electric current is an important factor that may influence the oxidation/reduction cycle for electrogeneration of Ce(IV). Therefore, the effect of electric current varying from 0.05 to 0.4 A on the Ce (IV) yield was investigated and the current efficiency was calculated, according to Eq. (2). Fig. 2 shows the Ce(IV) yield percentage increased with increasing electrolysis time during 50 min electrolysis. Furthermore, increasing electric current increased the Ce(IV) yield percentage. That is, more Ce(IV) was obtained when using larger electric current and longer electrolysis time. The Ce(IV) yield percentage reached 53%, the highest percentage in this study using 0.4 A after 50 min electrolysis. Fig. 2 also shows the current efficiency decreased with increasing electrolysis time and electric current. After 50 min electrolysis, the CE was 48.3% at 0.05 A, about double that at 0.4 A. If the electric current increased, the side reaction (Eq. (5)), may occur more intensively; consequently, the CE decreased. Besides, the fact that applying higher electric current caused higher anodic potentials, and thus favored the formation of platinum oxides that are detrimental for the Ce(IV) generation [34] may cause the lower value of CE.

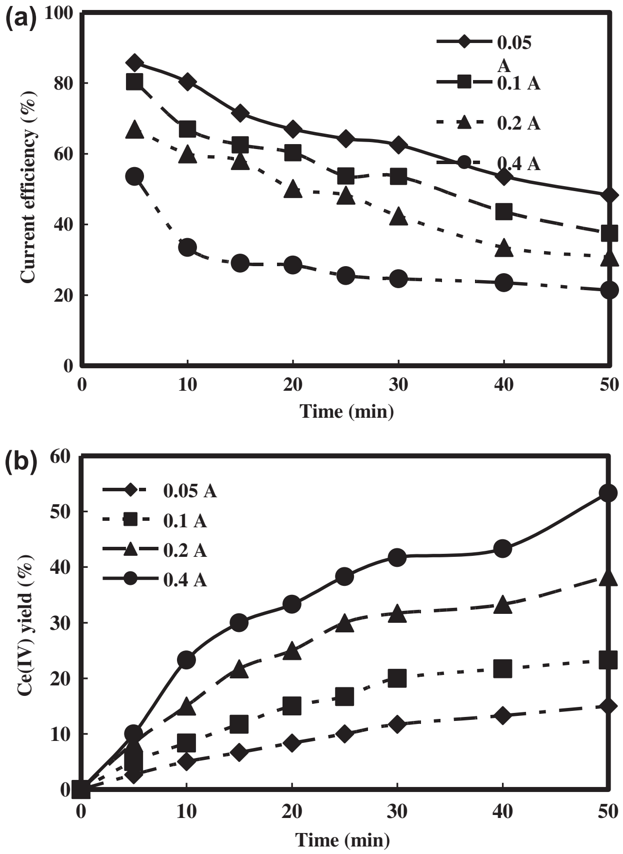

Fig. 2. Variations of (a) current efficiency and (b) Ce(IV) yield with time for the Ce(III) oxidation (PVA = 100 mg L^{-1}, t = 50 min, T = 323 K, HNO_3 = 0.5 M, and $[Ce(III)]_{initial}$ = 0.01 M).

3.2. Effects of electric current on PVA destruction efficiency

The PVA in the solution was destructed by the electrogenerated Ce(IV) as follows:

$$\begin{aligned} PVA + Ce(IV) &\rightarrow \text{organic compounds} \\ &\rightarrow CO_2 + H_2O + Ce(III) \end{aligned} \tag{9}$$

Fig. 3 illustrates the effect of different electric current on the destruction efficiency of PVA. As the electric current increased, PVA destruction efficiencies increased. After 50 min of electrolysis, 84, 90, 92, and 93% of the original PVA were destructed at electric currents of 0.05, 0.1, 0.2, and 0.4 A, respectively. The reduced Ce(III) can be electrooxidized to Ce(IV) according to Eq. (4). Therefore, the electrogenerated Ce(IV) can be reused as the oxidant for the continuous destruction of PVA. However, no significant improvement in the PVA destruction efficiency was observed while the electric current increased from 0.2 to 0.4 A.

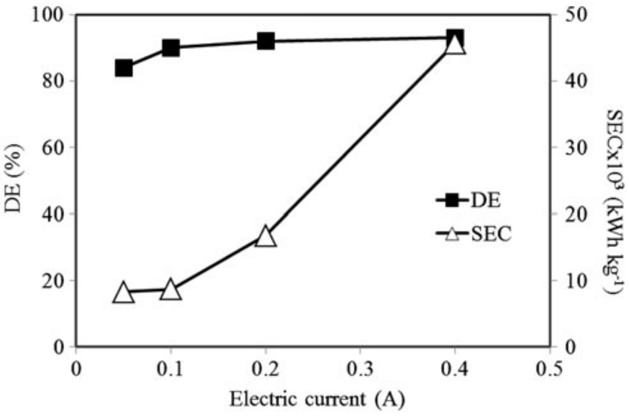

Fig. 3. Effect of electric current on the SEC and PVA destruction efficiency (PVA = 100 mg L^{-1}, t = 50 min, T = 323 K, HNO_3 = 0.5 M, and $[Ce(III)]_{initial}$ = 0.01 M).

In order to obtain the optimum electric current when concerning the energy efficiency, the SEC [35,36] for destroying 1 kg PVA at a specified certain electric current was calculated. Fig. 3 also shows the SEC values after 50 min of electrolysis at different electric currents. It can be evidently seen that increasing electric current had a significant effect on SEC. When the electric current varied from 0.05 to 0.4 A, we observed a dramatic increase in the SEC value from 8.35 to 45.7 kWh kg^{-1} for PVA destruction. When the current density was increased from 0.05 to 0.1 A, the PVA destruction efficiency increased, appreciably, from 84 to 90%, and the SEC value increased only slightly. However, as the current density was increased from 0.1 to 0.4 A, the PVA destruction efficiency was slightly improved from 90 to 93%, whereas the corresponding SEC increased significantly from 8.71 to 45.7 kWh kg^{-1}. Consequently, while considering the minimum SEC values for over 90% PVA destruction efficiency at different currents, an electric current of 0.1 A can provide the best performance for the present electrochemical oxidation.

3.3. Effects of acid concentration

The selection of the electrolyte plays a very important role in MEO processes. The soluble ability of the metal salts of the acid is critical. Sulfuric acid possesses low solubility of cerium and therefore leads to fractional oxidation of organics. In comparison with sulfuric acid, nitric acid is chosen in the present study because it has good solubility for cerium salts. Hence, in the case of cerium–MEO system, a high acid concentration of 1–5 M was usually used [37]. However, such a high acid concentration can cause the other environmental problems. Therefore, we used comparatively low acid concentration in this study. The effects of various acid concentrations on PVA destruction efficiency were described in Fig. 4. The PVA destruction efficiency increased with increasing acid concentration from 0.1 to 1 M. When the acid concentration was 0.1, 0.25, 0.5, and 1 M, the destruction efficiency was 44, 87, 92, and 94% after 50 min, respectively. This phenomenon was probably derived from the increasing formation yield of Ce(IV) while increasing acid concentration [38]. However, if the concentration of nitric acid was higher than 0.5 M, the destruction efficiency did not increase significantly. Fig. 4 also indicates that the SEC decreased from 9.67 to 2.09 kWh kg^{-1} when the concentration of the nitric acid increased from 0.1 to 1 M. Although there was a significant downward trend for the SEC while the concentration of nitric acid increased, the SEC was not significantly changed by increasing acid concentration from 0.5 to 1 M. Consequently, when simultaneously considering the destruction efficiency and SEC, a 0.5 M concentration of nitric acid was the optimal concentration with reasonable destruction efficiency at a relatively low SEC.

3.4. *Effects of temperature*

In this study, the effects of various solution temperatures on the destruction of 100 mg L^{-1} PVA were investigated at 303, 313, 323, 333, and 343 K, as shown in Fig. 5. After 50 min of electrolysis, it was observed that the maximum PVA destruction was found at 343 K. The PVA destruction reached 43, 63, 92, 94, and 96% for temperatures of 303, 313, 323, 333, and 343 K, respectively. The electrochemical reaction rate and chemical reaction rates usually increase with increasing solution temperature. Therefore, the destruction efficiency increased with the increasing electrogeneration of Ce(IV). Besides, the temperature rise may cause effective destruction of the passivation on the anode surface and reduce the degree of polarization of the electrode and decrease overpotential, resulting in inhibiting the generation of oxygen [39]. Therefore, at higher temperature, the electrogeneration rate of Ce (IV) in the reaction cell was found well.

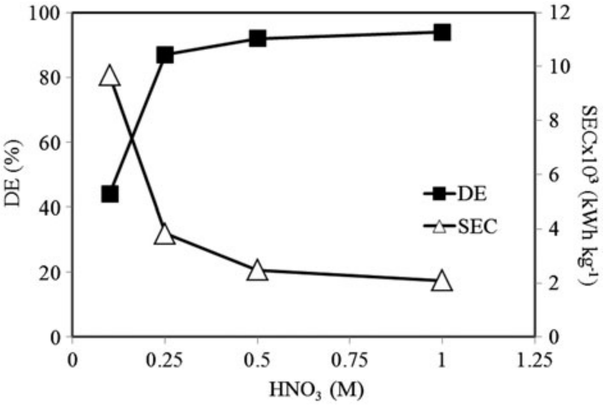

Fig. 4. Effect of nitric acid concentrations on the SEC and PVA destruction efficiency (PVA = 100 mg L^{-1}, t = 50 min, T = 323 K, current = 0.1 A, and $[Ce(III)]_{initial}$ = 0.01 M).

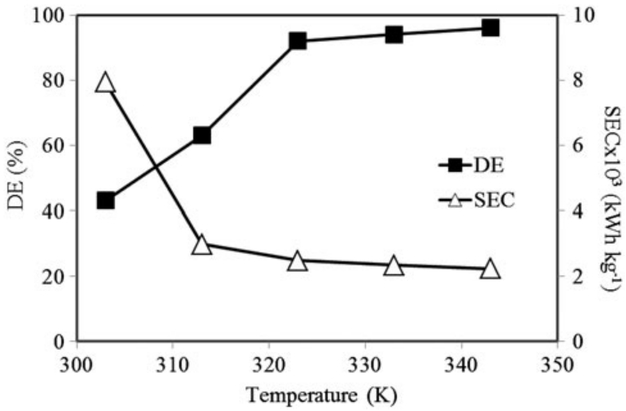

Fig. 5. Effect of temperature on the SEC and PVA destruction efficiency (PVA = 100 mg L^{-1}, t = 50 min, HNO_3 = 0.5 M, current = 0.1 A, and $[Ce(III)]_{initial}$ = 0.01 M).

Fig. 5 also shows the SEC values calculated on the PVA destruction efficiency after 50 min of electrolysis at different temperatures. The SEC values decreased significantly, by approximately 50%, when the temperature increased from 303 to 313 K. While the temperature was 313, 323, 333, and 343 K, the SEC value for PVA destruction was 2.98, 2.48, 2.34, and 2.23 kWh kg^{-1}, respectively. Consequently, on consideration of the destruction efficiency and SEC values for PVA destruction, a temperature of 323 K offers the best performance with reasonable destruction efficiency and a relatively low SEC.

3.5. *PVA destruction kinetics of MEO*

The PVA destruction kinetics was described by a pseudo-kinetics model in which the rate constant depends on the temperature. The pseudo-kinetic rate equation for representing the destruction rate in PVA concentration in the aqueous solution was described by the following *m*th order reaction kinetics:

$$\frac{dC}{dt} = -kC^m \tag{10}$$

where C represents the PVA concentration, m is the order of reaction, k is the reaction rate constant, and t

Table 1
Kinetic rate constants with pseudo-first-order and pseudo-second-order models for PVA destruction at various temperatures

	Pseudo-first-order model		Pseudo-second-order model	
Temperature (K)	$k_1 \times 10^{-2}$ (min^{-1})	R^2	$k_2 \times 10^{-2}$ (L mol^{-1} min^{-1})	R^2
303	0.82	0.99	0.01	0.89
313	1.63	0.99	0.03	0.87
323	4.53	0.99	0.22	0.73
333	8.65	0.99	1.16	0.68
343	10.6	0.99	2.62	0.79

is the time. For a pseudo-first-order reaction, the above Eq. (10) becomes:

$$\ln\left(\frac{C_t}{C_0}\right) = -k_1 t \tag{11}$$

The slope of the plot of ln C_t/C_0 vs. time gives the value of the rate constant k_1, min^{-1}. Here, C_0 is the initial concentration in mol L^{-1}, C_t is the concentration value in mol L^{-1} at time t, and t is the time.

For a pseudo-second-order reaction, the above Eq. (10) becomes:

$$\frac{1}{C_t} - \frac{1}{C_0} = k_2 t \tag{12}$$

The slope of the plot of $1/C_t$ vs. time gives the value of the rate constant k_2, L mol^{-1} min^{-1}. The values of k with pseudo-first-order and second-order models for PVA destruction for various temperatures are determined graphically and are shown in Table 1, respectively. The conformity between experimental data and the model values was evaluated using correlation values (R^2). As shown in Table 1, regardless of the temperature, the R^2 value for the pseudo-first-order model was relatively higher than that for the pseudo-second-order model. Consequently, the first-order kinetic model fits well with the observed data of the MEO process for temperature. To understand the relationship between temperature and the rate of a reaction, we can assume that the rate constant depends on the temperature of the reaction. The pseudo-first-order rate constant is expressed by the Arrhenius equation.

$$\ln k = \ln A - \frac{E_a}{RT} \tag{13}$$

where A is the proportionality constant of the reaction, E_a is the activation energy (kJ mol^{-1}), R is the gas constant (8.314 J mol^{-1} K^{-1}), and T is the temperature (K). The Arrhenius equation can be used to determine the activation energy of a reaction. According to this equation, a plot of ln k vs. $1/T$ should produce a straight line with a slope of $-E_a/R$, as shown in Fig. 6. An activation energy of 78.27 kJ mol^{-1} was calculated using the slope of the fitted equation (least-squares correlation coefficient = 0.9226).

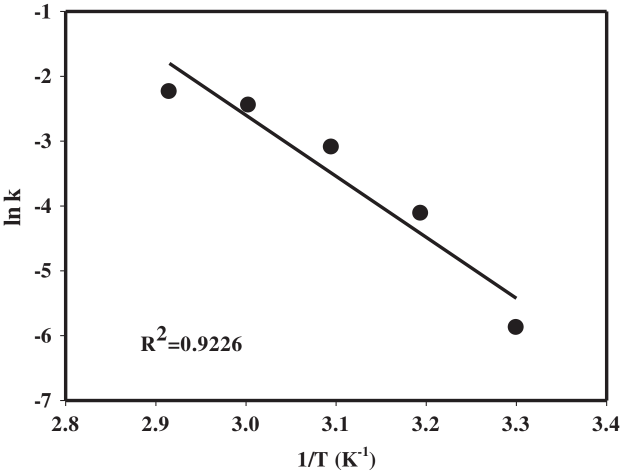

Fig. 6. Pseudo-first-order kinetic rate constant vs. reciprocal of temperature in absolute scale (PVA = 100 mg L^{-1}, t = 50 min, HNO_3 = 0.5 M, current = 0.1 A, and [Ce(III)]$_{\text{initial}}$ = 0.01 M).

4. Conclusions

In this study, the MEO for destruction of PVA from aqueous solution was investigated. The MEO procedure successfully generated Ce(IV) as the mediator to destroyed PVA in a batch reactor. The effects of various parameters were evaluated for PVA destruction such as the electric current, concentrations of nitric acid, and temperature. The applied electric current of 0.1 A was regarded as the optimum value, providing reasonable destruction efficiency and SEC; with the same considerations, the nitric acid concentration of 0.5 M and the solution temperature of 323 K were found to be the optimum values for the present experiment. The experimental results revealed that the kinetics of PVA destruction can be described by the pseudo-first-order model. Besides, the value of activation energy was calculated to be 78.27 kJ mol^{-1} based on pseudo-first-order rate constants from the Arrhenius equation.

Acknowledgment

The authors would like to thank the National Science Council of Taiwan, ROC for financially supporting this study under contract numbers NSC 100-2628-E-273-001-MY3 and NSC100-2221-E-241-013.

References

[1] Y. Tokiwa, G. Kawabata, A. Jarerat, A modified method for isolating poly (vinyl alcohol)-degrading bacteria and study of their degradation patterns, Biotechnol. Lett. 23 (2001) 1937–1941.

[2] J.A. Giroto, R. Guardani, A.C.S.C. Teixeira, C.A.O. Nascimento, Study on the photo-Fenton degradation of polyvinyl alcohol in aqueous solution, Chem. Eng. Process. 45 (2006) 523–532.

[3] H. Schonberger, A. Baumann, W. Keller, Study of microbial degradation of polyvinyl alcohol (PVA) in wastewater treatment plants, Am. Dyestuff Rep. 86 (1997) 9–18.

[4] J.G. Lim, D.H. Park, Degradation of polyvinyl alcohol by *Brevibacillus laterosporous*: Metabolic pathway of polyvinyl alcohol to acetate, J. Microbiol. Biotechnol. 11 (2001) 928–933.

[5] R. Solaro, A. Corti, E. Chiellini, Biodegradation of poly (vinyl alcohol) with different molecular weights and degree of hydrolysis, Polym. Adv. Technol. 11 (2000) 873–878.

[6] E. Chiellini, A. Corti, B. Politi, R. Solaro, Adsorption/desorption of polyvinyl alcohol on solid substrates and relevant biodegradation, J. Polym. Environ. 8 (2000) 67–79.

[7] A. Corti, R. Solaro, E. Chiellini, Biodegradation of poly (vinyl alcohol) in selected mixed microbial culture and relevant culture filtrate, Polym. Degrad. Stabil. 75 (2002) 447–458.

[8] J. Chen, Y. Zhang, G.C. Du, Z.Z. Hua, Y. Zhu, Biodegradation of polyvinyl alcohol by a mixed microbial culture, Enzyme Microb. Technol. 40 (2007) 1686–1691.

[9] S.I. Tsujiyama, T. Nitta, T. Maoka, Biodegradation of polyvinyl alcohol by *Flammulina velutipes* in an unsubmerged culture, J. Biosci. Bioeng. 112 (2011) 58–62.

[10] L.C. Lei, X.J. Hu, P.L. Yue, S.H. Bossmann, S. Göb, A.M. Braun, Oxidative degradation of poly vinyl alcohol by the photochemically enhanced Fenton reaction, J. Photochem. Photobiol., A 116 (1998) 159–166.

[11] S.H. Bossmann, E. Oliveros, S. Gob, M. Kantor, A. Goppert, L. Lei, P.L. Yue, A.M. Braun, Degradation of polyvinyl alcohol (PVA) by homogeneous and heterogeneous photocatalysis applied to the photochemically enhanced Fenton reaction, Water Sci. Technol. 44 (2001) 257–262.

[12] Y.X. Chen, Z.S. Sun, Y. Yang, Q. Ke, Heterogeneous photocatalytic oxidation of polyvinyl alcohol in water, J. Photochem. Photobiol., A 142 (2001) 85–89.

[13] A. Grönroos, P. Pirkonen, J. Heikkinen, J. Ihalainen, H. Mursunen, H. Sekki, Ultrasonic depolymerization of aqueous polyvinyl alcohol, Ultrason. Sonochem. 8 (2001) 259–264.

[14] S.J. Zhang, H.Q. Yu, Radiation-induced degradation of polyvinyl alcohol in aqueous solutions, Water Res. 38 (2004) 309–316.

[15] A.K. Bajpai, N. Vishwakarma, Adsorption of polyvinylalcohol onto Fuller's earth surfaces, Colloids Surf., A 220 (2003) 117–130.

[16] S.K. Behera, J.H. Kim, X.J. Guo, H.S. Park, Adsorption equilibrium and kinetics of polyvinyl alcohol from aqueous solution on powdered activated carbon, J. Hazard. Mater. 153 (2008) 1207–1214.

[17] Y.S. Won, S.O. Baek, J. Tavakoli, Wet oxidation of aqueous polyvinyl alcohol solution, Ind. Eng. Chem. Res. 40 (2001) 60–66.

[18] A.M.T. Silva, R.N.P. Vaz, R.M. Quinta-Ferreira, J. Levec, Gas–liquid–solid reactions of polyvinyl alcohol on oxidation treatments fro environmental pollution remediation, Can. J. Chem. Eng. 81 (2003) 566–573.

[19] S. Kim, T.H. Kim, C. Park, E.B. Shin, Electrochemical oxidation of polyvinyl alcohol using a RuO_2/Ti anode, Desalination 155 (2003) 49–57.

[20] W.L. Chou, C.T. Wang, K.Y. Huang, Investigation of process parameters for the removal of polyvinyl alcohol from aqueous solution by iron electrocoagulation, Desalination 251 (2010) 12–19.

[21] W.L. Chou, Removal and adsorption characteristics of polyvinyl alcohol from aqueous solutions using electrocoagulation, J. Hazard. Mater. 177 (2010) 842–850.

[22] C.T. Wang, W.L. Chou, K.Y. Huang, Treatment of polyvinyl alcohol from aqueous solution via electrocoagulation, Sep. Sci. Technol. 45 (2010) 212–220.

[23] L.J.J. Janssen, L. Koene, J. Chem, The role of electrochemistry and electrochemical technology in environmental protection, Chem. Eng. 85 (2002) 127–136.

[24] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol. 38 (2004) 11–41.

[25] J.C. Farmer, F.T. Wang, P.R. Lewis, L.J. Summers, Destruction of chlorinated organics by cobalt(III)-mediated electrochemical oxidation, J. Electrochem. Soc. 139 (1992) 3025–3028.

[26] V.V. Kokovkin, S.J. Chung, S. Balaji, M. Matheswaran, I.S. Moon, Electrochemical cell current requirements for toxic organic waste destruction in Ce(IV)-mediated electrochemical oxidation process, Korean J. Chem. Eng. 24 (2007) 749–756.

[27] S.J. Chung, K. Pillai, A sustainable environmentally friendly NOx removal process using Ag(II)/Ag(I)-mediated electrochemical oxidation, Sep. Purif. Technol. 65 (2009) 156–163.

[28] S. Balaji, S.J. Chung, R. Thiruvenkatachari, I.S. Moon, Mediated electrochemical oxidation process: Electro-oxidation of cerium(III) to cerium(IV) in nitric acid medium and a study on phenol degradation by cerium(IV) oxidant, Chem. Eng. J. 126 (2007) 51–57.

[29] B. Balazs, Z. Chiba, P. Hsu, P. Lewis, L. Murguia M. Adamson, Destruction of hazardous and mixed wastes using mediated electrochemical oxidation in a silver(II) nitric acid bench scale system, Proceedings

of the sixth International Conference on Radioactive Waste Management and Environmental Remediation, ICEM 97, New York, NY, Am. Soc. Mech. Eng. (1997) 541–545.
[30] Y. Wei, B. Fang, T. Arai, M. Kumagai, Electrolytic oxidation of Ce(III) in nitric acid and sulfuric acid media using a flow type cell, J. Appl. Electrochem. 35 (2005) 561–566.
[31] T. Raju, C.A. Basha, Electrochemical cell design and development for mediated electrochemical oxidation-Ce(III)/Ce(IV)system, Chem. Eng. J. 114 (2005) 55–65.
[32] J.H. Finley, Spectrophotometric determination of polyvinyl alcohol in paper coatings, Anal. Chem. 33 (1961) 1925–1927.
[33] K.L. Huang, T.S. Chen, K.J. Yeh, Regeneration of Ce (IV) in simulated spent Cr-etching solutions using an undivided cell, J. Hazard. Mater. 171 (2009) 755–760.
[34] T.H. Randle, A.K. Kuhn, Kinetics and mechanism of the cerium(IV)/cerium(III) redox reaction on a platinum electrode, J. Chem. Soc. Faraday Trans. 79 (1983) 1741–1756.
[35] W.L. Chou, C.T. Wang, S.Y. Chang, Study of COD and turbidity removal from real oxide-CMP wastewater by iron electrocoagulation and the evaluation of specific energy consumption, J. Hazard. Mater. 168 (2009) 1200–1207.
[36] W.L. Chou, C.T. Wang, K.Y. Huang, Effect of operating parameters on indium (III) ion removal by iron electrocoagulation and evaluation of specific energy consumption, J. Hazard. Mater. 167 (2009) 467–474.
[37] Z. Chiba, Mediated electrochemical oxidation of mixed wastes, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-JC-112669, April 1993.
[38] J. Varela, S. Oberg, T.M. Neustedter, N. Nelson, Non-thermal organic waste destruction: Characterization of the CerOx system 4, Environ. Prog. 20 (2001) 261–271.
[39] N.I. Kharabadze, Anode process in strongly acidic Mn sulfate solution, Elektrokhim. Margantsa, Akad. nauk. Gruz. SSR 2 (1965) 267–270.