Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.880380

54 (2015) 325–331
April

Taylor & Francis
Taylor & Francis Group

Electrochemical oxidation of D-fructose solution using the Box–Behnken design methodology

Chen Lim Tay*, Shuey Lee Fam

Department of Chemical and Petroleum Engineering, School of Engineering and Science, Curtin University Sarawak Campus, CDT 250, 98000 Miri, Sarawak, Malaysia
Tel. +60 85 443939; Fax: +60 85 443837; email: taycl@curtin.edu.my

Received 12 September 2013; Accepted 1 January 2014

ABSTRACT

The electrochemical oxidation of D-fructose solution was studied using a Box–Behnken design. Seventeen batch runs of electrochemical oxidation were conducted based on three sets of operating conditions generated using Design-Expert software. The effects of D-fructose concentration, applied voltage and NaOH concentration on oxidation percentage and oxidation rate were studied. As revealed by ANOVA, the D-fructose and NaOH concentrations significantly affected the oxidation percentage, and the applied voltage and NaOH concentration significantly affected the oxidation rate. Functional models for the oxidation percentage and oxidation rate were generated and reported. The electrochemical oxidation of D-fructose was optimised by maximising the D-fructose concentration and minimising the applied voltage and NaOH concentration. The models were validated by comparing the adjusted optimised solution with the experimental data. A 62.78% electrochemical oxidation percentage and an oxidation rate of 12.20 mM/L h were achieved using 82% D-fructose with 0.14 M NaOH and a 10 V applied voltage.

Keywords: Electrochemical oxidation; D-fructose; Box–Behnken; Wastewater treatment; Optimisation; Modelling

1. Introduction

Electrochemical oxidation has been widely studied in waste management to treat high-COD wastewater using direct anodic oxidation and/or indirect oxidation methods. Such wastewater is commonly discharged from landfills [1,2] and livestock effluent [3], textile [4,5], refractory [6], sugar [7,8] and food and fruit processing industries [9]. The direct anodic oxidation method involves the application of metal oxide and catalytic metal alloy anodes, such as titanium-based dimensionally stable anodes [10] and boron-doped diamond and metal alloy electrodes [11,12], where direct oxidation occurs at the electrode surface [13]. In contrast, the indirect oxidation method involves the reduction of chlorine, hypochlorous acid and/or hypochlorite to oxidise the organic compounds near the anode and/or in the bulk of the solution in alkaline media. However, the effects of the addition of NaCl on the indirect oxidation may depend on the anodic material [14].

Recently, the electrochemical oxidation of simulated sugar industrial effluent containing a saccha-

---

*Corresponding author.

rose mixture solution has been reported using a RuO_2-coated titanium anode [7], iron, carbon and SS304 stainless steel [8]. A maximum COD removal of 80% was achieved by both the reported studies. The effects of current density, initial COD concentration and flow rate on COD removal were studied using a Box–Behnken design. Guven and co-workers studied the effects of applied voltage, NaCl concentration and waste concentration on the COD removal and initial COD removal rate using the CCD method. An iron electrode provided the highest percentage of COD removal; however, the resultant high turbidity indicated iron corrosion and $Fe(OH)_3$ formation.

In the present study, we focus on the electrochemical oxidation of D-fructose solution in alkaline media, as D-fructose is a prevalent substituent that contributes to the high COD of wastewater from the wine [15] and fruit processing industries [16]. The electrodes were comprised of 304 stainless steel due to its good corrosion resistance and moderate oxidation efficiency before the optimisation. The effects of D-fructose concentration, applied voltage and NaOH concentration on the oxidation percentage and oxidation rate are analysed using statistical tests. The electrochemical oxidation is modelled, and the optimised solution is predicted and compared with the experimental results.

2. Materials and methods

A 0.1 M D-fructose (HmbG Chemicals) solution was prepared by dissolving 18.016 g of D-fructose in a 1 L volumetric flask. Next, 4 g of sodium hydroxide (NaOH; UNIChem Chemical Reagent) was added to provide an alkaline supporting electrolyte. Both the anode and cathode were comprised of stainless-steel plates (SS304) with dimensions of 20 cm (length) × 5 cm (width) (immersed length: 12 cm). The stainless-steel plates were connected with alligator clips and wires to the DC power supply (GPC-3030) with a working voltage of 5–15 V. The D-fructose solution was stirred gently with a magnetic stirrer to yield a homogenous mixture while avoiding vortex formation or aeration.

The D-fructose concentration, pH and temperature of the solution were monitored and recorded in 1 h intervals. The D-fructose concentration of a 1 mL sample taken from the reactor was measured using a refractometer (Reichert r2mini) in Brix %, and the solution pH was simultaneously measured using a pH metre (Eutech Instruments) by placing the pH electrode in the reactor.

The Box–Behnken design methodology was used to generate an experimental design with three factors and three levels using Design-Expert 8.0. The three independent variable levels were: the D-fructose concentration (20–100%), applied voltage (5–15 V) and NaOH concentration (0.05–0.20 M). The total number of experiments required was 17, as defined by $N = 2k(k-1) + C_0$, where k is the number of factors and C_0 is the number of central points (5 for this experiment) [17]. The performance of the electrochemical oxidation of the D-fructose solution was evaluated by analysing the responses for oxidation percentage (%) and oxidation rate (mM/L h).

3. Results and discussion

The various concentrations of D-fructose (0, 0.01, 0.05 and 0.10 M) were calibrated at different concentrations of 0, 0.05, 0.13 and 0.20 M NaOH, as shown in Fig. 1. The Brix percentage of the solution increased as the D-fructose concentration and NaOH concentration increased. These calibrated results were used in the calculation of the D-fructose concentration before and after the electrochemical oxidation treatment based on

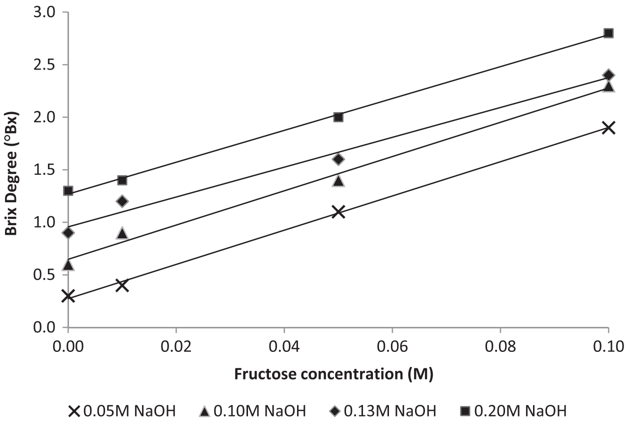

Fig. 1. Calibration data for various D-fructose concentrations for 0.05, 0.10, 0.13 and 0.20 M NaOH.

Table 1
Calibration equation with R^2 value for different concentrations of NaOH

NaOH concentration (M)	Calibration equation	R^2
0.05	$y = 16.29x + 0.2734$	0.9987
0.10	$y = 16.29x + 0.6484$	0.9912
0.13	$y = 14.194x + 0.9513$	0.9854
0.20	$y = 15.161x + 1.2685$	0.9984

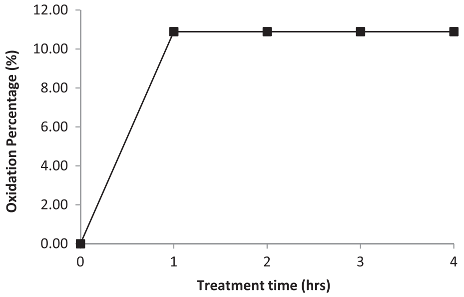

Fig. 2. D-fructose oxidation percentage after 4 h of treatment with 0.10 M NaOH and a 10 V applied voltage at an initial temperature of 25˚C.

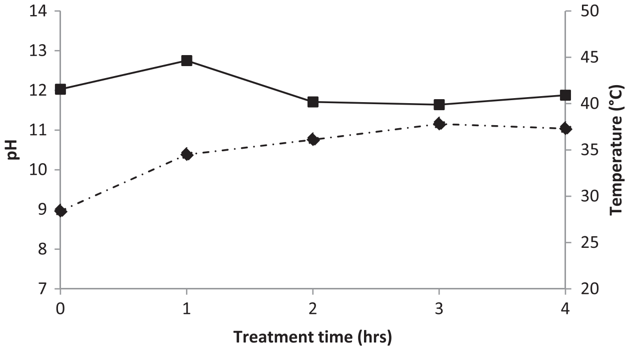

Fig. 3. Temperature and pH profile for a 4 h treatment with 0.10 M NaOH and a 10 V applied voltage.

the Brix degree (˚Bx). The calibration equations and R^2 values for different NaOH concentrations are shown in Table 1.

The preliminary electrochemical oxidation of D-fructose solution was conducted using 0.10 M D-fructose with 0.10 M NaOH at a 10 V applied voltage. The D-fructose concentration, pH and temperature of the solution were monitored at 1 h intervals, and the results are shown in Figs. 2 and 3. After 1 h of treatment, 10.9% of the D-fructose had been oxidised, and the oxidation had reached equilibrium. The pH of the solution slowly decreased from the initial value of 12.03 to the final value of 11.88 after 4 h. The decrease of the solution pH could be due to the formation of the 2-keto-D-gluconic acid as a major product [18]. The temperature of the solution increased gradually from 28.4 to 37.3˚C after 4 h due to the exothermic electrochemical oxidation process.

The effects of D-fructose concentration, applied voltage and NaOH concentration on the oxidation percentage and oxidation rate were further investigated with 17 batch runs from the Box–Behnken design and are presented in Table 2. Generally, increasing the applied voltage and NaOH concentration increased the oxidation percentage and oxidation rate. The highest oxidation percentage (71.80%) and oxidation rate (17.18 mM/L h) were achieved for a 100% D-fructose with a 10 V applied voltage and 0.20 M NaOH. The runs with operating conditions of 60% D-fructose, 10 V applied voltage and 0.13 M NaOH used five replicates, and the observed oxidation percentage and oxidation rate were in the ranges of 67.30–100% and 8.81–14.09 mM/L h, respectively.

The experimental data were further analysed using ANOVA and regression testing, as shown in Table 3.

Table 2
Experimental parameters and results for various runs generated by Design-Expert using the Box–Behnken method

Runs	Fructose (%)	Applied voltage (V)	NaOH (mol/L)	Oxidation percentage (%)	Oxidation rate (mM/L h)
1	60	5	0.2	56.39	4.94
2	100	10	0.05	10.95	3.07
3	100	5	0.13	13.86	3.52
4	20	5	0.13	82.30	3.52
5	60	10	0.13	83.04	12.33
6	100	15	0.13	37.23	8.81
7	60	10	0.13	67.30	8.81
8	20	10	0.05	61.16	3.07
9	60	5	0.05	9.74	1.53
10	60	15	0.05	19.47	3.07
11	60	15	0.20	75.10	11.54
12	20	15	0.13	100.00	10.57
13	60	10	0.13	100.00	14.09
14	60	10	0.13	94.21	12.33
15	20	10	0.20	69.44	4.95
16	100	10	0.20	71.80	18.14
17	60	10	0.13	71.17	10.57

Table 3
ANOVA and regression analyses for D-fructose oxidation percentage and oxidation rate

Source	Sum of squares	Degree of freedom	Mean square	*F*-value	*p*-value Prob > *F*
Oxidation percentage					
Model	13441.77	9	1493.53	5.72	0.0157
Residual	1826.92	7	260.99		
Lack of fit	1025.92	3	341.97	1.71	0.3024
Pure error	801.00	4	200.25		
$R^2 = 0.8803$, Adjusted $R^2 = 0.7265$, Adeq. Precision = 7.394					
Oxidation rate					
Model	328.50	9	36.50	5.17	0.0208
Residual	49.46	7	7.07		
Lack of fit	33.36	3	11.12	2.76	0.1757
Pure error	16.11	4	4.03		
$R^2 = 0.8691$, Adjusted $R^2 = 0.7009$, Adeq. Precision = 7.488					

The final equations for the oxidation percentage and oxidation rate are expressed in Eqs. (1) and (2) by comparing the significant values, lack of fit, pure error and R^2 of the models.

Oxidation percentage:

$$\begin{aligned} Y_1 = & -47.42183 - 0.74177^{*}A + 15.74777^{*}B \\ & + 1029.16667^{*}C + 0.0070875^{*}AB + 4.38083^{*}AC \\ & + 5.98667^{*}BC - 0.0036356^{*}A^2 - 0.75918^{*}B^2 \\ & - 4264.80^{*}C^2 \end{aligned} \tag{1}$$

Oxidation rate:

$$\begin{aligned} Y_2 = & -15.82848 + 0.032204^{*}A + 3.04573^{*}B \\ & + 74.00000^{*}C - 0.00220^{*}AB + 1.09917^{*}AC \\ & + 3.37333^{*}BC - 0.00932344^{*}A^2 - 0.14117^{*}B^2 \\ & - 502.53333^{*}C^2 \end{aligned} \tag{2}$$

In Eqs. (1) and (2), A is the D-fructose concentration, B is the applied voltage and C is the NaOH concentration. The quadratic models for the responses of oxidation percentage and oxidation rate were selected based on their high R^2 values (0.8803 and 0.8691, respectively) and low *F*-values for lack of fit (1.71 and 2.76, respectively). In the ANOVA test, the Prob > *F* for the oxidation percentage and oxidation rate was 0.0157 and 0.0208, respectively. As Prob > *F* is less than 0.05 for both models, they are deemed significant. There is a 1.57% chance that the *F*-value for the oxidation percentage, 5.72, and a 2.08% chance that the *F*-value for the oxidation rate, 5.17, could occur due to noise.

The effects of D-fructose concentration and applied voltage during the electrochemical oxidation on the oxidation percentage and oxidation rate are shown in Fig. 4(a) and (b). According to the ANOVA analysis, the D-fructose concentration significantly affected the oxidation percentage but not the oxidation rate. However, the statistical data show the opposite trend for the effect of the applied voltage on the oxidation percentage and oxidation rate. The oxidation rate of the D-fructose solution increased with increasing applied voltage. Based on Eq. (2), the optimum oxidation rate of the D-fructose solution, 12.27 mM/L h, could be achieved using 12 V of applied voltage with 100% D-fructose and 0.13 M NaOH. A higher applied voltage overcomes the resistance between the electrodes much better, due to the low ionic conductivity of the solution and enhances the electrochemical reaction rate [8].

Fig. 5(a) and (b) shows the effects of D-fructose concentration and NaOH concentration on the oxidation percentage and oxidation rate when a 10 V applied voltage was used in the treatment process. The D-fructose and NaOH concentrations significantly affected the oxidation percentage during the treatment. The optimum oxidation percentage was obtained using 0.14 M NaOH and 20% D-fructose. This NaOH concentration facilitated the degradation of D-fructose [19], increased the ionic conductivity and reacted with the major product of electrochemical oxidation, 2-keto-D-gluconic acid, maintaining the reaction equilibrium in the forward direction.

The combination of the effect of applied voltage and NaOH concentration produced dramatic changes in the oxidation percentage and oxidation rate, as

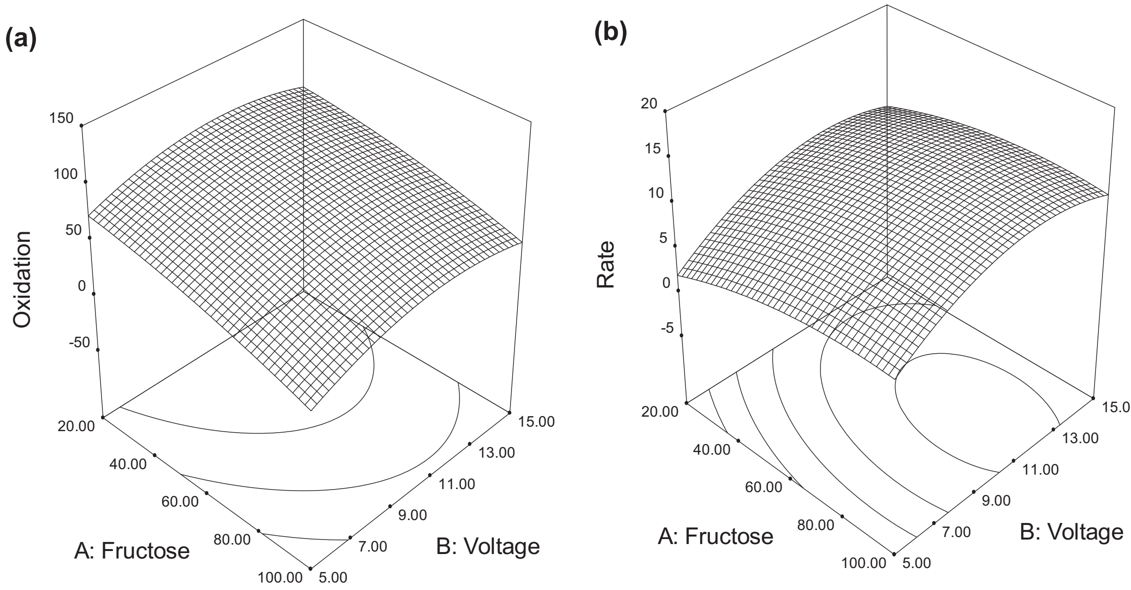

Fig. 4. Effects of D-fructose concentration and applied voltage on (a) oxidation percentage and (b) oxidation rate for 0.13 M NaOH.

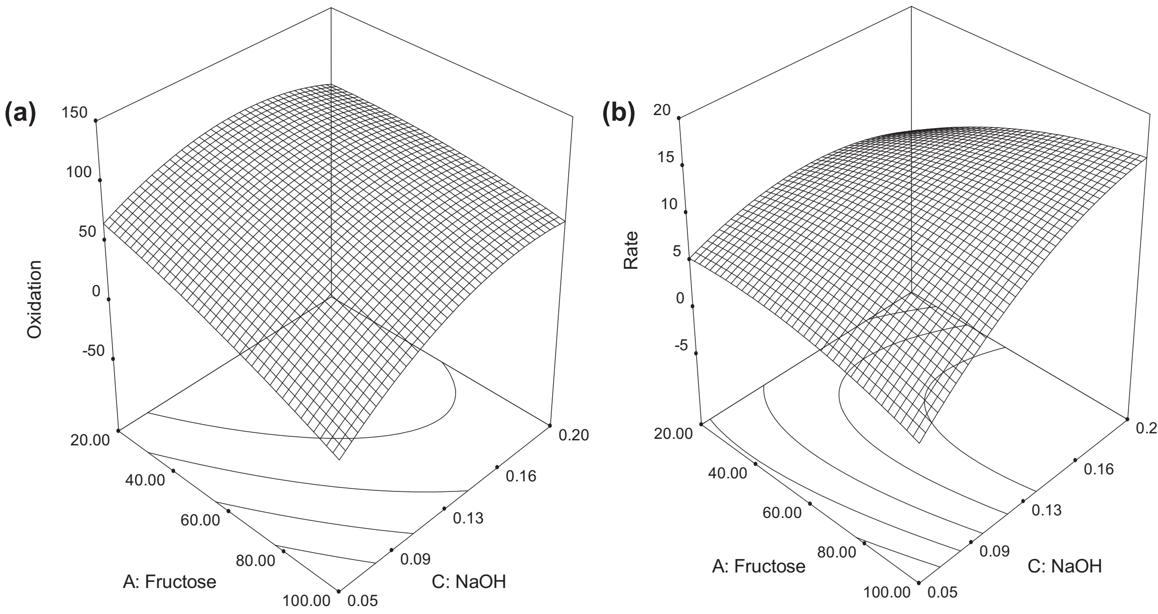

Fig. 5. Effects of D-fructose and NaOH concentrations on (a) oxidation percentage and (b) oxidation rate for a 10 V applied voltage.

shown in Fig. 6(a) and (b). The model predicted that the highest oxidation percentage (69.15%) would be obtained using 0.18 M NaOH and a 11.30 V applied voltage, and the highest oxidation rate (16.42 mM/L h) would be obtained using 0.20 M NaOH and a 12.0 V applied voltage. By optimising the applied voltage and NaOH concentration, the highest combination of oxidation percentage (65%) and oxidation rate (16.3 mM/L h) was achieved for 100% D-fructose by applying 13.34–13.46 V and adding 0.20 M NaOH.

The electrochemical oxidation conditions and process for D-fructose solution were optimised using the models generated in Eqs. (1) and (2) by Design-Expert. To achieve the economically optimal oxidation percentage and oxidation rate, the D-fructose concentration was maximised and the voltage and NaOH

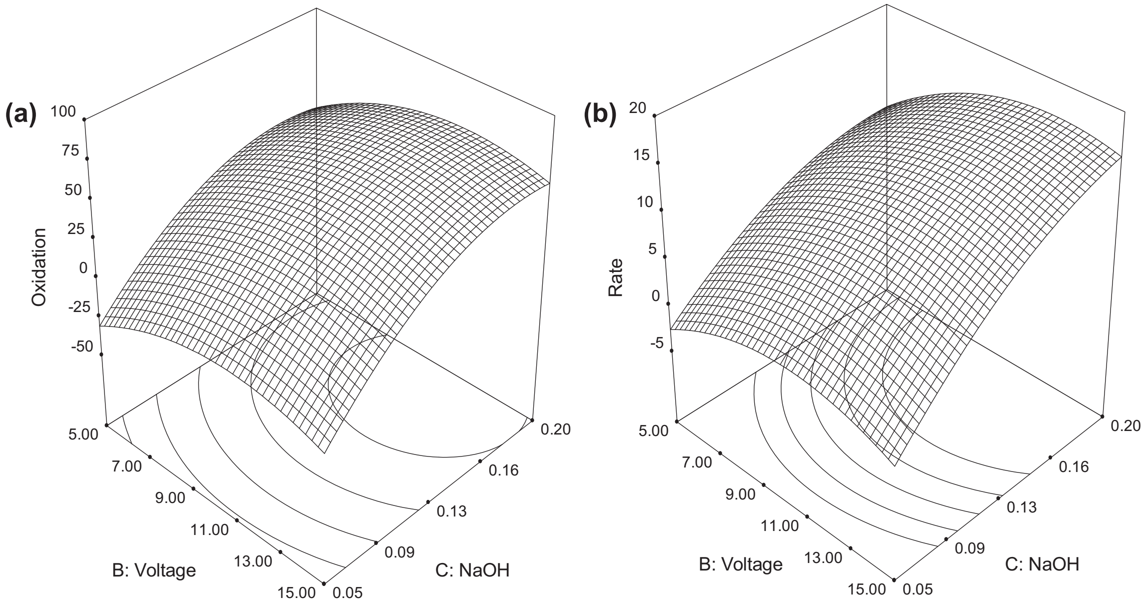

Fig. 6. Effects of applied voltage and NaOH concentration on (a) oxidation percentage and (b) oxidation rate for 100% D-fructose.

Table 4
Comparison of optimisation and experimental results

Solution	Fructose concentration (%)	Applied voltage (V)	NaOH concentration (mol/L)	Oxidation percentage (%)	Oxidation rate (mM/L h)	Desirability
Suggested	81.59	9.41	0.14	72.0455	12.437	0.619
Adjusted	82.00	10.00	0.14	73.8453	12.931	0.698
Experiment	82.00	10.00	0.14	62.7812	12.200	

concentration were minimised to reduce the operation cost. The model produced only one solution, as reported in Table 4. To validate the suggested optimal conditions, the electrochemical oxidation conditions were readjusted to facilitate the experimental process. A D-fructose concentration of 82% was supplemented with 0.14 M NaOH and subjected to an applied voltage of 10 V. The validation results revealed a 14.98% error for the oxidation percentage and a 5.65% error for the oxidation rate compared to the adjusted optimisation condition. This model has provided a moderate prediction for the oxidation percentage with an acceptable accuracy in the oxidation rate.

4. Conclusion

The electrochemical oxidation of D-fructose has been studied by analysing the effects of D-fructose concentration, applied voltage and NaOH concentration. The effects of applied voltage and NaOH concentration significantly affected the oxidation percentage and oxidation rate for the highest D-fructose concentration. Electrochemical oxidation models for oxidation percentage and oxidation rate have been generated by statistical analysis and compared with the experimental results. An oxidation percentage of 62.78% and an oxidation rate of 12.2 mM/L h were achieved under the operating conditions of 82% D-fructose, 10 V of applied voltage and 0.14 M NaOH. The experimental results are comparable to the predicted optimisation solution generated from models. These models can be used as a preliminary guide for the investigation of the COD removal of sugars as the main component in wastewater under alkaline conditions.

References

[1] Y. Deng, J.D. Englehardt, Electrochemical oxidation for landfill leachate treatment, Waste Manage. 27 (2007) 380–388.

[2] M.J.K. Bashir, M.H. Isa, S.R.M. Kutty, Z.B. Awang, H.A. Aziz, S. Mohajeri, I.H. Farooqi, Landfill leachate treatment by electrochemical oxidation, Waste Manage. 29 (2009) 2534–2541.

[3] I. Ihara, K. Umetsu, K. Kanamura, T. Watanabe, Electrochemical oxidation of the effluent from anaerobic digestion of dairy manure, Bioresour. Technol. 97 (2006) 1360–1364.

[4] C.R. Costa, F. Montilla, E. Morallón, P. Olivi, Electrochemical oxidation of acid black 210 dye on the boron-doped diamond electrode in the presence of phosphate ions: Effect of current density, pH, and chloride ions, Electrochim. Acta 54 (2009) 7048–7055.

[5] J.B. Parsa, M. Rezaei, A.R. Soleymani, Electrochemical oxidation of an azo dye in aqueous media investigation of operational parameters and kinetics, J. Hazard. Mater. 168 (2009) 997–1003.

[6] L.C. Chiang, J.E. Chang, S.C. Tseng, Electrochemical oxidation pretreatment of refractory organic pollutants, Water Sci. Technol. 36 (1997) 123–130.

[7] P. Asaithambi, M. Matheswaran, Electrochemical treatment of simulated sugar industrial effluent: Optimization and modeling using a response surface methodology, Arab. J. Chem. (in press), doi: 10.1016/j.arabjc.2011.10.004.

[8] G. Güven, A. Perendeci, A. Tanyolaç, Electrochemical treatment of simulated beet sugar factory wastewater, Chem. Eng. J. 151 (2009) 149–159.

[9] A. Deligiorgis, N.P. Xekoukoulotakis, E. Diamadopoulos, D. Mantzavinos, Electrochemical oxidation of table olive processing wastewater over boron-doped diamond electrodes: Treatment optimization by factorial design, Water Res. 42 (2008) 1229–1237.

[10] M. Zhou, L. Liu, Y. Jiao, Q. Wang, Q. Tan, Treatment of high-salinity reverse osmosis concentrate by electrochemical oxidation on BDD and DSA electrodes, Desalination 277 (2011) 201–206.

[11] A.Y. Bagastyo, D.J. Batstone, K. Rabaey, J. Radjenovic, Electrochemical oxidation of electrodialysed reverse osmosis concentrate on Ti/Pt–IrO_2, Ti/SnO_2–Sb and boron-doped diamond electrodes, Water Res. 47 (2013) 242–250.

[12] X. Zhu, J. Ni, P. Lai, Advanced treatment of biologically pretreated coking wastewater by electrochemical oxidation using boron-doped diamond electrodes, Water Res. 43 (2009) 4347–4355.

[13] S. Raghu, C.W. Lee, S. Chellammal, S. Palanichamy, C.A. Basha, Evaluation of electrochemical oxidation techniques for degradation of dye effluents—A comparative approach, J. Hazard. Mater. 171 (2009) 748–754.

[14] O. Scialdone, S. Randazzo, A. Galia, G. Silvestri, Electrochemical oxidation of organics in water: Role of operative parameters in the absence and in the presence of NaCl, Water Res. 43 (2009) 2260–2272.

[15] L. Malandra, G. Wolfaardt, A. Zietsman, M. Viljoen-Bloom, Microbiology of a biological contactor for winery wastewater treatment, Water Res. 37 (2003) 4125–4134.

[16] A. Abdullah, H. Mat, Characterization of solid and liquid pineapple waste, Reaktor 12 (2008) 48–52.

[17] S.L.C. Ferreira, R.E. Bruns, H.S. Ferreira, G.D. Matos, J.M. David, G.C. Brandão, E.G.P. da Silva, L.A. Portugal, P.S. dos Reis, A.S. Souza, W.N.L. dos Santos, Box-Behnken design: An alternative for the optimization of analytical methods, Anal. Chim. Acta 597 (2007) 179–186.

[18] A.W. Heinen, J.A. Peters, H. van Bekkum, The oxidation of fructose on Pt/C catalysts: The formation of d-threo-hexo-2,5-diulose and the effect of additives, Carbohydr. Res. 304 (1997) 155–164.

[19] B.Y. Yang, R. Montgomery, Alkaline degradation of invert sugar from molasses, Bioresour. Technol. 98 (2007) 3084–3089.