2P4-9

Proceedings of Symposium on Ultrasonic Electronics, Vol. 33 (2012) pp. 225-226
13-15 November, 2012

Optimization of the Ultrasonic Oxidation Kinetics of Diethyl Phthalate Using the Factorial Design with Response Surface Methodology (RSM)

Pengpenng Qiu[1‡], Beomguk Park[1], and Jeehyeong Khim[1]
([1]School of Civil Enviro.and Arch.Eng,Korea Univ.)

1. Introduction

Diethyl phthalate (DEP) is an ubiquitous pollutant in the aquatic environment due to their widely use as plasticizers, detergent bases and aerosol sprays. Besides, it has high toxity to humans' reproductive organs.Therefore, it is very urgent to take some measures to deal with it.

Sonolysis process, as an emerging technology of AOPs, has attracted a lot of researchers' interest because of its application for a wide range of contaminants. During ultrasonic process, Frequency and electrical power, as two key and effective factors of ultrasound, are usually became their main focus to optimize sonolysis process[1, 2]. However, the optimization method they have used was just considering one factor at one time so that the cross effect between frequency and electric power was ignored.

In this study, factorial design with RSM was used to optimize the effect of frequency and electric power on the ultrasonic oxidation kinetic constant k of DEP by considering the cross effect of these two. After that, Arrhenius Empirical Equation was utilized to evaluate the relationship of reaction constant k with solution temperature based on the optimal frequency and electric power.Also, the activation energy E_a was obtained.

2. Materials and methods

DEP (99.5% pure grade) was obtained from Aldrich. Hexane (99.5%, HPLC grade) was purchased from Fisher and Fluka. The sono-reactor was made up of a glass cup-horn type with 2 L [12.5×22 cm] capacity equipped with a cup-horn type ultrasonic transducer as shown **Fig. 1**. The initial solution volume and concentration were 500 ml and 1 mg/L, respectively. DEP was analyzed by Gas Chromatography Mass Spectrometry (GC-MS). GC/MS analysis was performed using an Agilent 6890 Plus gas chromatograph equipped with a 5973N quadruple mass spectrometer system (Agilent, Palo Alto, CA). Design expert V 8.0.6 (US, Stat-Ease Inc) was used to design the experiment and analyze the experimental data.

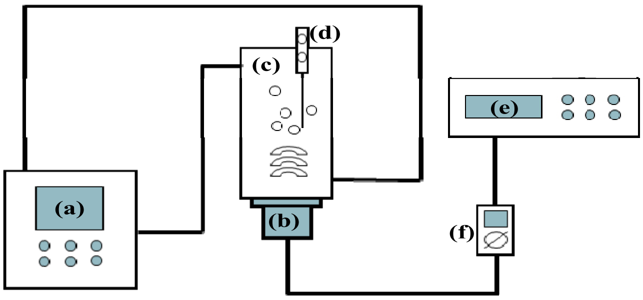

Fig. 1 Experimental set-up. (a): water jacket; (b): transducer; (c): reactor; (d): thermometer; (e): ultrasound generator; (f): power meter

3. Results and discussion

3.1 Factorial Design evaluation

Experimental data from **Table I** was inserted into the Design Expert and polynomial regression was used to analyze the data. In this process Analysis of Variance (ANOVA) was used to identify the importance of the parameters of the model related to the target through "Fisher's test". To check the significance of each factor, p value was used with a standard that P-value <0.005 means the factor is significant.

At last, a final function (1) between ultrasonic oxidation kinetic constant k and frequency and electric power was obtained. (A: frequency; B: electric power).

$$k = 0.037 - 4.90\times10^{-4}A - 1.08\times10^{-3}B + 1.5\times10^{-5}AB + 9.65\times10^{-7}A^2 - 2.41\times10^{-8}A^2B$$

Adj $R^2 = 0.99$; Pre $R^2 = 0.97$. (1)

Fig. 2 shows the 3-D relationship between the reaction constant k and frequency and electric power. As shown in the curve, the optimal frequency existed in the range of 300 kHz and 400 kHz. The kinetic constant was increased with increase of electric power.

By using the optimization function, an optimal frequency and electric power was obtained. They are 370 kHz and 80 W, respectively with the k value of 0.082 min^{-1}. However, this result is different from that of other researches. For example, Na et al. (2012) investigated that the optimal frequency for degradation of DEP by ultrasound was 300 kHz. This difference may be come from the cross effect.

Table I The kinetic constant k (min^{-1}) at different frequencies and electric powers.

Electric power(W) / Frequency (kHz)	40	60	80
100	0.005	0.007	0.012
300	0.029	0.05	0.079
500	0.049	0.058	0.065

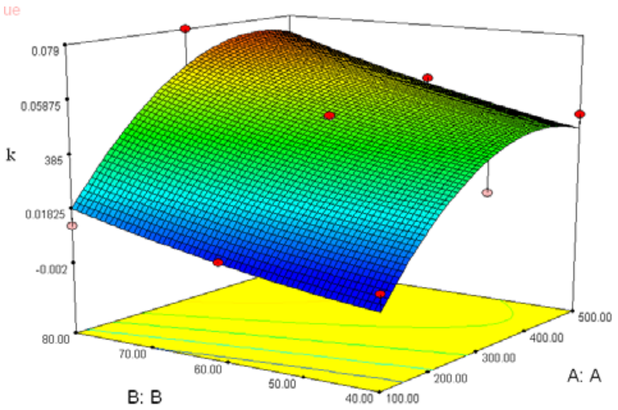

Fig. 2 The reaction constant k versus frequency and electric power

3.2 Arrhenius Equation Evaluation

After the optimal frequency and electric power was identified, Arrhenius Empirical equation (2) was used to evaluate the relationship of reaction constant k with solution temperature [3]. In this study, temperature of 10, 25, and 40°C was considered. The reaction constant k of these three temperatures are 9.44×10^{-2}, 7.93×10^{-2}, and 6.37×10^{-2} min^{-1}, respectively .

$$k = Ae^{(-E_a/RT)}$$

By rearranging the Arrhenius equation, and plot the curve between ln k' and 1/T (K^{-1}), as shown in the **Fig. 3**.

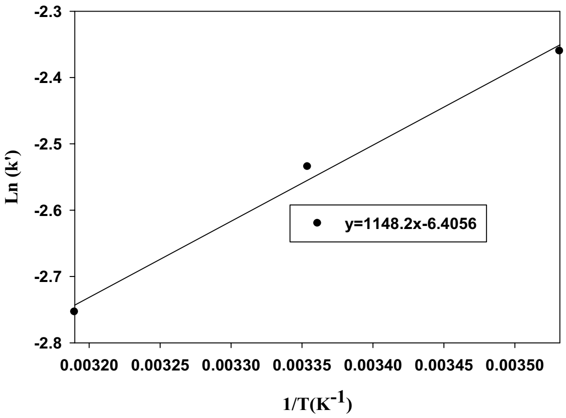

Fig. 3 ln(k') versus 1/T

The plot of ln k' as function of 1/T gives the activation energy of 9.55 kJ/mol.

Acknowledgment

This work was supported by the Basic Science Research Program through a National Research Foundation of Korea (NRF) grant funded by the Ministry of Education, Science and Technology (KRF-2009-0092799)

References

1. R. Chand ,N. Ince ,P. Gogate and D. Bremner :Purif.Tech. **67**(2009)103.
2. J. Kang , H. Hung , A. Lin and M. Hoffman:Environ.Sci.Tech.**33**(1999)3199.
3. S. Na , Y. Ahn , M. Cui , J. Khim: J Environ Manage **101**(2012)104.
4. N. Jose,S. Sengupta and J.Basu: Fuel **90**(2011)626.