

Statistical Modeling of Electrochemical Removal of Sodium in Fermented Food Composts

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Abstract—Electrochemical removal of sodium ion from fermented food composts was analyzed and statistically modeled by response surface methodology (RSM). Empirical models were developed to describe relationships between the operating variables (operation time, current density and water contents) and three responses (removal efficiency, energy expenditure and energy efficiency). Statistical analysis indicated that operation time and current density have significant effect on all responses. Good agreement between predicted and measured values confirmed the usefulness of the model. The models were verified by additional experimental at optimum conditions.

Key words: Statistical Modeling, Sodium Removal, Compost, Response Surface Methodology

INTRODUCTION

Composting has been a good means of recycling organo-rich wastes because the resulting composts can be used as fertilizer and soil conditioner. Korean food-wastes, which have particularly high contents of water and salt, mainly sodium chloride, are known to be difficult to compost [Kim, 1994]. It has been more than ten years since fermentation by the particular microorganism groups has been applied to treat the food-wastes in Korea [Kim, 1994]. However, the resulting composts have not been directly used as fertilizer because concentration of the sodium chloride is too high. This high level of sodium ion has been known to cause several toxic effects on animals and plants [Lechno et al., 1997; Lutts and Kinet, 1995; Hagsten and Perry, 1976]. For composts to be used as fertilizer, the sodium chloride level should be no more than 1% (w/w) in Korea. Therefore, a novel technology, which is economically feasible, must be developed to meet the sodium chloride regulation in fermented food composts.

Electrochemical treatment is a good candidate for the treatment of food composts [Baek, 1999]. In order to get an insight into this system and increase the removal and energy efficiencies, it is necessary to set up a suitable model for the process.

Response surface methodology (RSM) is a useful statistical technique for the investigation and optimization of complex processes. A response of interest is influenced by several variables, so the objective is to optimize the response. The theoretical and fundamental bases of RSM have been widely reviewed [Box and Draper, 1987]. RSM has been successfully applied in many areas such as foods, chemicals, and biological processes [Ismail et al., 1998; Sen, 1997; Shi et al., 1996; Carter et al., 1986]. However, it has not yet been reported as a means to study and to construct a model for the elec-

trochemical treatment of composts. In this work, the operating parameters for the electrochemical removal of sodium chloride from fermented food composts have been investigated and analyzed by RSM, and model equations have been presented. These model equations given in this research can be used for predictions of performance of the system and for establishment of scale-up parameters.

MATERIALS AND METHODS

Commercial grade nitric acid (60%) was purchased from Dong Yang Chemical Co. (Korea) and used for sample pretreatment. Standard solutions for atomic absorption spectrometer were prepared by using concentrated solutions of 1,014 ppm sodium (Cica-Merck, Japan) and 1,000 ppm calcium (Mallinckrodt Chemical Inc., USA). Direct current power supply was provided by First Science Co. (Korea) and the peristaltic pump used for continuous flow of electrolytes was the Eyela SP-23 (Japan).

Fermented food composts, which had been processed for a month in a composting plant of Taejon, were used as starting materials. Sample composts were rested at 80 °C in a drying oven for 24 h. Compost slurries with different water contents were prepared by mixing the known amounts of compost with pre-calculated amounts of tap water.

The whole experimental setup is very similar to that described previously [Baek et al., 2000]. In this work, electrolytes were supplied by the hydraulic gradient from the anode tank, while the peristaltic pump was located in the cathode side for continuous draining of the wastewater.

Experimental parameters were constructed according to a 3-factor central composite design with the axial points at $\alpha = \sqrt{2}$ in the coded units. This allowed the effects of each factor and their interactions to be considered (Table 1). A quadratic model was fitted to the experimental data by using the SAS statistical software (ver. 6.12) [SAS Institute, 1990]. The model obtained is as follows:

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Table 1. Central composite experimental design and results

Independent variables (Coded value)			Independent variables (Original values)			Dependent variables		
X ₁	X ₂	X ₃	T (h)	C (mA/cm ²)	W	RE	EE	EF
-1	-1	-1	12	1	3.5	60	11.32	5.30
-1	-1	1	12	1	5.5	62	12.13	5.11
-1	1	-1	12	3	3.5	67	18.28	3.66
-1	1	1	12	3	5.5	73	21.23	3.43
1	-1	-1	36	1	3.5	81	36.43	2.22
1	-1	1	36	1	5.5	67	18.08	3.70
1	1	-1	36	3	3.5	96	112.36	0.85
1	1	1	36	3	5.5	95	109.37	0.87
-1.414	0	0	7	2	4.5	58	9.52	6.09
1.414	0	0	42	2	4.5	96	139.15	0.69
0	-1.414	0	24	0.596	4.5	68	19.61	3.47
0	1.414	0	24	3.414	4.5	95	84.64	1.12
0	0	-1.414	24	2	3.09	77	45.67	1.68
0	0	1.414	24	2	5.91	82	38.71	2.11
0	0	0	24	2	4.5	78	23.42	3.33
0	0	0	24	2	4.5	76	23.28	3.41
0	0	0	24	2	4.5	81	26.43	3.06
0	0	0	24	2	4.5	79	25.18	3.13

T, C and W mean operation time, current density and water content, respectively. Water content, W, was expressed as liquid to solid ratio. Coded variables (X₁, X₂ and X₃) have following relations. X₁=(T-24)/12, X₂=(C-2)/1 and X₃=(W-4.5)/1. The dependent variables RE, EE and EF mean removal efficiency, energy expenditure and energy efficiency, respectively. All experiments were randomly performed.

$$Y = a_0 + a_1 X_1 + a_2 X_2 + a_3 X_3 + a_{12} X_1 X_2 + a_{13} X_1 X_3 + a_{23} X_2 X_3 + a_{11} X_1^2 + a_{22} X_2^2 + a_{33} X_3^2 \quad (1)$$

where Y is the measured response for each test, a₀ is the intercept term, a₁, a₂ and a₃ are linear coefficients, a₁₂, a₁₃ and a₂₃ are interactive coefficients, a₁₁, a₂₂ and a₃₃ are quadratic coefficients and X₁, X₂, and X₃ are also coded independent variables. In this system, response surfaces were removal efficiency, energy expenditure and energy efficiency. The removal efficiency means the amount of sodium ion removed divided by amount of initial sodium ion. The energy expenditure was explained as consumed energy per unit volume of composts during operation in the unit of kWh/m³. The energy efficiency was defined as removal efficiency per energy expenditure in the unit of %/kWh/m³. A range of values for each factor was selected for investigation. The water contents were adjusted 3.5, 4.5 and 5.5 as liquid to solid ratios based on the previous experiments. Current densities lay between 1 and 3 (mA/cm²) considering the economic feasibility. Operation time was properly chosen so that the values fell within the extremes with which the reactor was safely operated.

For the analysis of ions, the dried solid sample should be converted into a liquid sample to perform the analysis of sodium and calcium concentration by atomic absorption spectroscopy (AAS, Perkin Elmer-3300, USA). A method proposed by Baek et al. [2000] was established by using a microwave digestion apparatus (CEM-MDS 2100, USA) combined with nitric acid treatment. Detailed procedures are schematically depicted in Fig. 1. In this process, energy expenditure is an important variable for the industrial application. Energy expenditure was calculated by using the equation sug-

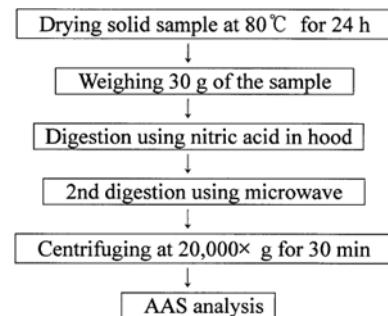


Fig. 1. Pretreatment procedures of solid samples using modified nitric acid method [Baek et al., 2000].

gested in the previous work [Baek, 1999].

RESULTS AND DISCUSSION

Preliminary tests showed that electrochemical treatment was feasible for the removal of sodium from food composts. Removal efficiency increased with current density and operation time: a maximum of 96% removal for 36 h operation at the current density of 3 mA/cm² [Baek et al., 2000].

It is generally understood that the presence of water in composts facilitates the mobility of ions. Therefore, the water content was taken as the third important variable in addition to the two variables, operation time and current density. Table 1 represents the experimental conditions and results of removal efficiency (RE), energy expenditure (EE) and energy efficiency (EF) according to the 3-

factor central composite design. Through the regression and various statistical tests such as T-test and F-test, each statistical model for the RE, EE, and EF can be formulated by Eq. (2) within a confidence level of 90%.

$$RE=79.52+10.89 X_1+8.26 X_2+3.12 X_1 X_2-2.87 X_1 X_3 \quad (2a)$$

$$EE=31.16+33.07 X_1+22.93 X_2+15.00 X_1^2+18.89 X_1 X_2 \quad (2b)$$

$$EF=2.98-1.45 X_1-0.92 X_2+0.41 X_1^2 \quad (2c)$$

where X_1 =(operation time (h)-24)/12, X_2 =current density (mA/cm²)-2 and X_3 =(mass of water)/(mass of composts)-4.5.

The coefficients of determination (r^2) for the model were 0.95 (RE), 0.90 (EE) and 0.92 (EF). The results indicated that the model developed for response variables RE, EE and EF appears to be adequate, that is, it was statistically acceptable at $P<0.01$ level. P-value

means probability that real value of each parameter is outside the range of estimated parameter. P-value was calculated by using t-value, parameter estimate/standard error, and degree of freedom.

The regression coefficients of the three models were obtained and tested for adequacy and fitness by analysis of variance (Table 2). The coefficients of linear effect for the two factors, operation time and current density, significantly affected all dependent variables ($P<0.01$). Among the cross-interaction terms, the considerable contributions to removal efficiency were operation time (X_1) with current density (X_2), and water content (X_3) with operation time (X_1). The coefficients of the quadratic effect of operation time (X_1) were significant on EE and EF ($P<0.1$).

The most relevant variables in all equations were operation time (X_1) and the current density (X_2). The water contents are less effective for EE and EF probably because the electrical conductivity of treated slurry is high enough. Thus, water content term (X_3) was deleted in the modeling of EE and EF. The empirical model represented the interactions between two parameters and predicted each dependent variable from the data of current density and operation time. Fig. 2, Fig. 3 and Fig. 4 show the contour plot of Eq. (1), where the stationary points are saddles. Fig. 2 shows RE is enhanced as current density and operation time increase. Operation time was shorter in the case of higher water content with same current density to reach desired removal efficiency. EE is directly proportional to current density and operation time shown in Fig. 3. As shown in Fig. 4, EF is highly dependent on operation time and current density, but independent of water content. Removal efficiency is linearly proportional to energy expenditure, while energy expenditure is linearly proportional to current density at operation time of 24 h.

In given experimental conditions, no response surfaces have optimum points. For good removal efficiency, therefore, it had better be treated for a long period with a high current density. In this pro-

Table 2. Least squares fit and parameter estimates (significance of regression coefficients)

	Model term	Parameter estimate	Standard error	p-value
Removal efficiency	Intercept	79.528	1.888	0.0000
	X_1	10.895	1.156	0.0000
	X_2	8.265	1.156	0.0001
	X_3	0.005	1.156	0.9961
	X_1^2	-2.292	1.416	0.1443
	X_2^2	3.125	1.416	0.0581
	X_3^2	-0.041	1.416	0.9773
	$X_1 X_2$	-2.875	1.416	0.0768
	$X_1 X_3$	2.125	1.416	0.1719
	$X_2 X_3$	-1.041	1.416	0.4830
Energy expenditure	Intercept	31.168	8.450	0.0061
	X_1	33.051	5.175	0.0002
	X_2	22.938	5.175	0.0022
	X_3	-2.285	5.175	0.6705
	X_1^2	15.000	6.339	0.0455
	X_2^2	18.895	6.338	0.0176
	X_3^2	3.892	6.339	0.5563
	$X_1 X_2$	3.137	6.338	0.6339
	$X_1 X_3$	2.187	6.338	0.7389
	$X_2 X_3$	-1.076	6.339	0.8694
Energy efficiency	Intercept	2.987	0.296	0.0000
	X_1	-1.458	0.181	0.0000
	X_2	-0.902	0.181	0.0011
	X_3	0.141	0.181	0.4597
	X_1^2	0.413	0.222	0.1002
	X_2^2	-0.112	0.222	0.6272
	X_3^2	-0.134	0.222	0.5608
	$X_1 X_2$	0.239	0.222	0.3138
	$X_1 X_3$	-0.188	0.222	0.4220
	$X_2 X_3$	-0.331	0.222	0.1745

P-value means probability that real value of each parameter is outside range of estimated parameter. P-value was calculated using t-value, parameter estimate/standard error, and degree of freedom. Grey boxes indicate the statistically significant values within a confidence level of 90%.

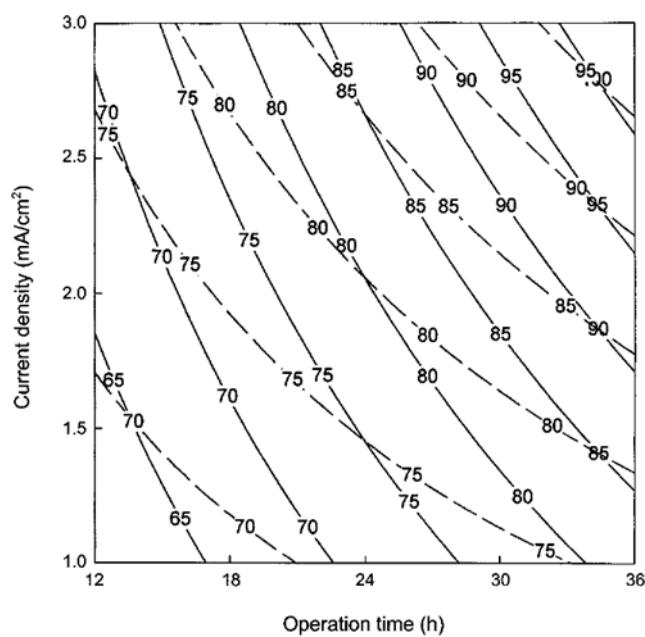


Fig. 2. Contour plot of removal efficiency. Hairline is the contour of removal efficiency when water content is 3.5 as liquid to solid ratio, while dotted line is the contour when the content is 5.5 as liquid to solid ratio.

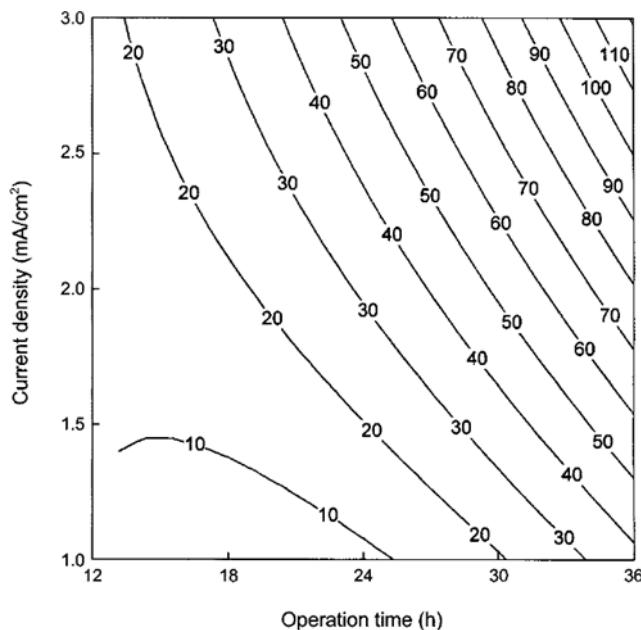


Fig. 3. Contour plot of energy expenditure.

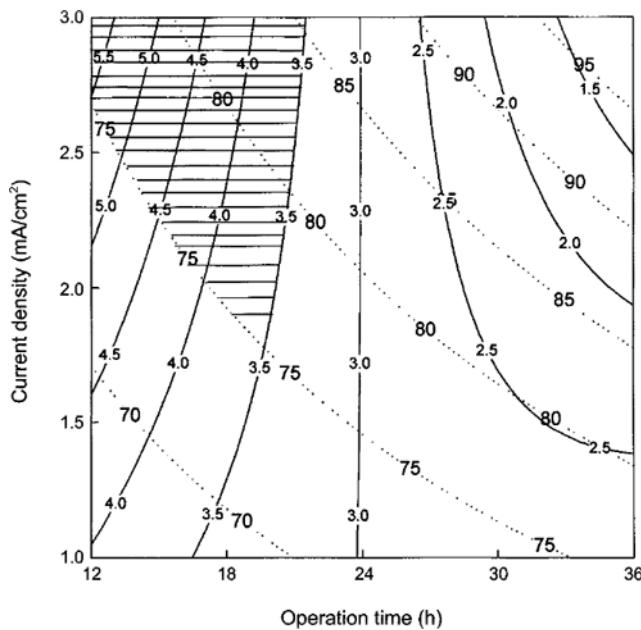


Fig. 4. Contour plot of energy efficiency. Hairline is the contour of energy efficiency, while dotted line is the contour plot of removal efficiency when the content is 5.5 as liquid to solid ratio.

cess, the condition which gives the highest energy efficiency with satisfying 75% removal efficiency was chosen as the optimum experimental condition. Fig. 4 shows energy efficiency in terms of operation time and current density with removal efficiency. Optimum condition was 15 h operation time with 2.5 mA/cm² current density, when energy efficiency was approximated to 4%/kWh. Adequacy of the model for predicting optimum response values, RE, EE and EF, was tested by using the same reactor. The experimental results for RE, EE and EF under these conditions showed a so-

dium removal of 74-78% (mean 76%), energy expenditure of 17.2-20.5 kWh (mean 18.5 kWh) and energy efficiency of 3.8-4.3%/kWh (mean 4.1%/kWh). The experimental results and the predicted data were not statistically different at the 5% significant level, indicating that the model was adequate for the removal of sodium from fermented food composts.

Removal efficiency was regressed to energy expenditure in the exponential form with correlation coefficient (r^2) of 0.93. The removal efficiency had limit value of 96% as in previous work. Another regressed equation between energy expenditure and energy efficiency shows good correlation in the form of exponential decay with correlation coefficient of 0.9686. Nonlinear regression between removal efficiency and energy efficiency also shows the form of exponential decay with r^2 of 0.9114. The regressed equations are as follows:

$$EE (\text{kWh}) = 43.05 + 52.72 (1 - e^{-0.0372 \times RE (\%)}) \quad (3a)$$

$$EF (\%/\text{kWh}) = 0.89 + 8.03 e^{-0.0526 \times EE (\text{kWh})} \quad (3b)$$

$$EF (\%/\text{kWh}) = -2.20 + 32.05 e^{-0.0242 \times RE (\%)} \quad (3c)$$

CONCLUSIONS

Through statistical analyses, mathematical models have been developed for electrochemical removal of fermented food composts. In the given system, removal efficiency can be predicted as terms of operation time, current density, and mass ratio of water and composts. Two operating variables, operation time and current density have considerably influenced the removal efficiency and energy expenditure. Optimum condition was 15 h operation with 2.5 mA/cm² current density in this given system. This model equation can be used for prediction of scale-up parameters.

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