

# Analysis of Siloxane Adsorption Characteristics Using Response Surface Methodology

Jin-Kyu Park<sup>1</sup>, Gyeong-Mi Lee<sup>1</sup>, Chae-Young Lee<sup>2</sup>, Kwang-Beom Hur<sup>3</sup>, Nam-Hoon Lee<sup>1†</sup>

<sup>1</sup>Department of Environmental Engineering, Anyang University, Anyang 430-714, Korea

<sup>2</sup>Department of Civil Engineering, The University of Suwon, Suwon 445-743, Korea

<sup>3</sup>Korea Electric Power Corporation, Daejeon 305-706, Korea

## Abstract

A central composite design and response surface methodology were applied to investigate the optimum conditions for maximum adsorption capacity in activated alumina as an adsorbent. The optimized conditions were determined for adsorption capacity using variables of flow rate and temperature. It was found that flow rate and temperature greatly influenced the adsorption capacity, as determined by analysis of variance analysis of these variables. Statistical checks indicated that second order polynomial equations were adequate for representing the experimental values. The optimum conditions for adsorption capacity were 0°C and 2,718 mL/min, with the estimated maximum adsorption capacity of 17.82%. The experimental adsorption capacity was 17.75% under these optimum conditions, which was in agreement with the predicted value of 17.82%.

**Keywords:** Adsorption capacity, Biogas, Response surface methodology, Siloxane

## 1. Introduction

Worldly consumption of fossil fuel has multiplied greenhouse gas emission, which has stimulated researchers' interest in development of renewable energy instead of traditional energy sources. Biogas production from municipal solid wastes or organic wastes is one of the renewable energy sources and is getting more attention because of the attractiveness of simultaneous waste treatment and electrical generation [1, 2].

However, to use biogas as an energy source, several trace compounds such as hydrogen sulfide, ammonia and siloxanes should be removed [3]. Among these compounds, siloxanes have negative influence on the capability and life duration of generators [4]. Siloxanes are a subgroup of silicones, containing Si-O bonds with organic radicals (mostly methyl-groups) bound to Si [5]. The structure of the siloxane is linear or cyclic. Several technical methods (e.g., adsorption, gas chilling, and absorption) are commercially available to remove the siloxanes today [6]. In adsorption, the most widely used method, various adsorbents and different conditional variables (e.g., flow rate, temperature, and concentration) have been applied to find an optimal condition for increasing adsorption capacity [6-8]. For the traditional searching procedure, one conditional variable at a time is changed without any changes to other variables for finding an optimal condition. This method may produce a certain optimum stage, however, interdependent influence or relations for various

conditional variables are not considered in general.

Therefore, an alternative searching procedure involving a statistical tool (e.g., factorial experimental design and response surface methodology [RSM]) should be adopted to solve this complexity [9]. RSM is a collection of mathematical and statistical techniques used to model and analyze problems in which a response of interest is influenced by several variables [10].

In this study, characteristics of the siloxane adsorption with various flow rates and temperatures were analyzed using alumina as an adsorbent of the siloxane. To improve the conventional test method which searches for the effect of each variable, RSM was applied to investigate the individual and interactive effects of flow rate and temperature on adsorption capacity.

## 2. Materials and Methods

### 2.1. Adsorption Test

The experimental equipment for this study is presented in Fig. 1. Activated alumina (Duksan Co., Ansan, Korea), an adsorbent of siloxane, was circular-shaped with a white color and its density was 0.6 g/cm<sup>3</sup>. The setup consisted of an adsorption column (12 mm, diameter; 120 mm, length) filled with 5 g of dried granular activated alumina (65.7% porosity) heated until 300°C for approximately 2 hr. The gas used in this column was adsorbed

© This is an Open Access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0/>) which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

Received March 07, 2012 Accepted May 23, 2012

<sup>†</sup>Corresponding Author

E-mail: nhlee@anyang.ac.kr

Tel: +82-31-467-0891 Fax: +82-31-467-0789

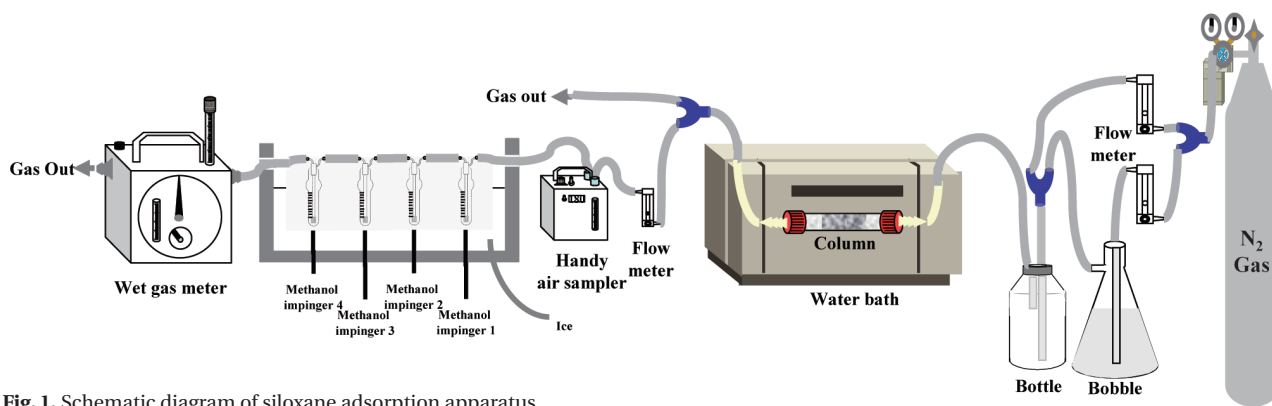


Fig. 1. Schematic diagram of siloxane adsorption apparatus.

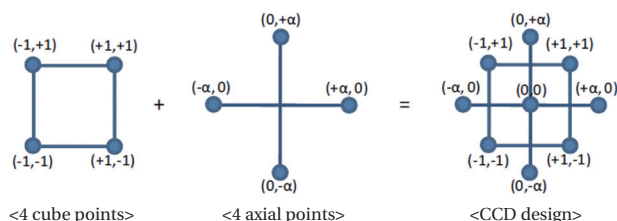


Fig. 2. Central composite design (CCD): 4 cube points, 4 axial points, and 5 replicates at the central point (0,0) [12].

in three impingers containing 6 mL of methanol. The inside of an ice box was steadily kept at a lower temperature of  $4 \pm 2^\circ\text{C}$ . The gas flow rate into the impingers was 100 mL/min constantly, with discharging of extra gas to the outside. In the last part of the impingers, a wet gas meter was installed to keep the total gas input constant. A gas chromatography/mass spectrometry (GC-MS) system (QP5050A; SIMADZU, Kyoto, Japan) equipped with a ZB-5 column ( $0.25 \mu\text{m} \times 0.25 \text{ mm} \times 30 \text{ m}$ ; Zebtron, Newport Beach, CA, USA) was operated to analyze the siloxane stored in three impingers.

In this study, octamethylcyclotetrasiloxane (D4; Acros Organics, Fair Lawn, NJ, USA) and decamethylcyclopentasiloxane (D5; Merck-Schuchardt, Hohenbrunn, Germany) were used as

siloxane test materials and are major components of siloxanes in biogas. To generate constant input concentration of the siloxane without any dependence of input gas rate and gas temperature, nitrogen gas is injected into two parts separately. One part of nitrogen gas injection was fed to a glass bottle containing a standard siloxane solution (D4, 100 ppm; D5, 70 ppm), and it was mixed with the other nitrogen gas injection before being introduced into the adsorption column. The siloxane solution was vaporized into the nitrogen gas. The average concentration of the injected siloxane mixture to the adsorption column was  $250 \mu\text{g}/\text{m}^3$ . Teflon pipe (5 m) was installed between mixing chamber and adsorption columns in a water bath for constant gas temperature.

## 2.2. Central Composite Design and Data Analysis

A central composite design is a second order factorial design including a central point and axial points [11]. If the number of independent variables is  $k$ , the points of factorial experiments are  $2^k$  and axial points are  $2k$ . Therefore, if the number of repeats at a central point is  $n$ , the total number of experiments is  $2^k+2k+n$ . As an example, Fig. 2 shows four ( $2^k = 4$ ) points as cube points, four ( $2k = 2$ ) axial points, and one center point (0, 0). Therefore if  $k$  is equal to 2, the minimum number of experimental points is 9 for central composite design.

In this research, the applied flow rate and adsorption tem-

Table 1. Central composite design

Standard time	Code		Experimental		Experimental order
	Temperature ( $X_1$ )	Flow ( $X_2$ )	Temperature ( $X_1, ^\circ\text{C}$ )	Flow rate ( $X_2, \text{mL}/\text{min}$ )	
1	-1	-1	6	1,080	Random
2	1	-1	34	1,080	
3	-1	1	6	3,000	
4	1	1	34	3,000	
5	-1.414	0	0	2,050	
6	1.414	0	40	2,050	
7	0	-1.414	20	700	
8	0	-1.414	20	3,400	
9	0	0	20	2,050	
10	0	0	20	2,050	
11	0	0	20	2,050	
12	0	0	20	2,050	
13	0	0	20	2,050	

perature as independent variables with the siloxane adsorption capacity as a dependent variable were examined with 13 experiments (Table 1). A central point was replicated 5 times in order to investigate experimental error.

Factorial design levels were codified from -1 to +1. The usage of axial point ( $\alpha$ ) is for indicating rotatability. In central composite design,  $\alpha$  is presented as  $[2^k]^{1/4}$  and calculated as 1.414 in this experiment. The ranges for adsorption temperature and flow rate were 0-40°C and 700-3,400 mL/min (linear velocity, 0.1-0.5 m/sec), respectively.

The experimental design was analyzed using the RSM. The variables,  $X_i$ , were coded as  $x_i$  according to Eq. (1), such that  $X_0$  corresponded to the central value [11]:

$$x_i = (X_i - X'_i) / \Delta X_i \quad (1)$$

Where,

$x_i$ : dimensionless coded value of an independent variable

$X_i$ : actual value of an independent variable for the  $i$ -th test

$X'_i$ : actual value of an independent variable at the central point

$\Delta X_i$ : step change

Regression analysis for the experimental results was performed using Minitab software ver. 14 (Minitab Inc., State College, PA, USA), and Eq. (2) was applied to search the optimum conditions.

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{12} X_1 X_2 \quad (2)$$

Where,

Y: predicted response

$X_1, X_2$ : independent variables

$\beta_0$ : constant coefficient

$\beta_1, \beta_2$ : linear coefficients

$\beta_{11}, \beta_{22}$ : quadratic coefficients

$\beta_{12}$ : interaction coefficient

### 3. Results and Discussion

#### 3.1. Adsorption Capacity of Siloxane

In this study, as an index of the adsorption performance, the adsorption capacity (the weight of the adsorbed siloxanes/the weight of the adsorbent) was calculated [7]. The results of the siloxane adsorption capacity depending on various flow rates and temperatures in the adsorption column filled with activated alumina are shown in Fig. 3. The 1,080 mL/min of flow rate with two separate temperatures, 6°C and 34°C, produced adsorption capacities of 15.42% and 11.93%, respectively. The temperature of 6°C produced better adsorption capacity. When flow rate was fixed to 2,050 mL/min with various temperatures (i.e., 0°C, 20°C, and 40°C), adsorption capacities were 17.5% (0°C) and 13.41% (40°C), respectively. The results of the adsorption capacity when flow rate was 3,000 mL/min with temperatures of 6°C and 34°C were 16.90% and 14.31%, respectively. From these experimental results, we clearly see that reduced temperature provides better conditions for the adsorption capacity with fixed flow rate. Ricaurte Ortega and Subrenat [13] reported that the increase in the temperature reduced the adsorption capacity. The reason for decreased adsorption capacity when temperatures were increased might be that the adsorption process between siloxane and activated alumina relies more on physical than chemical adsorption.

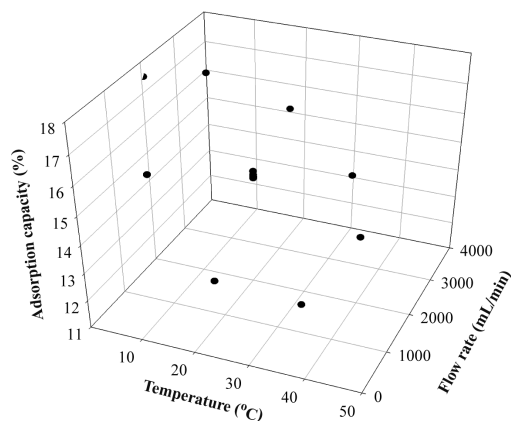


Fig. 3. Scatter plot for adsorption capacity as a function of temperature and flow rate.

Alternatively, we tried to study the pattern of fixed temperature with various flow rates. When temperature was fixed to 20°C with diverse flow rates (700 mL/min, 2,050 mL/min, and 3,400 mL/min) the adsorption capacities were increased to 12.69%, 14.75-14.99%, and 15.7%, respectively.

Adsorbates must be transported through the boundary layer that surrounds the adsorbents when gas is flowing past them. The distance of transport is determined by the flow rate past the adsorbent. Higher flow rate results in shorter distance. Therefore, when gas flow rate was increased, the siloxane was transported more quickly through the boundary layer. After passing through this boundary layer, siloxane was transported more quickly through the adsorbent's pores to the available adsorption sites. This rapid diffusion into pores of adsorbent might generate more reactions on the adsorbent with increased adsorption capacity [14].

#### 3.2. Model Fitting

Based on the above results, second order polynomial equations for the adsorption capacity fitted in terms of coded and uncoded factors were obtained, as shown in Eqs. (3) and (4):

$$\text{Parameter estimate from coded data} \\ Y = 14.832 - 1.5828X_1 + 1.1483X_2 + 0.2151X_1^2 - 0.2049X_2^2 - 0.1372X_1X_2 \quad (3)$$

$$\text{Parameter estimate from uncoded data} \\ Y = 13.6726 - 0.1341X_1 + 0.00233X_2 + 0.00108X_1^2 - 2.2497 \times 10^{-7}X_2^2 - 1.0167 \times 10^{-6}X_1X_2 \quad (4)$$

Where,  $X_1$  and  $X_2$  represent temperature and flow rate, respectively.

Table 2 shows experimental results and predicted values with ranges of 11.93-17.50% and 12.24-17.64%, respectively.

#### 3.3. Validation of the Model

In this study, we applied two different methods (i.e., graphical and numerical methods) to validate the model. Graphical methods utilize residual analysis between the values of dependent variables and predicted values from a regression equation. Fig. 4

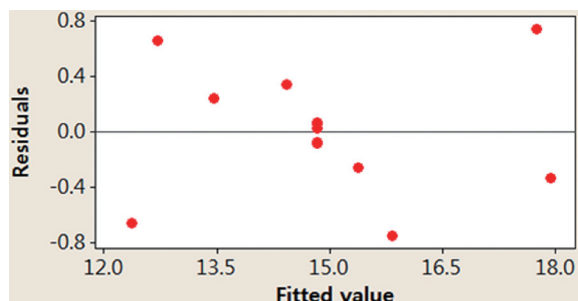


Fig. 4. Residuals vs. fitted values for adsorption capacity.

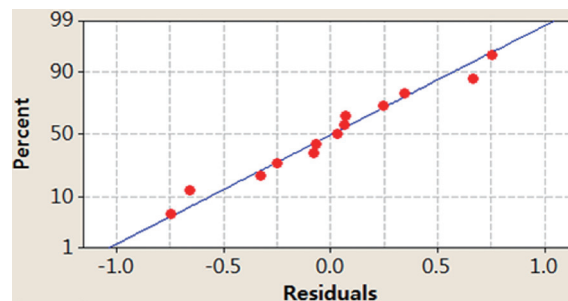


Fig. 6. Normal probability plots for adsorption capacity.

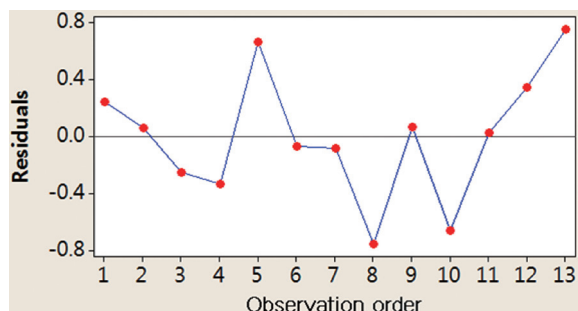


Fig. 5. Residuals vs. observation orders of data for adsorption capacity.

presents randomly distributed residuals and predicted values in a scatter diagram within  $\pm 0.8$ . In Fig. 5, each residual is plotted against an index of observation orders of data, which was used to check for any drift in the process. As previously shown in Figs. 4 and 5, we are not able to see any pattern of residual distribution. From this result, we may say that each residual is independent. Fig. 6 is a graph to check the normality distribution of the residuals. In this figure, experimental points are close to the center cross line, which means the test follows the normal distribution relatively well.

The model was then checked using a numerical method employing analysis of variance (ANOVA). The results of ANOVA are shown in Table 3. The value of  $p > F$  less than 0.05 indicates that this model is significant. For this model, the value of  $p > F$  (0.000)

Table 2. Central composite design and the results obtained

Run	Experimental design		Results	
	Temperature ( $X_1$ )	Flow ( $X_2$ )	Y1, Adsorption capacity (%)	
			Experimental	Predicted
1	-1	-1	15.42	15.17
2	+1	-1	11.93	12.24
3	-1	+1	16.96	17.64
4	+1	+1	14.31	14.31
5	-1.414	0	17.50	17.51
6	+1.414	0	13.41	13.09
7	0	-1.414	12.69	12.77
8	0	+1.414	15.79	15.99
9	0	0	14.99	14.83
10	0	0	14.76	14.83
11	0	0	14.80	14.83
12	0	0	14.75	14.83
13	0	0	14.86	14.83

Table 3. Analysis of variance results for the adsorption capacity

Source	Degree of freedom	Sum of squares	Mean squares	F-value	$p > F$
Model	5	28.0686	5.6137	255.65	0.000
Residual	7	0.1537	0.0220	-	-
Lack of fit	3	0.1150	0.0383	3.97	0.108
Pure error	4	0.0387	0.0097	-	-
$R^2$	0.9946				
Adjust $R^2$	0.9907				

shows statistically strong significance. The fit of the model was also expressed by the coefficient of determination  $R^2$ , which was found to be 0.9946, which indicates a good agreement between experimental and predicted values. The lack of fit measures the

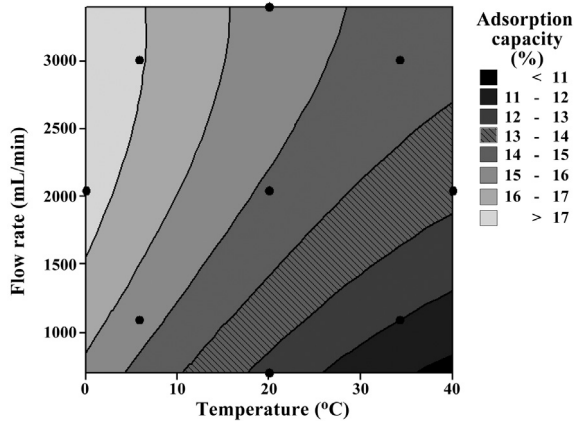


Fig. 7. Two dimensional response surface plots for adsorption capacity.

	Temperature (°C)	Flow (mL/min)
Maximum	40.0	3,400
Optimum	0.0	2,718
Minimum	0.0	700
Total satisfaction = 0.99969		
Adsorption capacity = 17.82 D = 0.99969		

Fig. 8. Response optimization plot.

variation of the data around the fitted model. When the  $p$ -value for the lack of fit is more than 0.05, there is a statistically significant lack-of-fit at the 95% confidence level, which means that the model is adequate [15]. In this study, the  $p$ -value (0.108) for the lack of fit showed that the model was valid.

### 3.4. Optimization and Verification of the Model

The  $p$ -values of the linear, quadratic and interaction terms, shown in Table 4 with 95% confidence, showed that all the terms were significant. The effects of the linear terms from temperature ( $X_1$ ) and flow rate ( $X_2$ ) presented were significant. In terms of temperature, negative effect was presented. In the non-linear effects of temperature ( $X_1$ )  $\times$  temperature ( $X_1$ ) and flow rate ( $X_2$ )  $\times$  flow rate ( $X_2$ ), quadratic terms showed that it was significant in the model. Flow rate ( $X_2$ )  $\times$  flow rate ( $X_2$ ) has a negative effect. Finally, the interaction effect with 0.025 as the  $p$ -value presented significance of the adsorption capacity attributed to the mixture effects from temperature and flow rate.

In Fig. 7, a two contour line graph shows the effects on adsorption capacity based on flow rate and temperature. The optimum status (i.e., temperature below 5°C and flow rate over 1,500 mL/min) for adsorption capacity was presented in the two contour line graph. In the case of response surface graph, depending on the shape of the response surface, we can find the optimum conditions. However, this study had some difficulties in finding the optimum conditions under the given conditions because the contour lines are raised continuously. It seems more research is necessary to find the optimum conditions under 0°C.

The optimum conditions under the given conditions were predicted using Minitab software. Fig. 8 shows the optimum values at the top of the graph at 0°C and 2,718 mL/min, with a maximum adsorption capacity (17.82%).

In order to verify the model, experiments were performed to compare the experimental results with corresponding predicted values. Table 5 shows that the experimental adsorption capacity of 17.75% and the predicted value of 17.82% corresponded well. The experiment results were close to the model prediction. Additionally, this study confirmed that the RSM method is appropriate for optimizing the adsorption capacity.

Table 4. Estimation of the second-order response surface parameters (coded unit)

Source	Parameter	Coefficient	Standard error	T-value	$p > T$
Constant	$B_0$	14.8320	0.06627	223.811	0.000
Linear	$X_1$	-1.4901	0.05239	-28.443	0.000
	$X_2$	1.0388	0.05239	19.828	0.000
Quadratic	$X_1^2$	0.2637	0.05618	4.694	0.002
	$X_2^2$	-0.3435	0.05618	-6.114	0.000
Interaction	$X_1X_2$	0.2103	0.07409	2.838	0.025

Table 5. Confirmation experiments at optimum conditions

Item	Temperature (°C)	Flow rate (mL/min)	Adsorption capacity (%)
Experimental value	0	2,718	17.75 (0.1528)
Predicted value	0	2,718	17.82
Error (%)	-	-	0.37

( ): standard deviation.

## 4. Conclusions

This research applied response surface methodology to find the optimum conditions of temperature and flow rate for siloxane adsorption capacity in activated alumina as an adsorbent. The results are shown below: 1) With faster flow rate, increased temperature minimizes siloxane adsorption capacity on activated alumina because the adsorption mechanism has a preference for physical adsorption instead of chemical adsorption relying on activate energy; 2) Under the conditions of constant temperature, flow rate and adsorption capacity have a positive relation. When gas flow rate was increased, siloxane was transported more quickly through the boundary layer. After passing through this boundary layer, siloxane was transported more quickly through the adsorbent's pores to the available adsorption sites. This rapid diffusion into pores of adsorbent might generate more reactions on the adsorbent with increased adsorption capacity; 3) From statistical analysis on siloxane adsorption capacity, second order polynomial equations were confirmed by the ANOVA result, with a *p*-value lower than 0.05; and 4) In numerical optimization, optimal conditions (i.e., 0°C and 2,718 mL/min for temperature and flow rate, respectively) were obtained with 17.82% adsorption capacity. Additionally, the three verification tests showed small error rate (0.37%) using the obtained model.

## Acknowledgments

This work was supported by the Power Generation & Electricity Delivery of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea Government Ministry of Knowledge Economy (Development of Biogas Pretreatment Fuel System for 5MW-GT) (no. 2009T100200127).

## References

- Münster M, Lund H. Comparing waste-to-energy technologies by applying energy system analysis. *Waste Manag.* 2010;30:1251-1263.
- Holm-Nielsen JB, Al Seadi T, Oleskowicz-Popiel P. The future of anaerobic digestion and biogas utilization. *Bioresour. Technol.* 2009;100:5478-5484.
- Arnold M, Kajolinn T. Development of on-line measurement techniques for siloxanes and other trace compounds in biogas. *Waste Manag.* 2010;30:1011-1017.
- Ohannessian A, Desjardin V, Chatain V, Germain P. Volatile organic silicon compounds: the most undesirable contaminants in biogases. *Water Sci. Technol.* 2008;58:1775-1781.
- Dewil R, Appels L, Baeyens J, Buczynska A, Van Vaeck L. The analysis of volatile siloxanes in waste activated sludge. *Talanta* 2007;74:14-19.
- Ajhar M, Travasset M, Yüce S, Melin T. Siloxane removal from landfill and digester gas - a technology overview. *Bioresour. Technol.* 2010;101:2913-2923.
- Matsui T, Imamura S. Removal of siloxane from digestion gas of sewage sludge. *Bioresour. Technol.* 2010;101 Suppl 1:S29-32.
- Schweigkofler M, Niessner R. Removal of siloxanes in biogases. *J. Hazard. Mater.* 2001;83:183-196.
- Hong C, Haiyun W. Optimization of volatile fatty acid production with co-substrate of food wastes and dewatered excess sludge using response surface methodology. *Bioresour. Technol.* 2010;101:5487-5493.
- Montgomery DC. Design and analysis of experiments. 6th ed. Hoboken: John Wiley & Sons; 2005.
- Molinuevo-Salces B, García-González MC, González-Fernández C, Cuetos MJ, Morán A, Gómez X. Anaerobic co-digestion of livestock wastes with vegetable processing wastes: a statistical analysis. *Bioresour. Technol.* 2010;101:9479-9485.
- Trinh TK, Kang LS. Application of response surface method as an experimental design to optimize coagulation tests. *Environ. Eng. Res.* 2010;15:63-70.
- Ricaurte Ortega D, Subrenat A. Siloxane treatment by adsorption into porous materials. *Environ. Technol.* 2009;30:1073-1083.
- Kim JS, Kim MC, Kang EJ, Kim MS. H<sub>2</sub>S adsorption characteristics of KIO<sub>3</sub> impregnated activated carbon. *J. Korean Oil Chem. Soc.* 2002;20:72-79.
- An SW, Yoo JY, Choi JY, Park JW. Adsorption characterization of Cd by activated carbon containing hydroxyapatite using response surface methodology (RSM). *J. Korean Soc. Water Qual.* 2009;25:943-950.