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# Assessment of MOF-801 synthesis for toluene adsorption by using design of experiment methodology

**Sangmin Lee*, Min Hyung Lee**, Kye Sang Yoo*,**,†, and Seongho Song*****

*Department of Chemical & Biomolecular Engineering, Seoul National University of Science and Technology, Seoul 01811, Korea
**Department of Energy & Chemical Engineering, Graduate School of Convergence Science, Seoul National University of Science and Technology, Seoul 01811, Korea
***Division of Statistics and Data Science, Department of Mathematical Sciences, University of Cincinnati, Cincinnati, OH 45221, USA

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**Abstract**−A sequential design of experiments was used to optimize the MOF-801 synthesis process for toluene adsorption. First, mixture design was employed on optimizing precursor concentration. Three chemical materials, fumaric acid, N,N-dimethylformamide and formic acid, were selected to optimize their composition using extreme vertices design methods. By analysis of variance (ANOVA), the model was expected to be acceptable for statistical prediction. The optimal precursor composition for the synthesis of MOF-801 was predicted on a molar basis as fallows: $ZrOCl_2 \cdot 8H_2O$ : fumaric acid : dimethylformamide : formic acid=1.0 : 1.7 : 43.3 : 39.5. Thereafter, $2^3$ factorial design was selected to investigate the effect of synthesis reaction conditions such as temperature, time and stirring speed. By the statistical analysis of eight adsorption runs, stirring speed could be excluded in further investigation. Central composite design with synthesis time and temperature was performed to optimize the synthesis process. The results were estimated using the quadratic model equation derived through nine synthesis experiments. Using this model, it was predicted that MOF-801 prepared under the synthesis time and temperature of 158 °C and 12 h, respectively, had the maximum amount of toluene adsorption. Indeed, after synthesizing MOF-801 with the optimized synthesis conditions, an actual adsorption capacity of the samples was 151.9 mg/g, close to the predicted value of 95.5%.

Keywords: MOF-801 Synthesis, Toluene Adsorption, Design of Experiments, Optimization

## INTRODUCTION

Volatile organic compounds (VOCs) in the atmosphere turn easily into the main source of the ozone layer and secondary organic aerosols (SOA), which can cause serious environmental pollution and health problems [1-5]. Among VOCs, toluene is one of the substances that contributes to ozone and SOA formation [6]. Thus, the presence of toluene in the atmosphere can cause serious health problems. For that reason, many VOC removal technologies have been developed, such as adsorption, condensation, incineration, and biodegradation. Among them, adsorption is one of the most advantageous methods for VOC removal because of its ease of application and high efficiency [7-10]. In the methodology, various porous materials were used as an adsorbent, including porous polymer [9], activated carbon [11], zeolite [12], and mesoporous silica [13]. However, these materials have low VOC adsorption capacity due to excessively open mesoporous channels. Moreover, these materials are difficult to modify because the basic unit is chemically hard. Therefore, the development of efficient VOC adsorbents with flexible framework structures has become a research goal in considerable attention [7].

The metal-organic framework (MOF) forms a new kind of porous material including metal ions or clusters, and organic ligands that construct unique network structures with high surface area, pore volume, and pore tunability. Various MOFs have been studied on adsorption using ZIF-68 [14], MIL-100(Cr), MIL-101(Cr) [15,16], IRMOF-1, MIL-47 [17], MIL-101(Fe), and UiO-66(Zr) [7,18]. These adsorbents have higher VOC adsorption capacity than conventional mesoporous materials. In general, MOFs are composed of two materials divided into secondary building units (SBUs) and linkers [19]. SBUs are inorganic clusters containing one or more metal ions organized by oxygen or nitrogen. These clusters are bonded to each other through an organic molecule that is a linker. So, numerous MOF structures can be generated due to many possible combinations of SBU and linker. Furthermore, additional precursor, e.g., monocarboxylic acid, also plays a role in forming the coordination of metal ions. The additives control the deprotonation rate of organic linkers or act as competitive linkers as a modulator. Since the concentration of the additives is generally higher than the linker, the metal ions initially form a coordination sphere from their molecule. However, linkers can form one or more bonds with metal ions, so they replace additives during the synthesis reaction. Thus, additives can affect the nucleation rate and the crystal growth process, leading to form crystals with different size and morphology.

†To whom correspondence should be addressed.
E-mail: kyoo@seoultech.ac.kr

Zirconium-based MOFs are the most intensively studied due to their excellent stability and structural diversity [20]. Among them, MOF-801 is synthesized with fumaric acid as an organic linker to generate an fcu topology based on 12 linked $[Zr_6O_4(OH)_4]^{12+}$ clusters [21-23]. The strong covalent combination and high coordination of the SBUs can create a very stable framework. The pore structure of MOF-801 with two types of tetrahedral pore and an octahedral pore is favorable to adsorption. Moreover, MOF-801 can be easily synthesized in aqueous media due to its high aqueous solubility, a clear advantage in terms of environmental impact [22]. For the reasons, optimizing the synthesis process of MOF-801 can achieve commercialization in many fields as a useful adsorbent. However, as the synthesis process of MOF-801 is diversified and the number of precursors increase, the research burden for the optimization increases significantly. Therefore, the traditional trial and error method has critical drawbacks in terms of time and cost increasing.

Using an appropriate statistical design of experiment (DOE), the number of experiments can be reduced to obtain informative outcomes. Specifically, DOE proposes an experimental method suitable for the purpose of the experiment and plans the experiment to obtain maximum information within the minimum number of experiments through data processing and statistical data analysis. DOE methods known so far include factorial, response surface, mixture, and Taguchi method. Generally, conventional DOE methods are just applied to simple process analysis. In fact, a typical application in the industrial field is the quality control area. Recently, analysis and optimization of complicated processes were performed by combining the DOE methods. Such sequential design of experiments can be used for both the selecting of crucial factors and their optimization. In this study, three DOE methods were consecutively used to assess MOF-801 synthesis processes. Initially, a mixture design method was used to determine the optimal precursor conditions for synthesis of MOF-801. Subsequently, a two-step design was performed to optimize the synthesis process conditions. All data for DOE analysis were based on the toluene adsorption capacity. This result could be utilized directly to industrialize for toluene adsorption process.

## EXPERIMENTAL

### 1. Preparation of MOF-801

Zirconium(IV) oxychloride octahydrate ($ZrOCl_2 \cdot 8H_2O$, 98%), N,N-dimethylformamide (hereafter DMF, 99.8%), fumaric acid (hereafter FUMA, 99.0%), formic acid (hereafter FA, 98%) and methanol (99.8%) were purchased from Sigma-Aldrich. All the chemicals were used without further purification. Initially, $ZrOCl_2 \cdot 8H_2O$ and FUMA were added into a beaker and dissolved in a mixed solution of DMF and FA. The amount of the precursors was adjusted to the designed concentration. The solution was then stirred at room temperature for ten minutes to form a uniform solution. The stirring spread was controlled by homogenizer. Thereafter, the mixture was transferred to Teflon-lined stainless-steel autoclave and kept at the desirable temperature and time. The product mixture was then centrifuged to recover the solid product, which was washed with DMF and methanol, alternatively. The product was then dried at 75 °C for 12 h.

### 2. Toluene Adsorption

The adsorbent sample was activated in a helium atmosphere at 150 °C for 2 hours before toluene adsorption. A toluene breakthrough test was performed using stainless steel tube at atmospheric pressure. For each run, 20 mg of adsorbent was loaded into the bed. Toluene gas with a balanced air concentration of 1,000 ppm (0.1%) passed through the fixed bed at a flowrate of 100 ml/min. Toluene was analyzed using gas chromatography (YL6500GC, Younglin Co., Ltd., Korea) equipped with flame ionization detectors. The column installed was BR-5 (Bruker, capillary 30 m×0.25 mm), and the oven temperature was kept constant at 200 °C. Breakthrough curves were used to investigate the performance of the adsorbents toward toluene. The adsorption capacity (q) was as the total mass of the adsorbed toluene per unit weight of MOF-801 (mg/g). It was calculated using following equation:

$$q = \frac{QC_{in}}{m}\int_0^{t_s}\left(1-\frac{C_{out}}{C_{in}}\right)dt$$

where $C_{in}$ and $C_{out}$ were influent and effluent concentrations of toluene ($mg/m^3$). Q was the volumetric flow rate ($m^3$/min), m was the total mass of MOF-801 (g), and $t_s$ (min) was the time to reach saturation. The calculation was performed using MATLAB.

## RESULTS AND DISCUSSION

The optimization of adsorbent manufacture is essential to the design and operation of adsorption processes. Traditional experimental methods are often time consuming, require relatively huge sample volumes, and hardly disclose any statistical results. However, design of experiments can be a desirable way to overcome these limitations. Especially, sophisticated characterizations of adsorbent such as $N_2$ isotherm, XRD and SEM can be excluded due to the significance of DOE using results of minimized adsorption experiment without any other experiments. In this study, the relationship between the synthesis conditions of MOF-801 and the toluene adsorption capacity was directly predicted through the DOE methods. The results obtained were used to design the subsequent experiment by statistical analysis. All statistical assessments were performed using the latest version of Minitab software.

### 1. Mixture Design

At first, mixture design method was applied to determine desirable composition of precursors in MOF-801 synthesis. This method is a special class of response surface design to analyze the product consisting of several components or ingredients. The experimental design is effective in industrial development involving formulations or mixtures. In the method, the result is a function of the proportions of the individual components in the mixture. Among the precursors, $ZrOCl_2 \cdot 8H_2O$ as a reference was excluded from the designated factors. Thus, three chemicals, FUMA, DMF and FA, were selected to optimize the composition for synthesis of MOF-801. In this study, extreme vertices design, one methodology in mixture design was employed that introduces additional constraints on the design as the lower and upper bound of the proportion of an ingredient is no longer 0 to 1. The proportions do not all have the same ranges. Indeed, the ranges used in the design were as follows: FUMA+DMF+FA=1, $0.05 \le$ FUMA $\le 0.25$, $0.3 \le$ DMF $\le 0.7$,

**Table 1. Analysis of variance (ANOVA) for mixture design model**

| Source | DF | Seq SS | Adj SS | Adj MS | F-Value | P-Value |
|---|---|---|---|---|---|---|
| Regression | 5 | 9,785.1 | 9,785.1 | 1,957.0 | 12.90 | 0.002 |
| Linear | 2 | 3,476.0 | 4,030.7 | 2,015.3 | 13.29 | 0.004 |
| Quadratic | 3 | 6,309.1 | 6,309.1 | 2,103.0 | 13.87 | 0.002 |
| FUMA×DMF | 1 | 218.2 | 2,447.3 | 2,447.3 | 16.14 | 0.005 |
| FUMA×FA | 1 | 5,348.2 | 4,935.9 | 4,935.9 | 32.54 | 0.001 |
| DMF×FA | 1 | 742.7 | 742.7 | 742.7 | 4.90 | 0.063 |
| Residual error | 7 | 1,061.7 | 1,061.7 | 151.7 | | |
| Total | 12 | 10,846.8 | | | | |

0.2≤FA≤0.5. The values were based on molar concentration of the materials. Actually, a modified molar ratio was used to facilitate the design of the mixture method. It was designed by reducing the moles of DMF and FA to 1/10. After that, in the actual experiment, the number of moles of both substances was converted into ten times from the designed value.

Thirteen compositions of three precursors based on mol ratio were designed by Minitab software. MOF-801 samples were prepared with the predetermined precursor concentrations under identical reaction conditions, time, temperature and stir speeds. Toluene adsorption experiments were then performed with the MOF-801 samples to obtain their toluene adsorption capacity. First, analysis of variance (hereafter ANOVA) was calculated as presented in Table 1. ANOVA can assist to find whether the differences between groups of data are statistically significant. $R^2$ value of the model used in mixture design is 91.0%. This means the analysis results of this model were fairly reliable. Among the values in Table 1, we focused on the p-value that is a measure of the probability that an observed difference could have occurred just by random chance. The lower the p-value (usually less than 0.05), the greater the statistical significance. The p-value of the regression analysis was 0.002, which

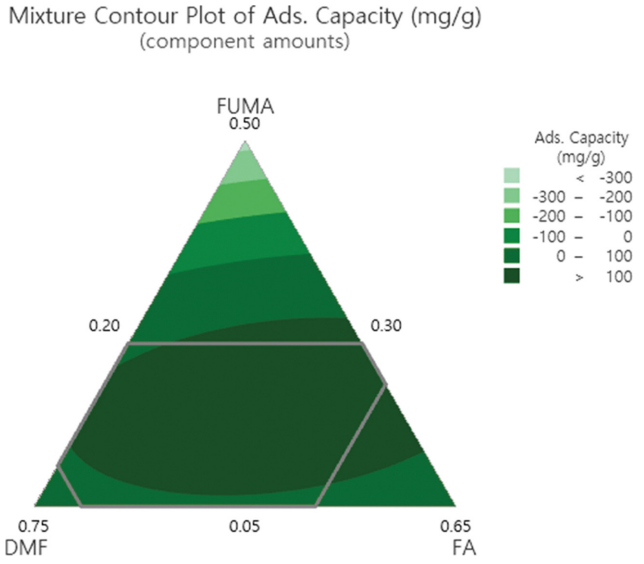


**Fig. 1. Mixture contour plot of toluene adsorption capacity of MOF-801 synthesized with various modified mol faction of precursors.**

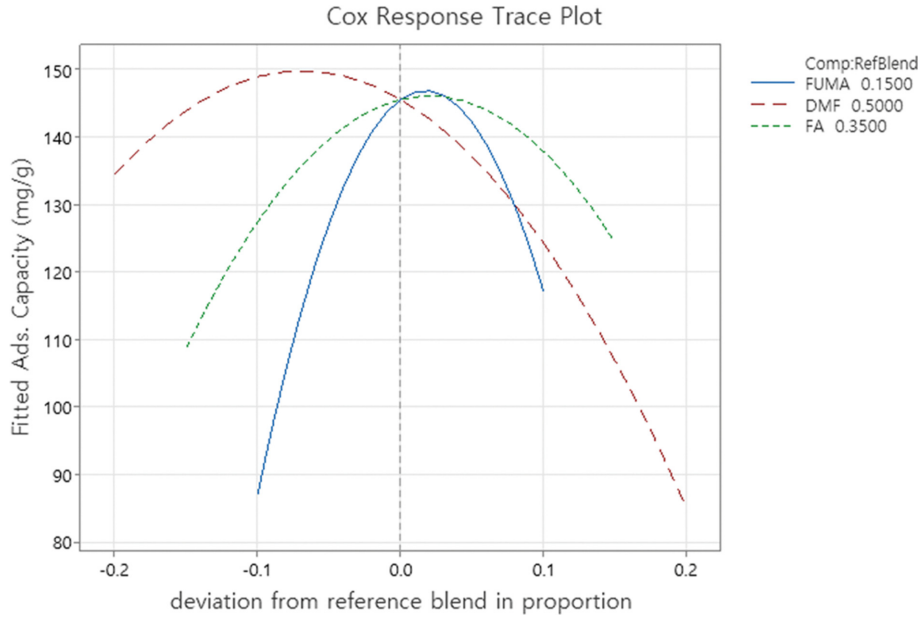


**Fig. 2. Cox response trace plot of toluene adsorption capacity of MOF-801 based on precursor composition.**

represents the statistical significance of the model. Specifically, p-value of linear and quadratic terms of model was 0.004 and 0.002, respectively. Only, the value of DMF×FA in quadratic was slightly high level. Thus, the predicted results generated by the mixture design used in this study are highly trustworthy for further study.

A mixture contour plot of toluene adsorption capacity of MOF-801 samples synthesized with various modified mol faction of precursors is presented in Fig. 1. A section with an adsorption amount of 100 mg/g or more was schematically predicted at the bottom of the triangle. It was predicted that the adsorption performance decreased rapidly as the ratio of fumaric acid increased in the synthesis of MOF-801 samples. Cox response trace plot showing the effects of changing each mixture component while holding all others in a constant ratio is illustrated in Fig. 2. The trace curves show the effect of changing the corresponding component along an imaginary line (direction) connecting the reference blend to a vertex. The plot can identify the most influential components and then plot them on a contour or surface plot. Indeed, the effect of FUMA on the adsorption capacity is clearly observed in the plot. This trend is in a good agreement with addressed above. Moreover, the existence of optimum composition is detected at all three components.

The optimum molar ratio of three precursors for MOF-801 synthesis was determined by response optimizer tool that shows how different experimental settings affect the predicted responses for a stored model. As shown in Fig. 3, MOF-801 synthesized under the modified mol ratio of 0.1723 : 0.433 : 0.3945 was predicted to show the highest performance. The predicted maximum adsorption capacity of toluene was 149.8 mg/g. The real composition of precursors for the optimized MOF-801 synthesis was as follows: $ZrOCl_2 \cdot 8H_2O$ : FUMA : DMF : FA=1 : 1.7 : 43.3 : 39.5 (molar basis). Thus, more specific values were predicted using statistical DOE method. An overlaid contour plot can define an area where the predicted means of one or more response variables were in an acceptable range as illustrated in Fig. 4. Overlaid contour plots allow us to visually identify an area of compromise among the various responses.

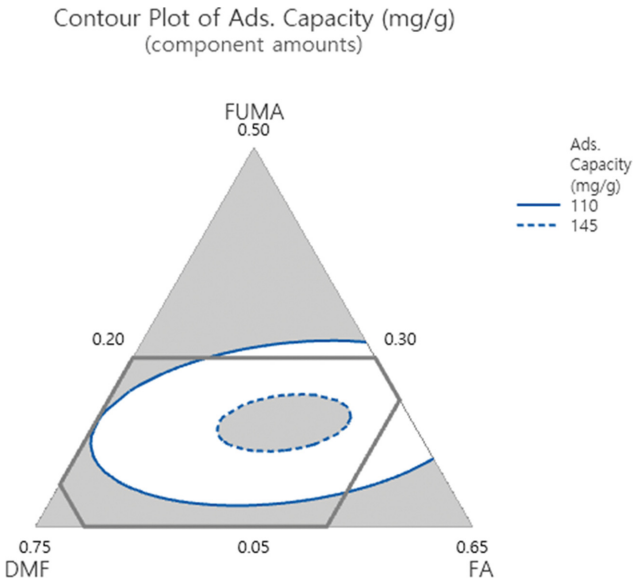


**Fig. 4. Overlaid contour plot of toluene adsorption capacity of MOF-801 synthesized with various modified mol faction of precursors.**

**Table 2. Factor and level for general factorial design**

| Factor | Level | |
|---|---|---|
| | Low (−1) | High (+1) |
| Temp. (°C) | 80 | 150 |
| Time (h) | 6 | 12 |
| Speed (rpm) | 0 | 1,000 |

**2. Factorial Design**

In previous study, the optimal composition was derived among the precursors used in MOF-801 synthesis. The next step is to consider optimization for the synthesis reaction conditions. There are three major factors for MOF-801 synthesis: temperature, time and stirring speed of the precursor mixture. Factorial designs allow the effects of a factor to be estimated at several levels of the other factors, yielding conclusions that are valid over a range of experimental conditions. As a screening step, eight experimental runs were selected by $2^3$ (2 levels, 3 factor) factorial design as illustrated

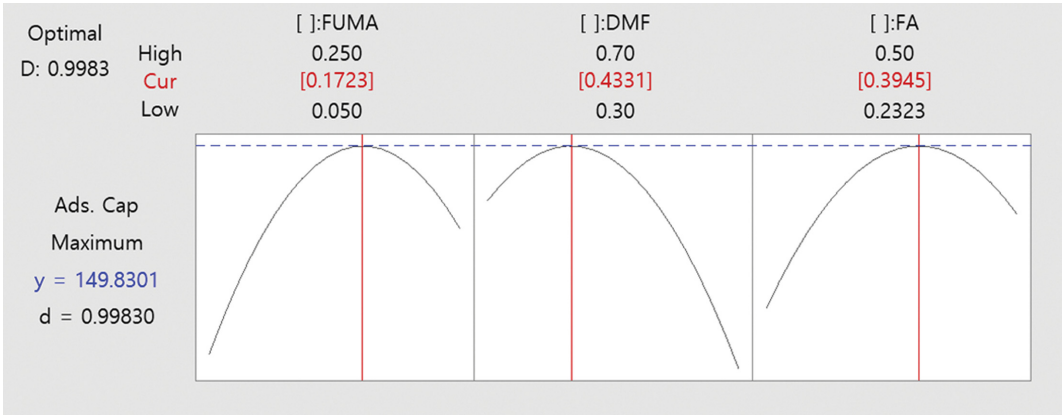


**Fig. 3. Response optimization plot for the maximum adsorption capacity of MOF-801 synthesized with various modified mol faction of precursors.**

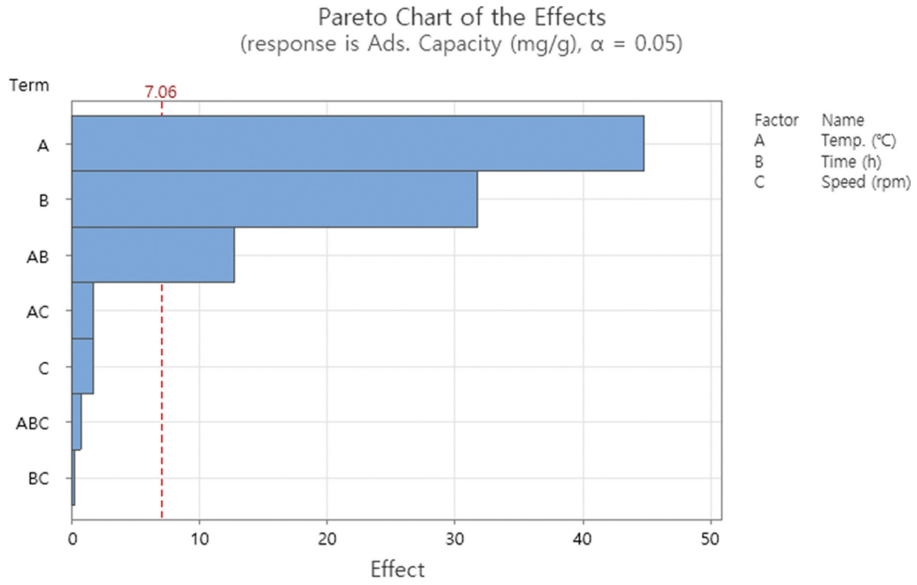


**Fig. 5. Pareto chart of the effects of synthesis conditions of MOF-801 on toluene adsorption capacity designed by full factorial method.**

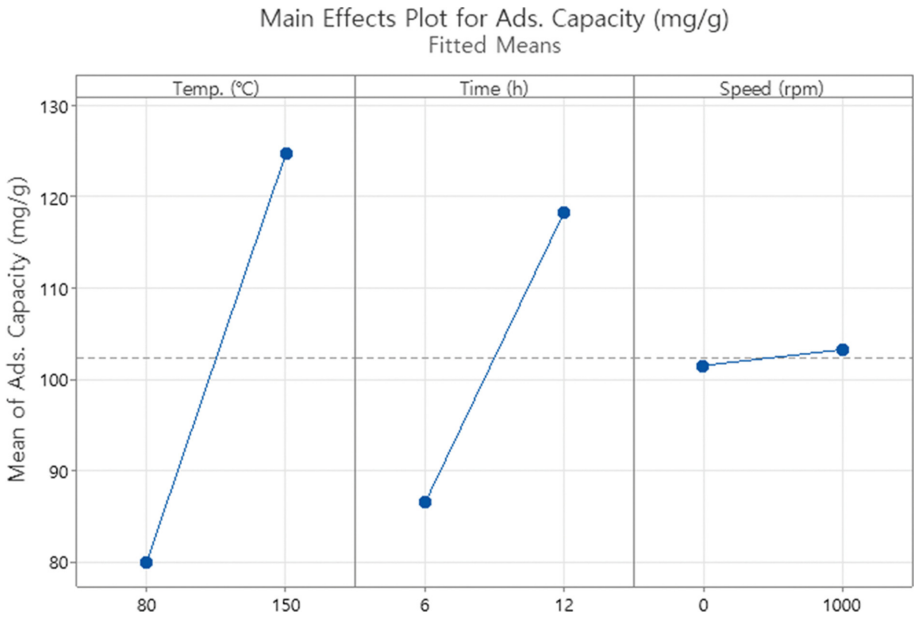


**Fig. 6. Main effects plot for toluene adsorption capacity of MOF-801 synthesized with various synthesis conditions designed by full factorial method.**

in Table 2. Based on the design, eight different MOF-801 samples were prepared by various synthesis conditions. Then, toluene adsorption experiments were carried out under the identical adsorption conditions.

Statistical analysis was executed to investigate the significance of input factors and their interactions with output responses. Initial, a Pareto chart was obtained to compare the importance of the factors as shown in Fig. 5. The relative importance was observed on the Pareto chart to compare the relative importance and statistical significance between the main factor and the interaction. Factors that cross the baseline shown in 7.06 within the chart were considered potentially important factors. Therefore, temperature (A), time (B), and AB (interaction between temperature and time) as chart terms were significant synthesis conditions for determining the adsorption capacity of MOF-801 samples. This implied the stirring speed (C) might be ignored in the optimization of synthesis reaction condition. Moreover, main effects plot was used to examine differences between level means for one or more factors. There was a main effect when different levels of a factor affected the response differently. A main effects plot illustrated the response mean for each factor level connected by a line as presented in Fig. 6. When the line was not horizontal, then there was a main effect. The steeper the slope of the line, the greater the magnitude of the main effect. This result was in a good agreement with the Pareto chart. Interac-

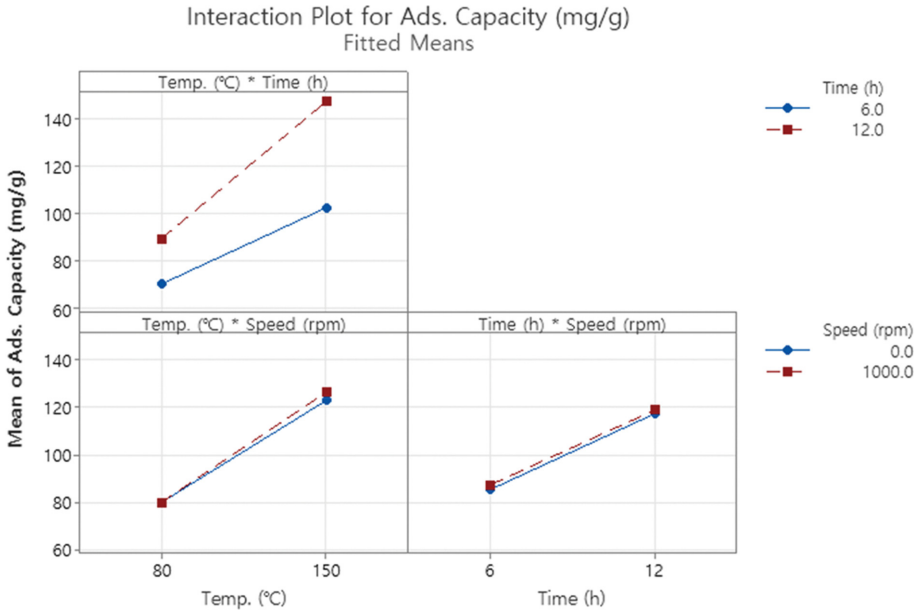


**Fig. 7. Interaction plot for toluene adsorption capacity of MOF-801 synthesized with various synthesis conditions designed by full factorial method.**

tion plot shows how the relationship between one categorical factor and a continuous response depends on the value of the second categorical factor. This plot displays means for the levels of one factor on the x-axis and a separate line for each level of another factor. In case of no interaction, two lines appear parallel. On the other hand, a nonparallel line is observed in the case of interaction existence. Analysis of the interactions between factors was performed as shown in Fig. 7. There were parallel lines between stirring speed and the other two factors; therefore, there was little interaction between them. Although insignificant, there was an interaction between synthesis temperature and time. Based on the results, stirring speed could be excluded for further investigation.

**3. Response Surface Method**

The major factors for optimizing MOF-801 synthesis as a toluene adsorbent were determined in the previous section. Response surface method (hereafter RSM) was employed on completing the statistical optimization. RSM is a set of advanced DOE techniques for better understanding and optimizing the response. This methodology is often used to refine models after determining important factors using factorial designs. Due to the utilization of quadratic regression model, RSM can provide understanding or mapping a region of a response surface, finding the levels of variables to optimize a response, and selecting the operating conditions to meet specifications. Practically, the central composite design (hereafter CCD), one of the RSM methods, was used in this study. CCD can fit a full quadratic model, including information from a correctly planned factorial experiment. Hence, it is useful to model a response variable with curvature by adding center and axial points to a previously done factorial design.

An experiment was designed using the CCD method to optimize both main factors, synthesis temperature and time. The factors and levels for the design are presented in Table 3. Some levels (−1 & +1) were already used in the factorial design. Nine experimental runs were suggested, and toluene adsorptions were performed accordingly. The results obtained from CCD were fitted to a quadratic polynomial equation to explain the dependence of adsorption capacity on the design variables as follows:

**Table 3. Factor and level for central composition design**

| Factor | Level | | | | |
|---|---|---|---|---|---|
| | $-\alpha$ | −1 | 0 | +1 | $+\alpha$ |
| Temp. (°C) | 50 | 80 | 115 | 150 | 180 |
| Time (h) | 4 | 6 | 9 | 12 | 14 |

$$\text{Adsorption Capacity (mg/g)} = -168 + 2.22 \times \text{Temperature (°C)} + 25.4 \times \text{Time (h)} - 0.00952 \times \text{Temperature}^2\,(°C) - 1.475 \times \text{Time}^2\,(h) + 0.0643 \times \text{Temperature (°C)} \times \text{Time (h)}$$

The linear correlation ($R^2$) that was used to evaluate the correlation between the actual and predicted responses was obtained from the developed model to be 0.951. This indicated that 95.1% of the variation for adsorption capacity was described by the variables studied and only 4.9% of the variation was not described by the model. Furthermore, the model adequacy was also examined by ANOVA. The results of the quadratic response surface model fitting in the form of ANOVA are presented in Table 4. ANOVA subdivides the complete variation of the results into variation associated with the model and the one associated with experimental errors, indicating whether the variation from the model is significant or not. This evaluation was performed by P-value to be a good predictor of the experimental data. The P-value obtained herein was 0.046, thus indicating the qualification of the model. Specifically, square terms were slightly more accurate than the linear term.

Contour and surface plots for toluene adsorption capacity of MOF-801 synthesized with various temperature and time are shown

**Table 4. Analysis of variance (ANOVA) for central composition design**

| Source | DF | Adj SS | Adj MS | F-Value | P-Value |
|---|---|---|---|---|---|
| Model | 5 | 9,648.3 | 1,929.7 | 9.53 | 0.046 |
| Linear | 2 | 833.3 | 416.6 | 2.06 | 0.274 |
| Temp. | 1 | 805.2 | 805.2 | 3.98 | 0.140 |
| Time | 1 | 608.7 | 608.7 | 3.01 | 0.181 |
| Square | 2 | 1,278.0 | 639.0 | 3.16 | 0.183 |
| Temp.×Temp. | 1 | 1,146.0 | 1,146.0 | 5.66 | 0.098 |
| Time×Time | 1 | 945.1 | 945.1 | 4.67 | 0.119 |
| 2-Way Interactions | 1 | 182.2 | 182.2 | 0.90 | 0.413 |
| Temp.×Time | 1 | 182.2 | 182.2 | 0.90 | 0.413 |
| Error | 3 | 607.3 | 202.4 | | |
| Total | 8 | 10,255.6 | | | |

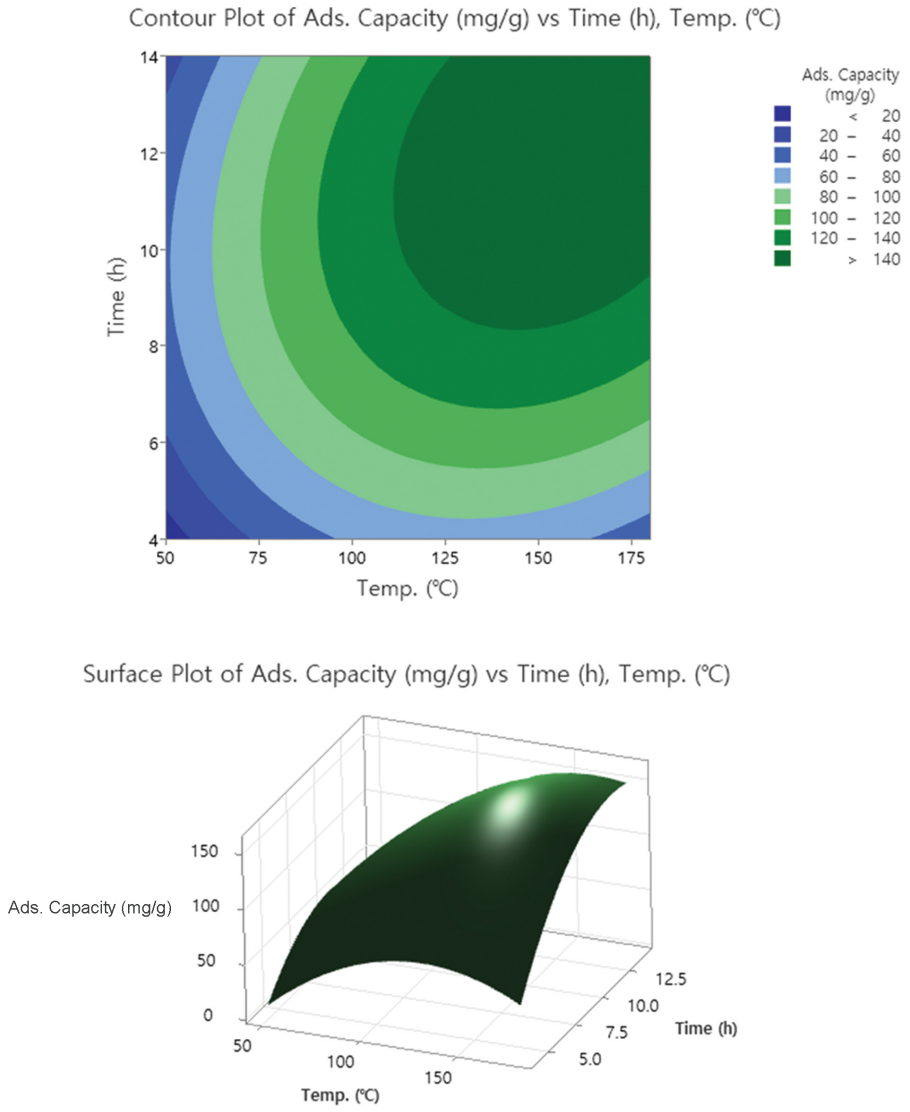


**Fig. 8. Contour and surface plots for toluene adsorption capacity of MOF-801 synthesized with various synthesis conditions designed by response surface method.**

in Fig. 8. A contour plot shows a two-dimensional view in which a contour is created by connecting points with equal response values. The surface plot displays the three-dimensional relationship in two dimensions of both variables and the response variable expressed

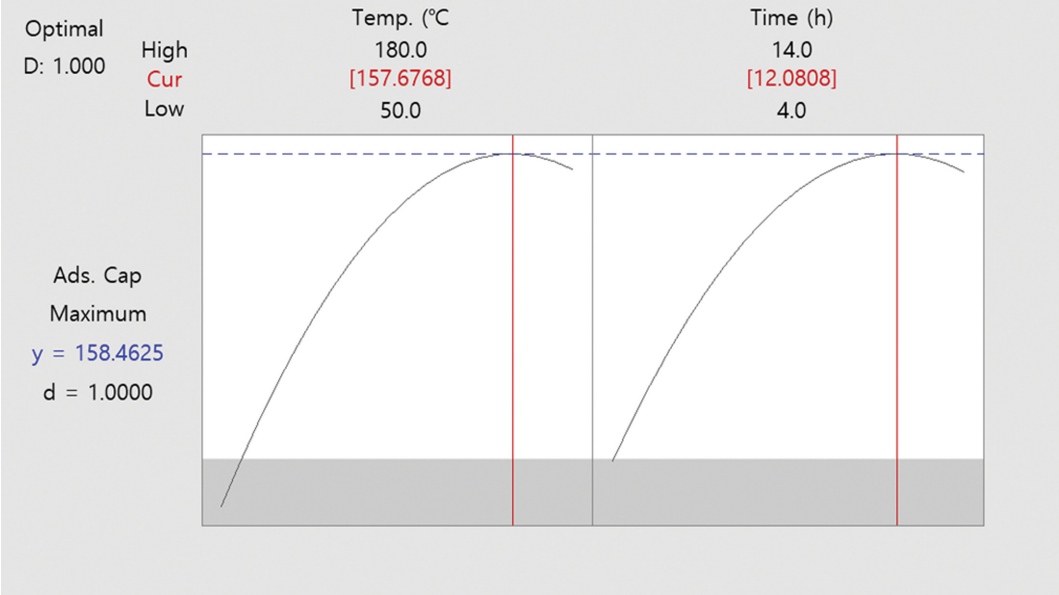


**Fig. 9. Response optimization plot for the maximum adsorption capacity of MOF-801 synthesized with various synthesis conditions designed by response surface method.**

as a smooth surface. As the synthesis temperature and time increased, the adsorption capacity of the adsorbent improved, as presented in the contour plot. Interestingly, synthesis conditions showing the highest adsorption capacity were clearly observed in the surface plot. The optimization of synthesis condition was investigated with response optimizer tool showing how different experimental settings affect the predicted responses for a stored model. The maximum adsorption capacity of MOF-801 was predicted as presented in Fig. 9. MOF-801 synthesized at 158 °C for 12 h was calculated to have a maximum toluene adsorption of 158.5 mg/g. In fact, after synthesizing MOF-801 with the optimized synthesis conditions, a toluene adsorption experiment was performed under the same conditions. The adsorption capacity of the samples was 151.9 mg/g. This is close to the predicted value of 95.5%. Therefore, this statistical methodology is suitable for application to an actual process.

## CONCLUSIONS

The main objective of this study was to optimize the synthesis conditions of MOF-801 for the adsorption process to remove toluene using statistical design of experiment methodology. Among the four precursors, Zirconium(IV) oxychloride octahydrate, N,N-dimethylformamide, fumaric acid, formic acid, three components except Zr source were optimized using mixture design method. The linear correlation ($R^2$) value of the model was 91.0% and p-value of regression was 0.002. Thus, the prediction analysis of this model was reliable. The predicted precursor composition of MOF-801 synthesis showing maximum adsorption was 149.8 mg/g. Sequential design of experiments were employed on optimization of three synthesis conditions: synthesis temperature and time, and stirring speed. Using $2^3$ factorial designs with eight experiments as a screening step, stirring speed was predicted to be eliminated for further step due to its negligible effect on adsorption capacity. For the optimization of synthesis conditions, the central composite design was used to design nine experimental runs. The design was fitted to a quadratic polynomial equation with $R^2$ of 0.951. Moreover P-value obtained herein was 0.046, indicating the statistical significance of the proposed model. MOF-801 synthesized at 158 °C for 12 h was predicted to show a maximum toluene adsorption of 158.5 mg/g. This is close to the actual value of 95.5%. We hope that our investigation helps to further move this technology forward to industrial implementation and shed more light into toluene removal using MOF type of adsorbent.

## ACKNOWLEDGEMENTS

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