# $NO_x$ adsorbent formulation research by uniform design

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## Abstract

In order to develop a nitric oxides adsorbent, some kinds of natural minerals were used in the presented study. A series of adsorbents were prepared according to uniform design and the adsorbing abilities were determined. The regression equations were drawn and the best formulation named JA was obtained from the equations. JA was prepared according to the formulation, and the adsorbability was also determined. Results showed that the absorbent JA can adsorb 156.7mg of NO and 289.9mg of $NO_2$ simultaneously in 3 hrs and the saturated adsorption quantity of $NO_x$ is 22.2% in experiment conditions, which is far better than that of active carbon. Comparing with traditional orthogonal design, experiments designed by uniform design can attain the purpose by fewer experiments. It can also obtain quantitative regression equations accurately on the basis of the results of the experiments. The equations are also helpful in results analysis.
*Keywords: formulation experiment design, uniform design, $NO_x$ adsorbent.*

## 1 Introduction

Most $NO_x$ in the atmosphere exist as NO and $NO_2$. The $NO_x$ produced by human activity are primarily discharged from flue gas and secondly from chemical processes; for instance, nitric acid production, nitration process, explosive material production and nitric acid pickling process. In the above mentioned chemical processes $NO_x$ is always discharged together with nitric acid mist.

There are many researches on $NO_x$ in flue gas, such as selective catalysis reduction (SCR), selective nocatalysis reduction (SNCR), etc. This presented study is aimed at the $NO_x$ of low concentration discharged from chemical processes.



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## 2 Materials and methods

### 2.1 Natural minerals as the raw materials

Many natural minerals with porous, stratified or catenarian structures have good adsorbing ability, such as bentonite, sepiolite, zeolite, kaolinite, etc. Because of their low cost, more and more researches on natural minerals are being carried out in the field of environment protection research. Adebowale et al. [1] modified kaolinite clay mineral with orthophosphate to adsorb Pb and Cd ions from aqueous solutions of the metal ions. Sanchez-Martin et al. [2] studied the efficiency of a series of clay minerals (montmorillonite, illite, muscovite, sepiolite and palygorskite) modified with the cationic surfactant octadecyltrimetylammonium bromide (ODTMA) in the adsorption of the pesticides penconazole, linuron, alachlor, atrazine and metalaxyl. Tahir and Rauf [3] studied the ability of bentonite to remove malachite green from aqueous solutions.

In this paper, three kinds of minerals zeolite, bentonite and attapulgite (marked as A, B and C respectively) were selected as the raw materials of the adsorbent. They were mixed with slaked lime (marked as D) to produce composite adsorbent. The adsorbent formulation was acquired by the specific design of experiment and the determination of the adsorb abilities.

### 2.2 Experiment design method

Formulation designs are commonly used in many industry processes and science researches. In these cases, the quality of the production is not determined by the total amount of the ingredients but by the proportion of them. Therefore, the essential work in formulation experiment design is to determine the relationship between the formulation and the experiment index through the selected experiment points. Basing on the experiment results the best formulation can be finally acquired.

In this paper, the study is aimed to obtain an optimized proportion of the raw materials A, B, C and D (as mentioned above) for the final absorbent, using the method of formulation design.

Many kinds of formulation experiment design methods are available, such as simplex–lattice design, simplex–centroid design, etc. [4]. Since the experiment points of simplex–lattice design and simplex–centroid design are not distributed uniformly in the experiment range and the boundary points are in the majority, uniform design which was invented by Chinese mathematicians Fang Kaitai and Wang Yuan was singled out for this study. It can conquer the shortcomings of other methods.

The experiments were designed as an unconstraint formulation design. The selected raw materials A, B, C and slaked lime (D) were considered as four factors of the experiments. In order to obtain a good regression result, the amount of experiments can not be less than two times of the number of the factors, reasonably, 3~4 times, thus every factor was divided into 12 levels.

Table $UM_{12}*(12^4)$ was selected and the 12 formulations of the adsorbents were listed in Table 1. The values of $x_1$, $x_2$, $x_3$ and $x_4$ represent the weight percentage of slaked lime (D) and mineral A, B, C in the adsorbent formulation respectively.

Table 1: Design of adsorbents formulations.

| Serial No. | formulation | | | |
|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | $x_4$ |
| 1 | 65.3 | 11.2 | 4.89 | 18.6 |
| 2 | 50.0 | 1.05 | 22.4 | 26.5 |
| 3 | 40.7 | 23.0 | 25.7 | 10.6 |
| 4 | 33.7 | 4.28 | 59.4 | 2.58 |
| 5 | 27.9 | 33.2 | 4.87 | 34.1 |
| 6 | 22.9 | 8.50 | 25.7 | 42.9 |
| 7 | 18.5 | 44.3 | 23.3 | 14.0 |
| 8 | 14.5 | 13.5 | 63.0 | 8.99 |
| 9 | 10.9 | 57.6 | 1.31 | 30.2 |
| 10 | 7.49 | 19.4 | 21.3 | 51.8 |
| 11 | 4.35 | 76.1 | 10.6 | 8.95 |
| 12 | 1.41 | 26.0 | 57.4 | 15.1 |

### 2.3 Preparation of the adsorbent

Mix the raw materials together according to the proportions listed in Table 1, then add some water and stir into mud. Shape the mud into pillared granules with the diameter of 2mm. After the granules were dried and activated by calcining the final adsorbent is produced.

### 2.4 Determination of the adsorb abilities

For the convenience in using the bench-scale system, the final adsorbent was broken and sieved so as to get the granules with the diameter of 1~1.6 mm. Stuff the sieved granules to a tubular adsorber with the inside diameter of 13.86 mm and the length of 180 mm. The adsorbent was stuffed to 12 cm high in the adsorber. The experiment system is shown in Figure 1.

The inlet gas is a mixture of NO and air. A part of NO will react with $O_2$ in the air to $NO_2$, thus there are actually NO, $NO_2$ and air in the inlet gas. The humidity of the gas was adjusted by a humidity control system. The outlet gas was discharged through an absorption bottle filled with NaOH solution. The concentration of NO and $NO_2$ were analyzed by Monitor Labs 8840 $NO/NO_x$ Analyzer.

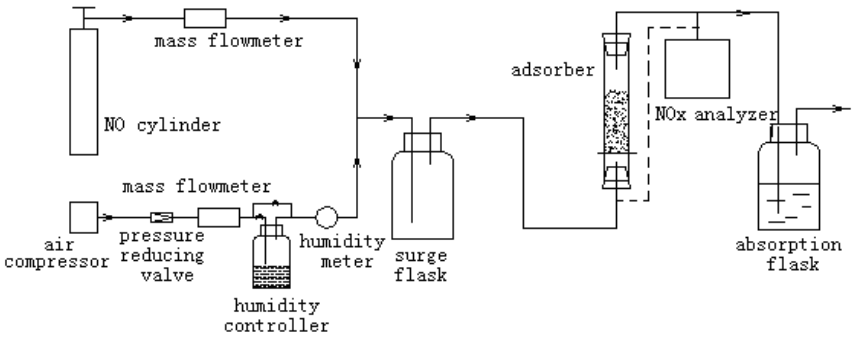


Figure 1: System for adsorb ability determination.

Table 2: Results of $NO_x$ adsorption quantity in 3 hrs.

| No. | adsorption quantity in 3 hrs (mg) | |
|---|---|---|
| | NO,$y_1$ | $NO_2$,$y_2$ |
| 1 | 107.60 | 275.51 |
| 2 | 96.75 | 269.84 |
| 3 | 88.15 | 270.46 |
| 4 | 84.62 | 264.54 |
| 5 | 88.31 | 275.63 |
| 6 | 74.73 | 265.65 |
| 7 | 68.38 | 264.66 |
| 8 | 46.37 | 259.98 |
| 9 | 57.70 | 253.94 |
| 10 | 14.06 | 238.05 |
| 11 | 25. 15 | 243. 23 |
| 12 | −39. 29 | 229. 18 |

## 3 Results and discussion

### 3.1 Adsorption quantity of $NO_x$ in 3 hrs

Adsorption quantity of $NO_x$ can be calculated by integral operation on the differences between the concentrations of inlet and outlet.

The inlet concentrations were: NO: 599mg/$m^3$ (447ppm), $NO_2$: 891 mg/$m^3$ (434ppm). The ambient temperature was 29~31°C. The relative

humidity was controlled between 69% and 71%. The space velocity was 6000 $h^{-1}$. The results of $NO_x$ adsorption quantity in 3 hrs is listed in Table 2.

Based on the data of Table 2, the following regression equations were acquired using SPSS software:

$$y_1=0.064x_1x_2+0.039x_1x_3+0.038x_1x_4-0.020x_2x_3 \quad (1)$$

$$y_2=1.958x_1+2.328x_2+2.480x_3+2.241x_4+0.027x_1x_2 +0.015x_1x_3+0.034x_1x_4-0.009x_3x_4 \quad (2)$$

where $y_1$ is the NO adsorption quantity (mg) in 3 hrs, and $y_2$ is the $NO_2$ adsorption quantity (mg) in 3 hrs.

Obviously:

$$x_1+x_2+x_3+x_4=100 \quad (3)$$

Solve the systems of equations constituted of eqn. (1), (3), and eqn. (2), (3) using Microsoft Excel. The following results can be acquired: for the variables $x_1$=50, $x_2$=50, $x_3$=0, $x_4$=0, a maximum of $y_1$ occurred at 160mg; and for $x_1$=45.84, $x_2$=54.16, $x_3$=0, $x_4$=0, the maximum of $y_2$ occurred at 295.54mg.

### 3.2 Comparison of the adsorb abilities between NO and $NO_2$

No.1 adsorbent is the best one of the 12 adsorbents in Table 2 by intuitive analysis. The removal efficiency of NO and $NO_2$ by No.1 in 3 hrs were compared in Figure 2.

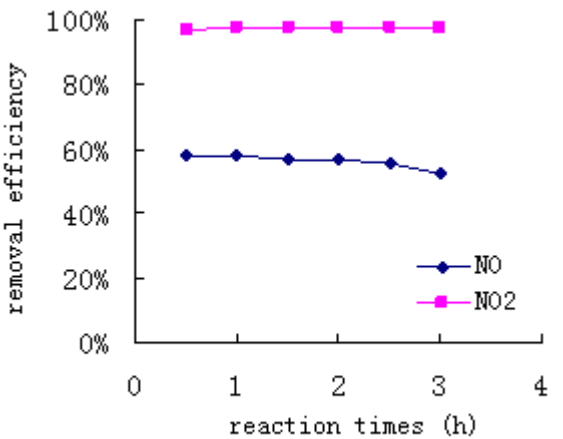


Figure 2: Comparison of removal efficiency between NO and $NO_2$.

It can be seen in Figure 2 that $NO_2$ is far easier to be removed than NO. The removal efficiency of $NO_2$ kept above the level of 97% in 3 hrs, while that of NO was around 52.8%~58.1%. Therefore the overall removal efficiency, and thus the final formulation of the absorbent should be determined by the adsorb ability for NO. The finally selected formulation named JA is: $Ca(OH)_2$ : zeilite =

50% : 50% (weight ratio) based on eqn. (1). Substitute $x_1$=50, $x_2$=50 into the regression eqn. (2), a predicted absorption value in 3 hrs for $NO_2$ can be acquired at 281.8mg. The adsorbent JA was prepared using the optimized formulation, and its real absorb abilities were determined with the same method, the results showed that the absorption quantities of JA in 3 hrs were 156.7mg for NO, and 289.9mg for $NO_2$, which were close to the predicted values, proving a high significance of the regressions, and an acceptable reliability of the equations.

### 3.3 Comparisons between JA and active carbon

The adsorb ability of active carbon was also tested in the same condition. The results showed that the $NO_x$ adsorption quantity of active carbon in 3 hrs was 166.2mg, which was 57.3% of the absorption quantity of JA. Furthermore, the concentration of the outlet NO was measured higher than the inlet concentration. Besides, there was also CO concentration detected in the outlet gas. Therefore, it can be deduced that $NO_2$ was reduced to NO at the surface of active carbon.

### 3.4 Breakthrough curve and saturated adsorption capacity of JA

JA was tested with the system (shown in Figure 1) continuously until it was totally broken through. The saturated adsorption quantity was also calculated. The breakthrough curve is shown in Figure 3.

13.0750g of JA was used in the testing. The removal quantity of NO was measured 654mg and that of $NO_2$ was 2249mg. It can be calculated that the adsorption capacity was 5.0% for NO, 17.2% for $NO_2$, thus 22.2% for $NO_x$ in the condition.

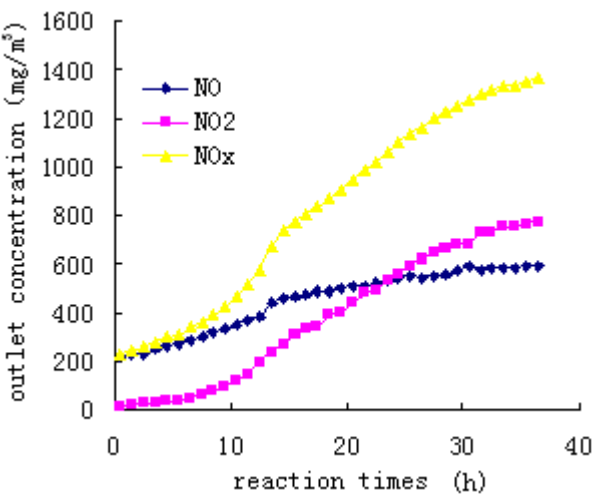


Figure 3: Breakthrough curve of JA.

### 3.5 Comparisons between uniform design and orthogonal design [5]

Compared with the traditional orthogonal design, the uniform design has the following advantages:

(1) The ingredient percentages in orthogonal design can not be taken as the levels of the factors because it would result in the summations not equal to 1.
(2) In uniform design, only one experiment is needed for each level of the factors, thus the experiment number is equal to the level number. As for orthogonal design, experiment number equals the square of level number.
(3) The levels of the factors in uniform design can be adjusted to avoid the reactants of top grade meeting with reactants of low grade, thus to prevent too violent or too slow reactions.

## 4 Conclusions

(1) Three kinds of natural minerals and slaked lime were introduced in the research. Uniform design was used in the experiments to develop a kind of $NO_x$ adsorbent. The best formulation has been acquired basing on the designed 12 experiments.
(2) In the experiment condition, the acquired best formulation of the absorbent is 1:1 (weight ratio) for $Ca(OH)_2$ and zeolite. Results showed that the absorbent JA can adsorb 156.7mg of NO and 289.9mg of $NO_2$ simultaneously in 3 hrs in the experiment condition, while the saturated adsorption quantity of $NO_x$ is 22.2%.

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