Chemical modification and characterization of clinoptilolite by 1,3-Phenylenediamine as a sorbent for the removal of NO\textsubscript{2}

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ABSTRACT
A novel sorbent was prepared through chemical modification of clinoptilolite zeolite using 1,3-phenylenediamine, and was characterized by Fourier transform infrared spectroscopy, differential thermal analysis and elemental analysis methods. The adsorption capacity of modified clinoptilolite was found to be 588.2 mg/g for NO\textsubscript{2} adsorption. The equilibrium data of NO\textsubscript{2} adsorption on modified zeolite were analyzed using Langmuir, Freundlich and Temkin models, which revealed that NO\textsubscript{2} adsorption by this modified zeolite follows Langmuir model. The adsorption mechanism was investigated by three simplified kinetic models, pseudo-first-order, pseudo-second-order and intra-particle diffusion.

Keywords: Zeolite; clinoptilolite; modification; NO\textsubscript{2}; adsorption capacity

1. Introduction
Clinoptilolite is the most abundant natural zeolite [1], which can be easily extracted from mines. The natural characteristics of clinoptilolite have made it a widely used sorbent [2]. Low cost and abundance are among the main advantages of this zeolite. From among all alimino-silicate groups, clinoptilolite contains the highest level of silicate and therefore, sorbents produced by acidic treatment of this zeolite may have molecular sieve properties of special interest. On the other hand, other research shows that natural zeolites can be used as a sorbent for purification of gases [2] and applied to remove nitrogen oxides (NO\textsubscript{x}) which are among pollutant gases [3]. Clinoptilolite has been found to be the best natural zeolite for purification of gases [4]. While natural zeolites have a lower capacity in removing gases than synthetic zeolites and activated carbons, their adsorption capacity can be enhanced through chemical modification, which may lead to a higher adsorption capacity in removing gases [5].

NO\textsubscript{2} is considered as one of the most harmful gases [6], which threatens human health. Short and long term exposure to NO\textsubscript{2} can induce health effectson humans, but these effects are different in character. Short term exposure to a very high concentration can result in severe pulmonary damage. Exposure of individuals with chronic lung diseases such as asthma and chronic obstructive pulmonary disease can cause short term responses such as changes in airway responsiveness or lung function. Chronic exposure to NO\textsubscript{2} has been associated with increased respiratory symptoms, especially when observed under indoor exposure. For these reasons, removal of NO\textsubscript{2} has received considerable attention.

In the light of the foregoing discussion, this paper aims to propose a new method for NO\textsubscript{2} removal from the air through chemical modification of clinoptilolite by 1,3-phenylenediamine. The adsorption capacity of modified clinoptilolitewere also investigated. The advantage of this approach is its high capacity in removing NO\textsubscript{2} compared to other sorbents.

2. Experimental
2.1. Materials
A sample of clinoptilolite from Aftar region (western Semnan, central Alborz Mountains, 200 Km to the east of Tehran, Iran) was used. Aftar zeolite region coordination is N35° 38’ 19.3” E053° 06’ 04.0” C. Clinoptilolite samples were prepared depending on the requirements of differential thermal analysis (DTA), fourier transform infrared spectroscopy (FTIR), elemental analysis, as well as application requirements in fixed-bed adsorption column and isotherm studies.

2.2. Instruments
Fourier transform infrared spectroscopy was conducted using FTIR analysis instruments (Thermo Nicolet Nexus 870, US) and thermal behavior was investigated using DTA/TGA thermal analysis instruments (Netzsch STA409PC Lluxx, Germany). Elemental analysis was carried out on an elemental analyzer instrument (Elementar Vario EL III, Germany). Finally, gas concentration was measured using a gas detector instrument with NO\textsubscript{2} electrochemical sensor (Senko SP2nd, Korea).

2.3. Reagents and solutions
1,3-phenylenediamine, 1,4-Dioxane, HCl and methanol were products of Merck (Darmstadt, Germany). 3-Glycidoxypropyltrimethoxysilane (GPTMS) was the product of Sigma-Aldrich (Missouri, USA). The stock solutions included 500 mg/L of 10% HCl, 50 mg/L of distilled 1,4-dioxane containing 5% GPTMS and 1000 mg/L of 0.1M HCl used to adjust the pH of the solutions.

2.5. Zeolite modification

In the first step, a 10 g sample of raw clinoptilolite which had been sieved to the grain size of 0.25–0.5 mm (G.S.=0.25-0.5 mm) was heated in the oven up to 150°C for 1 hr. The sample was then poured into a 10% HCl acid solution and stirred for 8 hrs. The zeolite was filtered using a filter paper and rinsed with distilled water so as to adjust to the pH of the distilled water. The sample was finally dried at 100°C. A 5 g sample of the product was poured into a distilled solution of 50 mL 1,4-dioxane containing 5% GPTMS and was refluxed for 16 hrs at 100°C. The product was filtered, washed with 30 mL distilled 1,4-dioxane and placed in a desiccator to dry.

In the second step, a solution was obtained from dissolving 10% of 1,3-phenylenediamine into 90% of water and the pH of the product was adjusted to 5 using a 0.1M HCl acid solution. The zeolite obtained from the first step was poured into a 50 mL solution obtained from the second step and stirred for 48 hrs. The product was then filtered using a filter paper.

Finally, the modified zeolite which showed a dark green color was washed with 30 mL of methanol and dried in ambient conditions (temperature=25°C and relative humidity=45%). The methodology used to modify clinoptilolite is summarized in Fig. 1.

2.4. Method

The NO₂ adsorption capacities were measured in a laboratory-scale, fixed-bed adsorption column, at room temperature (temperature=25°C and relative humidity=45%). The adsorbent was packed into a glass of adsorption column (length 110 mm, internal diameter 27 mm). In a typical test, 45 ppm of NO₂ went through the fixed-bed of adsorbent (modified zeolite, which was ground and sieved to the grain size of 0.25–0.5 mm) with a total inlet flow rate of 1.6 L/min. The concentrations of NO₂ in the outlet gas were measured using the gas detector.

2.6. Isotherm studies

Modified zeolites samples weighing 0.3 g to 1.7 g with an increasing rate of 0.1 g were put into the adsorption column, then NO₂ was passed through the modified samples for 10 min while its concentration (Cᵢ) and flow rate (Q) were 45 ppm and 1.6 L/min respectively. Variations in adsorption capacity of each sample were constantly measured by the gas detector.

3. Results and discussion

3.1. Characterization of modified clinoptilolite

3.1.1. Fourier transform infrared spectroscopy (FTIR)

Fig. 2A displays FTIR results for raw clinoptilolite where the bands for water, OH groups, silica oxides and aluminum oxides are demonstrated [7,8]. Fig. 2B demonstrates FTIR results for modified clinoptilolite where the band assigned to the stretching vibration modes of primary amine groups cannot be observed as it is overlapped by the OH-groups, which have a wide band centered at 3435 cm⁻¹. A comparison of the FTIR results of raw and modified clinoptilolite indicates that two extra bands have developed in the modified clinoptilolite, one of which is assigned to the stretching aliphatic C-H, associated with GPTMS occurring in the 3000 cm⁻¹ region. As can be seen from Fig. 2B, the other band appears near 1600 cm⁻¹ assigned to the stretching aromatic C=C which is associated with 1,3-phenylenediamine [9].

![Fig. 2. Fourier transform infrared spectroscopy of raw (A) and modified clinoptilolite (B).](image-url)
3.1.2. Differential thermal analysis (DTA)

Fig. 3 presents the results of DTA-TGA analysis for raw and modified clinoptilolite. As can be seen in Fig. 3A, zeolite has experienced a %1 weight loss up to 90ºC, which can be attributed to the initial loss of surface waters on zeolite sample and to the subsequent loss of OH groups. This weight loss is observed up to 1200ºC which leads to a total %14 weight loss. However, comparing the TG curve for the modified zeolite (Fig. 3B) with that of raw zeolite reveals an arc around 250-500ºC temperature range, showing the loss of both OH groups and 1,3-phenylenediamine in this region. This arc disappears after 500ºC (1,3-phenylenediamine has been lost), while zeolite sample weight loss continues steadily. A total %19 weight loss can be observed for the modified zeolite, %5 higher than the figure for raw zeolite, which is due to loss of 1,3-phenylenediamine in addition to the loss of OH-groups and water.

3.1.3. Elemental analysis

The results of elemental analysis is presented in Table 1, which confirms modification of raw zeolite samples where the content of nitrogen shows an increase from less than % 0.03 to % 0.33 due to the presence of NH₂ on 1,3-phenylenediamine following the modification process. Also, due to GPTMS bonds and subsequent 1,3-phenylenediamine bonds, the content of carbon has increased from % 0.54 to % 5.35, revealing the presence of an organic carbonic surface on zeolite samples.

![Fig. 3. DTA-TGA curve of raw (A) and modified clinoptilolite samples.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Analyte name</th>
<th>Analyte value (W/W%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>N</td>
<td>Less than &lt; 0.03</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>1.45</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.54</td>
</tr>
<tr>
<td>Modified</td>
<td>N</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>1.99</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>5.35</td>
</tr>
</tbody>
</table>

3.2. Isotherms of adsorption

Results of NO₂ adsorption onto modified clinoptilolite samples are presented in Fig. 4. Langmuir is an empirical model which assumes monolayer adsorption, with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites. Langmuir isotherm refers to homogeneous adsorption, where each molecule possesses constant enthalpies and sorption activation energy (all sites possess equal affinity for the adsorbate)[24].

![Fig. 4. Effect of modified zeolite mass in NO₂ adsorption (G.S.=0.25-0.5mm, Q =1.6 L/min, Cᵢ= 45ppm).](image)
The linear form of Langmuir equation can be written as (1) below [10]:

$$
\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}
$$

(1)

Where, $q_m$ is the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg/g). $K_L$ is the Langmuir constant (L/mg), $C_e$ is the equilibrium concentration of NO$_2$(mg/L) and $q_e$ is the amount adsorbed at $C_e$(mg/g).

The constants can be evaluated from the intercept and the slope of the linear plot of $C_e/q_e$ as a function of $C_e$(Fig. 5). A comparison of the experimental data with Langmuir isotherm model reveals that the results are compatible. Langmuir isotherm model can, therefore, be applied to analyze the adsorption capacity of modified clinoptilolite NO$_2$ removal. Langmuir parameters are computed from Equation (1) and displayed in Table 2.

Separation factor $(R_L)$ is a dimensionless parameter that can explain essential characteristics of the Langmuir equation. It is defined as [25]:

$$
R_L = \frac{1}{1 + \frac{C_e}{K_L q_m}}
$$

(2)

Where, $C_e$ denotes the adsorbate initial concentration (mg/L) and $K_L$ (L/mg) refers to the Langmuir constant. In this context, lower $R_L$ value indicates that adsorption is more favorable. In a more in-depth explanation, $R_L$ value indicates the adsorption nature to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable (0 < $R_L < 1$) or irreversible ($R_L = 0$). According to Table 2, the value of $R_L$ (=0.252) is in range of 0-1 and the adsorption nature of this sorbent is favorable.

![Fig. 5. Langmuir isotherm for NO$_2$ adsorption onto modified zeolite.](image1)

Freundlich isotherm is an empirical model that can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. At present, Freundlich isotherm is widely applied in heterogeneous systems especially for highly interactive species on activated carbon and molecular sieves (as in zeolites). A linear form of the Freundlich equation can be mathematically represented as [11]:

$$
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e
$$

(3)

Where, $1/n$ is the heterogeneity factor and $K_F$ is the Freundlich constant (mg/g) (L/mg)$^{1/n}$. Therefore, a plot of $\ln q_e$ as a function of $\ln C_e$(Fig. 6) allows the $1/n$ and constant $K_F$ to be determined. $1/n$ value below unity implies a chemisorption process while $1/n$ value above unity is indicative of cooperative adsorption [12]. As can be seen from the results of Freundlich isotherm model presented in Table 2, $1/n$ value for NO$_2$ adsorption onto modified zeolite is below unity and adsorption is a chemisorption process.

![Fig. 6. Freundlich isotherm for NO$_2$ adsorption onto Modified zeolite.](image2)

Temkin isotherm model is another model which was applied in this investigation. Temkin equation is excellent for predicting the gas phase equilibrium when organization in a tightly packed structure with identical orientation is not necessary. Conversely, complex adsorption systems including the liquid-phase adsorption isotherms are usually not appropriate to be represented. Temkin isotherm model can be represented as in (4) below [13]:

$$
q_e = \frac{R T}{A_T} \ln A_T C_e
$$

(4)

The linear form of the equation can be expressed as follows:

$$
\ln q_e = B \ln A_T + \ln C_e
$$

(5)

Where, $B = \frac{R T}{A_T}$ and $A_T$ are the Temkin constant related to the heat of sorption (J/mol). $A_T$ is the Temkin isotherm constant (L/g), $R$ is the gas constant (8.314 J/mol °K) and $T$ is the absolute temperature (°K). Therefore, plotting $q_e$ as a function of $\ln C_e$(Fig. 7) enables one to determine the constants $A_T$ and $B$. Temkin parameters calculated from Equations 4 and 5 are listed in Table 2.
Redlich–Peterson isotherm model is a hybrid model enjoying the characteristics of both Langmuir and Freundlich isotherm models, involving three parameters which constitute an experimental equation. This model can represent adsorption equilibria over a wide concentration range and applicable either in homogeneous or heterogeneous systems due to its versatility. Redlich–Peterson equation can be represented as follows [14]:

\[
q_e = \frac{K_q \alpha_q}{1 + \alpha_q}
\]

\[
K_q, \alpha_q, \beta_q
\]

are three isotherm constants that characterize the isotherm. Constant \( \beta_q \) is an exponent which lies between 0 and 1 (0 < \( \beta_q \) < 1).

The closer constant \( \beta_q \) is to unity, the more strongly the adsorption process follows Langmuir model and the closer this constant is to zero, the more strongly the adsorption process follows Freundlich model. Calculating the logarithm of Equation 6, Redlich–Peterson linear model is obtained as:

\[
\ln \left( \frac{q_e}{x_e} \right) = \ln \beta_q + \ln \alpha_q
\]

Typically, a minimization procedure is adopted in solving the equations by maximizing the correlation coefficient, \( R^2 \), between the experimental data points and predictions of the theoretical model with solver add-in function of the Microsoft excel [15].

Thus, \( K_q, \alpha_q, \beta_q \) and \( R^2 \) were calculated for NO\(_2\) adsorption onto modified clinoptilolite, which are presented in Table 2. As the Table 2 shows, \( R^2 \) has been calculated for Langmuir, Freundlich, Temkin and Redlich-Peterson models. As can be seen, \( R^2 \) value is higher in Langmuir model than in Freundlich and Temkin models. Also, \( \beta_q \) value is closest to unity in Redlich–Peterson model, suggesting that NO\(_2\) adsorption on modified clinoptilolite follows Langmuir model rather than Freundlich model. Therefore, Langmuir model is considered to be the most convenient and compatible model for analyzing NO\(_2\) adsorption on modified clinoptilolite by 1,3-phenylenediamine.

The results of NO\(_2\) removal procedures reported by previous studies are presented in Table 3. As the table demonstrates, modified zeolite samples investigated in the current study exhibited a higher adsorption capacity than the maximum values obtained by the methods in the literature. This suggests that the new modification method can be successfully applied in NO\(_2\) adsorption.

**Table 2.** Isotherm parameters obtained using the linear method.

<table>
<thead>
<tr>
<th>Langmuir</th>
<th>Temperature</th>
<th>( q_{\text{max}} ) (mg g(^{-1}))</th>
<th>( K_L ) (L mg(^{-1}))</th>
<th>( R_L )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25 °C</td>
<td>588.2</td>
<td>0.066</td>
<td>0.252</td>
<td>0.9798</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Freundlich</th>
<th>Temperature</th>
<th>( K_F ) (mg g(^{-1})) (L mg(^{-1}))(^{1/n})</th>
<th>( n )</th>
<th>( 1/n )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25 °C</td>
<td>104.4</td>
<td>2.58</td>
<td>0.378</td>
<td>0.9684</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temkin</th>
<th>Temperature</th>
<th>( A_T ) (L g(^{-1}))</th>
<th>( B ) (J mol(^{-1}))</th>
<th>( B_T ) (J mol(^{-1}))</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25 °C</td>
<td>0.577</td>
<td>137.4</td>
<td>18.05</td>
<td>0.9590</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Redlich–Peterson</th>
<th>( \beta_q )</th>
<th>( \alpha_q ) (or B(dm(^{3})mg(^{-1}))(^{\beta_q}))</th>
<th>( K_R ) (or A (dm(^{3})g(^{-1})))</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.01</td>
<td>0.065</td>
<td>40</td>
<td>0.9913</td>
</tr>
</tbody>
</table>

**Table 3.** Comparing NO\(_2\) adsorption capacities obtained using different sorbent in the literature.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Sorbate</th>
<th>Max. capacity, mg/g</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-enriched active carbons from brown coal</td>
<td>NO(_2)</td>
<td>30</td>
<td>16</td>
</tr>
<tr>
<td>Y-Zeolite modified by Na</td>
<td>NO(_2)</td>
<td>450</td>
<td>3</td>
</tr>
<tr>
<td>Y-Zeolite modified by Cs</td>
<td>NO(_2)</td>
<td>460</td>
<td>3</td>
</tr>
</tbody>
</table>
3.3. Adsorption kinetics

To investigate the mechanism of NO$_2$ on modified clinoptilolite, the pseudo-first-order, pseudo-second-order and intraparticle diffusion equations were used to find out the adsorption mechanism.

3.3.1. Pseudo-first-order kinetic model

The pseudo-first-order equation is a simple kinetic analysis of adsorption in the following form:

$$\frac{dq_e}{dt} = K_1(q_e - q_i)$$  \hspace{1cm} (8)

Where, $K_1$ is the rate constant of pseudo-first-order adsorption. $q_e$ represents the amount of adsorption capacity (corresponding to monolayer coverage) and $q_i$ is the amount of adsorption at any time $t$. By applying definite integration with initial conditions ($q_i = q_i$ and $q_e = q_e$), Eq.(8) changes in form:

$$\log(q_e - q_i) = \log q_e - \left(\frac{q_i}{q_e}\right) t$$  \hspace{1cm} (9)

Where, $q_e$ and $q_i$ are the amount of NO$_2$ adsorbed (mg/g) at equilibrium and at any time $t$ and $K_1$ is the constant (min$^{-1}$). Therefore, a plot of $\log(q_e - q_i)$ vs $q_i$ as a function of $t$ gives a straight line for the pseudo-first-order adsorption kinetics (Fig. 8). The value of $K_1$ was obtained from the slope of the straight lines ($K_1 = 0.2319$) and the $q_i$ value was calculated from the intercept ($q_i = 26.47$).

![Fig. 8 Pseudo-first-order kinetic of NO$_2$ adsorption on modified clinoptilolite.](image)

3.3.2. Pseudo-second-order kinetic model

This model can be represented in the following form [21]:

$$\frac{dq_e}{dt} = K_2(q_e - q_i)^2$$  \hspace{1cm} (10)

Where, $K_2$ is the rate constant of pseudo-second-order adsorption.

By applying definite integration with initial conditions [21], Eq.(10) changes in form:

$$\frac{t}{q_e} = \left(\frac{1}{K_2 q_i^2}\right) + \left(\frac{1}{K_2 q_i}\right) t$$  \hspace{1cm} (11)

Therefore, a plot of $t/q_e$ as a function of $t$ gives a straight line for the pseudo-second-order adsorption kinetics (Fig. 9). The value of $K_2$ was obtained from the slope of the straight lines ($K_2 = 2.73 \times 10^{-5}$) and the $q_i$ value could be calculated from the intercept ($K_2 = 2.73 \times 10^{-5}$). Both $q_i$ and $q_{exp}$, values are completely compatible ($K_2 = 2.73 \times 10^{-5}$). Correlation coefficients for the pseudo-first-order and pseudo-second-order kinetic plots are high ($R^2 = 0.9471$ and $R^2 = 0.9783$, respectively) but the adsorption kinetics can be predicted better by the pseudo-second-order model.

3.4. Weber-Morris intra-particle diffusion model

Weber and Morris [22] introduced a graphical method to prove the occurrence of intra-particle diffusion and to determine if it was the rate-limiting step in adsorption process. This model is expressed as:

| Activated carbons with KOH | NO$_2$ | 43.5 | 6  |
| Activated carbons with CO$_2$ | NO$_2$ | 44.1 | 18 |
| Activated carbons impregnation with KOH | NO$_2$ | 384.7 | 19 |
| Activated carbons impregnation with NaOH | NO$_2$ | 183.8 | 19 |
| Activated carbons (obtained from wood-base) | NO$_2$ | 206 | 20 |
| Clinoptilolite Zeolite, modified by 1,3-phenylenediamine (our sorbent) | NO$_2$ | 588.2 | --- |

Table: Adsorption of NO$_2$ on modified clinoptilolite
\[ q_t = K_{diff} t^{1/2} \]  
(12)

Where, \( K_{diff} \) is intra-particular diffusion rate constant (mg/g min^{1/2}) and \( q_t \) is the amount adsorbed per unit mass of adsorbent (mg/g) at time \( t \).

Intra-particular diffusion was characterized using the relationship between specific sorption \( (q_e) \) and the square root of time \( (t^{1/2}) \). Therefore, a plot of \( q_t \) as a function of \( t^{1/2} \) allows intra-particle diffusion model to be explained.

If the regression of \( q_t \) versus \( t^{1/2} \) is linear passing through the origin, then intra-particle diffusion will be the sole rate-limiting step but if the regression of \( q_t \) versus \( t^{1/2} \) is linear and it does not pass through the origin, this suggests that the adsorption involves intraparticle diffusion but is not the only rate-limiting step [23].

Fig. 10 shows the Weber-Morris diffusion model. The deviation of straight lines from the origin indicates that intra-particle transport is not the rate-limiting step. The results indicate that at the beginning of the adsorption process, the NO\(_2\) gas diffused quickly among the particles and then intra-particle diffusion slowed down and stabilized.

**Fig. 9.** Pseudo-second-order kinetic of NO\(_2\) adsorption on modified clinoptilolite.

**Fig. 10.** Intra-particle diffusion kinetics for adsorption of NO\(_2\) on modified clinoptilolite.

### 4. Conclusion

In this study, a novel type of sorbent was obtained from chemical modification of clinoptilolite zeolite by 1,3-phenylenediamine using a process which is both convenient and cost-effective. The newly developed sorbent enjoys a high capacity in NO\(_2\) adsorption as well as high chemical stability. Zeolite samples modified using the new method exhibit a remarkably higher level of adsorption capacity in NO\(_2\) removal compared to other sorbents. Langmuir isotherm model was found to be the most compatible model for analyzing adsorption capacity of modified zeolite. The highest adsorption capacity obtained using Langmuir isotherm model was 588.2(mg/g). The \( K_L \) value showed that the modified clinoptilolite was favorable for the adsorption of NO\(_2\). The adsorption mechanism can be predicted better by the pseudo-second-order model. The results indicate that at the beginning of the adsorption process, the NO\(_2\) gas diffused quickly among the particles, then intra-particle diffusion slowed down and stabilized.

### References


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