Modification of diatomite zeolite for the removal of acetone volatile organic compound

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Abstract: In this work, the effect of diatomite zeolite of Iran was evaluated as an adsorbent for adsorption of acetone volatile organic compound (VOC). The diatomite zeolite was modified by acid treatment to enhance the capability of adsorbent against acetone sorption. The morphology and structure of diatomite zeolites were determined by using scanning electron microscope (SEM), X-ray fluorescence (XRF) and Brunauer–Emmett–Teller (BET) analysis. Based on results, the modified diatomite zeolites had a higher surface area and Si/Al ratio compared with diatomite. The sorption experiments results indicated that the highest adsorption capacity was obtained by the modified diatomite zeolite for acetone sorption. The regeneration was performed with air at temperatures of 80 and 160 °C. The effect of air humidity was also evaluated on the sorption of acetone using zeolite samples. The obtained results indicated the high capacity of modified diatomite zeolite for VOCs adsorption.

Key words: Natural Zeolite, Diatomite, Adsorption, Chemical Modification, Acetone

1. Introduction

Volatile organic compounds (VOCs) are a large groups of molecules including alkanes, ketones, aromatics, paraffin’s, olefins, alcohols, ethers, esters, halogenated and sulfur hydrocarbons [1]. VOCs emissions into environment is a serious challenge with respect to human’s health and environmental considerations [2]. The presence of VOCs in the atmosphere causes severe health problems including the eye and throat irritation, damage to liver and central nervous system. In addition, VOCs can contribute to global warming, stratospheric ozone depletion and tropospheric ozone formation. Therefore, development of effective treatments to remove these organic chemicals is necessary. Various techniques including condensation, thermal oxidation, catalytic oxidation, bio filtration, have been used for the removal of VOCs [3-5]. However, these techniques are associated with problems such as excessive time requirements, high costs and high energy consumption. In this way, the adsorption process due to its simplicity, moderate operational conditions and economic feasibility is mostly preferred [6]. Several adsorbents such as silica gel, zeolites, mesoporous materials and activated carbons have been used for VOCs sorption [7-14]. Among adsorbents, activated carbons and zeolites are widely used in the VOCs sorption. However, the main problems of activated carbon are added fire risk, hygroscopic with pore clogging, low mechanical stability and regeneration difficulties which limits the using of activated carbon for the removal of VOCs [15]. Both natural and synthesized zeolites due to the excellent ion exchange and molecular sieving properties are widely used in VOCs treatment [16]. The use of synthesized zeolites due to the more expensive is limited [16]. The Brønsted and Lewis acid sites of zeolites are responsible of VOCs removal by adsorption onto the natural zeolites [17]. Among zeolites, diatomite due to its high permeability and porosity as well as high surface area has been widely used for the removal of different elements [18]. Kamelabad area of Iran has the main source of diatomite.

In the present study, an Iranian natural zeolite of diatomite was selected as an adsorbent for the removal of typical VOCs, i.e. acetone. Additionally, the surface of natural zeolite was modified using HCl to improve the sorption efficiency of diatomite. The effect of humidity on the acetone sorption was investigated. Also, the isotherm model was estimated for acetone sorption.

2. Experimental

2.1 Materials

The row diatomite zeolite powders were provided from Kamelabad mines of Iran. At first, natural clay
particles were washed by distilled water to remove impurities, and were dried at 110°C for 8 h. Then, dried samples were powdered in a ball mill consisting of distilled water in 250 rpm for 5 h. Finally, slurry samples were dehumidified using spray dryer in 140°C according to the previous study [19]. For modification of zeolites, the prepared diatomite powders were poured into 500-mL flasks containing 250 mL of 0.1 N HCl under stirring for 4 h [20]. Acetone with 99.8% purity were purchased from Merck (Darmstadt, Germany). The vapor concentration of the selected VOCs was obtained by vaporizing liquid acetone in a thermally controlled saturator chamber.

2.2 Adsorption experiments

The adsorption experiments were carried out in a fixed-bed reactor (5 mm ID), using 1 g of zeolite sample. During the adsorption and desorption steps, the carrier gas flow rates were fixed at 5 L h⁻¹. Adsorption of VOC onto the sample contained in the fixed bed reactor was carried out at constant temperature, 25°C, while the thermal desorption was conducted in the temperatures of 80 and 160°C. The equilibrium adsorption data were determined after 1 h. The effect of relative humidity (RH) on the sorption efficiency was investigated in the range of 0-40% RH. Moisture was supplied into the system by mixing a humidified stream with the incoming VOC gas stream at the adsorbed inlet. The equilibrium data of acetone sorption onto the zeolite samples were evaluated at 25°C for 1 h in the range of 0-10⁴ ppmv. Each experiment was repeated triplicate and the results were given as averages. The amount of VOCs sorption onto the zeolite samples was evaluated as follows:

\[ q_{\text{ads}} = \frac{F}{m} \int_{0}^{t} (C_{\text{in}} - C_{\text{out}}) \, dt \]  

(1)

Where \( q_{\text{ads}} \) is the adsorbed amount of the VOC (μmol g⁻¹), \( C_{\text{in}} \) and \( C_{\text{out}} \) are the initial and final concentrations of the acetone (μmole dm⁻³) at the adsorbed inlet and outlet streams as a function of time, respectively is the volumetric flow rate (dm³ s⁻¹) and \( m \) is the adsorbent mass (g). Aluminum from the zeolite structure took place.

2.3 Characterization tests

The morphology of Nano clays was characterized using a scanning electron microscope (SEM, JEOL JSM-6380) after gold coating. The X-ray fluorescence (XRF, Philips instrument) was used to evaluate the elemental compositions of NZ and modified NZ. The surface area of zeolite samples were measured by Brunauer–Emmett–Teller (BET) method. After acid treatment of natural zeolite, the surface area and the Si/Al ratio were measured. The VOCs concentrations at the inlet and outlet streams were determined using gas chromatography (Shimadzu, Japan).

3. Results and discussion

3.1 Characterization of zeolite samples

The SEM image of the diatomite nanoparticles is presented in Fig. 1. As shown, the diatomite nanoparticles with the average particle size of 70 nm were produced. The physical and chemical surface characteristics of diatomite and modified diatomite are listed in Table 1. As shown, The BET surface areas of the natural and modified zeolite samples were found to be 25 and 81 m²/g, respectively. After acid treatment of natural zeolite, the surface area and the Si/Al ratio increased [19]. Chemical modification using HCl dissolves amorphous materials that could be blocking zeolite framework, generating new pores and increasing clinoptilolite specific surface area. Pore opening expansion could result also from a decationisation process which led to a decrease in diffusion resistance inside the zeolite framework [19]. The increase in Si/Al ratio after acid treatment due to extracting
**Table 1.** Physicochemical properties of zeolite samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \text{S}_{\text{BET}} )</th>
<th>Pore size (nm)</th>
<th>( \text{SiO}_2 )</th>
<th>( \text{Al}_2\text{O}_3 )</th>
<th>( \text{Na}_2\text{O} )</th>
<th>( \text{CaO} )</th>
<th>( \text{K}_2\text{O} )</th>
<th>( \text{Fe}_2\text{O}_3 )</th>
<th>( \text{MgO} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diatomite</td>
<td>110</td>
<td>2.1</td>
<td>90.10</td>
<td>5.20</td>
<td>1.70</td>
<td>0.7</td>
<td>0.7</td>
<td>1.0</td>
<td>0.6</td>
</tr>
<tr>
<td>Modified diatomite</td>
<td>125</td>
<td>2.5</td>
<td>94.50</td>
<td>2.50</td>
<td>1.00</td>
<td>0.5</td>
<td>0.4</td>
<td>0.7</td>
<td>0.5</td>
</tr>
</tbody>
</table>

3.2 Adsorption of acetone onto the NZ and modified NZ

Adsorption kinetics of the acetone by the diatomite and modified diatomite at 25 °C are shown in Fig. 2. As shown, the highest adsorption capacity (mmol of adsorbate per gram of zeolite) was found to be 2.35 mmol g\(^{-1}\) for acetone by the modified diatomite. The higher adsorption capacity of modified diatomite for acetone sorption compared with diatomite could be attributed to the higher surface area of modified diatomite. Moreover, the equilibrium time for acetone sorption onto the both diatomite and modified diatomite were found to 60 min, respectively.

![Adsorption rates of acetone onto the diatomite and modified diatomite.](image)

3.3 Regeneration of diatomite and modified diatomite

The saturated diatomite and modified diatomite were recovered at temperatures of 80 and 160 °C under dry air during 60 min and the results of sorption efficiency after 5 cycles, are shown in Fig. 3. As shown, the adsorption capacity decreased significantly from one cycle to 5 cycles at temperature of 80 °C. This decline could be attributed to the accumulation of the adsorbed or chemically reacted of selected VOCs in the porous zeolite samples. The less steric hindrance of acetone is favorable to both external and internal diffusion mechanisms which control the mass transfer from the solid to the gas phase. Additionally, the increase in the desorption temperature from 80 to 160 °C improved the regeneration efficiency. The slight decrease in the regeneration efficiency at 160 °C could be attributed to the partial decomposition of zeolite sites by oxidation. At low temperature, the larger decreases in the regeneration efficiencies from one cycle to another could be explained by incomplete regeneration.
3.4 Effect of humidity on the sorption efficiency

The effect of humidity on the sorption efficiency of acetone is investigated in the range of 0-40% RH. The result is illustrated in Fig. 4. As shown, the sorption efficiencies of d and modified NZ for acetone reduced under wet conditions. The presence of residual moisture onto the surface adsorbent significantly decreased the acetone adsorption capacity. This behavior could be attributed to the condensation of water at the active surface of zeolite samples instead of adsorption process.

Figure 3. Regeneration of NZ and modified NZ at temperatures of (a), 80 and (b) 160 ºC for adsorption of acetone.
3.5 Adsorption isotherms

The adsorption isotherms of acetone using zeolite samples are shown in Fig. 5. Langmuir and Freundlich isotherm models were used to describe the equilibrium data of acetone. Langmuir isotherm model is an equation which indicates a homogeneous surface adsorption with uniform energies of active sites. This model can be expressed as follows [21]:

\[
q_{ads} = \frac{q_{m}bp}{1+bp}
\]  
(2)

where \(q_{ads}\) refers to the uptake of a VOCs per unit mass of adsorbent, \(q_{m}\) is the monolayer adsorption amount, b is the adsorption equilibrium constant, and P is the partial pressure at equilibrium of the adsorbate in the bulk gas phase.

Freundlich isotherm is an equation which indicates heterogeneous surface adsorption with no uniform energies of active sites. This model can be expressed as follows [22]:

\[
q_{ads} = kp^n
\]  
(3)

where k is the adsorption equilibrium constant and n is the empirical constant. The parameters of isotherm models were calculated by nonlinear regression of \(q_{e}\) versus P using MATLAB software. The results are shown in Table 2. By comparing the correlation coefficients, it was found that the equilibrium data of acetone onto the both zeolite samples were well described by Langmuir isotherm model \((R^2 > 0.986)\) compared with Freundlich \((R^2 > 0.963)\) isotherm model.

<table>
<thead>
<tr>
<th>Sample</th>
<th>VOC</th>
<th>Freundlich isotherm</th>
<th>Langmuir isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(K_f) (torr×mmol/g)</td>
<td>n</td>
<td>(R^2)</td>
</tr>
<tr>
<td>NZ</td>
<td>Acetone</td>
<td>0.852</td>
<td>3.120</td>
</tr>
<tr>
<td>Modified NZ</td>
<td>Acetone</td>
<td>1.625</td>
<td>3.02</td>
</tr>
</tbody>
</table>
Conclusion

In the present study, the performance of diatomite zeolite of Iran was investigated for the adsorption of acetone. The zeolite samples were chemically modified by HCl treatment. The higher surface area and porosity of modified diatomite was observed after acid treatment. The selectivity of acetone sorption onto the diatomite and modified diatomite was in order of modified diatomite > diatomite. The regeneration efficiency of diatomite and modified diatomite was less at 80 °C after five cycles, while a higher regeneration efficiency was achieved at 160 °C. The investigation of humidity on the sorption efficiencies of zeolite samples indicated that the acetone sorption capacities onto the both zeolite samples decreased by increasing humidity. The equilibrium data of acetone sorption by using both zeolite samples were well described by the Langmuir isotherm model.

References


[21]. Fabrication of PVA/GO nanofibers by electrospinning process for the removal of lead (II) and copper (II) ions from aqueous solutions
