Removal of acetone volatile organic compound using modified clinoptilolite natural zeolite of Iran

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In the present study, the effect of natural zeolite adsorbent of Iran on the adsorption of acetone volatile organic compound (VOC) was evaluated. An Iranian natural zeolite of clinoptilolite and modified clinoptilolite by acid treatment were used as adsorbents for the investigation of adsorptive characteristics of acetone. The structure of clinoptilolite zeolitic samples were determined using X-ray fluorescence (XRF) and Brunauer–Emmett–Teller (BET) analysis. Based on results, the modified NZ had a higher surface area and Si/Al ratio compared with NZ. The results of sorption experiments indicated that the highest adsorption capacity was obtained by the modified NZ 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 known Freundlich and Langmuir isotherm models were used to describe the equilibrium data of acetone. The obtained results suggests in the development of NZs for adsorption of VOCs.

Keywords: Natural Zeolite, Adsorption, Chemical Modification, Acetone, Di-methyl Benzene

1. INTRODUCTION

Volatile organic compounds (VOCs) are a large groups of molecules including alkanes, ketones, aromatics, paraffins, 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, biofiltration, and adsorption 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, adsorption method can be considered as an effective and widely used process due to its simplicity, moderate operational conditions and economic feasibility [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, natural clinoptilolite kinds are inexpensive materials and easily available in Semnan mines of Iran. Additionally, the physical and chemical characteristics of natural zeolites can improve by the acid treatment [18].

In the present study, an Iranian natural zeolite of clinoptilolite 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 NZ. The effect of humidity on the VOCs sorption was investigated. Also, the isotherm model was estimated for VOCs sorption.

2. EXPERIMENTAL

2.1. Materials

A natural zeolite of clinoptilolite was supplied by the Iranian mining company (Semnan region). Before being chemically treated, the NZs were washed by distilled water to remove impurities, and dried at 80◦C for 24 h. Then dried NZs were sieved to 0.3-0.5 μm. 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 adsorber 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:

$$q_{ads} = \frac{F}{m} \int_0^t (C_{in} - C_{out}) dt \qquad (1)$$

where q_{ads} is the adsorbed amount of the VOC (μmol g^{-1}). Cin and Cout are the initial and final concentrations of the acetone ($\mu mole$ dm^{-3}) at the adsorber inlet and outlet streams as a function of time, respectively. F is the volumetric flow rate (dm^3 s^{-1}) and m is the adsorbent mass (g).

2.3. Characterization tests

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 physical and chemical surface characteristics of NZ and modified NZ 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 rat after acid treatment due to extracting aluminum from the zeolite structure took place.

3.2. Adsorption of acetone onto the NZ and modified NZ

Adsorption kinetics of the acetone onto the NZ and modified NZ at 25˚C are shown in Fig.1. As shown, the highest adsorption capacity (mmol of adsorbate per gram of zeolite) was found to be 1.75 mmol g_{-1} for acetone by the modified NZ. The The higher adsorption capacity of modified NZ for acetone sorption compared with NZ could be attributed to the higher surface area of modified NZ. Moreover, the equilibrium time for acetone sorption onto the both NZ and modified NZ were found to be 45 and 60 min.

3.3. Regeneration of NZ and modified NZ

The saturated NZ and modified NZ 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.2. 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.
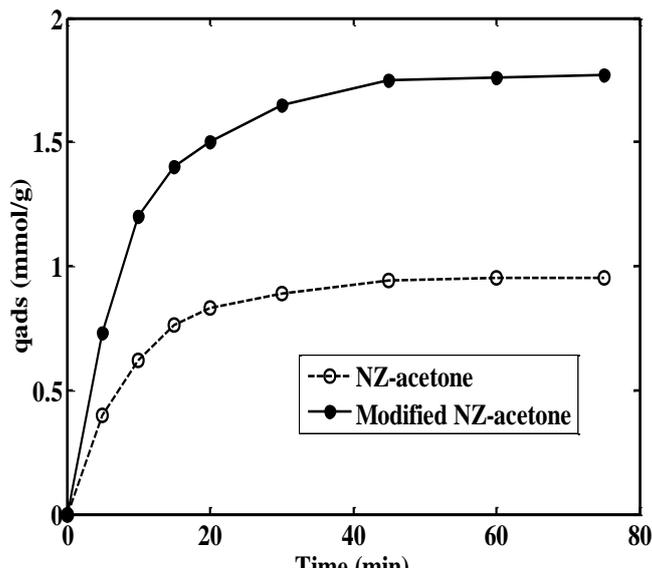
Fig.1. Adsorption rates of acetone onto the NZ and modified NZ.

Table 1. Physicochemical properties of zeolite samples

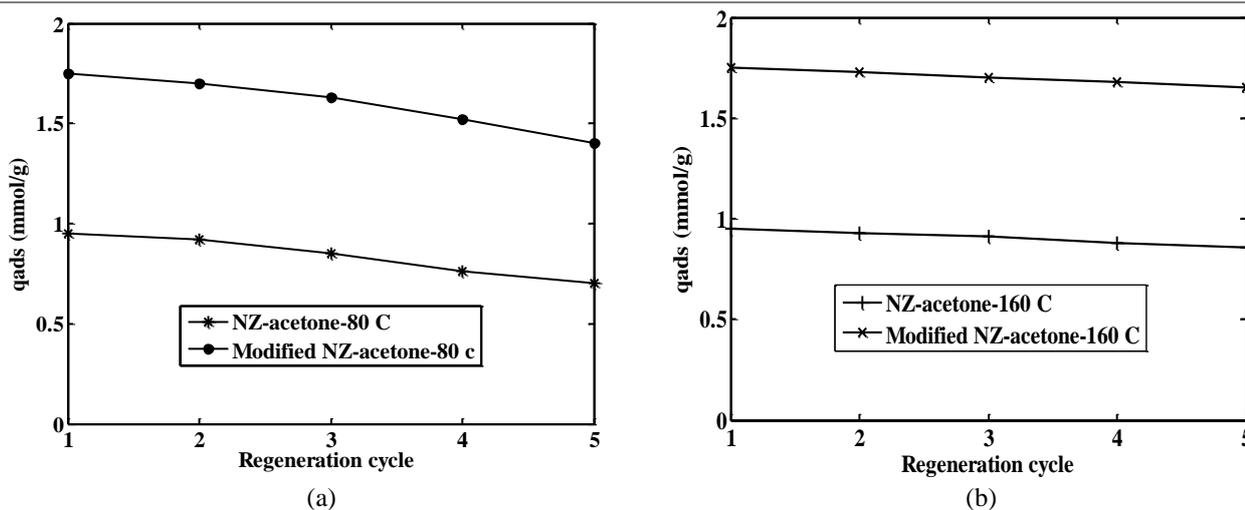| Sample	S_{BET}	Pore size (nm)	SiO_2	Al_2O_3	Na_2O	CaO	K_2O	Si/Al ratio
NZ	25	2.3	71.10	16.20	4.20	6.20	2.30	4.57
Modified NZ	81	2.9	80.50	12.50	1.50	4.20	1.3	6.57

(a)

(b)

Fig.2. Regeneration of NZ and modified NZ at temperatures of (a), 80 and (b), 160 °C for adsorption of acetone.

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. 3. As shown, the sorption efficiencies of NZ 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.
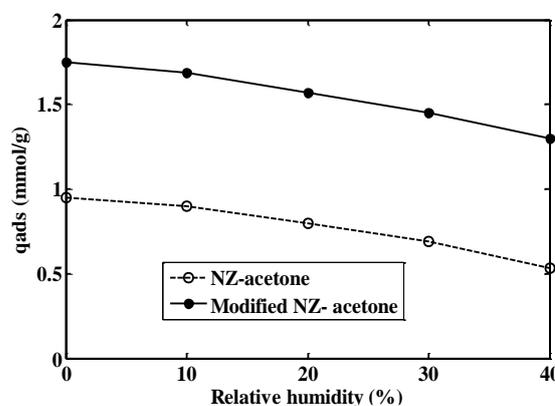

Fig.3. Effect of humidity on the acetone sorption using NZ and modified NZ.

3.5 Adsorption isotherms

The adsorption isotherms of acetone using zeolite samples are shown in Fig. 4. 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 [20]:

$$q_{ads} = \frac{q_m bp}{1 + bp} \qquad (2)$$

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 nonuniform energies of active sites. This model can be expressed as follows [21]:

$$q_{ads} = kp^{\frac{1}{n}} \qquad (3)$$

where k is the adsorption equilibrium constant and n is the empirical constant. The parameters of isotherm models were calculated by nonlinear regression of qe 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 (R2 > 0.986) compared with Freundlich (R2 > 0.963) isotherm model.
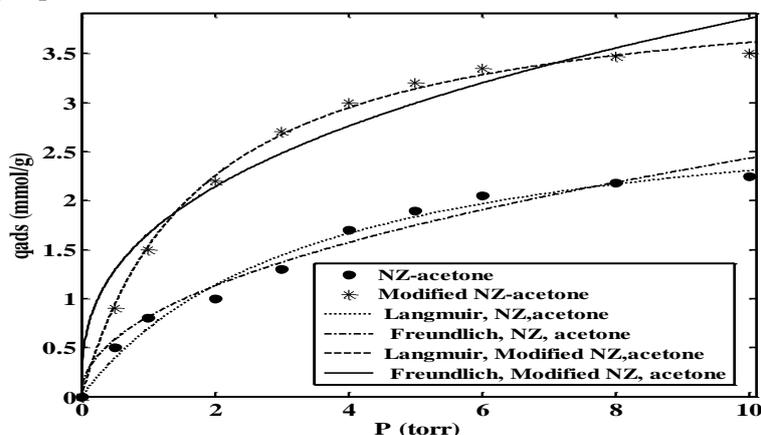

Fig.4. Experimental data, Langmuir and Freundlich isotherms of acetone sorption using NZ and modified NZ.

Table 2. Isotherm parameters for acetone sorption onto the zeolite samples

Sample	VOC	Freundlich isotherm			Langmuir isotherm		
		K_F (torr^{-n}mmol^{-1}g^{-1})	n	R^2	q_{max} (mmol/g)	b (torr^{-1})	R^2
Modified NZ	Acetone	1.534	2.925	0.953	4.645	0.53	0.991

4. CONCLUSION

In the present study, the performance of NZ of Iran including clinoptilolite was investigated for the adsorption of acetone. The zeolite samples were chemically modified by HCl treatment. The higher surface area and porosity of modified NZ was observed after acid treatment. The selectivity of acetone sorption onto the NZ and modified NZ was in order of modified NZ > NZ. The regeneration efficiency of NZ and modified NZ was less at 80 °C after five cycles, while a higher regeneration efficiency was achieved at 120 °C. The investigation of humidity on the sorption efficiencies of zeolite samples indicated that the acetone sorption capacities onto the NZ and modified NZ decreased by increasing humidity. The equilibrium data of acetone and di-methyl benzene were well described by the Langmuir isotherm model.

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