Removal of Ammonia from Air, using Three Iranian Natural Zeolites

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Abstract

Ammonia in air can be hazardous to human and animal life and should be removed from the environment. Recently the removal of environmental pollutants such as ammonia by means of natural and modified zeolites has attracted a lot of attention and interests. In this study the capability of three Iranian natural zeolites (Clinoptilolite) in point of view of removal of ammonia from air was investigated. Through this research, different zeolites from various regions of Iran including Semnan, Meyaneh, and Firoozkooh resources were considered to be studied. These samples of zeolites were ground and granulized into 425 µm to 4 mm and were utilized in dynamic sorption experiments. Curves of sorption were plotted and breakthrough and saturated points of zeolite samples were obtained. The adsorption capacities at different ammonia concentrations, temperatures, and flow – rates were also calculated. Results obtained showed that, the natural Iranian zeolite (Clinoptilolite) was identified to be more efficient adsorbent than the others to remove ammonia from the air. In the same conditions, the obtained breakthrough time for clinoptilolite sample of Meyaneh was longer than the others (135min), while, the adsorption capacity of Semnan clinoptilolite was higher than adsorbents (6.30 mg /g) (*P*<0.0001).

Keywords: *Ammonia removal, Adsorbent, Iranian natural zeolites, Clinoptilolite.*

Introduction

Ammonia is a colorless, diffusive at 760 mmHg, with a hot odor which is hazardous at concentration of more than 50 ppm (1). This gas is used extensively in the chemical industries. Its production in The USA has been increased from 5.8×10^6 ton/year in 1964 and 11.5×10^6 ton/year in 1974 to 25.5×10^6 ton in 1990 (2). The amount of ammonia released yearly during industrial and agricultural processes, has been estimated to be about 113-244 $\times 10^6$ ton world wide (2). In Iran also a considerable amount of ammonia is released into the environment from different industries such as oil refineries, petrochemical complexes and fertilizer manufacturing, causing variety of problems associated with the control systems (3). Emission of NH_3 as a pollutant from sources can cause human and environmental ef-

fects such as eye and throat irritation, cough, acute pulmonary effects, pulmonary edema, pneumonia, biological nitrification and finally death of aquatic organism (4). According to the above mentioned reasons, controlling of this pollutant essentially is required. So far, different methods such as washing out with water (scrubbing)**,** condensation and biological methods are used for removal and control of NH_3, which they have disadvantages (5). Nowadays the development of alternative treatment techniques such as using solid sorbents as a natural adsorbent (e.g. natural zeolites in this study) has a great interest for scientists. Zeolite, molecular sieves, as a well known category of aluminosilicate which exists both naturally and synthetically, shows a very good capability in gas separation technology. The abundance of natural zeolite resources in Iran can play a great role to develop this technology. Zeolite is a

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well known category of crystalline mineral which hydrated aluminosilicate of alkaline and alkaline earth elements with a typical formula of $M_{x/n}$ $[(AlO_2)_x(SiO_2)_y]$ $_w.H_2O$. In geological concerns, natural zeolites can be formed in active volcanic environmental under hydrothermal conditions, as well as sedimentary origins crystalline framework of zeolites structure contains a variety of channels and pores.

According to the published results, zeolites are suitable adsorbent for different polar and nonpolar molecules such as CO_2, SO_2, NO_2, NO, H_2S, NH_3, H_2O, aliphatic hydrocarbons, aromatic hydrocarbons, alcohols, ketons, and other similar molecules (6- 8). Use of natural zeolite as a sorbent is considerably increased in different industries (9).

Adsorption, ion–exchanging and catalytic behavior of different zeolites, has made them as an interesting material for different industrial and environmental applications. Early studies on the application of zeolites as adsorbents, were reported in 1938 when Barrer published some cientific information of the properties and characteristics of zeolites (10). Natural and synthetic zeolites have been known as an important material in modern technology for extracting and removal of pollutant from air and other waste stream (10).

Nowadays, production and utilization of zeolites for industrial processes has made the method to be one of the important scientific fields of research and study (11).

This paper presents the results obtained from the study on dynamic adsorption experiments on some zeolites from different regions of Iran for NH_3 removal from air.

Materials and Methods

Three different Iranian natural Clinoptilolites were obtained from semnan (Z_s), Meyaneh (Z_m) and Firoozkooh (Z_f) regions of Iran.

The samples were grond (Maxillary grinder) and particle size of 2-4 mm, 1-2 mm, and 425 µm-1mm were selected for further studies. All of the sorption experiments were done on a dynamics system. A simple schematic of the designed system is shown in Fig. 1.
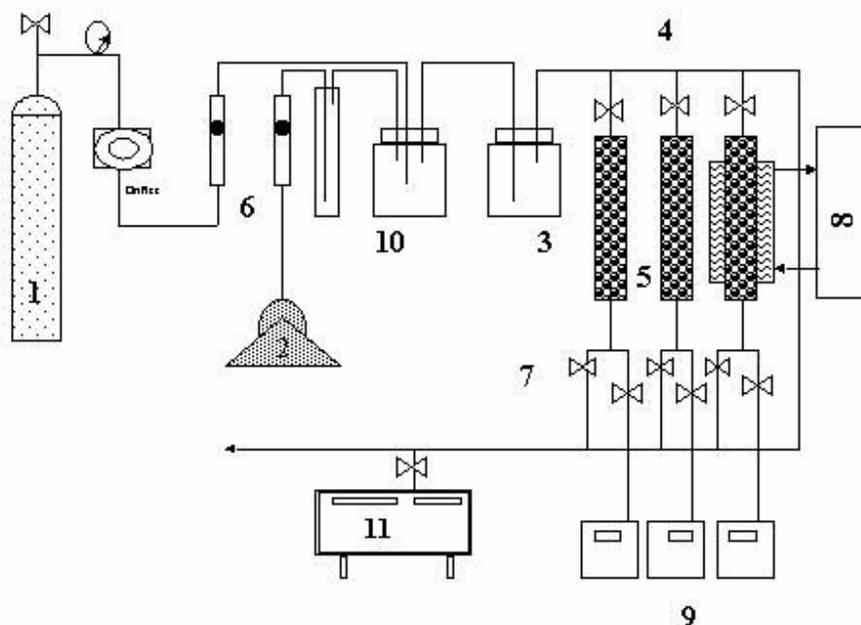
Fig. 1: Schematic diagram of the designed system for study of dynamic adsorption of NH_3

The components of system in figure (1) is as follows:

NH$_3$ gas supplier

Air supplier pump

Mixer of air and NH$_3$

Distributor of mixed gasses through columns

Zeolites bed (columns)

Flow meter

Valves and connections

Thermometer

Gas meter

Humidity adsorbent (cilicagel)

NH$_3$ analyzer

During the experiments, the flow rate (exhaust) of NH$_3$ and air was adjusted at range of cm^3/ min by a flowmeter followed by mixing thoroughly NH$_3$ and air in the connected bottles to the system. Before entering the mixed gas to the columns, concentration of the ammonia was measurd by a gas chromatogtaph equipped with, propak N column, TCD detector, as well as by a portable analyzer of NH$_3$ (multi-warn Drager, Germany) with an electrochemical sensor.

After fixing the concentration in system, the entrance value of columns with 10 g zeolite was opened followed by adjusting the flow – rate of the gas by flow – meter at the required level. Starting time, temperature, pressure, flow – rate and the numeral of gas meters were recorded. Concentration of NH3 at the outlet of the columns was measured before breakthrough point every 5 min and after breakthrough up to saturated point every 15min.

The column temperature was also adjusted by water circulation system.

Results

In order to characterize the zeolite samples, X- ray fluorescence method (XRF) was used. The obtained results from chemical analysis of the samples are shown in Table 1.

Table 1: Chemical composition of the zeolite samples, by X-ray fluoresence

Components	Contents wt%		
	Z_s	Z_f	Z_m
SiO$_2$	64.4	67.24	67.35
Al$_2$O$_3$	12.80	11.71	11.73
Fe$_2$O$_3$	1.31	0.58	0.88
TiO$_2$	0.31	0.42	0.34
CaO	2.37	3.04	2.34
MgO	1.15	1.16	1.21
Na$_2$O	1.13	1.19	0.88
K$_2$O	2.64	1.48	1.72
P$_2$O$_5$	0.21	no	no
LoI	13.47	13.19	12.94
Total	99.55	100.4	99.43

no = not observed

* Loss on iginiton

The X-ray diffraction patterns and thermal analysis of the samples were also obtained. According to the results of used characterization techniqus, all of the investigated natural zeolites were Clinoptilolite and belong to the hulandite (HEU) group. The results of column adsorption experiments including breakthrough volume and time, saturated piont and time for different zeolites are illustrated in Table 2 and Figs. 2,3 and 4.

Table 2: The breakthrough and saturation point and adsorption capacity of natural clinoptilolite for NH3 (T = 22°C, amount of zeolite in each colum 10g, particle size 1-2 mm).

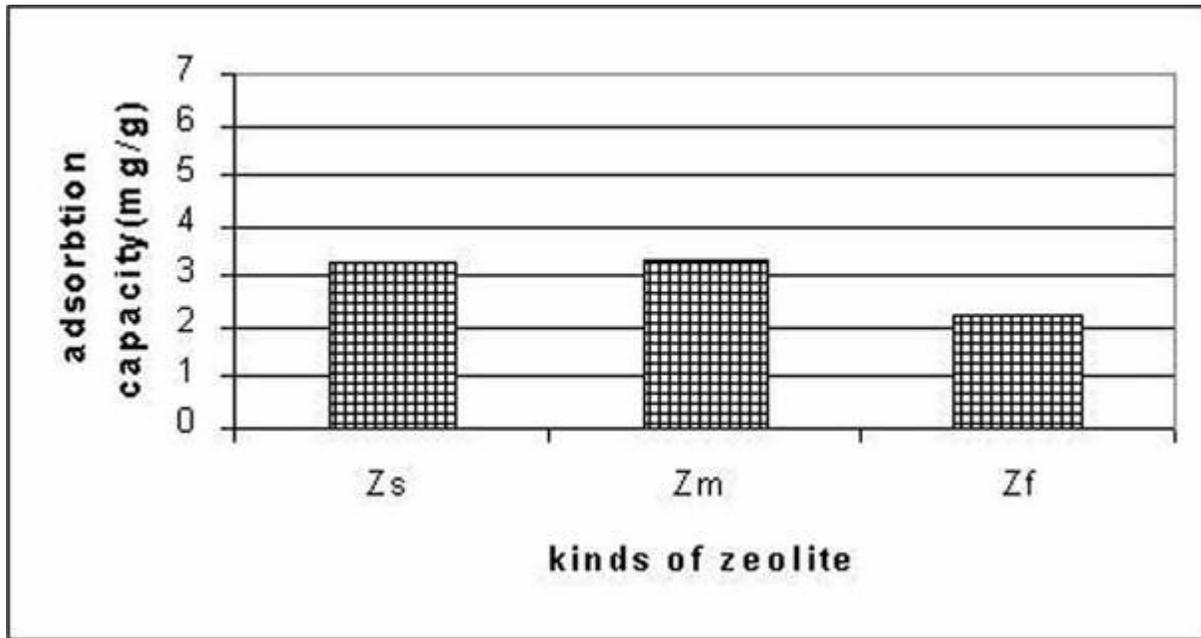| Zeolite type Experiment Parameters	Z_s	Z_m	Z_f
Inlet mean concentration into column (ppm)	180	180	180
Mean flow-rate (lit/min)	2.1	2.1	2.1
Saturated time (min)	130	135	90
Saturated time (min)	252	225	242
Adsorption capacity up to brakthrough (mg/g)	3.25	3.37	2.25
Adsorption capacity up to brakthrough (mg/g)	6.30	5.62	6

Fig. 2: Ammonia adsorption capacity up to breakthrough point for different Iranian natural clinoptilolite (T = 22°C)
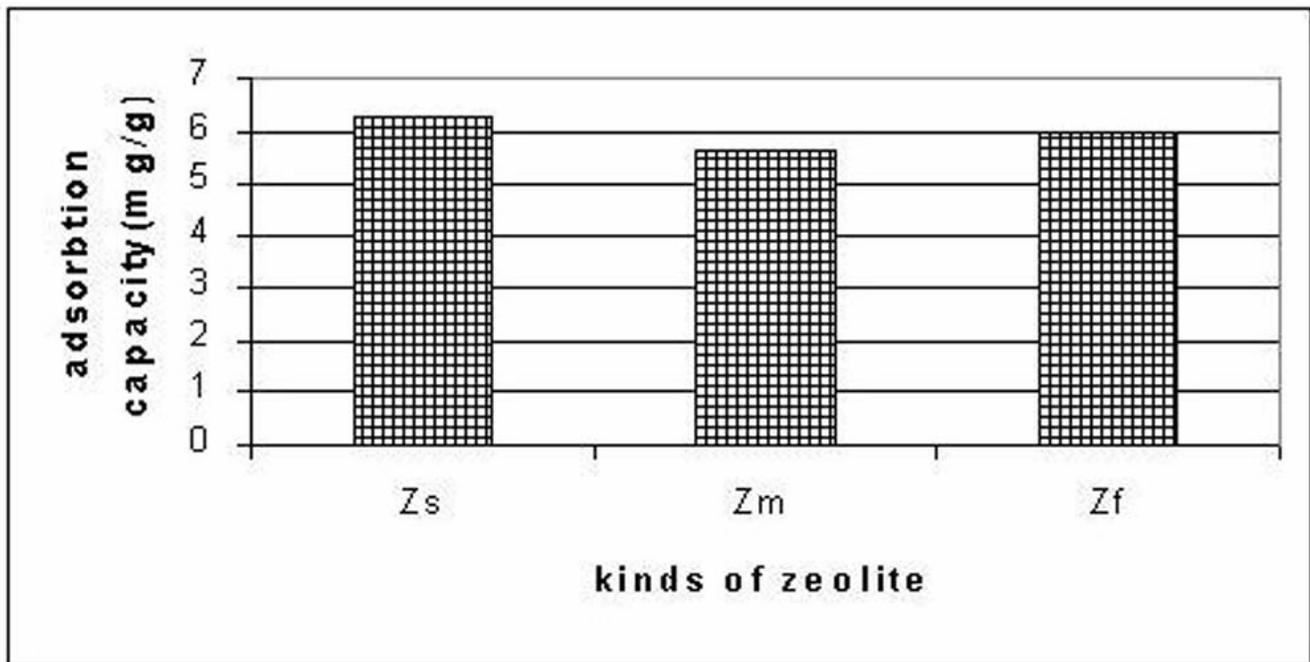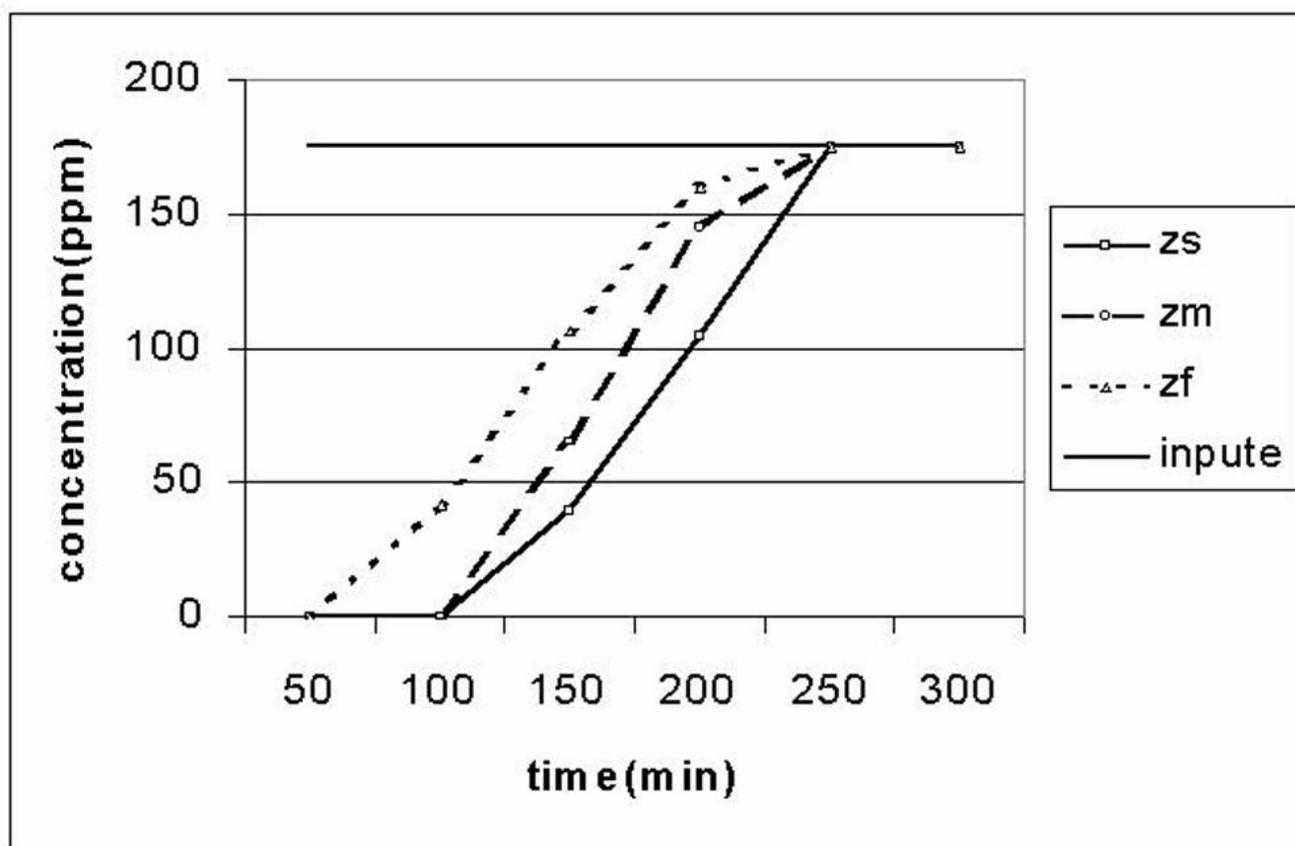

Fig. 3: Ammonia adsorption capacity up to saturation point for different Iranian natural clinoptilolite (T = 22°C)

Fig. 4: Breakthrough and saturation curves of NH3 adsorption on different Iranian natural clinoptilolite
(T = 22°C, adsorbent = 10 g , particle size 1-2 mm).

Discussion

The obtained results of the performed dynamic adsorption tests showed that all of the investigated Iranian natural Clinoptilolites could be suitable and efficient adsorbents for NH_3. The similarity of chemical behavior of NH_3 and H_2O molecules, can be mentioned as one of the main reasons for selectivity of zeolite toward NH_3. However, another parameter, i.e. the high dipolar moment of NH_3 can increase the adsorption selectivity. Investigation of Table 2 and Fig. 2, showed that the breakthrough adsorption capacity of Z_m sample is higher than other investigated samples (3.37 mg/g in comparison to 2.25 mg/g for Z_f and 3.25 mg/g for Z_s) and its breakthrough time is longer (135 min in comparison to 90 min for Z_f and 130 min for Z_s). The saturated point for Z_m is attained faster than Z_s and Z_f samples. The presence of the clay phase in the Meyaneh zeolite can be considered as a reason for longer breakthrough time. It is worth mentioning that, the clay phase can be considered as an adsorbent for gaseous molecules. It seems that, the kinetic reaction of ammonia adsorption on clay phase in the Meyaneh zeolite is faster in comparison to clinoptilolite phase (12).

The required time to attain saturation point for Z_m clinoptilolite (240 min) as well as adsorption capacity (6.30mg/g) is higher than other zeolite samples.The higher amount of aluminum and water content of this sample plays the main role for such a behavior.

In this study, the effect of temperature, particles size of zeolite sorbent as well as the flow – rate of the gas on the adsorption process were also

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evaluated. From the data obtained, It can be concluded that, as the column temperature increases from ambient temperature to 35°C and 60°C, breakthrough point will achieve in longer time and consequently the adsorption capacity is increased. Removal of H2O molecules from the zeolites framework by increasing the temperature can facilitate the NH_3 sorption processes. By releasing of H_2O molecules, the substitution of NH_3 molecules can be facilitated on the basis of data obtained from thermal analysis techniques.

Through this study, it was also clarified that, decreasing the sorbent particle size, from range of 1-2 mm to the range of 425 µm – 1 mm, the adsorption capacity as well as breakthrough time were considerably increased, although decreasing the particle size causes an increase in the pressure drop of the system. This process caused also a decrease in the flow – rate of the pump, which wasn't quantitatively measured. It is worth mentioning that, above process should be consider carefully optimizing the process for industrial application. These investigations also showed that, in the same conditions, an increase in gas flow – rate cause a decrease in breakthrough time and vice versa.

From the results obtained in this study, following conclusions can be made :

The investigated Iranian natural Clinoptilolite zeolites are suitable adsorbent for removal of ammonia from the polluted air streams.

In the same condition, Meyaneh Clinoptilolite had a longer breakthrough time (135min) while Semnan Clinoptilolite had higher adsorption capacity (6.30 mg/g), ($P<0.0001$).

According to the effect of the zeolite composition on the adsorption behavior, it seams that the modification of zeolite can improve the NH_3 adsorption efficiency.

Based on the above results, the investigated natural zeolites can be used for removal of NH_3, from the exhausted media of different industries. To optimize the conditions of removal process, further studies and researches shonld to be performed.

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