REMOVAL OF ACETALDEHYDE FORM INDOOR AIR USING NAA ZEOLITE AND MODERNITE

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT:
Indoor pollution nowadays can have serious effects on people’s health. The most common indoor pollutants in urban and industrial areas are volatile organic compounds – VOCs, which include acetaldehyde. Acetaldehyde vapors cause eye irritation, lung or respiratory tract problems and are considered cancerogenic. The aim of this research was to examine the adsorption properties of type NaA zeolite and Na-Form of modernite. Adsorption isotherms of acetaldehyde on the examined adsorbents were obtained by simulating adsorption in an indoor environment. The simulation chamber was set to the atmospheric pressure, the temperature of 25°C, and air humidity of 65%. The non-linear Langmuir model gave higher coefficients of determination (0.9675 and 0.9350, respectively) than those obtained using the Freundlich model (0.9563 and 0.9332, respectively), which is indicative of single-layer adsorption. Higher values of the Langmuir constant for the samples tested shows that there is only low affinity between the adsorbents examined and acetaldehyde. Maximum adsorption capacity (Q^0_m) in the monolayer obtained using the Langmuir model is 3.387 mg/g for NaA zeolite and 2.5293 mg/g for modernite. From this it can be fairly assumed that NaA zeolite as an adsorbent, is more suitable for removing acetaldehyde from indoor air.

KEYWORDS: acetaldehyde; zeolites; adsorption isotherms; maximum adsorption capacity

INTRODUCTION

Indoor air quality has become the focus of much research in recent years. Research has shown the presence of a large number of different pollutants which can have serious impact on human health. According to the World Health Organization, indoor air pollution – IAP, is responsible for 3.8 million deaths each year [1].

Indoor air pollution comes from various sources, and these are most commonly the materials that release pollutants into the air of the indoor environment. The sources can also come from different everyday activities, such as cooking, room heating, and similar human activities [2]. The most common indoor air pollutants present are carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NO_x), particulate matter (PM), aerosol, volatile organic compounds (VOCs), *etc*. VOCs are particularly dangerous due to their low boiling points, which allows them to be released into the air rather quickly. The most frequently occurring VOCs are toluene, acetaldehyde, methanol, ethanol, benzene, formaldehyde, *etc*. [3]. The presence of VOCs is recorded mostly in exhaust fumes [4], [5]. Apart from these, VOCs can come from different paints, varnishes, adhesives, wood preservatives, waxing and cleaning products, air fresheners, *etc*. [6], [7]. Acetaldehyde is one of the volatile organic compounds most commonly emitted into the air in urban and industrial areas. It is a product from incomplete combustion, mostly present in cigarette smoke, gases released from roasting coffee, automobile exhaust fumes, burning different organic waste material, *etc*. It is also, interestingly enough, the product of metabolic processes in plants. According to the research conducted so far, acetaldehyde vapors can cause eye and respiratory tract irritation, and are considered cancerogenic [8].

Reducing the content of volatile organic compounds in indoor environments has become one of the primary goals in air quality improvement. The simplest method for indoor VOC reduction is the use of natural ventilation or structural ventilation systems. Natural ventilation does not always give best results, especially during winter months. During winter, when the use of private incinerators is increased and the content of VOCs in the air is higher, natural ventilation can have the opposite effect. Structural ventilation systems also require outdoor air of good quality. This is the reason for an increased use of adsorbents (*e.g.*, activated charcoal) in removing certain air pollutants. Apart from that, the reduction of the content of VOCs in indoor air is increasingly achieved using adsorption processes, or by introducing suitable adsorbents.

An adsorption mechanism consists of dissolving VOCs in organic layers of adsorbents with large active surface areas [9], [10]. Much research is dedicated to the adsorption of VOCs on zeolites or activated charcoal in the absence of moisture. Under real conditions, water vapor is always present, and its content may sometimes exceed that of VOCs. Research in the past couple of years has shown that the presence of water vapor (moisture) affects the adsorption of gases and volatile compounds [11], [12]. For example, investigations into the adsorption of dichloroethane, ethyl acetate and benzene on metal–organic frameworks (MOFs) show that the adsorption of these volatile organic compounds decreases in the presence of humidity [13], [14].

The choice of the adsorbent depends on numerous factors, such as temperature, velocity, affinity of the adsorbent towards another adsorbent, *etc*. It is not easy to choose the right adsorbent because the choice is governed by the conditions in which the adsorbent is to be used, as well as by its characteristics (adsorption capacity, stability, hydrophilicity, hydrophobicity, *etc*.). The most commonly used adsorbents are activated charcoal, natural and synthetic zeolites, silica gel, and activated alumina [15].

The adsorbents chosen for the purpose of this research are hydrophilic synthetic NaA type zeolite (NaA zeolite) and Na-Forma modernite (Modernite), which were activated, *i.e*., dehydrated prior the experiments. Zeolites are microporous hydrated aluminosilicates of the elements in the first and the second groups of the periodic table, built up from an infinitely extended three-dimensional framework of [SiO_4] and [AlO_4] tetrahedrainter connected through a shared oxygen atom. Variations in the geometry of tetrahedra within the structure result in different forms of zeolites, characterized by cavities and/or canals. The cavity/canal size is determined by the “rings” made up from the aluminum and silicon tetrahedra. The rings can be four-membered, five-membered, six-membered, *etc*. Type NaA zeolite is characterized by a three-dimensional system of canals with an opening in the form of an eight-membered ring, 4.1 Å in diameter. Modernite is characterized by the main canal of elliptical shape made up from a twelve-membered ring whose dimensions are of 6.5x7.0 Å, and the so-called “side pockets” in the form of eight-membered rings whose dimensions are 2.6x5.7 Å [16]-[18].

The focus of investigation here is the efficiency of using type NaA zeolite and modernite to remove the acetaldehyde vapors from indoor air. The paper, therefore, presents the results of a simulation of an adsorption process in an indoor environment (atmospheric pressure, particular temperature and humidity) using the free diffusion mechanism.

MATERIALS AND METHODS

Adsorption of acetaldehyde was conducted on NaA zeolite and modernite $m≈0.5$g in 2.5 dm^3 adsorption chambers (Table 1). The adsorption chambers were first filled with humid air (relative humidity of RH=65%), and then acetaldehyde in batches of varying volumes (10-250μl) was injected. The temperature of the chambers was set at 25°C for an hour in order to allow for acetaldehyde to evaporate completely. After that, zeolite was subjected to the adsorption of acetaldehyde from the indoor environment prepared as described previously. The process of adsorption was conducted for three hours at the set temperature in the chambers. After the process completed, the gas phase analysis was conducted on a high sensitivity device which calculates total organic carbon (Shimadzu TOC high sensitive). The samples of zeolite were dried at 400 ºC for 2 hours in a vacuum prior to the experiment [15].

Table 1. Physical and chemical properties of NaA zeolite and modernite

Parameters	NaA zeolite	Modernite
Loss on ignition, w (%)	2.4	6.9
***L* Grey index**	90.0	84.5
***d*(10) (μm)**	1.4	2.3
***d*(50) (μm)**	3.4	8.8
***d*(90) (μm)**	5.7	-
SiO_2/Al_2O_3	1.98	13.5
Sodium content (Na),w (%)	22	4.3
***pH*(5%)**	-	9-11.5
Water adsorption (WA), 25°C/65RH/24h, w (%)	24,61	12,80

From the concentration of the organic carbon and acetaldehyde, it was possible to calculate the amount of adsorbed acetaldehyde using the following equation (1):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where:

q_e– the amount of the adsorbed acetaldehyde per gram of zeolite (mol/g)

C_0 – acetaldehyde concentration at the beginning of adsorption (mol/m^3)

C_e– equilibrium concentration of acetaldehyde (mol/m^3)

V- chamber volume (m^3)

m – mass of the adsorbent (g)

Equation (2) was used to calculate the constant for the Langmuir isotherm in a non-linear form:

$$q_e = \frac{Q_{max}^0 \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (2)$$

where:

q_e (mg/g) – adsorption capacity (equilibrium concentration of the adsorbed ions on the adsorbent),

Q_{max}^0 (mg/g) – maximum adsorption capacity of the adsorbent,

K_L (L/mg) – Langmuir adsorption equilibrium constant, referring to the adsorption energy.

Maximum adsorption capacity, Q_{max}^0, gives an insight into the saturation of the monomolecular layer on the surface of the adsorbent, whereas the Langmuir constant, K_L, refers to the adsorption energy [19].

Equation (3) was used to calculate the constant for the Freundlich isotherm:

$$q_e = K_F \cdot C_e^{\frac{1}{n}} \quad (3)$$

where:

q_e (mg/g)– adsorption capacity (equilibrium concentration of the adsorbed ions on the adsorbent),

n – function of the adsorption intensity (the higher *n* – the higher the adsorption intensity),

K_F $(mg/g)(L/mg)^{1/n}$ – Freundlich adsorption equilibrium constant, referring to the adsorption energy.

“Microsoft Excel” program was used to calculate the parameters in the non-linear models of the adsorption isotherms. In order to determine the regression analysis error, we used the non-linear Chi-square test (χ^2) according to Equation (4) [19], [20]:

$$\chi^2 = \sum_{i=n}^{n} \frac{(q_{e,observed} - q_{e,expected})^2}{q_{e,expected}} \quad (4)$$

RESULTS AND DISCUSSION

Modernite and NaA zeolite are very active hydrophobic zeolites with high thermal stability, widely used for removing undesirable tastes and odors. Due to its open three-dimensional structure modernite is also very efficient in removing larger molecules. These very properties are the reason why it was decided to perform the adsorption of acetaldehyde with these two types of zeolites for the purpose of this paper. Water adsorption on zeolites (modernite and NaA zeolite) was performed under conditions: *t*=25 °C, *RH*=65 %, atmospheric pressure and time of adsorption 24 hours. Obtained the results of water adsorption in Table 1.indicate that NaA zeolite has a higher affinity for water (*WA*=24.61%).Acetaldehyde adsorption was conducted in an experimental chamber under specific conditions: *t*=25°C, *RH*=65%, at the atmospheric pressure. The isotherm data were analyzed using the two most commonly used equilibrium models – Langmuir and Freundlich. The Langmuir isotherm is based on the assumption that a monomolecular layer of the adsorbent is formed and that there is no side interaction between the adsorbed molecules. On the other hand, the Freundlich isotherm is based on a multilayer adsorption on a heterogeneous surface [20].

The coefficients for determining the isotherm adsorption according to the Langmuir and the Freundlich models for the adsorbents tested are given in Table 2.

Table 2. Adsorption isotherm constants for Modernite and NaA zeolite using non-linear models (*t*=25°C, *RH* =65%, adsorption time=3h)

Model	Parameter	Adsorption parameter values	
		Modernite	NaA zeolite
Langmuir	K_L (dm^3/mg)	2.1538	7.915
	Q^0_m (mg/g)	2.5293	3.387
Adsorption parameter values	R^2	0.9350	0.9675
	R_L	0.1-0.9	0.2-0.9
	χ^2	0.322	0.17
Freundlich	*N*	1.5649	2.291
	K_F $(mg/g)//mg/dm^3)^n$	1.9832	3.705
Adsorption parameter values	R^2	0.9332	0.95632
	χ^2	2.86	8.66

Coefficients of determination obtained from the Langmuir model for NaA zeolite and modernite samples are high (0.9675 and 0.9350, respectively), *i.e.*, they are approaching 1 (Table 2). Coefficients of determination obtained from the non-linear Freundlich model (R^2) were somewhat lower (0.9563 and 0.9332, respectively). From this it can be concluded that this is a monolayer adsorption. The higher values of the Langmuir constant (K_L) for the tested samples show that the affinity between the tested adsorbents and acetaldehyde is pretty low. It can also be concluded that the tested adsorbents do not have much capacity for acetaldehyde adsorption because maximum adsorption capacity ($Q^0{}_m$) in the monolayer obtained based on the Langmuir model is 3.387 mg/g for NaA zeolite and 2.5293 mg/g for Modernite. The values of the R_L factor were in the interval of $0<R_L<1$, which can confirm if the process is favorable. If $R_L=0$ the process is irreversible, if $R_L=1$, then it is linear, whereas $R_L>1$ means that it is unfavorable.

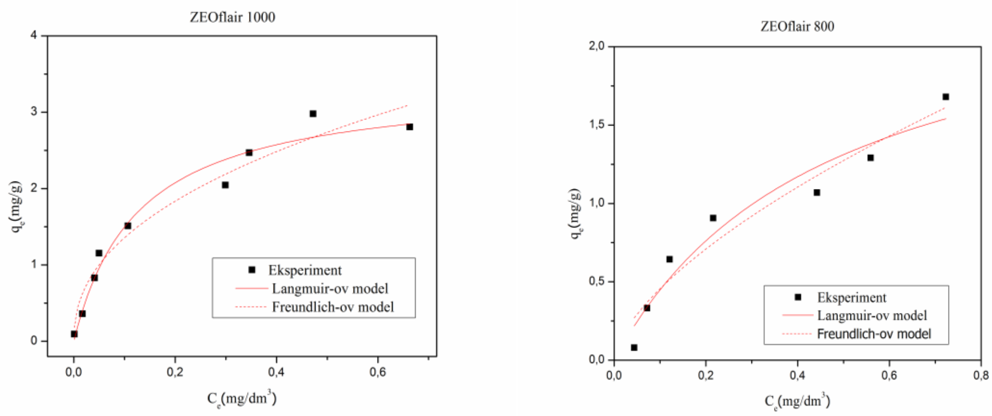

Figure 1. The use of non-linear Langmuir and Freundclih models for the adsorption of acetaldehyde on the adsorbents NaA zeolite and modernite (t=25°C, RH =65%, adsorption time =3h)

The results of the analyses (R_L=0.1-0.9 for modernite and R_L=0.2-0.9 for NaA zeolite) lead to the conclusion that both models are favorable. Figure 1 shows the use of non-linear Langmuir and Freundlich models for the experimental data of the equilibrium concentration of the adsorbed acetaldehyde on the adsorbents NaA zeolite and modernite.

The adsorption of acetaldehyde on NaA zeolite and modernite adheres more to the non-linear Langmuir model (Table 2, Figure 1).

CONCLUSION

Based on the results obtained from the adsorption of acetaldehyde vapors at the relative humidity of 65%, temperature of 25°C, the adsorption time of 3h and the atmospheric pressure, it can be concluded that the adsorption on modernite and NaA zeolite is a monolayer adsorption. This is confirmed by the obtained coefficients of determination, which are higher for the non-linear Langmuir model than those for the Freundlich non-linear model (According to Table 2).

Maximum adsorption capacity ($Q^0{}_m$) in the monolayer obtained according to the Langmuir model is 3.387 mg/g for NaA zeolite and 2.5293 mg/g for modernite. From this it follows that NaA zeolite is the more suitable of the two adsorbents for removing acetaldehyde from indoor air. It can also be concluded that, although zeolite has a higher affinity for water (water sorption capacity), the presence of water vapor, did not reduce the absorption capacity of acetaldehyde.

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