Scientific paper

Use of Total Organic Carbon Analyzer in Isotherm Measurements of Co-Adsorption of VOCs and Water Vapor from the Air

Dragana Kešelj,[1,*] Dragica Lazić[1] and Zoran Petrović[1]

[1] *Faculty of Technology, University of East Sarajevo, Karakaj 34A, 75400 Zvornik, BiH*

** Corresponding author: E-mail: dragana.keselj@tfzv.ues.rs.ba; draganakeselj@yahoo.com; Tel.: +38766253256*

Received: 04-05-2022

Abstract

The binary adsorption isotherms of volatile organic compounds (VOCs), and water vapor from the air have been the focus of much research in recent years. The content of adsorbed VOCs in the presence of water vapor can be determined by the volumetric or gravimetric method, in a static or dynamic mode. This study focuses on the adsorption technique in a static mode for isotherm measurement of the co-adsorption of VOCs and water vapor from the air using the gravimetric method. The content of VOCs is determined using a total organic carbon analyzer, while the amount of the adsorbed water was calculated from the difference between total adsorption (VOCs and water) and the adsorbed VOCs. This paper presents several adsorption isotherms with different VOCs (toluene, benzene, methanol, ethanol and isopropyl alcohol) and adsorbents (ZSM-5 zeolite, silica gel and Na-Form mordernite) in the presence of water vapor. The well-known adsorption isotherm models (Langmuir, extended Langmuir, Freundlich, extended Freundlich and Hill) were used to treat experimental results. The adjusted R-Squared (adj. R^2) values obtained for those non-linear models for isotherms (total adsorpton ($q_{e,tot}$) as a function of equilibrium concentration of VOC (C_e) and the adsorbed VOC (q_e) as a function of equilibrium concentration of VOC (C_e) are used to determine the best-fit isotherm model. The modeling results showed that the 3-parameter models could fit the data better than the 2-parameter model, with relatively higher adj. R^2. Experimental results demonstrate that the presented adsorption technique can be used for isotherm measurement of the co-adsorption of VOCs and water vapor from the air.

Keywords: Adsorption, adsorption isotherms, VOCs, water vapor

1. Introduction

The binary adsorption isotherms of VOCs and water vapor from the air have been the focus of much research in recent years.[1–7] Much research is also 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 vary and even exceed that of VOCs. The influence of relative humidity on VOCs diffusion and adsorption is still not well understood. Research in the past couple of years has shown that the presence of water vapor (moisture) affects the adsorption of gases and volatile compounds.[8–10] 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.[11] Very limited experimental research has been done on the effect of humidity on the diffusion coefficient.[12] The attraction between water molecules and methanol molecules may weaken the interaction forces between the solid surface and the methanol molecule and reduce the total adsorption capacity of methanol.[2,11] A piece of equipment that may be quicker and more effective at measuring pure CO_2 adsorption, pure H_2O adsorption, and co-adsorption is the DVS Vacuum.[12] This has previously been used by Su et al. to measure CO_2 and H_2O isotherms on an amine-functionalised Mg-MOF-74.[13] The DVS Vacuum uses a microbalance to measure the weight change of a sample subjected to various conditions. The temperature, pressure, and composition in the sorption chamber can be controlled

very accurately.[12,13] Today there are different devices which can perform adsorption of a variety of vapors (H_2O, MeOH, EtOH, C_6H_6 and other non-corosive vapors). A unique principle of the DVS Vacuum is the ability to control and measure sorbate entry and exit flows simultaneously while recording changes in sample mass.[12]

The determination of adsorption capacity can be done by volumetric or gravimetric method, in a static or dynamic mode. This study sets out to show how co-adsorption isotherms can be performed in a static mode, using a total organic carbon analyzer for gravimetric determination of the amount (mass) of adsorbed VOCs. The total adsorption of VOCs and water vapor was determined gravimetrically, from the difference in the mass of the adsorbent after and before the adsorption, while the amount of adsorbed water is calculated from the difference between total adsorption and the adsorbed VOCs.

2. Materials and Methods

2. 1. Materials

Zeolites, porous polymers, composites, aluminophosphates (AlPOs) and silica aluminophosphates (SAPOs), silica gels, activated carbons and metal organic frameworks (MOFs) are important classes of materials used in various sorption-based technologies. In order to obtain representative experimental data for the purpose of the analysis, the study included adsorbents of different physical and chemical properties.

The following adsorbents were used for the purpose of this study: highly silicate ZSM-5 zeolite – two samples with different molar ratio SiO_2/Al_2O_3 (*Adsorbent 1*- SiO_2/Al_2O_3 = 394 and *Adsorbent 2*- SiO_2/Al_2O_3 = 926), Na-Form mordernite (*Adsorbent 3*), and silica gel (*Adsorbent 4*) (Table 1). Molar ratio SiO_2/Al_2O_3 for adsorbents 1-3 is calculated based on their chemical analysis (mass percentages of SiO_2 and Al_2O_3), and refers to the ratio between the content of SiO_2 and Al_2O_3 expressed in mass per cent multiplied by the ratio between the molar masses of Al_2O_3 and SiO_2. For these adsorbents, apart from the content of SiO_2 and Al_2O_3, the analysis also included determining the content of Na in mass per cent. Loss of annealing for adsorbents 1–3 was calculated in the form of the percentage of the shrinkage in mass after heating at 950 °C, whereas Adsorbent 4 was analyzed for water residue, which also represents the loss of mass in percentages, but after drying at 160 °C. A low-temperature N_2 adsorption for the adsorbents used was employed to determine the pore size as well as the specific surface area using the BET method. The adsorbents were analyzed for the mean diameter of 50% of the particles (d(50)) and the mean diameter of 10% of the particles (d(10)) (Table 1) using a laser diffraction particle size analyzer (Mastersizer 3000).

The adsorbents were pre-dried to remove moisture before the experiments.

The chemicals used as adsorbates were toluene, benzene, methanol, ethanol and isopropyl alcohol. The physical properties of the five VOCs used as adsorbates are listed in Table 2.

Table 1. Physical and chemical characteristics of *Adsorbent 1, 2, 3* and *4*

Parameter	*Adsorbent 1*	*Adsorbent* 2	*Adsorbent 3*	*Adsorbent 4*
Loss of annealing, w %	2.5	3.1	6.9	–
d(10), μm	1.3	–	2.3	–
d(50), μm	2.5	< 10	8.8	15–35
Molar ratio SiO_2/Al_2O_3	384	926	13.5	–
Na content, w %	1.2	1.32	4.9	–
BET, m^2/g	355	434	420	450–550
Water residue, w %	–	–	–	< 10
pH (5%)	–	–	–	6–8
Pore size, nm	–	–	–	4.7–8

Table 2. Physicochemical properties of adsorbates

Chemical	Chemical formula	Density (g/cm^3)	Molecular weight (g/mol)	Boiling point (°C)	Vapor pressure (kPa)
Methanol	CH_3OH	0.792	32.04	64.7	13.02 (20 °C)
Ethanol	C_2H_5OH	0.7893	46.07	78.4	5.95 (20 °C)
Isopropyl alcohol	$(CH_3)_2CHOH$	0.7855	60.10	82.4	4.4 (20 °C)
Benzene	C_6H_6	0.8765	78.114	80.1	12.7 (25 °C)
Toluene	$C_6H_5CH_3$	0.866	92.14	110.6	2.8 (20 °C)

2. 2. Experimental Method and Analysis

The adsorbents were pre-dried to remove moisture before the experiments. A mass of 0.5 g of adsorbent is weighed into nine small glass jars with lids. The closed glass jars with adsorbents are placed in the adsorption chambers (2.5 L). Adsorption chambers (2.5 L) with closed glass jars were put in a climate chamber, where they were thermostated and filled with humid air at atmospheric pressure. Then the adsorption chambers were closed. A known volume of VOCs-in the range of 10–250 μL is injected into the adsorption chambers. After allowing all the VOCs to evaporate for an hour, a portion of the gas phase was taken and analyzed using a total organic carbon analyzer (Shimadzu TOC high sensitivity). It represents the concentration of the gas-phase VOCs (C_0).

For the purpose of the analysis, the manual injection kit is installed on the total organic carbon analyzer (Shimadzu TOC high sensitivity) (Figure 1).

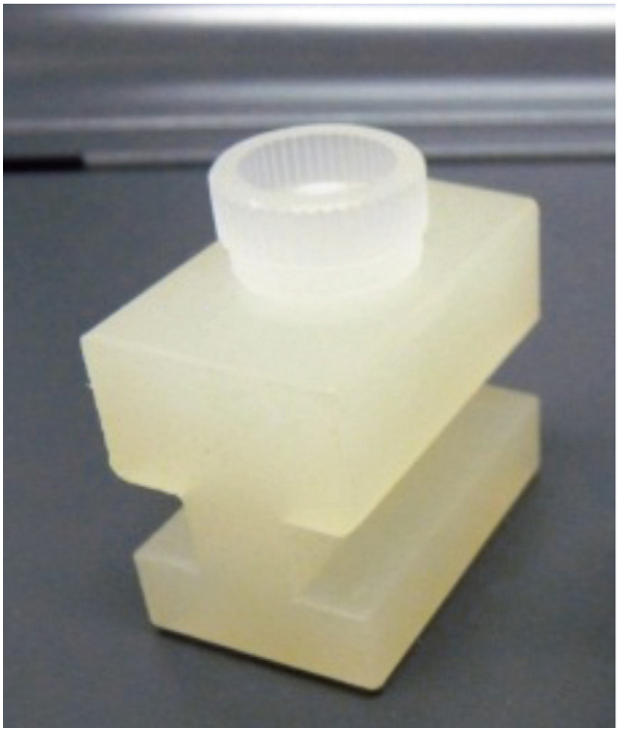

Figure 1. The manual injection kit

After determining the initial VOC concentration, the lids on the adsorbent jars are opened and the co-adsorption of VOC and water is performed. Part of the gaseous phase is taken again after equilibration and analyzed on a total organic carbon analyzer; this represents the equilibrium concentration of VOC (C_e). The amount of adsorbed VOC is calculated using the following equation (1):

$$q_e = \frac{(C_0 - C_e)V}{m_1} \quad (1)$$

where:

q_e – the amount of the adsorbed VOC per gram of adsorbent (g/g)

C_0 – VOC concentration at the beginning of adsorption (g/m^3)

C_e – equilibrium concentration of VOC (g/m^3)

V – adsorption chamber volume (m^3)

m_1 – mass of the adsorbent (g)

The total adsorption of VOCs and water vapor ($m_{e,tot}$) was determined gravimetrically, from the difference in the mass of the adsorbent before and after the adsorption.

$$m_{e,tot} = m_2 - m_1 \quad (2)$$

$$q_{e,tot} = \frac{m_{e,tot}}{m_1} \quad (3)$$

$q_{e,tot}$ – total mass of adsorbed VOC and water per gram of adsorbent (g/g)

m_2 – mass of the adsorbent after co-adsorption of VOC and water (g).

The mass of water adsorbed per gram of the adsorbent ($q_{e,w}$) was determined from the difference between the total mass of VOC and water adsorbed per gram of the adsorbent ($q_{e,tot}$) and the mass of VOC adsorbed per gram of the adsorbent (q_e):

$$q_{e,w} = q_{e,tot} - q_e \quad (4)$$

Freundlich and Langmuir isotherm models are used to discuss the equilibrium behavior of single-component adsorption. The Langmuir isotherm can be written as

$$q_e = \frac{q_0 K_L C_e}{1 + K_L C_e} \quad (5)$$

where:

q_o – is the maximum amount of adsorbed adsorbate (g/g),

C_e – is the equilibrium concentration of the adsorbate (g/m^3) and

K_L – is the Langmuir constant (m^3/g).

The Freundlich isotherm model mathematically is expressed as:

$$q_e = K_F \cdot C_e^{\frac{1}{n}} \quad (6)$$

where:

K_F – is adsorption capacity (m^3/g) and

$1/n$ – is adsorption intensity.

Freundlich and Langmuir models were used to discuss the equilibrium behavior of single-component adsorption.[15]

The models used for a single-component system are not always suitable for a multicomponent system.[15–19] Therefore, the single-component isotherm models were modified to suit a multicomponent system. There are

many models for analyzing adsorption equilibrium data, and in this study, apart from the non-linear Langmuir and Freundlich, we also used the extended Langmuir, extended Freundlich and Hill defined models in Origin software. Extended Langmuir and extended Freundlich are hybrid, three-parameter isotherm models, with another constant C added as the third parameter, apart from the constant B. A Hill isotherm model is a three-parameter isotherm model which refers to a modified Langmuir model with constants K I n.[20–22] introduced. An indicator of isotherm model suitability used in this study is adjusted R-Squared (adj. R^2), which is calculated as a function of Origin software by the following equation [23]:

$$Adj.R^2 = \left\{1 - \left[\frac{(1-R^2)(n-1)}{(n-k-1)}\right]\right\} \quad (7)$$

here,

n– represents the number of data points in our dataset,

k– represents the number of independent variables, and

R– represents the R-squared values determined by the model.

The coefficient of determination (R^2) is defined by the following equation:[21]

$$R^2 = \frac{\sum (q_e - q_{mexp})^2 - \sum (q_e - q_{cal})^2}{\sum (q_e - q_{mexp})^2} \quad (8)$$

where:

q_e –is the amount of the adsorbate adsorbed by the adsorbent during the experiment (g/g),

q_{cal} – is the amount of the adsorbate obtained by isotherm models (g/g), and

q_{mexp} – is the average value of q_e (g/g).

The advantage of the non-linear method is that the error distribution does not get altered as in the linear regression approach.

3. Results and Discussion

The adsorbents used in the study had different characteristics. *Adsorbents 1* and *2* are hydrophobic, with different specific surface areas (355 and 434 m^2/g, respectively) determined by low-temperature nitrogen adsorption. *Adsorbents 3* and *4* are hydrophilic. The adsorbates used in adsorption also had different characteristics: polar (methanol, ethanol), semi-polar (isopropyl alcohol) and non-polar (toluene, benzene).

The adsorbates were adsorbed on the adsorbents at atmospheric pressure, defined temperature (t) and relative humidity (rH). Based on the results obtained, we were able to obtain six isotherms

– co-adsorption of isopropyl alcohol -H_2O on *Adsorbent 1* (rH = 65%, t = 25 °C) (Figure 2);
– co-adsorption of methanol - H_2O on *Adsorbent* 2 (rH = 60%, t = 25 °C) (Figure 3);
– co-adsorption of methanol-H_2O on *Adsorbent* 3 (rH = 55%, t = 25 °C) (Figure 4);
– co-adsorption of ethanol - H_2O on *Adsorbent 3* (rH = 46%, t = 25 °C) (Figure 5);
– co-adsorption of toluene - H_2O on *Adsorbent 4* (rH = 70%, t = 22 °C) (Figure 6) and
– co-adsorption of benzene - H_2O on *Adsorbent 4 (rH = 50%, t = 26 °C)* (Figure 7*)*.

The obtained results show that co-adsorption of adsorbate (VOC) and water vapor occurred on all adsorbents. The shape of all isotherms indicates that there is a resemblance to type I or the lowest concentration part of type IV isotherm.

Analyzing the adsorption equilibrium data using a curve fitting tool (user-defined non-linear Langmuir and Freundlich, extended Langmuir, extended Freundlich and Hill models) in Origin software, adjusted R-Squared (R^2) and parameters of models were obtained and presented in Table 3.

The values of corresponding isotherm parameters obtained by fitting of experimental data on the co-adsorption of isopropyl alcohol -H_2O on *Adsorbent 1* based on the chosen isotherm models, shows a high value of adj. R^2. The highest value of adj. R^2 (adj.R^2 = 0.9688) for the total adsorbed isopropyl and water vapor and water ($q_{e,tot}$ = f (C_e)) was for the extended Freundlich. The model which gives the best description of adsorption of isopropyl alcohol from the water vapor- isopropyl alcohol binary system (q_e = f (C_e)) is the Freundlich model with adj.R^2 = 0.9566. Very close adj. R^2 was obtained for the extended Freundlich model for q_e = f (C_e) (adj. R^2 = 0.9495). The order of the isotherm models which best fits the experimental data of co-adsorption of isopropyl alcohol -H_2O on *Adsorbent 1* for co-adsorption of isopropyl alcohol –water vapor on *Adsorbent 1* for $q_{e,tot}$ = f (C_e) is the extended Freundlich >Hill> Freundlich> extended Langmuir> Langmuir (adj. R^2 values were 0.9688; 0.9479; 0.9191; 0.90259; 0.4420). On the other hand, for q_e = f (C_e) the best fitting non-lineare model for adsorption isotherms is Freundlich > Langmuir > extended Freundlich > Hill > extended Langmuir (adj.R^2 values were 0.9566; 0.9536; 0.9439; 0.9495; 0.94792).

The order of the isotherm models which best fit the adsorption of methanol and water vapor on *Adsorbent 2* $q_{e,tot}$ = f (C_e) is extended Langmuir = Hill > extended Freundlich > Langmuir > Freundlich (adj.R^2 were 0.99656; 0.99656; 0.9965; 0.9956; 0.93556). Whereas the order of the isotherm models that offers the best representation of measured data for methaonol in the methanol-water vapor binary system is extended Langmuir = Hill > extended Freundlich> Langmuir> Freundlich (adj.R^2 values were 0.99228; 0.99228; 0.98899; 0.9345; 0.85256).

The values of corresponding isotherm parameters obtained by fitting the experimental data of co-adsorption of methanol and water vapor on *Adsorbent 3* shows the following order of models Langmuir > extended Langmuir

= Hill > extended Freundlich > Freundlich (adj. R^2 were 0.9523; 0.94712; 0.94712; 0.9273; 0.77091). The order of the isotherm models that describe the adsorption of methanol from the binary system of methanol-water vapor on Adsorbent 3 ($q_e = f(C_e)$) is extended Freundlich > Freundlich > extended Langmuir > Hill > Langmuir (adj. R^2 values were 0.94633; 0.94362; 0.93194; 0.9298; 0.4100).

The order of the isotherm models which best fit the adsorption of toluene and water vapor on *Adsorbent 4* $q_{e,tot} = f(Ce)$ is Hill > extended Freundlich > Freundlich > ex-

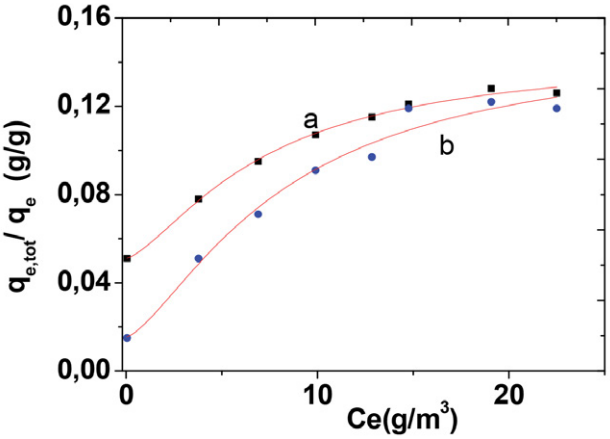

Figure 2. Adsorption Isotherms a- co-adsorption of isopropyl alcohol -H_2O; b- isopropyl alcohol on *Adsorbent 1* (rH = 65%, t = 25 °C)

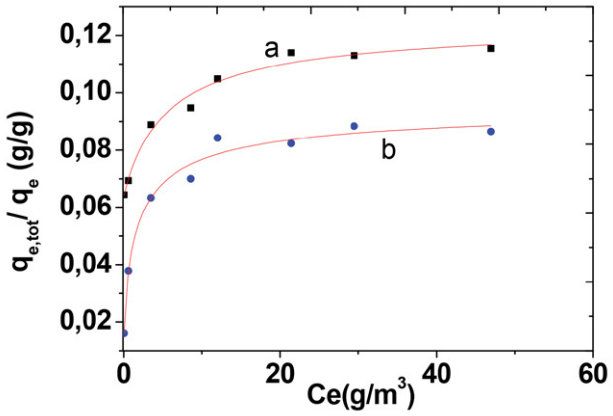

Figure 5. Adsorption Isotherms a- co-adsorption of ethanol – H_2O; b- ethanol on *Adsorbent 3* (rH = 46%, t = 25 °C)

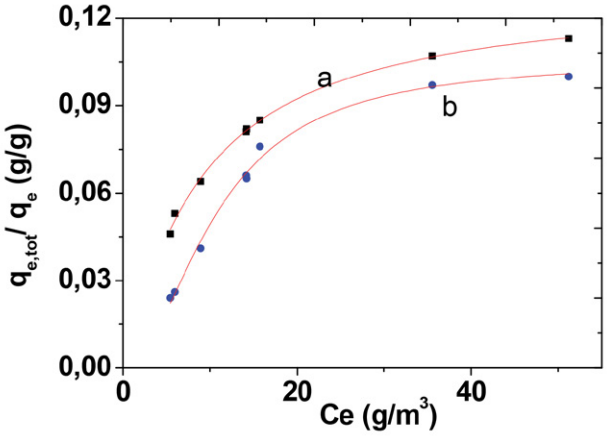

Figure 3. Adsorption Isotherms a-co-adsorption of methanol -H_2O; b- methanol on *Adsorbent 2* (rH = 60%, t = 25 °C)

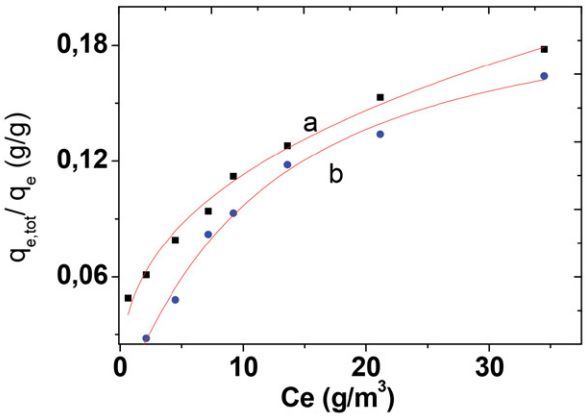

Figure 6. Adsorption Isotherms a-co-adsorption of toluene -H_2O; b-toluene on *Adsorbent 4* (rH = 70%, t = 22 °C)

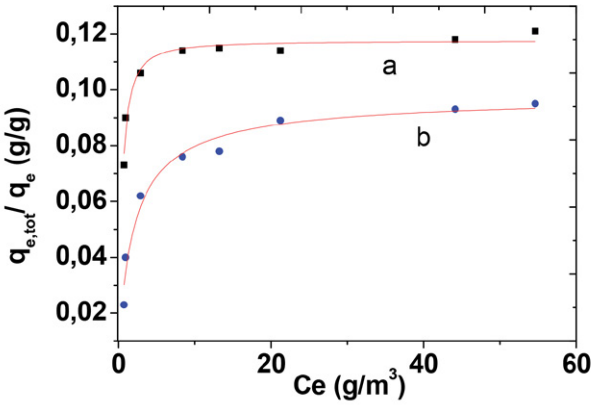

Figure 4. Adsorption Isotherms a- co-adsorption of methanol-H_2O; b- methanol on *Adsorbent 3* (rH = 55%, t = 25 °C)

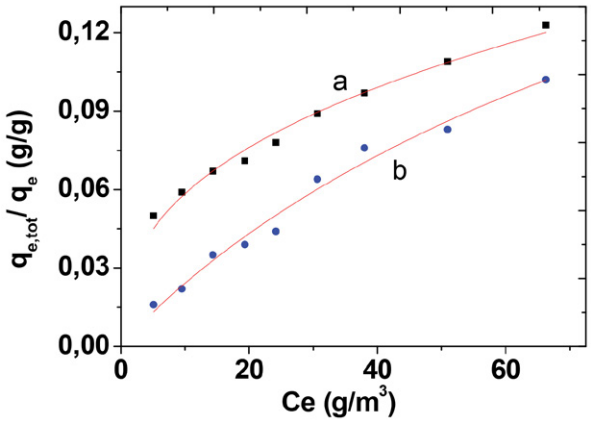

Figure 7. Adsorption Isotherms a-co-adsorption of benzene -H_2O; b- benzene on *Adsorbent 4* (rH = 50%, t = 26 °C)

Table 4. Langmuir, Freundlich, extended Langmuir, extended Freundlich and Hill isotherm parameters obtained by non-linear fitting for co-adsorption of VOC (isopropyl alcohol, methanol, ethanol, toluene, benzene) on adsorbents (*Adsorbents 1-4*)

Adsorbate /Adsorbent			**Isopropyl Alcohol/** *Adsorbent* **1**	**Methanol/** *Adsorbent* **2**	**Methanol/** *Adsorbent* **3**	**Ethanol/** *Adsorbent* **3**	**Toluene/** *Adsorbent* **4**	**Benzene/** *Adsorbent* **4**
Model								
Langmuir	$q_{e,tot}$	$K_L(m^3/g)$	0.3114	0.103	2.608	29.12	0.1554	0.06855
		$q_o(g/g)$	0.1448	0.1358	0.1192	0.1018	0.1989	0.1379
		Adj. R^2	**0.4420**	**0.9956**	**0.9523**	**0.4100**	**0.8835**	**0.8800**
	q_e	$K_L(m^3/g)$	0.1044	0.05112	0.592	1.17	0.0707	0.01073
		$q_o(g/g)$	0.1786	0.1466	0.0948	0.0859	0.2309	0.2444
		Adj. R^2	**0.9536**	**0.9345**	**0.9665**	**0.9309**	**0.9924**	**0.9804**
Extended Langmuir	$q_{e,tot}$	A(g/g)	21.2227	0.12882	0.11757	5.91215	17.70209	13.862
		$B(m^3/g)^{1/1-C}$	0.00335	0.08734	2.81094	0.01368	0.00271	0.00175
		C	0.81494	–0.12337	–0.25522	0.89807	0.62488	0.61706
		Adj. R^2	**0.90259**	**0.99656**	**0.94712**	**0.93194**	**0.98435**	**0.98037**
	q_e	A(g/g)	1.423	0.10571	0.09826	0.1045	0.2083	0.28798
		$B(m^3/g)^{1/1-C}$	0.0248	0.00973	0.57812	0.7981	0.06503	0.01038
		C	0.5645	–0.9534	0.12835	0.4779	–0.12623	0.05433
		Adj. R^2	**0.9439**	**0.99228**	**0.96259**	**0.9769**	**0.99217**	**0.97732**
Freundlich	$q_{e,tot}$	*1/n*	0.18441	0.34577	0.08446	0.10043	0.37272	0.38071
		$K_F(g/g)^n$	0.07084	0.03052	0.08891	0.07979	0.04787	0.02433
		Adj. R^2	**0.9191**	**0.93556**	**0.77091**	**0.94362**	**0.98705**	**0.98337**
	q_e	*1/n*	0.44875	0.49811	0.21789	0.19472	0.53652	0.73792
		$K_F(g/g)^n$	0.03162	0.01551	0.0425	0.04533	0.02587	0.0047
		Adj. R^2	**0.9566**	**0.85256**	**0.86869**	**0.92199**	**0.96059**	**0.97764**
Extended Freundlich	$q_{e,tot}$	A(g/g)	0.0664	0.12972	0.0858	0.07834	0.0507	0.36699
		B	0.1458	–5.05901	0.2511	0.09095	0.3091	–3.16602
		C	–0.1341	1.26742	0.2901	–0.05036	–0.04299	0.59346
		Adj. R^2	**0.9688**	**0.9965**	**0.9273**	**0.94633**	**0.9874**	**0.99296**
	q_e	A(g/g)	0.0334	0.11086	0.0362	0.07912	0.0108	0.32614
		B	0.3911	–16.4310	0.5556	0.01	1.415	–6.34167
		C	–0.03276	1.67984	0.2124	9.65401	0.1731	0.74606
		Adj. R^2	**0.9495**	**0.98899**	**0.9636**	**0.77668**	**0.9900**	**0.97957**
Hill	$q_{e,tot}$	V_{max} (g/g)	6.69483	0.12882	0.11757	1.03324	16.18856	16.65986
		K	$3.49 \cdot 10^{10}$	8.75983	0.43895	$6.341 \cdot 10^{9}$	$5.439 \cdot 10^{6}$	$2.577 \cdot 10^{7}$
		n	0.1869	1.12337	1.25522	0.10983	0.37542	0.38267
		Adj. R^2	**0.9479**	**0.99656**	**0.94712**	**0.9298**	**0.99217**	**0.98041**
	q_e	V_{max}(g/g)	4.26917	0.10571	0.09826	0.1045	0.2083	0.28798
		K	44168.7	10.71157	1.87509	1.54257	11.32094	125.2708
		n	0.45875	1.9534	0.87165	0.52191	1.12623	0.94567
		Adj. R^2	**0.94792**	**0.99228**	**0.96259**	**0.97687**	**0.98434**	**0.97732**

tended Langmuir > Langmuir (adj. R^2 values were 0.99217; 0.9874; 0.98705; 0.98435; 0.8835), whereas for q_e = f (Ce) the order is Langmuir > extended Langmuir > extended Freundlich > Hill > Freundlich (adj. R^2: 0.9924; 0.99217; 0.9900; 0.98434; 0.96059).

For the data obtained for co-adsorption of benzene-water vapor on *Adsorbent 4,* the order of the isotherm best fits for $q_{e,tot}$ = f (Ce) is extended Freundlich > Freundlich > Hill > extended Langmuir > Langmuir (adj. R^2 values were 0.99296; 0.98337; 0.98041; 0.98037; 0.8800), and for q_e = f (Ce) the order is Langmuir > extended Freundlich > Freundlich > extended Langmuir = Hill (adj. R^2 0.9804; 0.97957; 0.97764; 0.97732; 0.97732).

Figures 2–7 show the best fitting non-linear models for adsorption isotherms of VOC-water vapor co-adsorption.

The values of Adjusted R- Squared (R^2), which is an indicator of isotherm model suitability, obtained for all six adsorption isotherms for co-adsorption of VOC and water vapor, were lower for the two-parameter models

(Langmuir and Freundlich) than for the three-parameter models (extended Langmuir ~~are~~, extended Freundlich and Hill). This paper confirms that three-parameter models are more suitable for describing the isotherm measurements of VOC-water co-adsorption, i.e., multicomponent adsorptions. This can be explained by the fact that another constant is added to a two-parameter model, which allows additional factors characteristic for multicomponent systems to be introduced and quantified (such as the content of particular gaseous components, their molar mass, the surface area occupied by each of these components, etc.).

4. Conclusions

The adsorption equilibrium data of co-adsorption of VOC and water vapor from the air on the test adsorbents included the total adsorbed VOC and water vapor, adsorbed VOC, initial and equilibrium concentrations of VOC. The initial and equilibrium concentrations of VOC were determined using a total organic carbon analyzer. The experimental data for six co-adsorption isotherms of VOC-water vapor were analyzed. The analysis was performed using nonlinear models, which are considered to be a better tool for calculating isothermal parameters, and adj. R^2 was also used to determinate the best fitting isotherm to the experimental data. The values obtained for adj. R^2 indicate a good fit to isotherm models, which clearly demonstrates that the technique used in the present work is suitable for studying the co-adsorption of VOCs and water vapor from the air.

Acknowledgments

The authors would like to acknowledge the support provided by "Zeochem" doo, Zvornik for funding this work through the project "Adsorption isotherms of volatile organic compounds (VOC) on products of the company "Zeochem" d.o.o".

5. References

1. C. Gebald, J. A. Wurzbacher, A. Borgschulte, T. Zimmermann, *Environ. Sci. Technol.*, **2014,** *48*, 2497–2504. **DOI:**10.1021/es404430g
2. S. Xian, Y. Yu, J. Xiao, Z. Zhang, Q. Xia, H. Wang, Z. Li, *RSC Adv.*, **2015**, *5*, 1827–1834. **DOI:**10.1039/C4RA10463C
3. R. Veneman, N. Frigka, W. Zhao, Z. Li, S. Kersten, W. Brilman, *Int. J. Greenh. Gas Control*, **2015**, *41*, 268–275. **DOI:**10.1016/j.ijggc.2015.07.014
4. J. A. Thompson, S. I. Zones, *Ind. Eng. Chem. Res.*, **2020**, *59*, 18151–18159. **DOI:**10.1021/acs.iecr.0c03480
5. E. P. Hessou, L. A. B**é**d**é**, H. Jabraoui, A. Semmeq, M. Badawi, V. Valtchev, **2021**, *Molecules*, *26*, 5486. **DOI:**10.3390/molecules26185486
6. J. Rodrı´guez-Mirasol, J. Bedia, T. Cordero, J. J. Rodrı´guez, *Separation Science and Technology*, **2005**, *40*, 3113–3135. **DOI:**10.1080/01496390500385277
7. U. Sager, F. Schmid, *Chem. Eng. Technol.*, **2010,** *33,* **1203–1207. DOI:**10.1002/ceat.201000086
8. S.B. Bal'zhinimaev, A. E. Paukshtis, V. A. Toktarev, V. E. Kovalyov, A. M. Yaranova, E.A. Smirnov, S. Stompel, *Microporous Mesoporous Mater.,* **2019**, *277*, 70–77. **DOI:**10.1016/j.micromeso.2018.10.023
9. N. Astrath, J. Shen, D. Song, J. H. Rohling, F. B. G. Astrath, J. Zhou, T. Navessin, Z. S. Liu, C. Gu, X. Zhao, *J. Phys. Chem. B* **2009,** *113,* 8369–8374. **DOI:**10.1021/jp900796w
10. M. Kraus, U. Trommler, F. Holzer, F. D. Kopinke, U. Roland, **2018**, *Chem. Eng. J., 351*, 356–363, **DOI:**10.1016/j.cej.2018.06.128
11. K. Vellingiri, P. Kumar, A. Deep, K.H. Kim, *Chem. Eng. J.,* **2017**, *307*, 1116–1126. **DOI:**10.1016/j.cej.2016.09.012
12. J. Xu, J. S. Zhang, *Building and Environment*, **2011**, *46*, 1785–1796 **DOI:**10.1016/j.buildenv.2011.02.007
13. Surface Measurement Systems, "DVS Vacuum Dynamic Vacuum Vapor & Gas Gravimetric Sorption Analyzer." 2020. https://www.microtrac.com/products/gas-adsorption-measurement/surface-area-pore-size-distribution/belsorp-max-ii/
14. J. P Young, V. Martis, S. Garcia, M. van der Spek, CO-Adsorption And Pure-Component Isotherm Measurements On Direct Air Capture Adsorbents Using The Dvs VacuUM, TCCS-11 – Trondheim Conference on CO2 Capture, Transport and Storage Trondheim, Norway – June 21–23, **2021**, pp45–50
15. S. Kalam, S.A. Abu-Khamsin, M. S. Kamal, S. Patil, *ACS Omega*, **2021**, *6,* 32342−32348. **DOI:**10.1021/acsomega.1c04661
16. L. J. Dunne , G. Manos, *Phil. Trans. R. Soc. A*, **2018,** *376:* 20170151. **DOI:**10.1098/rsta.2017.0151
17. C. R. Girish, *International Journal of Civil Engineering and Technology,* **2017,** *8,* 80–86. http://www.iaeme.com/ijciet/issues.asp?JType = IJCIET&VType = 8&IType = 10
18. S. Divekar, A. Nanoti, S. Dasgupta, Aarti, R. Chauhan, P. Gupta, M. O. Garg, S.P. Singh, I. M. Mishra, *J. Chem. Eng. Data*, **2016**, *61,* 2629–2637 **DOI:**10.1021/acs.jced.6b00294
19. CM. Simon, E. Braun, C. Carraro, B. Smit, *PNAS*, **2017**, *114,* 287–296. **DOI:**10.1073/pnas.1613874114
20. X. Chen, *Information,* **2015**, *6*, 14–22. **DOI:**10.3390/info6010014
21. N. Ayawei, A. N.Ebelegi, D. Wankasi, *Journal of Chemistry,* **2017**, 2017, 1–11 **DOI:**10.1155/2017/3039817
22. T. A. Osmari, R. Gallon, M. Schwaab, E. Barbosa-Coutinho, J. Baptista Severo Jr., J. C. Pinto, *Adsorption Science & Technology,* **2013**, *31,* 433–458. **DOI:**10.1260/0263-6174.31.5.433
23. S. Dubey, D. Gusain, Y. C. Sharma, *Journal of Molecular Liquids*, **2016**, *219,* 1–8. **DOI:**10.1016/j.molliq.2016.01.021

Povzetek

V zadnjih letih je fokus raziskovanja na binarnih adsorpcijskih izotermah hlapne organske komponente (VOC) in vodne pare iz zraka. Količino adsorbirane VOC v prisotnosti vodne pare lahko določimo volumetrično ali gravimetrično, v statičnem ali dinamičnem načinu. Ta študija je osredotočena na adsorpcijsko tehniko v statičnem načinu za izotermne meritve koadsorpcije VOC in vodne pare iz zraka z uporabo gravimetrične metode. Količino VOC smo določili s pomočjo analizatorja celotnega dušika, medtem ko smo količino vode izračunali iz razlike med celotno adsorpcijo (VOC in voda) in količino absorbirane VOC. V članku predstavljamo nekaj adsorpcijskih izoterm za različne VOC (toluen, benzen, metanol, etanol in izopropilalkohol) in različne adsorbente (zeolite ZSM-5, silikagel in natrijevo obliko mordernita) v prisotnosti vodne pare. Za obravnavo eksperimentalnih podatkov smo uporabili dobro znane adsorpcijske modele (Langmuir, razširjeni Langmuir, Freundlich, razširjeni Freundlich in Hill). Za določitev najbolje prilegajočih izotermnih modelov smo uporabili prilagojene vrednosti R^2, ki smo jih dobili iz teh nelinearnih modelov (to je krivulj celotne količine adsorbiranih plinov ($q_{e,tot}$) v odvisnosti od ravnotežne koncentracije VOC (C_e)). Rezultati so pokazali, da dajo modeli s tremi parametri boljše rezultate za prileganje k meritvam kot modeli z dvema parametroma, torej z višjimi vrednostmi R^2. Eksperimentalni rezultati pokažejo, da to adsorpcijsko tehniko lahko uporabimo za izotermne meritve ko-adsorpcije VOC in vodnih par iz zraka.