Original Article

Adsorption of gas-phase n-hexane and benzene, toluene, ethyl benzene, and xylene onto compost; kinetics and isothermal studies

Mohammad Mehdi Amin, Bijan Bina, Amir Rahimi¹, Mohsen Heidari^{2,3}

Environment Research Center, Research Institute for Primordial Prevention of Noncommunicable Disease, Isfahan University of Medical Sciences (IUMS), Isfahan, Iran and Department of Environmental Health Engineering, School of Health, IUMS, Isfahan, Iran, ¹Chemical Engineering Department, College of Engineering, University of Isfahan, Isfahan, Iran, ²Department of Environmental Health Engineering, Student Research Center, School of Health, Isfahan University of Medical Sciences (IUMS), Isfahan, Iran, ³Department of Environmental Health Engineering, Faculty of Health, Hormozgan University of Medical Sciences, Bandar Abbas, Iran

Address for correspondence:

Dr. Mohsen Heidari, Department of Environmental Health Engineering, Environment Research Centre, School of Health, Isfahan University of Medical Sciences, Hezar Jerib Ave, Isfahan, Iran.

E-mail: moheidari84@gmail.com

ABSTRACT

Aims: In this study, the potential capability of compost in the simultaneous adsorption of gas-phase n-hexane and benzene, toluene, ethyl benzene, and xylene (BTEX) was studied.

Materials and Methods: Batch adsorption technique was used to assess the adsorption properties of compost. The pseudo-first and pseudo-second order kinetics were considered in order to identify the possible mechanism of the adsorption process. Moreover, the suitability of the adsorbent was evaluated using Langmuir, Freundlich and The Dubinin-Radushkevich isotherm models.

Results: After 24 h contact time, the adsorption capacity of one g compost was 1.42 mg n-hexane and BTEX for initial concentration of 7.74 mg/l. The adsorption capacities were in order of n-hexane < benzene < toluene < ethylbenzene < xylene. This order is in accordance to the ascending octanol-air partitioning coefficient (K_{OA}) order of the compounds (the lowest for n-hexane and the highest for xylene). The kinetics data proved a closer fit to the pseudo-second order model, while the isotherm experimental data were a good correlation to both Freundlich and Langmuir models.

Conclusion: The experimental data show that a material with an organic matrix, that is, raw compost, has a higher adsorption capacity for the gaseous compounds with higher K_{OA} . Overall look to the results of this study indicates that although the raw compost could adsorb gaseous n-hexane and BTEX, its capacity may not be sufficient for the continuous removal of VOCs from the air in the compost-based biofilters, in which biodegradation play a key role.

Key words: Adsorption, benzene, toluene, ethyl benzene, and xylene, compost, n-hexane



INTRODUCTION

Volatile organic compounds (VOCs) are considered to be some of the most hazardous air pollutants emitted from a variety of sources including industries and automobiles. These compounds, though in most cases are used in their liquid form, have the potential to vaporize at significant rates

Copyright: © 2014 Mobarakeh AS. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

This article may be cited as:

Amin MM, Bina B, Rahimi A, Heidari M. Adsorption of gas-phase n-hexane and benzene, toluene, ethyl benzene, and xylene onto compost; kinetics and isothermal studies. Int J Env Health Eng 2015;4:27.

into the ambient atmosphere.^[1] Among VOCs, benzene, toluene, ethyl benzene, and xylene (BTEX) and n-hexane are common components of many solvent mixtures and are mainly used in textile, polymer and varnishing industries. They are among the main air pollutants emitted from petrochemical industries.^[2-4] BTEX account for up to 59% (w/w) of gasoline pollutants.^[5,6] They are well-known VOCs of environmental and health concern. Benzene is a well-known carcinogen that has also been linked to leukemia. Chronic exposure to xylene and toluene has been associated with adverse effects on the nervous system, liver and the kidneys while chronic exposure to ethylbenzene has adverse effects on the respiratory system and the kidneys.^[5,7,8] Over-exposure to n-hexane has been related to dizziness and drowsiness and peripheral neuropathy of hands and feet.^[9]

Due to the ubiquity of VOCs in the environment and risk to human health, it is necessary to limit and control their emissions. The control techniques are broadly classified into two types: Destruction (thermal oxidation, catalytic oxidation, biofiltration) and recovery (adsorption, membrane separation, condensation).^[10,11] Adsorption is a reliable process to remove organic compounds from industrial waste gases and in some applications, to recover recyclable materials from process exhaust streams.^[12,13] Besides, adsorption and absorption phenomena are believed to be effective in the performance of biofilters, especially under transient conditions or shock loading since adsorption along with absorption may act as a buffer for biological activity.^[14]

Activated carbon is the most common material used extensively for the adsorption of various VOCs from the air.^[13] Some studies have been done on the adsorption capacity of other adsorptive materials, including diatomaceous earth (toluene),^[15] fibrous peat and ground tire rubber (GTR) (n-butyl acetate, toluene, m-xylene),^[16] zeolite (acetone and toluene),^[17] porous metal-organic frameworks (VOCs),^[18] and polymeric resin (trichloroethylene and benzene).^[10] Recently, Mohammadi-Moghadam *et al.* reported that Glycyrrhiza glabra Root (GGR) could adsorb around 2.2 mg/g toluene from the air under batch tests.^[19] Compost has also been used for the adsorption of different gas-phase pollutants.^[20,21] Moreover, it is a well-known packing material in biofiltration process, in which adsorption may play a role in the removal of VOCs.

To help evaluate the performance of a sorbent in the removal of gaseous-phase pollutants, it is important to understand the isotherm and kinetic characteristics between the adsorbent used and adsorbate.^[13] The sorption of a gasphase adsorbate onto a solid adsorbent is typically studied through three methods; namely: (a) Static volumetric method, (b) dynamic column method, and (c) gravimetric method.^[22] Moreover, there are some studies that evaluate the adsorptive properties of packing material, usually used in biofiltration system, through simple batch tests.^[16,19,23] This test is basically similar to static volumetric method. In this method, sorbent media are placed in an airtight chamber/ reactor with an initial gas concentration inside. As adsorption occurs, the gas-phase concentration decreases until an equilibrium state is reached. In static volumetric method, the gas-phase adsorbate concentration calculated through appropriate pressure-volume-temperature measurement,^[22] while in batch test the gaseous concentration is measured through direct sampling.

To the best of our knowledge, there appears to be relatively little information in the literature concerning multicomponent adsorption of VOCs on compost through batch test. Compost is a common filter media in the biofiltration of VOCs. In the other hand, adsorption phenomenon may have a significant role in the removal of gas-phase VOCs along with biodegradation within biofilm. Therefore, in this study, the potential capability of raw compost in simultaneous adsorption of common VOCs, including n-hexane and BTEX was explored. This may illustrate the scale of adsorption in compost-based biofilters treating the tested pollutants. Moreover, the effects of parameters such as contact time and adsorbate concentration on adsorption capacity were investigated. To describe the adsorption of n-hexane and BTEX onto compost, different adsorption kinetic and isotherm models fitted to the experimental data.

MATERIALS AND METHODS

Materials

Compost was provided from Isfahan Compost Company. Benzene (\geq 99%), toluene (99.5%), ethylbenzene (\geq 99%), xylene (99.5%) and n-hexane were purchased from Merck Co. The physicochemical properties of n-hexane and BTEX are presented in Table 1.^[24-28]

Preparation of the adsorbent

Compost was sieved through a 2-mm sieve to remove large particles and then sieved through a 1-mm sieve. Undesirable components such as glass and plastic were then removed manually. The sieved compost was presterilized at 120°C for 15 min in an autoclave and dried at 100°C for 24 h in the oven and subsequently cooled at room temperature in desiccators for 1 h.

Analytical methods

The concentrations of gaseous n-hexane and BTEX were analyzed by a gas chromatograph equipped with flame ionization detector (GC-FID) (Agilent GC, 7890A). The column used was an Agilent 19091S-433 capillary column, $30 \text{ m} \times 250 \,\mu\text{m} \times 0.25 \,\mu\text{m}$. The GC-FID method for the determination of BTEX and n-hexane was optimized as follows:

Amin, et al.: Adsorption of gas-phase n-hexane and BTEX

- · Injected sample volume: $100 \,\mu l$,
- · Carrier gas: Helium (purity 99.995%) with flow of 1.11 ml/min,
- Fuel gas: H_2 (30 ml/min),
- Detector temperature: 250°C,
- Oven temperature: 50°C for 1 min and increased with the rate of 10°C/min to 150°C for 10 min (total run time: 11 min).

To achieve calibration curve, known amounts of the compounds were injected into a glass bottle sealed with Teflon septum according to the standard procedure.^[29] Then, air samples were drawn from the bottles with a 1 ml gas tight syringe (Hamilton, USA), and directly injected into the GC.

Adsorption experiments

Batch adsorption experiments were carried out to determine the effect of parameters such as contact time and adsorbate concentration on the adsorption of gas-phase n-hexane and BTEX onto compost. All of the adsorption experiments were carried out in sterilized 250 ml glass bottles with PTFE airtight cap contained 1 g adsorbent. For the determination of isotherm properties, liquid compounds were injected into the bottles to obtain overall gas-phase concentrations of 1.68-16.12 mg/l and maintained at $25^{\circ}C \pm 1^{\circ}C$. The bottles were shaken by a rotary shaker at 300 rpm. After given time intervals, an aliquot of polluted gas was analyzed for the organic pollutants by GC-FID. The experiments were duplicated, and their average values were calculated. Blank samples (BTEX and n-hexane mixture without the adsorbent) were also used to determine the value of the components loss. The blank recoveries were calculated (80-93%) and the data were adjusted for them. The amount of the gaseous compounds that are adsorbed on the adsorbent can be expressed as follows:

$$q_e = \frac{(C_o - C_e) V}{m} \tag{1}$$

where $q_e (mg/g)$ is the adsorption capacity of compost for the compounds, $C_0 (mg/l)$ is the initial gas-phase concentration of compounds, $C_e (mg/l)$ is the equilibrium gas-phase concentration of the compounds, m (g) is the mass of the compost, and V (l) is the volume of the gas (or volume of the bottle, the adsorbent volume is negligible).

RESULTS

Effects of contact time

The adsorbed mass of n-hexane and BTEX per mass of compost (mg/g) in relation to the adsorbent-adsorbate contact time (t in hours) is presented in Figure 1. In general, the adsorption of the tested pollutants on the adsorbent was increased over time.

Adsorption kinetics

In this study, the experimental data obtained for the simultaneous adsorption of gaseous n-hexane and BTEX onto compost were fitted through two kinetic models including pseudo-first order and pseudo-second order models. The general form of the pseudo-first order kinetic is shown by the following equation:^[30]

$$q_t = q_e \left(1 - e^{-k_1 t} \right) \tag{2}$$

With a linear form of

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

where $q_e (mg/g)$ and $q_t (mg/g)$ are the adsorbed quantity of n-hexane and BTEX at equilibrium and at time (t),



Figure 1: The effects of contact time on n-hexane and benzene, toluene, ethyl benzene, and xylene adsorption by the compost (compost weight = 1 g, initial concentration = 24.4 mg/l)

Table 1: Physiochemical properties of n-hexane and BTEX compounds								
Characteristics	n-hexane	Benzene	Toluene	Ethylbenzene	Xylene			
Formula	$CH_3 (CH_2)_4 CH_3$	C ^e H ^e	C _g H _g CH ₃	C _e H _e CH ₂ CH ₃	$C_{e}H_{4}(CH_{3})_{2}$			
Molecular weight (g/mol)	ັ86.17 ⁷ ັ	78 [°] .1 [°] 1	92.14 [°]	ٽ106.16	10 ⁶ .16 [°]			
Water solubility at 20°C (mg/l)	9.5	1790	526	169	162			
Boiling point (°C)	68.5	80	111	136	138			
Vapor pressure at 25°C (mmHg)	124	75	21	7	9			
Log octanol-water partition coefficient, log Kow (Kow)	3.90 (7943.3)	2.13 (134.7)	2.73 (537.03)	3.15 (1412.5)	3.15 (1412.5)			
Log air-water partition coefficient,	1.867 (73.62)	-0.644 (0.227)	-0.566 (0.272)	-0.492 (0.322)	-0.550 (0.282)			
log K _{AW} (K _{AW})								
Log octanol-air partition coefficient,	2.033 (107.9)	2.774 (594.3)	3.296 (1977.3)	3.642 (4386.6)	3.700 (5008.9)			
log K _{oa} (K _{oa})								

BTEX: Benzene, toluene, ethyl benzene, and xylene

respectively. k_1 (1/h) is the pseudo-first order rate constant. k_1 and q_e values can be obtained by plotting ln ($q_e - q_t$) against t.

The experiment data were also analyzed by pseudo-second order model. This adsorption kinetic is shown by the following equation:^[30]

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{4}$$

With a linear form of

$$t / q_t = 1 / (k_2 q_e^2) + t / q_e \tag{5}$$

where q_e and q_t defined already for the pseudo-first order model. k_2 (g/mg/h) is the pseudo-second order rate constant. k_2 and q_e can be obtained by plotting t/ q_t versus t in Eq (5).

The experimental data obtained for the adsorption of gas-phase n-hexane and BTEX by compost at different time intervals were correlated with the above mentioned kinetics, which are presented in Figure 2. The values of regression coefficients obtained from the fitting the experimental data to the pseudo-first order and pseudo-second order kinetic models were in the range of 0.513-0.944 and 0.976-0.995, respectively. Furthermore, the pseudo-first and pseudo-second order kinetics presented overall equilibrium adsorption capacities of 2.88 mg and 5.10 mg n-hexane and BTEX per g dry compost, respectively [Table 2].

Adsorption capacity

In order to determine the adsorption isotherm (next section), it is necessary to evaluate the adsorption capacity of the adsorbent at various initial concentrations of adsorbate. The adsorption capacity of compost was assessed for initial n-hexane and BTEX concentrations ranged from 1.68 to 16.12 mg/l at 25°C after 24 h contact time. The overall adsorption capacities (q_e) of the pollutants are presented in Table 3.

Adsorption isotherms

The Langmuir adsorption isotherm, the Freundlich model and the Dubinin-Radushkevich (D-R) isotherm model are evaluated for the results of the adsorption experiments.

The general form of this isotherm is given by^[30]

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{6}$$

The linearized form of the Langmuir isotherm equation is written as

$$\frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m} \tag{7}$$

where q_e is quantity of n-hexane and BTEX adsorbed onto the dry support (mg/g), C_e is the equilibrium gas-phase concentration (mg/l), q_m is the monolayer or maximum adsorption capacity of the adsorbent (mg/g), and K_L is the Langmuir adsorption constant (l/mg) and is related to the free energy of adsorption.



Figure 2: (a) The pseudo-first order and (b) pseudo-second order kinetic fitted to the experimental data

Table 2: Parameters of pseudo-first order and pseudo-second order kinetics obtained from this study							
Adsorbate	Pseudo-first order			Pseudo-second order			
	k ₁	q _e	R ²	k ₂ (g/mg/h)	q _{e, calculated} (mg/g)	R ²	
n-hexane	0.09	0.32	0.513	0.87	0.61	0.976	
Benzene	0.20	0.59	0.944	0.67	0.86	0.997	
Toluene	0.14	0.57	0.747	0.65	1.05	0.995	
Ethylbenzene	0.12	0.69	0.686	0.45	1.27	0.989	
Xylene	0.12	0.75	0.721	0.40	1.33	0.989	
n-hexane and BTEX	0.13	2.88	0.754	0.11	5.10	0.992	

BTEX: Benzene, toluene, ethyl benzene, and xylene

The general form of Freundlich isotherm can be written as: $[^{30]}$

$$q_e = K_F C_e^{1/n} \tag{8}$$

With a linearized form of

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{9}$$

where K_F (mg/g [l/mg]^{1/n}) and n are parameters characteristic of the adsorbent-sorbate system, which must be determined by data fitting. They are indicative of the extent of adsorption and the degree of nonlinearity between gaseous concentration and adsorption and show the capacity and intensity of the adsorption, respectively.

The linear form of D-R isotherm can be shown as:^[19]

$$inq_e = inq_m - \beta O^2 \tag{10}$$

where $q_m (mg/g)$ is the theoretical saturation sorption capacity, β (kJ/mol) related to mean adsorption energy and ϵ is the Polanyi potential which is related to the equilibrium concentration as follows:

$$RTln(1+1/C_{e}) \tag{11}$$

where R is the gas constant (0.008314 kJ/mol/K) and T is the absolute temperature.

The experimental data for various equilibrium gaseous adsorbate concentrations were fitted to the linear Langmuir, Freundlich and D-R models through plotting $1/q_e$ versus $1/C_e$ [Figure 3a], C_e/q_e versus C_e [Figure 3b] and $\ln q_e$ versus ϵ^2 [Figure 3c], respectively. The regression coefficients obtained from the fitting the experimental data to the Langmuir, Freundlich and D-R isotherm equations were in the ranges of 0.970-0.981, 0.975-0.988, and 0.733-0.853, respectively. The isotherm constants and correlation coefficients of the adsorption of n-hexane and BTEX onto compost are calculated and presented in Table 4.

DISCUSSION

The effect of contact time

Figure 1 shows that the adsorption of n-hexane and BTEX was rapidly increased during first 75 min (n-hexane = 59%, Benzene = 55%, toluene = 64%, ethylbenzene = 67% and xylene = 64%) and then they continue to increase at a relatively low speed with contact time up to 24 h. The higher rate of adsorption at the beginning of the adsorption time may be due to the availability of abundant adsorption sites, which are reduced as the time goes forward.^[19] It must also consider that the available adsorbate concentration is reduced over time.

Adsorption kinetics

Adsorption kinetic models are used generally to determine the controlling mechanism of adsorption and the efficiency of the adsorbents for the removal of pollutants.^[4,31] As is evident in

Table 3: The capacity of various materials in the adsorption of VOCs								
Gas-phase adsorbate	Adsorbent	Contact time (h)	Initial concentration (mg/l)	Adsorption capacity (mg/g)	Study			
n-hexane and BTEX	Compost	24	1.68 3.36 7.74 11.2 16.12	0.40 0.66 1.43 2.21 3.51	This study			
Toluene Toluene m-xylene m-xylene Toluene Hexane	Fibrous peat GTR** Fibrous peat GTR GGR* perlite	48 48 48 48 12 72	10 10 10 10 6.93 10	4.3 22.1 12.6 95.5 2.2 0.19	[16] [16] [16] [20] [24]			

*Glycyrrhiza glabra root, **Ground tire rubber. BTEX: Benzene, toluene, ethyl benzene, and xylene, VOCs: Volatile organic compounds

Table 4: Langmuir, Freundlich and D-R isotherm parameters for the simultaneous adsorption of n-hexane and BTEX onto compost

Adsorbate	Langmuir isotherm			Freundlich isotherm		D-R isotherm	
	q _m (mg/g)	K, (l/mg)	R,	K _F (I/g)	n	q_ (mg/g)	E (kj/mol)
n-hexane	0.84	0.24	0.51	0.16	1.07	0.35	1.82
Benzene	1.03	0.26	0.50	0.21	1.09	0.43	1.88
Toluene	1.23	0.28	0.48	0.27	1.09	0.50	2.02
Ethylbenzene	1.63	0.26	0.50	0.35	1.05	0.59	2.10
Xylene	1.70	0.26	0.50	0.36	1.05	0.60	2.11
n-hexane and BTEX	6.41	0.05	0.51	0.29	1.07	2.08	0.75

BTEX: Benzene, toluene, ethyl benzene, and xylene, D-R: Dubinin-Radushkevich

Amin, et al.: Adsorption of gas-phase n-hexane and BTEX



Figure 3: (a) Langmuir isotherm model, (b) Freundlich isotherm model, and (c) Dubinin-Radushkevich isotherm model for the simultaneous adsorption of n-hexane and benzene, toluene, ethyl benzene, and xylene onto compost

the Figure 2a and b, the experimental data for each of adsorbates examined best fit the pseudo-second order kinetics model, providing correlation coefficient (R^2) values higher than that of pseudo-first order. The comparison between the experimental adsorption capacity obtained from the contact time effect experiments (q_{exp} : 4.88 mg/g) and the calculated adsorption capacity (q_{cal} : 5.1 mg/g) [Table 2] shows that the q_{cal} value is close to q_{exp} value for the pseudo-second order kinetics. Also, the q_e values obtained by pseudo-second order model were in order of n-hexane < benzene < toluene < ethylbenzene < xylene which is in agreement with that obtained experimentally.

Adsorption capacity

The adsorption capacity of the compost was increased by the increasing gas-phase n-hexane and BTEX concentrations.

This may be due to an increase in driving forces including van der Waal's force to the active sites of the adsorbent that originated from high concentrations of the compounds.^[19] In this study, the initial concentrations ranged from 1.68 to 16.12 mg/l was selected to evaluate adsorption capacity of compost at various concentrations and to determine the adsorption isotherm. Hernández-Meléndez et al. applied the gas-phase hexane concentrations ranged from 4 to 24.8 mg/l to determine adsorption isotherm of this compound onto various biofilter bed materials. They selected the initial concentration of 10 mg/l to compare adsorption capacity of various filter bed materials.^[23] Moreover initial concentration of 6.93 mg/l and 10 mg/l VOCs have been used to evaluate adsorption capacity of various filter bed materials.^[16,19] The ranges of applicable inlet concentration of VOCs for biological air treatment and adsorption systems are usually up to 5 and 10 mg/l, respectively.^[32] Therefore, the initial concentration of 7.74 mg/l is a conservative measure to evaluate the adsorption capacity of compost as a biofilter bed material. At this concentration, the adsorption capacities were in the order of n-hexane (0.21 mg) <benzene (0.25 mg) < toluene (0.28 mg) < ethylbenzene(0.34 mg) < xylene (0.35 mg). This order may be related to the different affinity of the gaseous species to the organic matter (based on $K_{\Omega A}$) and approximately molecular weight [Table 1].

The octanol-air partition coefficient (K_{OA}) is the ratio of a chemical concentration in octanol to that in air at equilibrium. It is useful for predicting the partitioning behavior between air and solid matrices. It is possible to estimate K_{OA} from the octanol-water partition coefficient (K_{OW}) and air-water partition coefficient (K_{AW}) as:^[33]

$$K_{OA} = K_{OW}/K_{AW}$$
(12)

As shown from Table 1, the K_{OA} values for the subjected compounds are in the order of n-hexane (2.033) < benzene (2.774) < toluene (3.296) < ethylbenzene (3.642) < xylene (3.700). The higher K_{OA} , the higher tendency of gas-phase species to the organic matrices.^[33]

According to Table 3, for initial gas-phase n-hexane and BTEX concentration of 7.74 g/m³, the overall adsorption capacity of compost was 1.43 mg/g. With respect to the initial concentration of gaseous adsorbates, contact time and adsorbate type reported in other studies, it is approximately concluded that the capacity of compost for the adsorption of VOCs is lower than GTR, GGR, and fibrous peat and higher than perlite [Table 3].^[16,19,23] Oh *et al.* in a study focused on the adsorptive properties of biofilter packing materials on toluene removal reported that the compost is a well-known and good media in the biofiltration of VOCs, in which the elimination capacities as high as 180 g VOCs/m³/h have been reported.^[34] In general, this adsorption capacity of compost

does not guarantee the effective continuous and long-term removal of VOCs in compost-based biofilters, in which biological degradation play a key role. In Oh *et al.* study, it was concluded that the adsorption capacity of the packing materials would have been exhausted within a day and the removal of toluene relied primarily on biological degradation after the 1st day of operations.^[20]

Adsorption isotherms

The equilibrium adsorption isotherm is fundamental to describe the interactive behavior between the adsorbate and the adsorbent and is useful for designing any sorption system.^[4,35] For the interpretation of the isotherm determination experimental data, three yet very frequently applied isothermal models were used in their linear form: (1) The Freundlich model, (2) the Langmuir model and (3) the (D-R) isotherm. The Langmuir adsorption isotherm is fundamentally used for the sorption of gases on a solid surface. This isotherm assumes that the adsorption occurs at specific homogeneous sites within the adsorbent and has found successful application in many studies of monolayer adsorption.^[36] This isotherm predicts the maximum monolayer adsorption capacity of the adsorbent.^[4,19] The Freundlich model is an empirical expression that assumes a heterogeneous adsorbent surface with sites that have different energies of adsorption and are not equally available. The Freundlich isotherm model is usually explained for multilayer adsorption on a heterogeneous adsorbent surface. It is more widely used but provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model.^[36,37] The D-R is more generally used to distinguish between physical and chemical adsorption.

With respect to the regression coefficients presented in Figure 3, both Freundlich and Langmuir isotherms were well adapted to the description of n-hexane and BTEX adsorption on compost. It is reported in some studies that the adsorption of toluene, m-xylene and n-butyl acetate onto fibrous peat and GTR,^[16] toluene onto GGR,^[19] and hexane onto peat moss and pine sawdust^[23] are described well by the freundlich equation. Delhomenie *et al.* in a study conducted on the adsorption of toluene on the compost-based pellets in a bench-scale biofilter (i.e., dynamic column method) reported that both Langmuir and frundlich models are valid to describe the adsorption equilibrium.^[21]

The essential characteristic of the Langmuir isotherm can be described by the equilibrium parameter, R_1 , calculated by:

$$R_{L} = \frac{1}{(1 + K_{L}C_{0})}$$
(13)

where K_L is the Langmuir constant and C_0 is the initial gaseous compound concentrations (mg/l). R_L is a dimensionless factor

used to determine whether the adsorption process is favorable or unfavorable. The adsorption process for $0 < R_L < 1, R_L > 1$, $R_L = 1$, and $R_L = 0$ are favorable, unfavorable, linear, and irreversible, respectively.^[36]

Moreover, the extent of Freundlich isotherm exponent, n, specify the intensity of the adsorption process; the higher values of n (more than 1) the stronger adsorption bond between adsorbent and adsorbate.^[4] The n and R_L values calculated to be >1 and between 0 and 1, respectively, for the adsorption of all gaseous compounds onto compost [Table 4], indicating that the adsorption of the n-hexane and BTEX onto compost is favorable.

In order to determine the type of adsorption process, it is necessary to determine the mean adsorption energy, E (kJ/mol) that is related to the β constant obtained from D-R isotherm as

$$E = \frac{1}{\sqrt{2\beta}} \tag{14}$$

The value of E determines the type of adsorption process, as the physical and chemical adsorptions are occurred at E < 8 kJ/mol and E > 16 kJ/mol, respectively. The chemical ion exchange generally occurred at E values between 8 and 16 kJ/mol.^[4,19] As seen from Table 4, the E values are below 2.11 kJ/mol, indicate that the adsorption of gaseous n-hexane and BTEX onto compost has physical nature. The E value reported by Mohammadi-Moghadam *et al.* for the adsorption of gaseous toluene onto GGR was 1.38 kJ/mol, that is, physical adsorption was occurred.^[19]

CONCLUSION

In this study, simultaneous adsorption of gas-phase n-hexane and BTEX onto the raw compost was explored. The adsorption capacity decreases in the following order: xylene \rightarrow ethylbenzene \rightarrow toluene \rightarrow benzene \rightarrow n-hexane with an overall adsorption capacity of 1.43 mg n-hexane and BTEX per g dry compost (initial concentration = 7.74 mg/l). The adsorption of gaseous n-hexane and BTEX onto the raw compost was well described by the pseudo-second order kinetic. The Freundlich and Langmuir models well fitted to the experimental data, providing n and R_L values slightly more than one and between 0 and 1, respectively, indicating the adsorption process is favorable. Generally compost is a relatively potential adsorbent for the removal of gas-phase n-hexane and BTEX. Its capacity increase as the octanol-air partitioning coefficient (K_{OA}) of adsorbates increases. It may be also concluded that the adsorption capacity provided by compost may not be sufficient for the continuous removal of VOCs from air in compost-based biofilters compared to biological degradation.

Amin, et al.: Adsorption of gas-phase n-hexane and BTEX

ACKNOWLEDGMENTS

This paper is the result of PhD thesis approved in the Isfahan University of Medical Sciences (IUMS). The authors wish to acknowledge to Vice Chancellery of Research of IUMS for the financial support, Research Project, no 391249.

REFERENCES

- 1. Rene ER, Murthy DV, Swaminathan T. Effect of flow rate, concentration and transient-state operations on the performance of a biofilter treating xylene vapors. Water Air Soil Pollut 2010;211:79-93.
- Iranmanesh E, Halladj R, Zamir SM. Microkinetic analysis of n-Hexane biodegradation by an isolated fungal consortium from a biofilter: Influence of temperature and toluene presence. Clean Soil Air Water 2013;00:1-8.
- Prenafeta-Boldú FX, Guivernau M, Gallastegui G, Viñas M, de Hoog GS, Elías A. Fungal/bacterial interactions during the biodegradation of TEX hydrocarbons (toluene, ethylbenzene and p-xylene) in gas biofilters operated under xerophilic conditions. FEMS Microbiol Ecol 2012;80:722-34.
- Nourmoradi H, Nikaeen M, Nejad MH. Removal of benzene, toluene, ethylbenzene and xylene (BTEX) from aqueous solutions by montmorillonite modified with nonionic surfactant: Equilibrium, kinetic and thermodynamic study. Chem Eng J 2012;191:341-8.
- Rahul, Mathur AK, Balomajumder C. Performance evaluation and model analysis of BTEX contaminated air in corn-cob biofilter system. Bioresour Technol 2013;133:166-74.
- Gallastegui G, Ramirez A, Elias A, Jones JP, Heitz M. Performance and macrokinetic analysis of biofiltration of toluene and p-xylene mixtures in a conventional biofilter packed with inert material. Bioresour Technol 2011;102:7657-65.
- Amin MM, Hatamipour MS, Momenbeik F, Khiadani Hajian M, Mohammadi-Moghadam F. Soil remediation via bioventing, vapor extraction and transition regime between vapor extraction and bioventing. Int J Environ Health Eng 2014;3:1.
- Amin MM, Hatamipour MS, Momenbeik F, Nourmoradi H, Farhadkhani M, Mohammadi-Moghadam F. Toluene removal from sandy soils via *in situ* technologies with an emphasis on factors influencing soil vapor extraction. ScientificWorldJournal 2014;2014:416752.
- ATSDR. Toxicological Profile Information Sheet. USA: Agency for Toxic Substances and Disease Registry, Department of Health and Human Services, Public Health Service; 1999.
- Liu P, Long C, Li Q, Qian H, Li A, Zhang Q. Adsorption of trichloroethylene and benzene vapors onto hypercrosslinked polymeric resin. J Hazard Mater 2009;166:46-51.
- 11. Ruddy EN, Carroll LA. Select the best VOC control strategy, Chem Eng Prog 1993;89:28-35.
- Zhang W, Qu Z, Li X, Wang Y, Ma D, Wu J. Comparison of dynamic adsorption/desorption characteristics of toluene on different porous materials. J Environ Sci (China) 2012;24:520-8.
- Yun JH, Choi DK. Equilibria and dynamics for mixed vapors of BTX in an activated carbon bed. AIChE J 1999;45:751-60.
- Pagans E, Font X, Sánchez A. Adsorption, absorption, and biological degradation of ammonia in different biofilter organic media. Biotechnol Bioeng 2007;97:515-25.
- Mudliar S, Giri B, Padoley K, Satpute D, Dixit R, Bhatt P, *et al.* Bioreactors for treatment of VOCs and odours-a review. J Environ Manage 2010;91:1039-54.
- Alvarez-Hornos FJ, Izquierdo M, Martínez-Soria V, Penya-Roja JM, Sempere F, Gabaldón C. Influence of ground tire rubber on the transient loading response of a peat biofilter. J Environ Manage 2011;92:1978-85.

- Lee DG, Kim JH, Lee CH. Adsorption and thermal regeneration of acetone and toluene vapors in dealuminated Y-zeolite bed. Sep Purif Technol 2011;77:312-24.
- Yang K, Xue F, Sun Q, Yue R, Lin D. Adsorption of volatile organic compounds by metal-organic frameworks MOF-177. J Environ Chem Eng 2013;1:713-8.
- Mohammadi-Moghadam F, Amin MM, Khiadani Hajian M, Momenbeik F, Nourmoradi H, Hatamipour MS. Application of Glycyrrhiza glabra root as a novel adsorbent in the removal of toluene vapors: Equilibrium, kinetic, and thermodynamic study. J Environ Public Health 2013;2013:986083.
- Oh DI, Song J, Hwang SJ, Kim JY. Effects of adsorptive properties of biofilter packing materials on toluene removal. J Hazard Mater 2009;170:144-50.
- 21. Delhomenie MC, Bibeau L, Heitz M. A study of the impact of particle size and adsorption phenomena in a compost-based biological filter. Chem Eng Sci 2002;57:4999-5010.
- Pei J, Zhang JS. Determination of adsorption isotherm and diffusion coefficient of toluene on activated carbon at low concentrations. Build Environ 2012;48:66-76.
- Hernández-Meléndez O, Bárzana E, Arriaga S, Hernández-Luna M, Revah S. Fungal removal of gaseous hexane in biofilters packed with poly(ethylene carbonate) pine sawdust or peat composites. Biotechnol Bioeng 2008;100:864-71.
- CSID:236. Available from: http://www.chemspider.com/Chemical-Structure.236.html. [Last accessed on 2014 Jun 22, 15:43].
- CSID:1108. Available from: http://www.chemspider.com/Chemical-Structure.1108.html. [Last accessed on 2014 Jun 22, 16:10].
- CSID:7219. Available from: http://www.chemspider.com/Chemical-Structure.7219.html. [Last accessed on 2014 Jun 22, 16:32].
- CSID:7521. Available from: http://www.chemspider.com/Chemical-Structure.7521.html. [Last accessed on 2014 Jun 22, 16:40].
- CSID:7767. Available from: http://www.chemspider.com/Chemical-Structure.7767.html. [Last accessed on 2014 Jun 22, 16:45].
- 29. Lodge JP. Methods of Air Sampling and Analysis. New York: Lewis Publishing Inc.; 1989.
- Song X, Zhang Y, Yan C, Jiang W, Chang C. The Langmuir monolayer adsorption model of organic matter into effective pores in activated carbon. J Colloid Interface Sci 2013;389:213-9.
- Zhang Z, Hara IM, Kent GA, Doherty WO. Comparative study on adsorption of two cationic dyes by milled sugarcane Bagasse. Ind Crops Prod 2013;42:41-9.
- Muñoz R, Villaverde S, Guieysse B, Revah S. Two-phase partitioning bioreactors for treatment of volatile organic compounds. Biotechnol Adv 2007;25:410-22.
- Meylan WM, Howard PH. Estimating octanol-air partition coefficients with octanol-water partition coefficients and Henry's law constants. Chemosphere 2005;61:640-4.
- Znad HT, Katoh K, Kawase Y. High loading toluene treatment in a compost based biofilter using up-flow and down-flow swing operation. J Hazard Mater 2007;141:745-52.
- Fan L, Luo C, Sun M, Li X, Qiu H. Highly selective adsorption of lead ions by water-dispersible magnetic chitosan/graphene oxide composites. Colloids Surf B Biointerfaces 2013;103:523-9.
- 36. Ghaneian MT, Dehvari M, Jamshidi B. A batch study of hexavalent chromium removal from synthetic wastewater using modified Russian knapweed flower powder. Int J Environ Health Eng 2014;3:16.
- Chen H, Wang A. Kinetic and isothermal studies of lead ion adsorption onto palygorskite clay. J Colloid Interface Sci 2007;307:309-16.

Source of Support: Isfahan University of Medical Sciences, Conflicts of Interest: None declared.