



Breakthrough of toluene vapours in granular activated carbon filled packed bed reactor

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ABSTRACT

The objective of this research was to determine the toluene removal efficiency and breakthrough time using commercially available coconut shell-based granular activated carbon in packed bed reactor. To study the effect of toluene removal and break point time of the granular activated carbon (GAC), the parameters studied were bed lengths (2, 3, and 4 cm), concentrations (5, 10, and 15 mg l⁻¹) and flow rates (20, 40, and 60 ml/min). The maximum percentage removal of 90% was achieved and the maximum carbon capacity for 5 mg l⁻¹ of toluene, 60 ml/min flow rate and 3 cm bed length shows 607.14 mg/g. The results of dynamic adsorption in a packed bed were consistent with those of equilibrium adsorption by gravimetric method. The breakthrough time and quantity shows that GAC with appropriate surface area can be utilized for air cleaning filters. The result shows that the physisorption plays main role in toluene removal.

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1. Introduction

Air quality has caused much serious concern recently since it is directly related to human health. Volatile organic compounds (VOCs) are pollutants present in gas and/or liquid streams of many industrial applications, which are controlled by increasingly stringent environmental regulations. In the colour printing works, ethyl acetate and toluene are among the key pollutants included in exhaust air. Ethyl acetate is a kind of irritative and explosive compound with fragrant odor, which is harmful to respiratory systems of mankind. Toluene is a toxic and hydrophobic compound listed in Title III of the 1990 Clean Air Act Amendment proposed by US-EPA.

These contaminants may cause infection to eyes, nose and could even cause cancer, if people are exposed for a long time. They are very harmful for both human health and environment, even at very low concentrations [1–4]. It can be remarked that they are: (1) agents that destroy the ozone stratospheric layer, (2) precursors of photochemical oxidants, (3) agents of the acid rain, (4) elements of the climatic change, (5) agents that affect the nervous system and (6) carcinogenic and mutagenic agents.

The relevant enterprises are thus required to adopt appropriate technologies to reduce those VOCs in the emissions. The current control technologies for these VOCs, such as thermal incineration and wet scrubbing, are usually costly, especially in cases when the

concentrations of these pollutants are not high. The most important methods used for treating VOC gaseous streams are [5–9] (1) absorption, (2) adsorption, (3) condensation, (4) thermal oxidation, (5) catalytic oxidation and (6) photocatalytic oxidation. All these methods provide good results when using the appropriate conditions of concentration, flow and temperature. Many of the gaseous streams involved in industrial processes contain VOC at very low concentrations. Both legislation and human health determine that these streams must be treated to remove the organic compounds.

Adsorption on porous carbon [10–14] is the best method for removal of VOC, H₂S and CS₂ and other odourous compounds from air circulating in ventilation systems, and canisters of carbon are placed in most new automobiles to prevent gasoline vapours from being vented to the air. Because of the large surface area and it's, hydrophobic properties, of activated carbon high adsorption capacity are one of the best options. They are useful for adsorbing molecules such as low molecular weight chlorinated aliphatics and non-chlorinated aromatics are generally treated with air stripping or GAC [15] with molecular weights between 45 and 130 [2,8,13]. The adsorption of organic pollutants can be carried out employing different adsorbents.

Activated carbon adsorption has been considered to be one of the promising methods for controlling VOCs of low concentrations. Activated carbon is characterized with heterogeneously porous structures. Activated carbons have been used for a number of years in air cleaning applications. Generally activated carbon can be made from a variety of raw materials such as peat, coal, nut shell, lignite, saw dust and synthetic polymers [16,17]. Manufactured as grains or

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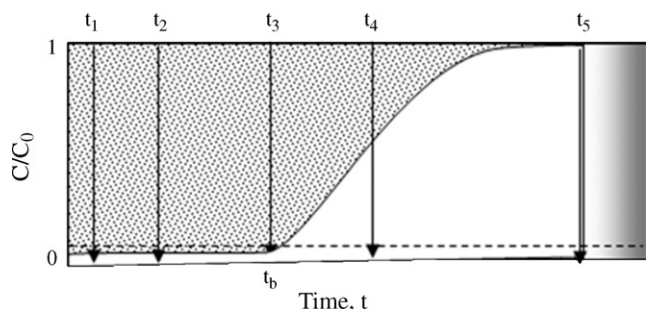


Fig. 1. Breakthrough curve for adsorption.

powdered material, activated carbon is particularly suited for the adsorption and removal of gases and odours in the air [18].

The principle objective of the present study is to find the percent adsorption and breakthrough curve of toluene. The breakthrough curve (transient response of the adsorbent bed to a step-change in the influent concentration) is reflective of the adsorbents performance under dynamic conditions. A relatively larger breakthrough time and gradual increase in the concentration following breakthrough are desirable.

1.1. Mass transfer zone

The mass transfer zone (MTZ) is the active surface of the activated carbon in which adsorption occurs (Fig. 1). When the gas starts flowing in to the bed, the top of the adsorbent in contact with the gas stream quickly adsorbs the pollutant during first contact. The gas stream leaving the bed is practically free from VOC. As the volume of polluted fluid getting through the bed increases, an adsorption zone of mass transfer gets defined. In this MTZ, adsorption is complete and the concentration of pollutant in the bed varies from 100% to approximately 0% of C_0 . This adsorption zone then moves downwards through the bed in relation to time until the breakthrough occurs. When this zone reaches the end of the bed the pollutant in the gas stream cannot be adsorbed any longer. This moment is called “breakpoint” the plot obtained after this point gives the concentration history and is called breakthrough curve.

From a practical point of view, this point allows to determine the pollutant concentration in stream and the volume treated (V_b). For most adsorbent–adsorbate systems, the breakthrough curve is obtained after an outlet concentration of 50% has been reached. To facilitate the calculations of the bed adsorption capacity, the breakthrough curve is often fixed at 50% (t_4) sometimes at 10% (t_3) of the inlet concentration according to the target quality of outlet stream. When the mass transfer zone leaves the bed (t_5), the bed is completely saturated, adsorption in the bed does not occur and the outlet stream which leaves the bed has the same concentration as one enters. The quantity of the adsorbed pollutant at breakpoint can be obtained from the following relation [19,20]

$$q_b = \frac{Q_v t_{0.2\%} C_0}{m_c} \quad (1)$$

where $t_{10\%}$ is the outlet concentration 0.2% of the inlet; C_0 is the inlet pollutant concentration (mg l^{-1}); Q_v volumetric flow rate (l/min); M_c quantity of adsorbent (g).

2. Materials

Commercially available coconut shell-based carbon, were used for the study. Table 1 shows the characteristics of the carbon used for benzene removal study.

For pressure measurement the wire pressure transmitter with integral sensor of 691 series of gauge pressure with adjustable zero

Table 1
Characteristics of the activated carbon.

Parameters	Activated carbon
Raw material	Coconut shell
BET surface area (m^2/g)	1000
Bulk density (g/ml)	0.5
Particle density (g/ml)	0.85
Ash content (on dry basis) (%)	3.59
Moisture content (%)	5.0
pH_{zpc}	5.3
Conductivity ($\mu\text{S/cm}$)	94.0
Particle size, mesh	8–20
Elemental analysis (%)	
C	66.0
H	3.5
N	0.331
O	29.6
S	0.56
Acidic surface functional groups (meq/g)	
Carboxylic	
Phenolic	0.105
Lactonic	0.006
Carbonyl	0.003
	Nil
FTIR frequencies	
OH stretching (intermolecular diamer)	3450
CO stretching (aldehydic)	1725
=CH stretching (alkenes)	3040

Table 2
Physical properties of adsorbates used for the study.

Sl. no	Characteristics	Toluene
1	Molecular formula	C_7H_8
2	Molecular weight (g mol^{-1})	92.11
3	Dipole moment (dB)	0.4
4	Molecular diameter	0.467
5	Molecular length	0.568
6	Dielectric constant	2.3
7	Heat of vapourization (kJ mol^{-1})	39.2
8	Bulk liquid density (cm^3/g) at 25 °C	0.867
9	Saturated vapour pressure (atm) at 25 °C (kPa)	0.037

point and full scale in the range 0–2 bar of Instrument Research Associates (IRA) Pvt. Ltd. has been used.

3. Analytical methods

Concentrations of VOC were analyzed by using a Nucon (model-5765) gas chromatograph equipped with a capillary column type AT-5 (60 m \times 0.53 mm \times 1 μm film thickness, temperature limits: –20 to 350 °C) and with a flame ionization detector. The injector, oven and detector temperature were maintained at 220, 50, and 250 °C, respectively. The hydrogen gas was used as the fuel and nitrogen was used as the carrier gas at a flow rate of 20 ml/min. The calibration curve was prepared by injecting known amounts of the VOC into a sealed bottle equipped with a Teflon septum according to the standard procedure [21]. For the calibration, air samples are drawn by a 1 ml gas lock syringe (Hamilton–Bonaduz–Schweiz) and analyzed by gas chromatograph. The air samples were drawn from the various sampling ports by using a gas lock syringe and analyzed. Table 2 shows the physical properties of toluene used for the study.

4. Experiment

Fig. 2 shows the schematic diagram of experimental set-up. The experiments were carried out under dynamic condition. Known quantity of carbon was weighed and filled in the 11 ml volume of glass tubes and closed air tightly. The glass tube has provision

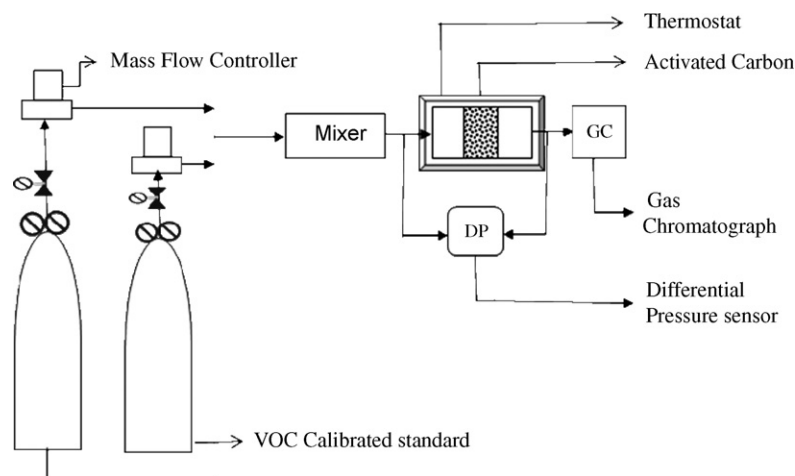


Fig. 2. Schematic experimental set-up.

of inlet/outlet with festo connector. The pressure sensor has been connected through this inlet/outlet to maintain and measure the required pressure inside the tube. After the assurance of leak proof, the VOC was allowed to flow from the cylinder through the adsorption bed by mass flow controller at required flow rate. The entire set up was fitted in the thermostatic controlled oven for various temperatures. The inlet and outlet concentration were measured at regular intervals by gas chromatograph to find out the breakthrough for various pollutants.

5. Results and discussion

Tables 1 and 2 show the physiochemical properties of adsorbents and adsorbates. The properties will also influence the adsorption capacity and breakthrough time of the GAC. But in our present study it has been observed that bed depth, concentration and flow rate influence the adsorption capacity and breakthrough time under dynamic condition. The effect of these parameters on the toluene removal, breakthrough and adsorptive capacity with GAC in packed bed are discussed in detail.

5.1. Effect of bed depth

To find out the effect of bed length on the breakthrough and adsorption capacity of toluene vapours, the experiments were carried out in 5 mg l^{-1} of toluene passed at the flow rate of 30 ml/min at different bed lengths i.e. 2, 3, and 4 cm. The data were shown in Fig. 3 and Table 3.

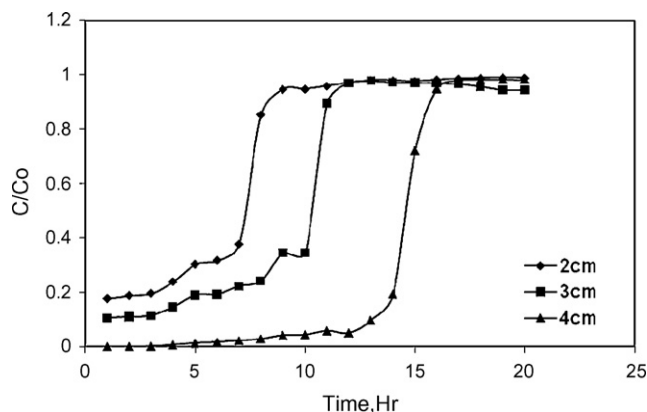


Fig. 3. Breakthrough curve for different bed depth (toluene).

The tests with different bed lengths give breakthrough curves of the same characteristic 'S' shape for systems with a favourable isotherm shape. In Fig. 3 and Table 4, we can observe that for a given permissible value, say, 0.2 mg l^{-1} , if we closely observe the breakpoint time for toluene at 2 cm bed length is 7.5 h, at 3 cm bed length is 10.5 h and at 4 cm bed length is 14.9 h. These results show that the breakthrough volume varies with increasing the bed length. This is because of mass transfer phenomenon takes place in the process. But with longer beds, the mass transfer zone is a smaller fraction of the bed length, and a greater fraction of the bed is utilized. When bed length is decreases, axial dispersion phenomenon predominates in the mass transfer and reduces the diffusion of adsorbate in to adsorbent. The pollutant has not enough time to diffuse into the carbon. Subsequently, the treated volume of gas stream also will decrease.

The concentration profile in the mass transfer zone acquires a characteristic shape and width that do not change as the zone moves down the bed for the ideal adsorption systems. Breakthrough curve analysis is mainly considered in practice to analyze the effect of bed length on adsorption. This is because bed length mainly affects the breakpoint time. Moreover, an increase in the bed adsorption capacity (q_b) was also observed with increase in bed depth, the data's were shown in Table 3. The adsorption capacity for 2 cm bed length is 401.79 mg/g , 3 cm bed length is 403.85 mg/g and 4 cm bed length 406.36 mg/g . The capacity of the solid is obtained by integration of a complete breakthrough curve or from separate equilibrium tests. Increase in the adsorption capacity with bed length, because increase in quantity of carbon subsequently increases the available specific surface of the adsorbent for more

Table 3

Adsorption breakthrough data for toluene on different bed length, 30 ml/min , 4 cm bed length, 5 mg l^{-1} .

Depth (cm)	Mass (g)	t_b (h)	Capacity (mg/g)
2	2.8	7.5	401.79
3	3.9	10.5	403.85
4	5.5	14.9	406.36

Table 4

Adsorption breakthrough for toluene on different concentration 20 ml/min , 3 cm bed length.

Initial concentration (mg l^{-1})	t_b (h)	Capacity (mg/g)
5	15.5	461.30
10	10	476.19
15	7.5	535.71

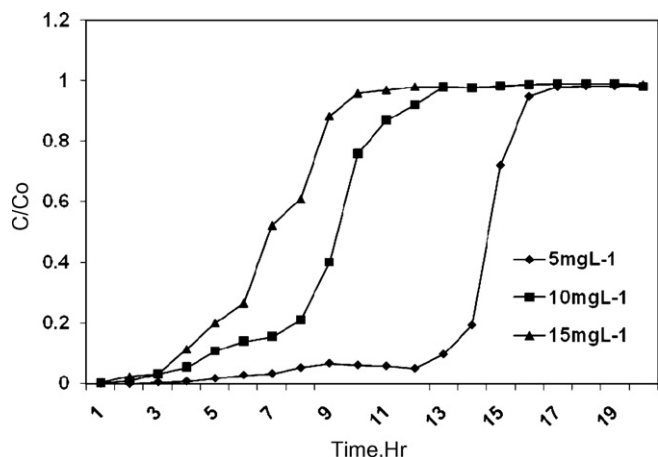


Fig. 4. Effect of concentration on breakthrough curve of toluene.

fixation binding sites. Then it follows that a delayed breakthrough leads to larger volume of treated gas stream.

5.2. Effect of concentration

To study the effect of concentration on the breakthrough time and adsorption capacity the concentration was varied at 5, 10, and 15 mg l^{-1} at the flow rate of 20 ml/min and the bed length is 3 cm. The results were shown in Figs. 4 and 5 and Table 4. Fig. 4 shows breakthrough curves of toluene at different concentrations. There were good breakthrough curve shapes. The sudden change in shape of the curve from 5 to 10 mg l^{-1} but only a shift in curve from 10 to 15 mg l^{-1} may be attributed to the intermolecular, interlayer and intralayer interactions of molecules, which may be possible after a certain concentration is crossed [22]. However, the concentration of gas stream gradually increases at outlet, because the resistance of mass transfer. It can also be observed from Fig. 4 that at the lowest concentration the percentage removal is above 90% after 3 h also. It is an indication that at low concentration the bed saturates very slowly.

From the above three curves it was observed that the saturation time of the bed (age of the adsorption column) is more when the concentration is lower; which is very much obvious. At higher concentration the bed saturates very early, the change in behaviour is sudden and drastic from 5 to 10 mg l^{-1} , i.e. there is a total change in the trend of the curve itself. But when concentration is changed from 10 to 15 mg l^{-1} there is only a shift towards lesser age of filter but not change in trend of the curve. The adsorption capacity for 5, 10, and 15 mg l^{-1} at the flow rate of 20 ml/min is 461.30, 476.19,

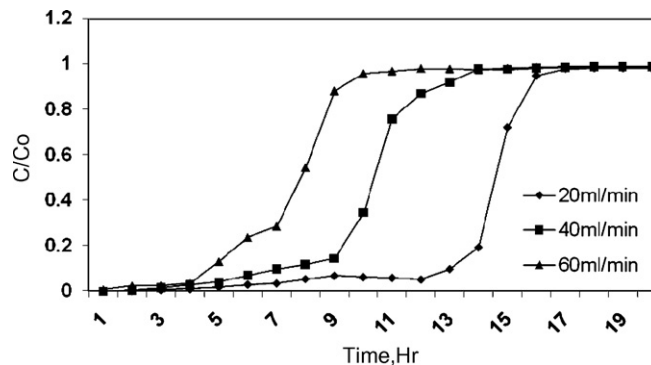


Fig. 6. Effect of flow rate on breakthrough toluene at 25 mg l^{-1} .

Table 5

Adsorbent breakthrough for toluene on different flow 3 cm column depth, 5 mg l^{-1} .

Flow (ml/min)	t_b (h)	Capacity (mg/g)
20	15	357.14
40	11	523.80
60	8.5	607.14

and 535.71 mg/g , respectively. This may be due to the interlayer and intralayer interactions. As the concentration increases over a certain threshold value there are chances of molecules adhering or branching to the molecules in their near neighborhood thus keeping the adsorption still going on [23,24].

The effect of moderate changes in feed concentration on the breakthrough curve can be predicted, since the width of the mass transfer zone does not change. The equilibrium capacity is determined from the adsorption isotherm, and the break point time is proportional to the capacity of the solid and to the reciprocal of the feed concentration. Laboratory tests using higher than expected concentrations of a pollutant may be made to shorten the time for breakthrough test. Very large differences in concentration may lead to errors in scale up because of a change in the mass transfer co-efficient.

5.3. Effect of flow rate

To examine the effect of the flow rate through the bed depth, the flow rate varied from 20, 40, and 60 ml/min at 5 mg l^{-1} of toluene and 3 cm bed length. The results are given in Figs. 6 and 7 and Table 5. Fig. 7 shows that at the flow rate increased the amount of adsorption reduced, at lower flow rates there was linear behaviour and at higher flow rates there was a sudden decrease in the percentage removal. The fact that the section area of the column is

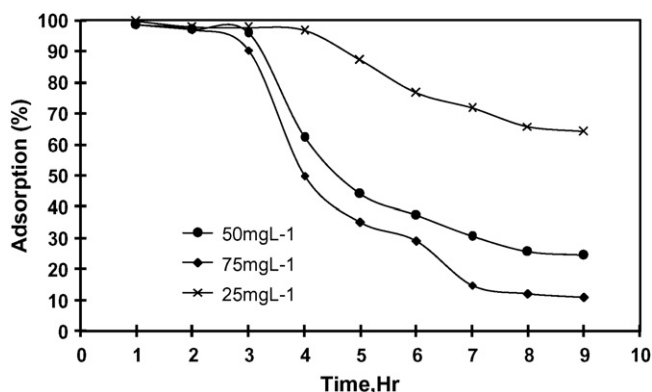


Fig. 5. Effect of concentration on adsorption at 60 ml/min toluene.

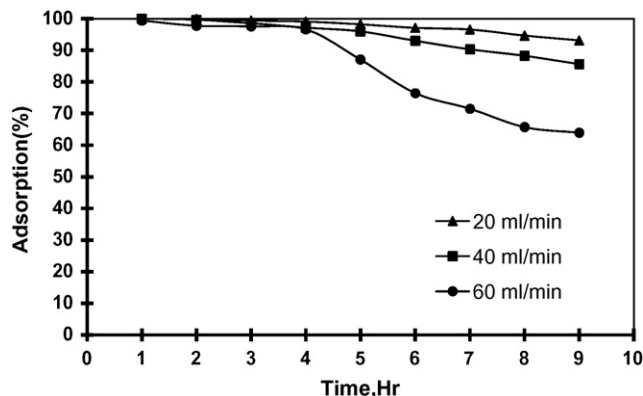


Fig. 7. Effect of flow rate on percent adsorption at 5 mg l^{-1} of toluene.

uniform implies that the linear flow rate through the bed is directly proportional to the overall volumetric flow rate through the packed bed and the uptake of pollutant on to the carbon decreases, when the linear flow rate through the bed increases and the residence time available for each molecule to get adsorbed on the adsorption sites reduces. Hence many molecules escape unadsorbed as the flow rate increases. Also at higher flow rates there are chances of already adsorbed molecules getting desorbed and thus getting carried away with the feed flow. An increase in the flow rate reduces the volume treated efficiently until breakthrough point and therefore decreases the service time of the bed. This is due to the decrease in contact time between the pollutant and adsorbent at higher flow rates. As the adsorption rate is controlled by intraparticle diffusion, an early breakthrough occurs leading to low bed adsorption capacity. These results are also in agreement with those referred to the literature [25].

When the flow rate decreases, the contact time in the column is longer, intraparticle diffusion then becomes effective. The adsorption capacity also increases for 20 ml/min is 357.14 mg/g, 40 ml/min is 523.80 mg/g and 60 ml/min is 607.14 mg/g. Thus the pollutants have more time to diffuse amidst the particles of carbon and a better adsorption capacity is obtained. At a lower flow rate, the carbon gets saturated early, certainly because of a increased contact time, a larger amount of pollutants adsorbed on the carbon and a weak distribution of the gas stream into the column, which leads to lower diffusivity of the gas stream amidst the particles of the carbon. This shows an increase in the uptake of the pollutant due to the intraparticle phenomena. Therefore the volume treated, the breakthrough time and bed adsorption capacities were reduced, and a wide volume of gas stream is purified with efficient elimination.

Fig. 6 shows that, for any given permissible limit of the concentration the breakpoint time decreases with increasing value. This observation can be made at all concentrations. The theoretical 'S' shaped curve is obtained for higher flow rates, but at lower flow rate the curve tends to show a linear behaviour, up to the number of experimental hours considered here. This is a clear indication that for any given permissible limit the adsorption column saturates slowly at lower flow rates and much earlier when the flow rate is high. This is because at higher flow rates more molecules compete for the adsorption sites at a given time and hence the bed saturates earlier. The effect of flow rate can be explained mathematically by the equation below:

$$t = \frac{L \times \rho_b \times (W_{\text{sat}} - W_0)}{U_0 \times C_0} \quad (2)$$

where L is the length of bed, ρ_b is the bulk density of the carbon, W_0 weight of carbon at initial, W_{sat} is weight of carbon at equilibrium or saturated value, C_0 is the initial concentration, U_0 is the superficial velocity, which means that the break point time t , is inversely proportional to U_0 for a fixed volume of bed the velocity depends only on the flow rate. This means that the break point time is inversely proportional to flow rate. Hence as flow rate increases the break point time decreases.

This behaviour is clearly shown in the experiments carried out. It can be observed from Fig. 6 that the break point time is 15 h when the flow rate is 20 ml/min, 11 h at 40 ml/min and 8.5 h at 60 ml/min.

6. Conclusion

Experiments were carried out to study the breakthrough curve of toluene vapours on granular activated carbon. The various parameters considered were, flow rate, concentration, and length of bed on percentage adsorption and break point time. The percentage of adsorption was maximum at lower flow rates. At higher flow rates the percentage adsorption was less and break point

time was reached earlier. At higher concentration the adsorption percentage was lesser than that at the lower concentration. But the total amount of loading or adsorption capacity increased with the increase in concentration. This indicates that the multi layer adsorption takes place; inter layer and intralayer interactions between the adsorbed molecules. Increase in length of the bed provides a better adsorption percentage and higher breakpoint time.

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References

- [1] M. Tancredi, R.Z. Wilson, L.E. Crouch, The carcinogenic risk of some organic vapors indoors: a theoretical survey, *Atmos. Environ.* 21 (10) (1987) 2187–2205.
- [2] K.L. Foster, R.G. Fuerman, J. Economy, S.M. Larson, M.J. Rood, Adsorption characteristics of trace volatile organic compounds in gas streams on to activated carbon fibers, *Chem. Mater.* 4 (5) (1992) 1068–1073.
- [3] L.A. Wallace, E.D. Pellizzari, B.P. Leaderer, H. Zelon, L.S. Sheldon, Emissions of volatile organic compounds from building materials and consumer products, *Atmos. Environ.* 21 (1987) 385–393.
- [4] V. KGupta, N. Verma, Removal of volatile organic compounds by cryogenic condensation followed by adsorption, *Chem. Eng. Sci.* 57 (2002) 2679–2696.
- [5] E.N. Rudy, L.A. Carroll, Select the best VOC control strategy, *Chem. Eng. Prog.* 89 (1993) 28–35.
- [6] J. Benkhedda, J.N. Jaubert, D. Barth, L. Perrin, Experimental and modelled results describing the adsorption of toluene onto activated carbons, *J. Chem. Eng. Data* 45 (4) (2000) 650–653.
- [7] M.P. Cal, S.M. Larson, M.J. Rood, Experimental and modelled results describing the adsorption of acetone and benzene onto activated carbon fibres, *Environ. Prog.* 13 (1) (1994) 26–30.
- [8] A.F. Dolidovich, G.S. Akhremkova, V.S. Effremtsev, Novel technologies of VOC decontamination in fixed, moving and fluidized catalyst-adsorbent beds, *Can. J. Chem. Eng.* 77 (2) (1999) 342–355.
- [9] A.V. Vorontsov, E.N. Savinov, P.G. Smirniotis, Vibrofluidized and fixed-bed photocatalytic reactors: case of gaseous acetone photooxidation, *Chem. Eng. Sci.* 55 (2000) 5089.
- [10] M.K. Clark, B.W. Lykins, *Granular Activated Carbon*, Lewis Publ., MI, 1989, pp. 257–293.
- [11] P.N. Cheremisinoff, M.F. Ellerbush, *Carbon Adsorption Handbook*, Ann Arbor Sci., Ann Arbor, MI, 1978.
- [12] R.C. Bansal, J.B. Donnet, N. Stoeckli, *Active Carbon*, Marcel Dekker Inc., NY, 1988.
- [13] M.J. Rhul, Recovery of VOCs via adsorption onto activated carbon, *Chem. Eng. Prog.* 89 (7) (1993) 37–41.
- [14] E.D. Dimotakis, M.P. Cal, J. Economy, M.J. Rood, S.M. Larson, Chemically treated activated carbon cloths for removal of volatile organic carbons from gas streams: evidence for enhanced physical adsorption, *Environ. Sci. Technol.* 29 (7) (1995) 1876–1880.
- [15] M.H. Stenzel, S.U. Gupta, Air pollution control with granular activated carbon and air stripping, *J. Hazard. Waste Manage.* 35 (12) (1995) 1304–1309.
- [16] Y.-C. Chiang, P.-C. Chiang, C.-P. Huang, Effects of pore structure and temperature on voc adsorption on activated carbon, *Carbon* 39 (2001) 523–534.
- [17] R.R. Bansode, J.N. Lasso, W.E. Marshall, R.M. Rao, R.J. Portier, Adsorption of volatile organic compounds by pecan shell and almond shell-based granular activated carbons, *Bioresour. Technol.* 90 (2003) 175–184.
- [18] P. Navarri, D. Marchal, A. Ginestet, Activated carbon fibre material for VOC removal, *Filtr. Separat.* 2 (2001) 34–40.
- [19] L. Warren, Mc. Cabe, C. Julian, Smith, P. Harriott, *Unit Operations of Chemical Engineering*, 5th ed., McGraw-Hill, Inc. International Editions, 1993.
- [20] R.H. Perry, W.D. Green, Perry's *Chemical Engineers' Handbook*, 7th ed., Mc. Graw Hill International Editions, 1998.
- [21] J.P. Lodge, *Methods of Air Sampling and Analysis*, Lewis Publishing Inc., New York, 1989.
- [22] J.L. Riccardo, A.J. Ramirez-Pastor, F. Romá, Multilayer adsorption with multisite occupancy: an improved isotherm for surface characterization, *Langmuir* 18 (6) (2002) 2130–2134.
- [23] X. Hu, B. King, D.D. Do, Ternary desorption and displacement kinetics of gases in activated carbon, *Gas Separat. Purif.* 8 (3) (1994) 187–190.
- [24] X. Hu, B. King, D.D. Do, Ternary adsorption kinetics of gases in activated carbon, *Gas Separat. Purif.* 8 (3) (1994) 175–186.
- [25] D. Das, V. Gaur, N. Verma, Removal of volatile organic compound by activated carbon fiber, *Carbon* 42 (2004) 2949–2962.