Vapor phase adsorption of xylene on granular activated carbon – Experimental and theoretical breakthrough curves

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Experiments have been carried out to study adsorption of xylene (a volatile organic compound) on the granular activated carbon, using the experimental variables, such as inlet gas concentration (2400 – 6200 ppm), gas flow rate (50 mL/min) and height of the adsorbent bed (0.015 – 0.025 m). The breakthrough curves are then drawn between ratios of outlet gas concentration to inlet gas concentration and time for different operating conditions. A mathematical model is developed to predict the breakthrough curves of xylene on granular activated carbon. The model shows the effects of the gas-particle film mass transfer resistance, adsorbent pore diffusion and instantaneous local adsorption equilibrium at the pore surface. The experimental data and the corresponding model simulated results have been compared and are found to be in good agreement. The breakthrough time increases with increase in bed height and decreases with increase in inlet concentration.

Keywords: Adsorption, Breakthrough curve, Granular activated carbon, Vapor phase adsorption, Xylene

Rapid economic development and urban population growth have triggered a series of challenges to the endeavors of maintaining the clean air. Urban air quality is cause of public concern, largely as a result of instances of smog and health problems. New pollutants are being increasingly recognized. Air pollution sources have grown and so also the pollutants. Some of these have led to the emission of some hazardous air pollutants like volatile organic compounds. Volatile organic compounds (VOCs) are chemicals that have high vapor pressure exceeding 0.5 kPa at 25°C (ref.1), like benzene, toluene, xylene, formaldehyde and methylene chloride. Major VOC emission sources are automobiles exhaust (45%) followed by industrial sites (41%) and remaining from solid waste disposal and from miscellaneous sources2. The acute and chronic effects of VOCs on health and environment include eye irritation, nose irritation, throat irritation, cancer, liver damage and kidney damage. Hence, many VOCs have been identified as toxic and carcinogenic3,4. Approximately 235 million tons of VOCs are released per year into the atmosphere by man-made sources3. The subject has become important because of the impact on environment and human.

Recommended strategies for reducing organic vapors include product substitution or reformulation, thermal or catalytic incineration and activated carbon adsorption followed by regeneration or catalytic incineration of the highly concentrated stream5. The removal of volatile organic compounds commonly performed by adsorption is of great interest for the air quality control. The key parameter in adsorption process is the nature of porous solid medium. A high surface area or high micropore volume can be achieved due to the porous structure of the solid and thus high adsorptive capacity. The breakthrough curve is reflective of the adsorbent performance under dynamic conditions. A relatively larger breakthrough time and gradual increase in the concentration following breakthrough are desirable. There are various adsorbents available for VOC removal such as pyrolysed sewage-sludge, metal-organic frameworks MIL-101, Pt-catalysts by impregnation or doping of carbon aerogels, coconut shells based carbons, stainless steel microfibrous entrapped activated carbon composites, etc7-11. Hence, from the literature review it is evident that adsorption on porous carbon is a good option for the removal of VOCs. In the
present study granular activated carbon has been used as an adsorbent for removal of xylene.

The major objectives of this study include to: (i) set-up of an experimental test bench to study the adsorption phenomena for the removal of xylene by commercially available granular activated carbon, (ii) obtain breakthrough curves under varying operating conditions such as inlet concentrations, gas flow rate and height of the adsorbent bed, and (iii) develop a mathematical model to understand the adsorption mechanism and predict the breakthrough profiles.

Mathematical modeling

In this section, a mathematical model is presented to predict the time-dependent (unsteady state) concentration profiles of the xylene on a solid adsorbent under isothermal conditions. One important point that may be noted is that, in reality the steady-state condition never exists in the bed of adsorbing materials during adsorption. Hence, a finite adsorption rate always prevails in the bed. The steady-state is achieved only when the bed reaches saturation levels. The present mathematical model takes account of both external and internal mass transfer resistances as well as of non-ideal plug flow along the column. Simultaneously, instantaneous local adsorption equilibrium on the pore surface is considered. The following assumptions are made for developing the mathematical model for the adsorption of xylene on granular activated carbon:

(i) The system operates under isothermal conditions.
(ii) Intraparticle mass transport is due to Fickian diffusion, and is characterized by $D_e$. Mass transfer across the boundary layer surrounding the solid particles is characterized by the external-film mass transfer coefficient $k_m$.
(iii) Axial dispersion is considered to account for non-ideal flux along the longitudinal axis of the column.
(iv) The macroporous adsorbent particles are spherical and homogeneous in size and density.

The present model is based on three governing equations, namely: (a) species balance of the adsorbing component in the bed, (b) species balance of the component inside the pores of the adsorbent, and (c) instantaneous local adsorption equilibrium at the pore surface.

Based on the preceding assumptions, the mass balance of the adsorbing component in a cross-section of the column in a non-dimensional form yields:

$$ \left( \frac{\partial C_b^*}{\partial \tau} \right) = -\frac{1}{t_{res}} \left( \frac{\partial C_b^*}{\partial z^*} \right) + P \left( \frac{\partial^2 C_b^*}{\partial z^*^2} \right) - Z(C_b^* - C_{ps}^*) \quad \ldots (1) $$

where $t_{res} = \frac{L}{V_z}$, $P = \frac{D_L}{L^2}$ and $Z = \frac{3k_m}{R_p \epsilon_b}$

$$ C_b^* = \frac{C_b}{C_{b0}} $$

$$ z^* = \frac{z}{L} $$

and $C_{ps}^* = \frac{C_{ps}}{C_{b0}}$

where $C_b$ is the concentration of xylene in the bulk gas phase (kg/m$^3$); $C_{b0}$, the initial concentration of xylene in the gas phase (kg/m$^3$); $C_{ps}$, the concentration of xylene at the external surface of the adsorbent particle (kg/m$^3$); $L$, the length of the fixed bed (m); $V_z$, the interstitial velocity (m/s); $D_L$, the axial dispersion coefficient (m$^2$/s); $k_m$, the external-film mass-transfer coefficient (m/s); $R_p$, the radius of the adsorbent particle (m); $\epsilon_b$, the bed porosity; $C_b^*$, the dimensionless concentration of xylene in the bulk gas phase; $C_{ps}^*$, the dimensionless concentration of xylene at the external surface of the adsorbent particle; and $z^*$, the dimensionless length of the fixed bed column.

The dimensionless initial and boundary conditions for Eq. (1) are as follows:

at $t = 0$ and at all $z^*$, $C_b^* = 0$

at $t > 0$ and at $z^* = 0$, $C_b^* = 1$

at $z^* = 1$, $\frac{\partial C_b^*}{\partial z^*} = 0$

The intra-pellet mass transfer is due to the diffusion of xylene molecules through the pore and here Langmuir isotherm is assumed to describe the
equilibrium relationship between amount adsorbed and concentration of xylene in the pores. Hence, the mass balance of the adsorbing component inside the pores of the adsorbent in non-dimensional form is given by the following relationship:

\[
\frac{\partial C_p^*}{\partial t} = \frac{T \alpha (1 + KC_{b0}C_p^*)^2}{\alpha (1 + KC_{b0}C_p^*)^2 + \rho (1 - \alpha) q_m K} \left[ \frac{\partial^2 C_p^*}{\partial r^2} + \frac{2}{r^*} \frac{\partial C_p^*}{\partial r^*} \right]
\]

... (2)

where \( T = \frac{D_e^*}{R_p^*} \)

\[ C_p^* = \frac{C_p}{C_{b0}} \]

\[ r^* = \frac{r}{R_p} \]

where \( C_p \) is the concentration of xylene in the gaseous phase inside the pores (kg/m\(^3\)); \( \alpha \), the particle porosity; \( q_m \), the maximum adsorption capacity of the adsorbent (kg/kg); \( K \), the Langmuir isotherm constant (m\(^3\)/kg); \( \rho \), the particle density (kg/m\(^3\)); \( D_e^* \), the effective diffusivity (m\(^2\)/s); \( C_p^* \), the dimensionless concentration of xylene inside the pores of the adsorbent particle; and \( r^* \), the dimensionless radius of the adsorbent particle.

The non-dimensional initial and boundary conditions for Eq. (2) are as follows:

at \( t = 0 \), \( C_p^* = 0 \)

at \( r^* = 0 \), \( \frac{\partial C_p^*}{\partial r^*} = 0 \)

at \( r^* = 1 \), \( \frac{\partial C_p^*}{\partial r^*} = R (C_b^* - C_p^*) \) where \( R = \frac{k_m R_p}{D_e} \)

where \( q_m \) and \( K \) are the Langmuir isotherm parameters, which are usually obtained from the experimental adsorption data under equilibrium conditions. For the model simulation, \( q_m \) and \( K \) are used as adjusted parameter models for predicting the breakthrough curves under varying conditions.

**Numerical solution technique**

Since non-linear adsorption equilibrium is considered, the preceding set of partial differential equations (Eqs 1 & 2) was solved numerically by a reduction to a set of ordinary differential equations using the orthogonal collocation method\(^{13,14}\). Equation (1) was discretized in 14 collocation points including the boundary point and Eq. (2) was discretized in 8 collocation points including the boundary point. The solution of this set of coupled equations was performed by a mathematical algorithm, developed in MATLAB (v.7.1) software, implemented into a computer program. The program used the ODE15s solver from MATLAB that applies the variable order, variable step gear method. On a Pentium IV machine the CPU time of computation was found to be less than a minute.

**Experimental Procedure**

Commercially available granular activated carbon was used for the present study. It was procured from Loba Chemie Pvt. Limited, India. The experimentally determined characteristics of granular activated carbon used for xylene removal are given below:

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average particle diameter, mm</td>
<td>15</td>
</tr>
<tr>
<td>BET surface area, m(^2)/g</td>
<td>564</td>
</tr>
<tr>
<td>Pore volume, cm(^3)/g</td>
<td>0.32</td>
</tr>
<tr>
<td>Average pore diameter, Å</td>
<td>22.68</td>
</tr>
<tr>
<td>Particle density, kg/m(^3)</td>
<td>400</td>
</tr>
</tbody>
</table>

Xylene used in the experiments was of AR grade and was procured from Sd fine-Chem Limited, India.

**Experimental set - up**

Figure 1 is the schematic of the experimental set-up designed and used for carrying out adsorption experiments. The set-up consists of three sections, namely a gas preparation section, an adsorption section, and an analytical section. In the gas preparation section, carrier gas (nitrogen in this case) is bubbled in the liquid xylene contained in a vertical glass column (0.7 m long and 0.05 m diameter). Isothermal conditions are maintained in the column by circulating water at a fixed temperature around the column. The bubbler is made of SS of 6.35 mm diameter tube whose bottom end is closed and the outer surface is perforated with a hole of diameter 0.08 mm near the bottom and measured quantity of nitrogen is bubbled in the xylene liquid through the hole. Another part of nitrogen is sent directly to the mixing chamber for getting the desired dilution. The
resulting gas-vapor mixture from the mixing chamber is sent to the adsorption section consisting of a vertical glass column (I.D = 5 cm, L = 10 cm) filled with an adsorbent with provisions for the gas inlet and outlet. The effluent gas stream from the adsorption section is passed to the analytical section consisting of a gas chromatograph [MICRO-9100, Netel (India) Limited] with flame ionization detector (FID) and data station. A computer is connected to the data station to store the peak area. There is a provision of a by-pass line for measuring the inlet concentration of xylene through gas chromatograph.

**Procedural step**

Prior to start of the experiments the glass column was filled with xylene up to a certain height for getting the desired concentration of xylene in a gas-vapor mixture. Water was circulated at a fixed temperature around the column and a sufficient time was given (1 h) to attain the required temperature. The weighed amount of granular activated carbon was placed into the adsorption column and then supported by glass wool from both sides to avoid any carryover of adsorbent particles. Nitrogen gas at a measured flow rate bubbled through xylene and also it was sent directly to the mixing chamber for dilution at a fixed flow rate. The concentration of the inlet gaseous mixture was measured by GC prior to the start of the adsorption process. It took around 3 – 4 h for the inlet gas to reach the steady state and then this gaseous mixture was allowed to pass through the adsorption column. As the adsorption process started, the transient concentrations of exit gas from the adsorption column (breakthrough data) was monitored and measured by GC. The concentration of xylene in an unknown gas-vapor mixture was observed by using a calibration curve. Breakthrough curves are then drawn for different operating conditions. In each case breakthrough time is found out which is defined as time taken for the effluent concentration to reach 5% of the inlet concentration. The operating conditions used for the adsorption experiments are given below:

- **Inlet xylene concentration, ppm**: 2400 & 6200
- **Gas flow rate, mL/min**: 50
- **Weight of adsorbent, g**: 4 & 6.63
- **Bed height, m**: 0.015 & 0.025
- **Adsorption temperature, K**: 313

**Results and Discussion**

**Effect of bed height**

To determine the effects of bed height on the breakthrough characteristics, the experiments were carried out for varying bed height (0.015 and 0.025 m) at a constant inlet gas concentration of 6200 ppm and a constant gas flow rate of 50 mL/min. Figure 2 describes the experimentally obtained breakthrough curves for xylene under the various bed heights. The breakthrough time increases from 15500 s to 30300 s as the bed height increases from 0.015 m to 0.025 m. The increase in the breakthrough time with increase in the bed height as observed from Fig. 2 can be explained in terms of the total amount of adsorbent present in the bed. With increase in the bed
height which implies more amount of adsorbent under identical flow rates and inlet gas concentrations the bed will get saturated in a longer time.

Figure 2 also shows that the model predictions agree well with the experimental data. For the model predictions of the breakthrough curves under identical experimental conditions, the values of \( q_m \) and \( K \) had to be adjusted. The corresponding values of \( q_m \) and \( K \) obtained for a bed height of 0.015 m are 0.131 kg/kg and 57.569 m³/kg respectively. Similarly, for a bed height of 0.025 m, \( q_m \) and \( K \) values obtained are 0.127 kg/kg and 58.518 m³/kg respectively.

**Effect of inlet xylene concentration**

To determine the effects of inlet xylene concentration on the breakthrough characteristics, the experiments were carried out for varying xylene inlet concentration (2400 and 6200 ppm). For each run 4 g of the adsorbent was taken and the gas flow rate was set at 50 mL/min. Figure 3 describes the experimentally obtained breakthrough curves for xylene under the various gas inlet concentrations. The breakthrough time decreases from 18700 s to 15500 s as the inlet concentration increases from 2400 ppm to 6200 ppm. The increase in the breakthrough time with the decrease in inlet concentration levels as observed from Fig. 3 can be explained in terms of the total amount of xylene. With decrease in the inlet concentration under identical flow rates, the total amount of xylene (moles) entering the macro-pores of the adsorbent is less. Therefore, the saturation of the adsorbent bed is delayed and occurs in relatively longer time.

Figure 3 also shows that the model predictions agree well with the experimental data. Again for the model predictions of the breakthrough curves under identical experimental conditions, the values of \( q_m \) and \( K \) need to be adjusted. The corresponding values of \( q_m \) and \( K \) obtained for inlet concentration of 2400 ppm are 0.133 kg/kg and 57.424 m³/kg respectively. Similarly, for inlet concentration of 6200 ppm, \( q_m \) and \( K \) values obtained are 0.131 kg/kg and 57.569 m³/kg respectively.

**Simulation studies**

It has been found that the values of adjustable parameters \( q_m \) and \( K \) are almost the same. Hence, for further simulations \( q_m \) and \( K \) are selected to be 0.13 kg/kg and 57.5 m³/kg respectively. Here, simulations have been carried out in order to study the effects of some variables like flow rate, particle diameter and pore diffusivity on breakthrough curve which could not be observed experimentally. The average diameter of the adsorbent particle used in all experiments is 1.5 mm. Hence, the effect of different diameter of the adsorbent particles on breakthrough curves can also be predicted through simulation of adsorption column. The various parameters used in simulations studies such as \( Re, Sc, Pe \), mass transfer coefficient \( (k_m \text{ in m/s}) \), axial dispersion coefficient \( (D_L \text{ in m²/s}) \), and effective diffusivity \( (D_e \text{ in m²/s}) \) are reported in Table 1. The values of \( k_m \), \( D_L \) and \( D_e \) are found from the reported correlations.

<table>
<thead>
<tr>
<th>( Q ) mL/min</th>
<th>( D_p ) m</th>
<th>( V_i \times 10^4 ) m/s</th>
<th>( Re )</th>
<th>( Sc )</th>
<th>( Pe )</th>
<th>( D_L \times 10^8 ) m³/s</th>
<th>( k_m ) m/s</th>
<th>( D_e \times 10^8 ) m³/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0.0015</td>
<td>3.371</td>
<td>0.0383</td>
<td>1.656</td>
<td>0.2112</td>
<td>9.445</td>
<td>0.0116</td>
<td>1.6567</td>
</tr>
<tr>
<td>75</td>
<td>0.0015</td>
<td>6.369</td>
<td>0.0718</td>
<td>1.656</td>
<td>0.3943</td>
<td>5.059</td>
<td>0.0121</td>
<td>1.6567</td>
</tr>
<tr>
<td>50</td>
<td>0.001</td>
<td>4.2463</td>
<td>0.0319</td>
<td>1.656</td>
<td>0.1761</td>
<td>7.5524</td>
<td>0.0173</td>
<td>1.6567</td>
</tr>
<tr>
<td>50</td>
<td>0.002</td>
<td>4.2463</td>
<td>0.0638</td>
<td>1.656</td>
<td>0.3509</td>
<td>7.5793</td>
<td>0.0090</td>
<td>1.6567</td>
</tr>
<tr>
<td>400</td>
<td>0.0015</td>
<td>33.9</td>
<td>0.3831</td>
<td>1.656</td>
<td>1.8375</td>
<td>1.0856</td>
<td>0.0146</td>
<td>1.6567</td>
</tr>
</tbody>
</table>

\*\( Q \) is the volumetric flow rate (mL/min).
\**\( D_p \) is the diameter of the adsorbent particle (m).
Effect of gas flow rate

As observed from Fig. 4, both the breakthrough time and the total adsorption time decrease with the increase in flow rate. Here, the breakthrough time has decreased from 20540 s to 8563 s as the gas flow rate is increased from 40 mL/min to 75 mL/min. This is due to the increase in mass transfer coefficient with the increase in gas flow rate, resulting in the increase in adsorption rate, due to which the bed will get saturated in a shorter time.

Effect of particle diameter

As observed from Fig. 5, decrease in the particle size from 0.002 m to 0.001 m for same bed height results in significant increase in breakthrough time from 10910 s to 20840 s. The noticeable characteristic of the breakthrough responses, especially for the small size particles, is the abrupt increase in the concentration levels following the breakthrough of the bed, due to which time for bed saturation decreases. The decrease in breakthrough time in case of large size particles is attributed due to the longer diffusion path in the pores. However, the time of bed saturation increases due to the large adsorption surface area of the particle. Pre-determining such type of breakthrough characteristic of an adsorbing material is important for selecting the particle size.

Effect of pore diffusivity

The pore size of an adsorbent is a critical parameter in determining the breakthrough characteristics of an adsorbate. The smaller the pore size, the larger is the diffusion time of adsorbing species within the pores due to relatively smaller diffusivity. The larger diffusion time causes the adsorption process to be diffusion limited. In order to determine the conditions under which pore diffusion becomes limiting in adsorption of VOC, simulations have been carried out for varying effective diffusivity and gas flow rates.

Figure 6 describe the effect of pore diffusivity on breakthrough curves. Here, the gas flow rate of 40 mL/min has been chosen and it has been observed that adsorption rate remains unaffected over large values of diffusivity ($D_e$). At higher flow rates the adsorption rates will be significantly altered by variation in $D_e$.

From the above simulation results, it is concluded that (i) in general, the effect of pore diffusivity on adsorption rate is significant at high flow rates; implying adsorption process is limited by pore diffusion, and (ii) the effect of pore diffusivity on adsorption rate is almost negligible at low flow rates; implying the gas-particle film mass transfer controls the adsorption process.
Conclusion

The experimental studies reveal that the granular activated carbon is a potential adsorbent for capturing xylene at low concentration levels, due to its high BET surface area. The breakthrough time during adsorption considerably decreases with the increase in inlet concentration levels, suggesting utility of the adsorption method for controlling xylene from gaseous effluent at low concentration levels. The breakthrough time during adsorption is found to be increasing with increase in bed height, suggesting greater utilization of bed at greater bed heights. Furthermore, a mathematical model accounting for external-film and pore-diffusion mass-transfer mechanisms, axial dispersion and nonlinear isotherm was used to fit the experimental breakthrough curves. The model is found to reproduce adequately the experimental results once the best-fitting parameters are attained. Then the effect of gas flow rate, particle diameter and pore diffusivity on breakthrough curves are predicted through the developed mathematical model. The breakthrough time is increased with the decrease in particle radius and steeper breakthrough curves are obtained following breakthrough, suggesting the use of adsorbent with smaller diameter which also increase the length of bed utilized up to breakthrough and efficiency of the adsorbent. It is found that at low gas flow rates gas-particle film mass-transfer controls the overall adsorption process while at higher gas flow rates it is the pore diffusivity which controls the overall adsorption process.

References