Vapor Phase Adsorption of Homologous Aliphatic Ketones on Activated Spherical Carbon
Bhargavi R, Kadirvelu K, Kumar N S
Defence Bioengineering and Electromedical Laboratory, DRDO, Bangalore, India – 560075
bhargav.chemi@gmail.com
doi:10.6088/ijessi.00105020023

ABSTRACT

Volatile organic compounds (VOCs) contribute to more than half of the pollutants present in the atmosphere. Adsorption has been found to be a feasible and an effective method to separate and recover VOCs for further analysis. Activated Spherical Carbon (ASC) adhered onto woven fabric was used as the adsorbent for the present study. In this paper, we review the novel single vapor phase adsorption of homologous aliphatic ketone series - from propanone to hexanone onto ASC. The breakthrough time of propanone was fastest among all vapors; this behavior is attributed to its physico-chemical properties. The results show that physisorption plays a primary role in ketone removal. Another experiment was carried out to compare the adsorption trend of two pentanone isomers, wherein the breakthrough time of 2-pentanone was more than that of 3-pentanone. The breakthrough characteristic shows that activated spherical carbon with an appropriate surface area could be utilized in controlling the volatile organic compounds to maintain and improve the ambient air quality. ASC woven fabric is effective in use as an adsorbent material which is light in weight and also suitable for protective clothing.

Keywords: Volatile organic compounds, adsorption, activated spherical carbon, aliphatic ketones, pentanone isomers, breakthrough curve.

1. Introduction

On account of our daily activities, large quantities of VOCs are emitted into the environment by various means (Kunwar P et al., 2002). These emissions have contributed to acid rain, depletion of ozone layer and also has aided in the generation of precursors of photochemical reactions. VOCs can cause harmful effects to internal organs in the human body even at very low concentrations (Chi-Yuan Lu and Ming-Yen Wey, 2007); long time exposure may even cause cancer. VOCs are commonly found in substances such as paints, automotive exhausts, tobacco smoke, flue gases etc.

Adsorption has been recognized as the economically favorable and regenerative method for effectively controlling emissions of VOCs even at low concentrations (Debasish Das et al., 2004, N.Mohan et al., 2009 and Sampattrao D et al., 2006). The adsorbent is a porous solid medium, of which the adsorption capacity is characterized in terms of surface area and pore size distribution (K. Gurudatt et al., 1997). The mechanism of adsorption is dependent upon the size of the adsorbate in comparison with the pore width.

A good adsorbent must have a reasonably large surface area and a relatively larger pore network for the transport of molecules to the interior. There are varieties of commercially available adsorbents including activated carbon (K. Kadirvelu et al., 2005), silica, zeolites,
Alumina etc. Amongst them, activated carbon adsorption is considered to be one of the promising methods for controlling VOCs of low concentrations.

Activated carbon is a carbonaceous product having porous structure and is mainly prepared by carbonizing and activating organic substances. These have been used for many years quite successfully for adsorptive removal of heavy metals, waste water (C. Namasivayam and K. Kadirvelu, 1997, Catherine Faur-Brasquet et al., 2002, C. Faur-Brasquet et al., 2002 and D. Mohan and S. Chander, 2001), from industrial solid waste (K. Kadirvelu et al., 2005), gas streams (Mark P. Cal et al., 1997) and indoor air environments (Mark P. Cal et al., 1996 and Zheng-Hong Hueng et al., 2003). Activated carbon materials are extensively available in the form of granules or powder (Y. Chen et al., 2006). The detailed characteristics of adsorption of VOCs on activated carbon have been examined by Cheng (Wen-His Cheng, 2008 and Cheng et al., 2007). A brief study of removal of various VOCs using granular activated carbon has been investigated by Tsai Jiun-Horng et al. (Tsai Jiun-Horng et al., 2008).

Compared to activated carbon granules or powder, ASC has a significantly different micro porous structure. Because of its better performance, ASC can be adhered onto woven fabric to meet the requirements of specific applications. This type of handling enables ASC to be used in various filters such as air cleaning, solvent recovery and waste water treatment. It is particularly effective in shielding the toxic chemical and biological agents in the form of gases, liquids and solid aerosols. There are few studies concerning the breakthrough characteristics of single and binary vapors according to the fraction of each component among VOCs (Ehud Biron and Michael J.B. Evans, 1998 and Song-Woo Lee et al., 2007).

The major objectives of this study were as follows:

1) To study the single vapor phase adsorption characteristics of homologous aliphatic ketones series from propanone - hexanone on commercially available ASC adhered on woven fabric.

2) To compare the breakthrough curves of pentanone isomers.

2. Materials and Methods

2.1 Adsorbent and Adsorbates

Polystyrene sulfonate based ASC adhered on woven fabric was obtained from Vijay Sabre Safety Pvt Ltd., Mumbai, India. The adsorbent was dried for 12 hours at 120°C before the commencement of the experiment. The characteristics of ASC are summarized in the Table 1. Various parameters were analyzed according to IS 877:1989.

Table 1: Table showing the characteristics of ASC

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area (m²/g)</td>
<td>1156</td>
</tr>
<tr>
<td>Pore diameter (Å)</td>
<td>20.25</td>
</tr>
<tr>
<td>Total pore volume Vₜot (cc/g)</td>
<td>0.6215</td>
</tr>
<tr>
<td>Particle size</td>
<td>300-600 µm</td>
</tr>
</tbody>
</table>
Moisture, % 4.15  
Ash, % 9.69  
Solubility in water, % 1.54  
Solubility in 0.25 M HCl, % 8.17  
P\:H 3.1  
Decolorizing power, mg/g 256.02  
Adsorption capacity for CCl\(_4\), % 81.54  
Chloride content, % 15.06  
Sulphate content, % 7.18  
Cyanogen compounds, % NIL  
Conductivity µS/cm 46.7

All adsorbates used were of 99.9% analytical grade obtained from Merck, India. These were used without further purification and its physico-chemical properties are shown in the Table 2 (Y. Marcus, 1998 and F. Allan and M. Barton, 2000).

**Table 2**: Table showing the physico-chemical properties of homologous aliphatic ketone series

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Molecular formula</th>
<th>Molecular weight (g/mol)</th>
<th>Density (g/ml)</th>
<th>Boiling point (°C)</th>
<th>Vapor pressure (mmHg)</th>
<th>Polarity Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propanone</td>
<td>(\text{H}_3\text{C} \text{O} \text{CH}_3)</td>
<td>58.08</td>
<td>0.793</td>
<td>56</td>
<td>184</td>
<td>5.1</td>
</tr>
<tr>
<td>Butanone</td>
<td>(\text{H}_3\text{C} \text{O} \text{CH}_3)</td>
<td>72.11</td>
<td>0.805</td>
<td>80</td>
<td>71</td>
<td>4.7</td>
</tr>
<tr>
<td>2-pentanone</td>
<td>(\text{H}_3\text{C} \text{O} \text{CH}_3)</td>
<td>86.13</td>
<td>0.805</td>
<td>101</td>
<td>27</td>
<td>4.5</td>
</tr>
</tbody>
</table>
Vapor Phase Adsorption of Homologous Aliphatic Ketones on Activated Spherical Carbon

<table>
<thead>
<tr>
<th></th>
<th>Structure</th>
<th>分子量</th>
<th>μ</th>
<th>单位</th>
<th>语料库</th>
<th>语料库</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-pentanone</td>
<td>CH₃C(CH₃)₃O</td>
<td>86.13</td>
<td>0.813</td>
<td>101</td>
<td>36</td>
<td>4.5</td>
</tr>
<tr>
<td>2-hexanone</td>
<td>CH₃C(CH₂CH₂)₂O</td>
<td>100.16</td>
<td>0.810</td>
<td>126</td>
<td>14</td>
<td>4.2</td>
</tr>
</tbody>
</table>

### 2.2 Analytical methods

The high specific surface area of ASC was obtained from Smart Instruments Company Pvt Ltd., coded as SMART SORB 92/93. The concentrations of VOCs were analyzed by Agilent-7890A gas chromatograph equipped with a capillary column type HP-5 (30 m x 0.32 mm x 0.25 μm film thickness) with a flame ionization detector. For the analysis, the samples were drawn by a 1ml gas lock syringe (Hamilton-Bonaduz-Schweiz) and were analyzed by the gas chromatograph. The morphology of ASC was studied using Quanta 200 (FEI Company) scanning electron microscope.

### 3. Experiment

Adsorption experiments were performed using the experimental setup shown in the schematic diagram (Fig.1). Helium gas was passed into the impinger to vaporize the adsorbate through Mass Flow Controller (MFC). Then the vapor of the adsorbate was passed through a stainless tube with ASC adhered on woven fabric at its end. The inlet and outlet concentrations were measured at regular intervals by gas chromatograph to find out the breakthrough for VOCs. The concentration of the adsorbates was at 250 ppm.

![Experimental setup](image)

**Figure 1:** Experimental setup


_Bhargavi R, Kadirvelu K, Kumar N S_  
*International Journal of Environmental Sciences Volume 1 No.5, 2011*
4. Results and Discussion

4.1 Surface properties

Physical characteristics of porous materials such as surface area and pore structure are important in sorption processes. The surface area is the reactive zone where chemisorption and/or physisorption occur. Alternatively, pore size and shape will define the process performance, since kinetics of adsorption is directly related to adsorbate intraparticle diffusion. The Brunauer-Emmett-Teller (BET) surface area ($S_{\text{BET}}$) obtained from N$_2$ adsorption isotherms data, pore diameter and the calculated total pore volume ($V_{\text{tot}}$) data of ASC are given in Table 1. To better understand the surface structure, photomicrographs of the spherical carbon were taken by a scanning electron microscope. The ASC adhered onto the woven fabric is shown in the Fig. 2 (a). The enlarged view of the ASC and its surface are shown in the Figure. 2 (b) & (c) respectively.

![SEM image of spherical carbon adhered on fabric](image)

**Figure 2:** SEM image of the (a) spherical carbon adhered on fabric enlargement (100 X) (b) activated spherical carbon (enlargement 400X) (c) surface of the activated spherical carbon (enlargement 6000X)

4.2 Adsorption of homologous ketones series

The breakthrough characteristics of the adsorption of homologous ketones series on ASC have been discussed in detail, and the breakthrough curves are compared in Figure. 3. The breakthrough time was defined as the time when the outlet concentration was 20% of the inlet concentration. The breakthrough times of single vapor of propanone, butanone, 2-pentanone and 2-hexanone were found to be 140, 220, 400 and 520 minutes respectively.

The time needed to reach equilibrium for propanone, butanone, 2-pentanone and 2-hexanone vapor were 400, 560, 880 and 1200 minutes and the equilibrium adsorption capacities were found to be 24065mg/sq.m, 22240mg/sq.m, 30248mg/sq.m and 75926mg/sq.m respectively. The breakthrough time of propanone vapor among these vapors was the fastest and that of 2-hexanone was slowest.

To investigate the relations between equilibrium adsorption capacity and characteristics of the adsorbates (density, molecular weight, polarity index, boiling point and vapor pressure), XY plots were made and are illustrated in the Figure. 4 –Figure. 8. The equilibrium adsorption capacity is a function of both molecular weight and boiling point of the adsorbates and it follows the third order polynomials with the equations $y = 2.103x^3 - 435.9x^2 + 29784x - 64731$ and $y = 0.402x^3 - 87.73x^2 + 6212x - 11939$ respectively.
The correlation coefficients ($r^2$) between equilibrium adsorption capacity and molecular weight and that of boiling point were over 0.99, as illustrated in Figure 4 and Figure 5. The equilibrium adsorption capacity is also a function of polarity index and it exhibited a falling tendency. It follows second order polynomials with the equation $y=10692x^2 - 1E+06x - 11939$ having correlation coefficient 0.988, which is illustrated in Figure 6. The relation between equilibrium adsorption capacity and vapor pressure and that of density was poor, as illustrated in Figure 7 and Figure 8. From the results, it can be concluded that the higher the boiling point and molecular weight of the adsorbate, the higher the equilibrium adsorption capacity.

**Figure 3 and Figure 4:** Breakthrough curves of aliphatic ketones series and Correlation between equilibrium adsorption capacity and molecular weight of adsorbates

**Figure 5 and Figure 6:** Correlation between equilibrium adsorption capacity and boiling point of adsorbates and Correlation between equilibrium capacity and polarity index of adsorbates
Vapor Phase Adsorption of Homologous Aliphatic Ketones on Activated Spherical Carbon

Bhargavi R, Kadirvelu K, Kumar N S

International Journal of Environmental Sciences Volume 1 No.5, 2011

Figure 7 and Figure 8: Relation between equilibrium adsorption capacity and vapor pressure of adsorbates and Relation between equilibrium capacity and density of adsorbates.

The breakthrough curves of aliphatic ketone series can be explained by the difference of affinity between adsorbent and the adsorbates, and the physico-chemical properties of the adsorbates. The breakthrough curves, as seen in Fig.8, imply that as the methylene group in the homologous aliphatic ketone series increases, the breakthrough time also increases.

Vapor pressure is an important criterion in the adsorption process. In this homologous series, the vapor pressure decreases with increase in the carbon chain. This enhances the affinity of the adsorbates towards carbon. Other important criteria are boiling point, density and molecular weight. These parameters will increase with the addition of methylene group in the series, which enhances the affinity of the adsorbate on the adsorbent. Thus, it can be concluded that the physico-chemical properties play a major role in the adsorption process.

4.3 Adsorption of two isomers of pentanone:

The breakthrough curves of 2-pentanone and 3-pentanone on ASC are illustrated in Figure. 3 (b) and the breakthrough time was found to be 400 and 340 minutes respectively. The equilibrium adsorption capacity of the 3-pentanone was found to be 25580 mg/sq.m. Though the molecular weight, polarity index and boiling point are the same, the breakthrough time of 2-pentanone is more than that of 3-pentanone. This is attributed to the reduced vapor pressure of 2-pentanone. Hence the 3-pentanone molecules easily diffuse through the carbon as compared to 2-pentanone.

Figure 9: Breakthrough curves of two pentanone isomers
5. Conclusion

- The studies of single vapor phase adsorption of homologous aliphatic ketones and pentanone isomers on ASC gave rise to some significant conclusions.
- The breakthrough time of propanone was fastest when compared with the vapors of propanone, butanone, 2-pentanone and 2-hexanone.
- The physical properties of adsorbates play a major role in the adsorption process.
- The results showed that the breakthrough time increases as the carbon atoms in the ketone series increase.
- Though the physico-chemical properties are similar, the breakthrough time of 2-pentanone is more than that of 3-pentanone owing to the variation in the vapor pressure.
- The equilibrium adsorption capacity is a function of both molecular weight and boiling point of the adsorbates and it follows the third order polynomial trend.
- The function of polarity index follows second order polynomial trend.
- The relation between the equilibrium adsorption capacity with that of density and vapor pressure was poor.
- Decreasing adsorbent particle size increases the removal of VOCs.

In summary, the ASC adhered on woven fabric shows potential material for use as a highly effective adsorbent. It is lesser in weight and can be used in manufacturing protective clothing applications.

Acknowledgements

The authors thankful to Dr V C Padaki, Director, Dr. A S K Prasad, Associate Director, Defence Bioengineering and Electromedical Laboratory, Bangalore, for providing all the necessary facilities and encouragement. Authors are also thankful to Mr. R. Meghanath, Technician, who has helped for the experimental setup in this work.

6. References


