Comparison of Adsorption Characteristics for VOCs on Activated Carbon and Oxidized Activated Carbon

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In this investigation, the selected activated carbon is treated in NaOH solution or gas fluid with ozone from an ozone generator. FTIR, BET specific surface area and element analysis instruments were used to identify the difference in the chemical and physical characteristics between the activated carbon and oxidized activated carbon. The system of adsorption apparatus consists of a fixed adsorption column, quartz pan, electronic balance, and data acquisition system to measure the adsorption capacities and adsorption rates for VOCs under various operating conditions. VOCs, n-hexane, methyl-ethyl-ketone, and benzene were selected to evaluate the effect of adsorption characteristics on the activated carbon and oxidized activated carbon.

The results of chemical analysis with the FTIR instrument indicate the absorption bands and peaks measured at 1632 cm⁻¹ on the oxidized activated carbons (AOH₂O and AO₃) are much stronger than on the activated carbon (AC). This shows that carbonyl (conjugated C=O) of the functional group is predominantly found to increase on the oxidized activated carbons (AO and AOH₂O). Significant changes were observed for BET-specific areas for AOH₂O and AO, but the carbon contents of AOH₂O and AO decreased slightly. Moreover, the oxidized activated carbons showed greater affinity for polar adsorbate than did AC, and the overall effective mass transfer coefficients, kD of AO for various VOC adsorption were larger than those of AC and AOH₂O.

INTRODUCTION

The control of VOC emissions by adsorption has been successfully utilized in various industries. With the very unique characteristics, i.e., larger specific surface area and micropore volume, associated with the activated carbon, it has become the most popular adsorbent for VOCs control in the adsorption process. Unfortunately, in the manufacturing, storage, transportation, and operation processes of the activated carbon, it may be oxidized by oxygen, ozone or other oxidizer in the ambient environment. As a result, the activated carbon could change its chemical and physical characteristics thereby significantly effecting the adsorption of VOCs.

The gas-phase oxidation of carbon by ozone is interpreted by a mechanism involving two chemical reactions at independent areas of the surface, S₁₁ and C₂₂. The reactions at these sites are presented to be:

\[ C_{11} + O_3 \rightarrow C_{11}O_3 \]  \hspace{1cm} (1)

\[ C_{22} + O_3 \rightarrow C_{22}O + O_2 \]  \hspace{1cm} (2)

where C₁₁ and C₂₂ are the carbon atoms at edge sites S₁ and S₂, respectively. It should also be noted that a large amount of ozone may be adsorbed on the carbonaceous material (graphite, carbon black, and activated carbon) [1-4].

The oxidation of carbon by ozone dissolved in alkaline solution is believed to involve two mechanisms: (a) direct oxidation to CO₂, and (b) oxidation to form degradation products.

FIGURE 1. Schematic representation of the oxygen surface functional group on activated carbon.
that are soluble in alkaline solution, which subsequently oxidize to CO₂ [2]. The BET nitrogen area of treated activated carbon was abruptly reduced after his reaction [5, 6].

Moreover, it is found that the carbonaceous material surface (e.g., graphite or activated carbon) reacting with H₂O₂, O₃, or H₂SO₄ should obtain highly polar sites having the oxygen functional groups of -OH, -COOH, -CHO, -CO, and/or OSO₃H [3-8]. A schematic representation of surface oxides that are believed to be present on activated carbon surface is presented in Figure 1 [2].

The oxygen surface functional groups on the carbonaceous adsorbents distinctly increase adsorption capacities for polar adsorbates, such as methanol and water vapor, as well as the contribution of chemisorption, e.g., the hydrogen-bonded species formed [8]. From the analysis of adsorption energy distribution, it has been presented that the dispersive component of surface energy and the enthalpies of alkane adsorption decreased after oxidative pretreatment of carbons. This indicates that the oxidized carbons have less affinity for hydrocarbons than the untreated carbon surface [6].

As the quantity of oxygen bound chemically to the surface decreases from the amount of the raw carbon to that on carbons treated at ever higher temperature, a decrease of the thickness of the adsorption layer is also observed [8]. The adsorption rate for a polar molecule (such as water vapor) with ozone-treated activated carbons increases, although the BET nitrogen area decreases [5].

Because some functional groups are observable by IR or FTIR instruments, IR (or FTIR) spectral studies of activated carbon are important for: (1) providing information on structure, such as the oxygen functional groups on the activated carbons, (2) providing basic spectra of the activated carbon for comparison with spectra of the same carbon containing adsorbate, and (3) providing much information on the molecular forces involved for specific adsorbates [2, 9, 10]. The IR adsorption bands and peaks for various carbon material and the proposed sources of the IR signals are summarized in Table 1 [2].

In this research, the changes in the chemical and physical characteristics of activated carbon were investigated and identified when the original activated carbon was treated and oxidized with ozone in various treatment processes. The effect of adsorption characteristics (such as adsorption capacity and adsorption rate) of VOCs on activated carbon and modified (oxidized) activated carbon, was also discussed. The experimental results will be provided to evaluate the possible utilization of oxidized activated carbon.

EXPERIMENTAL CONSIDERATION

Materials

The activated carbon (coconut raw material and mesh 12 × 40) was dried in an oven for 24 hrs at 105°C. The two kinds of oxidized activated carbons were manufactured with raw activated carbon in various treatment (oxidized) processes. The VOCs, n-hexane, benzene, and methyl-ethyl-ketone (MEK)(Lab-Scan, analytical grade) were selected as adsorbates to evaluate the effect of adsorption characteristics on the activated carbon (AC) and oxidized activated carbons (AOH, and AO₃).

Oxidation Processes of Activated Carbon

(1) Activated carbon oxidized in liquid solution: 100 g of dry activated carbon (AC) were added to 500 ml of NaOH solution (pH = 11). The mixture was oxidized by introducing feed O₃ gas (75 mg/l) at a flow rate of 2.5 NL/min from the ozone generator (SG-01A) and stripping for 30 min. After removing the supernatant liquid, the oxidized activated carbon (AOH O₃) was rinsed with Milli-Q water and dried at 105°C for 24 hrs.

(2) Activated carbon oxidized in gas fluid: 15 g of activated carbon (AC) was put into the pyrex column (L = 50 cm, D = 3 cm), then gas fluid with 25 mg/l O₃ from the ozone generator was introduced at a flow rate of 2.5 NL/min for 30 mins. The oxidized activated carbon (AO₃) was put in an oven for 24 hrs at 105°C.

Each of the (oxidized) activated carbon (AC, AOH, and AO₃) was purged by introducing nitrogen and air in sequence until the weight of the samples did not change significantly. Then, the final products were stored in a desiccator.

Analytical Method

The FTIR, BET specific surface area and element analysis instruments were used to identify the difference in the chemical and physical characteristics between the activated carbon and oxidized activated carbon. 0.2 m sample was tested in the adsorption system to measure and evaluate the adsorption capacity and adsorption rate.

Adsorption Apparatus System

The adsorption capacities and adsorption rates were measured by the gravimetric method [11, 12] with an adsorption apparatus system shown in Figure 2. This consisted of an adsorption quartz column (D = 3 cm, L = 60 cm), a quartz pan...
### Table 1 Infrared Absorption Studies of Carbon Materials [2]

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Absorption Bands and Peaks (cm⁻¹)</th>
<th>Source of Infrared Signal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose char</td>
<td>3030</td>
<td>IR-T/A</td>
</tr>
<tr>
<td>Coal</td>
<td>2920, 2850</td>
<td>Aromatic C-H</td>
</tr>
<tr>
<td>Carbon black</td>
<td>1760</td>
<td>Aliphatic CH₂ &amp; CH₃ stretch</td>
</tr>
<tr>
<td>Channel black</td>
<td>1740</td>
<td>Lactone</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>1735</td>
<td>C=O stretch</td>
</tr>
<tr>
<td>Pyrolyzed polymer</td>
<td>1724-1754</td>
<td>Carbonyl</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>1710-1760</td>
<td>Carbonyl, carboxyl and lactone</td>
</tr>
<tr>
<td>Cellulose char</td>
<td>1704</td>
<td>C=O</td>
</tr>
<tr>
<td>Carbon black</td>
<td>1675-1775</td>
<td>Lactone</td>
</tr>
<tr>
<td>Cellulose char</td>
<td>1616</td>
<td>C=O</td>
</tr>
<tr>
<td>Coal</td>
<td>1605</td>
<td>Aromatic ring (ether or quinone)</td>
</tr>
<tr>
<td>Channel black</td>
<td>1600</td>
<td>Graphitic structure</td>
</tr>
<tr>
<td>Channel black</td>
<td>1600</td>
<td>Carboxyl</td>
</tr>
<tr>
<td>Channel black</td>
<td>1590</td>
<td>Carboxyl or aromatic group</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>1590</td>
<td>Aromatic structures and unconjugated carbonyl</td>
</tr>
<tr>
<td>Pyrolyzed polymer</td>
<td>1575-1550</td>
<td>Lactone</td>
</tr>
<tr>
<td>Carbon black</td>
<td>1550-1675</td>
<td>Quinone</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>1500-1670</td>
<td>C=O stretch, carboxyl</td>
</tr>
<tr>
<td>Cellulose char</td>
<td>1449</td>
<td>CH₂</td>
</tr>
<tr>
<td>Pyrolyzed polymer</td>
<td>1389-1351</td>
<td>Hydroxyl</td>
</tr>
<tr>
<td>Carbon black</td>
<td>1360</td>
<td>Graphitic structure</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>1340-1480</td>
<td>Phenol</td>
</tr>
<tr>
<td>Carbon black</td>
<td>1265-1275</td>
<td>Ether</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>1260</td>
<td>C=O-C vibration, lactone</td>
</tr>
<tr>
<td>Cellulose char</td>
<td>1250</td>
<td>Aromatic C=O</td>
</tr>
<tr>
<td>Channel black</td>
<td>1230</td>
<td>C-O stretch</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>1215</td>
<td>C=O absorption or phenox absorption</td>
</tr>
<tr>
<td>Channel black</td>
<td>1205</td>
<td>Condensed aromatic ring or H-bonded, conjugated carbonyl</td>
</tr>
<tr>
<td>Carbon black</td>
<td>1195-1205</td>
<td>Phenol</td>
</tr>
<tr>
<td>Coal</td>
<td>1160-1300</td>
<td>C=O stretch, phenol, aromatic ether, OH deformation, quinone</td>
</tr>
<tr>
<td>Coal</td>
<td>1030</td>
<td>C-O stretch, aromatic ether of type Ph-O-CH₂R</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>1000-1180</td>
<td>C-O stretch and vibration</td>
</tr>
<tr>
<td>Carbon black</td>
<td>1720</td>
<td>FTIR</td>
</tr>
<tr>
<td>Carbon fiber</td>
<td>1680</td>
<td>FTIR</td>
</tr>
<tr>
<td>Carbon black</td>
<td>1000-1400</td>
<td>FTIR</td>
</tr>
<tr>
<td>Coal</td>
<td>2920</td>
<td>FTIR</td>
</tr>
<tr>
<td>Coal</td>
<td>1735</td>
<td>FTIR</td>
</tr>
<tr>
<td>Coal</td>
<td>1690-1720</td>
<td>FTIR</td>
</tr>
<tr>
<td>Coal</td>
<td>1630-1650</td>
<td>FTIR</td>
</tr>
<tr>
<td>Coal</td>
<td>1600</td>
<td>FTIR</td>
</tr>
</tbody>
</table>

*D = 1.3 cm, H = 0.5 cm*, an electronic balance (Precisa 125 A, readability 0.1 mg) and a data acquisition system under various operating conditions.

### Adsorption Kinetics Procedures

An activated carbon sample of 0.2 gm was put in a quartz pan. Then it was hung with a platinum string which was connected with an electronic balance and a data acquisition system. \( N_2 \) gas fluid from a pressure tank was introduced to the VOCs generator to carry the organic vapour. The desired VOCs concentration was mixed and diluted by air fluid. The VOCs concentration was detected by a THC monitor and was controlled with +5 percent accuracy. The adsorption weight on the (modified) activated carbon versus the adsorption time was recorded by a data acquisition system.

### RESULTS AND DISCUSSION

From the result of chemical analyses by FTIR as shown in Figure 3, some functional groups of (oxidized) activated carbon are observed in spectra of FTIR, such as:

1. the peak at 780 and 878 cm⁻¹, attributable to \( \equiv C-H \) band
2. the peaks at 1055, 1269, and 1383 cm⁻¹, attributable to C-O absorption, probably phenol, aromatic ether, and OH deformation structure
3. the peaks at 1590 cm⁻¹, the well-known carbonaceous band which is variously attributed to aromatic structure and to unconjugated, chelated carbonyl group, and
4. the peaks at 1633 cm⁻¹ attributable to C-O stretch, probably carbonyl (conjugated C=O) and/or carboxyl structure.

Comparing the spectrum of activated carbon (AC) with the spectra of oxidized activated carbons (AOHO, and AO₁), the absorption bands and peaks measured at 1055 and 1633 cm⁻¹ on AOHO and AO₁ are much stronger than that on AC. This shows that the C-O and C=O functional groups on the oxidized activated carbons tend to increase from the oxidized processes of ozone.

Significant changes were observed for the specific surface area of BET nitrogen of AO and AOHO, The specific surface
The experimental data show that when AC is treated with ozone in NaOH solution, the surface chemical groups introduced onto the surface by oxidation may block the pores and hinder the favorable geometrical arrangement of adsorbed molecules over the surface. Also, the micropores may be enlarged to form macro pores and thus decrease the specific surface area.

The adsorption uptake curves for hexane on activated carbon (AC) and oxidized activated carbons (AOHO, and AO), at various inflow concentrations and 25°C are shown in Figures 4-6 and Table 2. The average adsorption rates for VOCs on the activated carbon and oxidized activated carbon (at the interval of adsorption time of 10 mins) are shown in Table 3. The adsorption capacities for nonpolar n-hexane on various adsorbents follow the sequence as:

\[ AC > AOHO > AO \]

The adsorption capacities and rates of AO, for n-hexane were much lower than those of AC and AOHO, although AO, has a larger specific surface area than those of AC and AOHO,. Element analyses show that the carbon content decreases when the AC is treated with ozone. The carbon content of AC, AOHO, and AO, are 84 percent, 83 percent and 80 percent, respectively. These results indicate that not only does the oxidation of activated carbon (AC) by ozone gas form the surface functional group, C-O and C=O, but also some 0, molecules are adsorbed on the surface. Because most of the adsorption active sites on AO, are covered by O, or O, the nonpolar hexane molecules adsorbed by van der Waals forces on the surface of AO, are lower than on that of AC.

The adsorption uptake curves for MEK on AC, AOHO, and

### Table 2 Comparison of Adsorption Capacities for Various VOCs on Activated Carbon (AC) and Oxidized Activated Carbons (AOHO, AO)

<table>
<thead>
<tr>
<th>VOC Adsorbate</th>
<th>Concentration (ppm)</th>
<th>Adsorption Capacity (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AC(AC/AC)</td>
<td>AOHO(AOHO/AC)</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>13400</td>
<td>123.5 (1.0)</td>
</tr>
<tr>
<td></td>
<td>6820</td>
<td>114.5 (1.0)</td>
</tr>
<tr>
<td></td>
<td>3410</td>
<td>106.5 (1.0)</td>
</tr>
<tr>
<td>MEK</td>
<td>4510</td>
<td>154.5 (1.0)</td>
</tr>
<tr>
<td>Benzene</td>
<td>4350</td>
<td>156.5 (1.0)</td>
</tr>
</tbody>
</table>

The adsorption uptake curves for hexane on activated carbon (AC) and oxidized activated carbons (AOHO, and AO), are shown in Figures 4-6. The trend of the first 10 mins of adsorption time as follows:

\[ AC > AOHO > AO \]
AOHOO > AC ~ AO, for adsorption capacity and AO > AOHOO > AC for average adsorption rate in the adsorption time of the first 10 mins.

These sequence results are significantly different from those of hexane. The more oxygen surface functional groups there are on carbonaceous adsorbents, the higher the affinity of the carbonaceous adsorbents to adsorb polar molecules are. Because MEK contains the carbonyl functional group (C=O), it has a significant dipole moment, \( u = 2.77 D \), and is a very polar molecule. The highly polar sites on AO and AOH0 indicate a strong chemisorption force for MEK polar adsorbates.

The adsorption uptake curves for benzene on activated carbon (AC) and oxidized activated carbons (AOH0, and AO,) at 25°C are shown in Figure 8. From the result, the adsorption capacities for 4350 ppm benzene on various adsorbents, AC, AOH0, and AO, are 156.5 mg/g, 167 mg/g and 132.5 mg/g respectively. The average adsorption rates in the first 10 mins are 0.77 mg/min (AC), 0.67 mg/min (AOH0,), and 0.63 mg/min (AO,). The structure of the benzene molecule is planar and the \( \pi \) electron density in benzene lies in doughnut-shaped regions both above and below the plane of the ring, although benzene is not a nonpolar molecule with no dipole moment. So, the oxygen surface function groups on activated carbon have more affinity for benzene than hexane, and have less affinity for benzene than for MEK.

Furthermore, attempts were made to use the first order kinetic equation of mass transfer to describe the adsorption rates of VOCs adsorption on activated carbon (AC) and oxidized activated carbons (AOH0, and AO,)

\[
\frac{dq}{dt} = k_D (q_e - q)
\]

\[
q_t = q_e (1 - e^{-kt})
\]

where \( q_e \) is the equilibrium amount of adsorbed adsorbate at equilibrium. The constant \( k_D \) is overall effective mass transfer coefficient and depends on the diffusivity \( D \) of the VOCs adsorbate into the adsorbent pores.

From this equation and experimental data, the \( k_D \) values can be calculated and obtained for \( q_t \). The results are presented in Table 4 and the correlation coefficients are above 0.95. The correlation coefficients are above 0.95. From the Table, the \( k_D \) values of AO for VOCs adsorption are larger than for AC and AOH0. These results also show that the lower the concentration of VOCs (such as n-Hexane) introduced, the lower the \( k_D \) value.

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<table>
<thead>
<tr>
<th>VOC Adsorbate</th>
<th>Concentration (ppm)</th>
<th>( k_D ) value (min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AC</td>
<td>AOH0</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>13400</td>
<td>0.1026 (0.998)</td>
</tr>
<tr>
<td></td>
<td>(0.0483) (0.0731)</td>
<td>(0.0976) (0.0987)</td>
</tr>
<tr>
<td></td>
<td>(0.0553) (0.0472)</td>
<td>(0.0537) (0.0978)</td>
</tr>
<tr>
<td></td>
<td>(0.0554) (0.0278)</td>
<td>(0.0966) (0.0310)</td>
</tr>
<tr>
<td></td>
<td>(0.0525) (0.0984)</td>
<td>(0.0997) (0.0315)</td>
</tr>
<tr>
<td></td>
<td>(0.0513) (0.0980)</td>
<td>(0.0982) (0.0982)</td>
</tr>
</tbody>
</table>

(\( R^2 \): correlation coefficient.)
CONCLUSIONS

In the manufacturing, storage, transportation, and operation processes, activated carbon may be oxidized by oxygen, ozone, or other oxidizer in the ambient environment. As a result, the activated carbon could change its chemical and physical characteristics which would have a significant effect on the adsorption of VOCs.

From this investigation, significant changes are observed for the specific surface areas of BET nitrogen of the oxidized activated carbon. The chemical analyses by FTIR instruments measured the absorption bands and peaks at 1632 cm$^{-1}$ on the oxidized activated carbons (AOHO, and AO$_2$) which is much stronger than on the original activated carbon (AC). The carbonyl (conjugated C=O) functional group was produced predominantly from the oxidation process by ozone. The adsorption capacities and adsorption rates for various VOCs on adsorbents (AC, AOHO, and AO$_2$) are significantly different and have more affinity for polar VOCs. The $k_D$ values of AO$_2$ for VOCs adsorption are larger than that of AC and AOHO. These results indicated that the micropores of the AO$_2$ activated carbon may be enlarged to form macropores. The micropore distributions and the quantities of oxygen surface functional group changes and effects for VOCs adsorption remain a topic of continued research in our laboratory.

ACKNOWLEDGMENT

We are grateful to the National Science Committee, Chinese, for financial support to pursue this project and also appreciate the AIChE for accepting this material for presentation at the National Summer Meeting of AIChE, 1992.

NOTATION

VOCs = vapor organic compounds
MEK = methy-ethyl-ketone
AC = original activated carbon
AO$_2$ = oxidized activated carbon (oxidized by ozone in gas fluid)
AOHO$_2$ = oxidized activated carbon (oxidized by ozone in NaOH solution)

$q_e$ = the amount of adsorbed adsorbate at equilibrium
$q_t$ = the amount of adsorbed adsorbate at t time

LITERATURE CITED