Removal of 4,6-dimethyldibenzothiophene from model diesel fuel using activated carbon with sulfo group

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Adsorption of 4,6-dimethyldibenzothiophene (DMDBT) from model diesel fuel was performed using commercial petroleum pitch based activated carbon treated by (NH\textsubscript{4})\textsubscript{2}S\textsubscript{2}O\textsubscript{8} in 1 M H\textsubscript{2}SO\textsubscript{4} and/or SO\textsubscript{3}. The treatment of (NH\textsubscript{4})\textsubscript{2}S\textsubscript{2}O\textsubscript{8} in 1 M H\textsubscript{2}SO\textsubscript{4} mainly increased the number of carboxyl groups, whereas the introduction of sulfo group was observed for SO\textsubscript{3} treatment.

The adsorption of DMDBT on each prepared activated carbon followed the tri-Langmuir isotherm. Carboxyl and sulfo groups on the activated carbon surface increased the amount of DMDBT adsorption in which the amount adsorbed for each sulfo group was 6 times greater than that for a carboxyl group. Increasing amounts of 1-methylnaphthalene as an inhibitor caused a decrease in the amount of DMDBT adsorption. However, 1-methylnaphthalene did not affect the adsorption on the sites of carboxyl and sulfo groups. When methanol was used as a polar solvent, adsorption on carboxyl group sites showed a decrease in the amount of DMDBT adsorption, while sulfo groups showed the opposite results. These results were attributed to the oxidation of DMDBT to sulfoxide and/or sulfone by sulfo group on the carbon surface.

**KEYWORDS** : Activated carbon, Adsorption, Sulfo group, Sulfur compounds, Oxidation

1. Introduction

Owing to strict environmental regulations, the removal of sulfur compounds from diesel fuel and gasoline is an important aspect of the worldwide effort to reduce atmospheric pollution caused by the emissions of not only sulfur oxides but particular matter from automobile engines\textsuperscript{1).} In Japan, the sulfur contents in diesel fuel are regulated to 10 mass ppm (mg-sulfur/kg-fuel) or less\textsuperscript{5). In the past decade, much effort has been devoted to the deep desulfurization of diesel fuel\textsuperscript{1). Hydrodesulfurization (HDS) has been commonly used in petroleum refining to reduce the sulfur level in fuel using chemical reaction under high temperature (300-400 °C) and high pressure (20-100 atm of H\textsubscript{2})\textsuperscript{4).} Although the HDS process is efficient in removing thiols, sulfides and disulfides, there are some refractory sulfur-containing compounds such as dibenzothiophene (DBT) and its derivatives against HDS reaction in diesel fuel to produce ultra low sulfur fuel.

Alternatively adsorptive removal using porous materials becomes a matter of concern as one of the most promising options to remove the refractory sulfur-containing compounds from diesel fuel\textsuperscript{5, 6-8) due to its low-energy consumption, the ambient operation temperature and atmospheric pressure\textsuperscript{9, 10).} A wide variety of novel materials are being developed and evaluated as adsorbents\textsuperscript{8, 14-22).} Activated carbons have been employed for the adsorptive removal as well, because they could be widely used as adsorbents due to their high surface area and receptivity for modification. Both physical and chemical properties of an activated carbon may play an important role in the desulfurization process. It has been demonstrated that pore volume with the diameter of less than 7 Å, which is similar in size to DBT and 4,6-dimethyldibenzothiophene (DMDBT) molecules, is critical to achieve a high performance of adsorption capacity\textsuperscript{10, 23-27).} This is owing to strong dispersive interaction between pores and similar size of the adsorbate molecule. Since the oxidation of activated carbon was also found to enhance the adsorption of sulfur compounds\textsuperscript{25, 27-32) caused by acid-base interaction between the basic thiophenes and the acidic surface functional groups\textsuperscript{34).}

Our recent study has shown that activated carbons with acidic surface functional groups, especially carboxyl group, increased the
amount of DMDBT adsorption as well\textsuperscript{33}. In non-polar solvent postulating diesel fuel, activated carbon with carboxyl group increased the amount of adsorption, whereas in polar solvent the opposite tendency was observed\textsuperscript{33}. Moreover, the influence of 1-methylnaphthalene (1 MN) as a competitive inhibitor in n-hexane solvent was examined at a constant concentration of DMDBT assuming practical application to diesel fuel. The increase in 1 MN concentration caused the decrease in the amount of DMDBT adsorption but did not affect the adsorption onto the carboxyl group as the adsorption site\textsuperscript{33}. Accordingly more acidic group such as sulfo group on the carbon is prospective as selective adsorption sites of DMDBT. Therefore, in this study introduction of sulfo group onto activated carbon surface and the effect of sulfo group on the adsorptive removal of DMDBT were examined to develop high capacity and selectivity adsorbents for DMDBT.

2. Experimental

2.1 Materials

The bead-shaped activated carbon, BAC (petroleum pitch as its raw material; Kureha Corporation, Japan), was used in this study. BAC was oxidized with a saturated solution of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} in 1 M H\textsubscript{2}SO\textsubscript{4} (1 g of carbon/10 mL of solution) at 25 °C for 12 days to introduce acidic functional groups, and then the oxidized BAC was washed with distilled water until the pH of washing water showed constant value\textsuperscript{34}. The oxidized BAC was heated at 623 K in the air for 2 h to decompose the sulfuric acid remaining in the carbon. The sample prepared by the oxidation was denoted as Ox.

Both BAC and Ox were treated with SO\textsubscript{3} at ambient temperature for 2 days to introduce sulfo group\textsuperscript{35}. Then, the treated samples were washed with distilled water until the constant pH value of washing water was obtained. The samples were also heated at 623 K in the air for 2 h to decompose the sulfuric acid remaining in the carbon. The samples prepared from BAC and Ox in this process were denoted as BAC-SO\textsubscript{3} and Ox-SO\textsubscript{3}, respectively.

2.2 Porous structure

The porous structure of the activated carbons was characterized by adsorption/desorption isotherms of nitrogen at 77 K. Approximately 0.1 g sample was degassed at 120 °C for 90 min prior to measurement. BET specific surface area (\(S_{\text{BET}}\)) was calculated using the volume of N\textsubscript{2} adsorbed at a relative pressure of 0.03-0.1. The total pore volume (\(V_{t}\)) was calculated from the amount of N\textsubscript{2} adsorption at \(P/P_0 = 0.96\). The micropore volume (\(V_{\text{mic}}\)) was obtained from \(\alpha_s\) plot using subtracting pore effect (SPE) method\textsuperscript{36}. The mesopore volume (\(V_{\text{meso}}\)) was calculated by the difference between \(V_t\) and \(V_{\text{mic}}\).

2.3 Boehm titration

The Boehm titration method was used to determine the amount of surface functional groups\textsuperscript{37,38}. Approximately 0.2 g sample was immersed in each 25 mL of NaOH, NaHCO\textsubscript{3}, and HCl solution at a concentration of 0.1 mol/L and in 25 mL of Na\textsubscript{2}CO\textsubscript{3} at a concentration of 0.05 mol/L. The glass flask containing each solution and sample was sealed and shaken for 4 days at 25 °C. The aliquot of 5 mL for each base was titrated with 0.05 mol/L HCl. For 5 mL of HCl solution, 10 mL of 0.1 mol/L NaOH was added, and then titrated with 0.05 mol/L HCl. The number of acidic sites was calculated with the assumption that NaOH neutralizes lactonic and phenolic groups as well as acidic groups which is equivalent to carboxyl group or more stronger acidic groups; Na\textsubscript{2}CO\textsubscript{3} neutralizes lactonic group and the acidic groups; and that NaHCO\textsubscript{3} only neutralizes the acidic groups. The number of basic groups was calculated from the amount of HCl consumed by the titration.

2.4 Energy dispersive X-ray spectrometer with a scanning electronic microscope (SEM-EDS)

An energy dispersive X-ray spectrometer with the scanning electronic microscope (SEM-EDS) was used to determine the chemical composition of BAC, Ox, BAC-SO\textsubscript{3} and Ox-SO\textsubscript{3}.

2.5 X-ray photoelectron spectroscopy (XPS)

The elements and surface functional groups on the activated carbon were analyzed by X-ray photoelectron spectroscopy (XPS) as well. The incident radiation used was a Mg\textsubscript{Kα} operated at 100 W (10 kV; 10 mA). XPS analysis was carried out under \(<10^{-7}\) Pa at ambient temperature. The chemical species of sulfur on the activated carbon surface was identified by reference data\textsuperscript{39-41}.

2.6 Adsorption isotherm measurements

The model diesel fuel (MDF) which contains 0.5-5.0 mmol sulfur per liter (mmol-S/L) was used as a mixture of n-hexane and DMDBT. The adsorption isotherms of DMDBT in MDF on BAC, Ox, BAC-SO\textsubscript{3} and Ox-SO\textsubscript{3} were determined at 298 K through batch test. Approximately 20 mg of activated carbons was weighed and put into 100 mL flask with 20 mL of MDF in which S content was adjusted to 0.5-5.0 mmol/L. The flasks were then covered with caps, and placed on a shaker with the agitation rate of 100 rpm for 2 days. Subsequently, the equilibrium concentration of DMDBT solution (\(C_e\)) was determined using gas chromatograph with hydrogen flame ionization detector (GC-FID). Then the amount of adsorption at equilibrium \(Q_e\) was calculated from the following equation:

\[
Q_e = \frac{(C_0 - C_e)v}{w} \hspace{1cm} (1)
\]

where \(Q_e\) is the amount of adsorption at equilibrium (mmol/g), \(C_0\) is the initial concentration of adsorbate (mmol/L), \(C_e\) is the equilibrium concentration of adsorbate (mmol/L), \(v\) is the volume of solution (L), and \(w\) is the weight of activated carbon (g).

2.7 Effect of inhibitory substance on the DMDBT adsorption

1-Methylnaphthalene (1 MN) was used as the inhibitory substance for DMDBT adsorption. Various contents of 1 MN solution were added into MDF to adjust the 1 MN concentration of 0.0, 0.9 and 2.2 wt%. S content was fixed as 0.5 mmol/L. The adsorption and sub-
sequent data analysis were carried out with the same procedure described in section 2.6.

2.8 Effect of solvent type on the DMDBT adsorption

Hexane and methanol were used as non-polar solvent and polar solvent, respectively. DMDBT was added into n-hexane or methanol to adjust the DMDBT concentration of 0.5 mmol/L. The adsorption and subsequent data analysis were carried out with the same procedure described in section 2.6.

2.9 Thermal analysis

Thermal analysis for Ox and BAC-SO3 was carried out before and after DMDBT adsorption. Approximately 20 mg of activated carbons was weighted and put into 100 mL flask with 20 mL of 5.0 mmol/L DMDBT solution. After the adsorption experiment, approximately 10 mg of samples was heated to 600 °C at a heating rate of 10 °C/min in a helium flow (flow rate of 100 mL/min), and derivative thermogravimetry (DTG) curves for the samples were obtained.

3. Results and Discussion

3.1 Textural properties

Table 1 presents the structural parameters of the activated carbons used in this study. The data in Table 1 indicated that $S_{BET}$ area and $V_i$ of both Ox and Ox-SO3 became slightly smaller, and also the $V_{mic}$ decreased in comparison with those of BAC. The decrease in those values of Ox was due to the destruction of the pore wall by long time oxidation process of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and the strong oxidant of SO$_3$ decreased each value of $S_{BET}$, $V_i$ and $V_{mic}$, respectively.

3.2 The amount of surface functional groups

Table 2 presents the surface acidic strengths of BAC, Ox, BAC-SO3 and Ox-SO3 obtained by Boehm titration. After carbon surface treatment by $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and/or SO$_3$, the total acidity was enhanced due to the increase in lactonic, phenolic groups as well as acidic groups, which would be equivalent to carboxyl group or more stronger acidic groups, while the total basic groups on the carbon surface contrarily decreased. The amount of acidic group equivalent to carboxyl group or more stronger acidic groups was followed in the order of Ox-SO3 > Ox > BAC-SO3 > BAC, which accounted for 1.16, 1.05, 0.34 and 0.00 meq./g, respectively. Moreno-Castilla et al. identified that the strong acidic group introduced by (NH$_4$)$_2$S$_2$O$_8$ treatment was carboxyl group. On the other hand, Yantasee et al. suggested that the SO$_3$ treatment introduced sulfo group, which was in accordance with our result as shown in Fig. 1. Therefore, high amount of carboxyl groups may be presented on the Ox surface, while the surface of BAC-SO3 may be dominated by sulfo groups.

3.3 The surface sulfur content determined by SEM-EDS

The surface sulfur content (wt%) determined by SEM-EDS is shown in Table 2. The results indicated that BAC, Ox, BAC-SO3 and Ox-SO3 contained 0.30, 0.04, 1.47 and 1.47 wt% of sulfur, respectively. The increase in the content was greatly pronounced for the sample subjected to SO$_3$ treatment. For BAC-SO3, the introduction of 1.17% sulfur content on the activated carbon surface corresponded to 0.37 meq./g of sulfur group. The value of 0.37 meq./g was almost the same contents with the acidic groups stronger than carboxyl group obtained by Boehm titration method. Accordingly, acidic groups stronger than carboxyl group on the surface of BAC-SO3 as well as Ox-SO3 could be expected as sulfur group.

3.4 Elemental composition and sulfur species contents determined by XPS

XPS data provide information on the chemical states of each element, and thus represent the functional groups presented on the carbon surfaces. The content of each element (wt%) and the amount of total sulfuric functional groups, sulfo group and thiol group (meq./g) for the BAC and BAC-SO3 is represented in Table 3. The amount of sulfuric functional groups were calculated by the surface sulfur content (wt%) and the ratio of peak area. The sulfur content of BAC-SO3 obtained by XPS analysis was 1.55 wt%, indicating almost the same

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**Table 1** Textural properties of BAC, Ox, BAC-SO3 and Ox-SO3.

<table>
<thead>
<tr>
<th>AC</th>
<th>$S_{BET}$ [m²/g]</th>
<th>$V_i$ [mL/g]</th>
<th>$V_{mic}$ [mL/g]</th>
<th>$V_{meso}$ [mL/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAC</td>
<td>1390</td>
<td>0.62</td>
<td>0.54</td>
<td>0.08</td>
</tr>
<tr>
<td>Ox</td>
<td>1220</td>
<td>0.58</td>
<td>0.51</td>
<td>0.07</td>
</tr>
<tr>
<td>BAC-SO3</td>
<td>1320</td>
<td>0.59</td>
<td>0.52</td>
<td>0.07</td>
</tr>
<tr>
<td>Ox-SO3</td>
<td>1070</td>
<td>0.53</td>
<td>0.47</td>
<td>0.07</td>
</tr>
</tbody>
</table>

**Table 2** Surface properties of BAC, Ox, BAC-SO3 and Ox-SO3.

<table>
<thead>
<tr>
<th>AC</th>
<th>Acidic* [meq./g]</th>
<th>Lactonic [meq./g]</th>
<th>Phenolic [meq./g]</th>
<th>Total acidic [meq./g]</th>
<th>Basic [meq./g]</th>
<th>Sulfur content [wt%]</th>
<th>Sulfur group [meq./g]</th>
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</thead>
<tbody>
<tr>
<td>BAC</td>
<td>0.00</td>
<td>0.16</td>
<td>0.10</td>
<td>0.26</td>
<td>0.60</td>
<td>0.30</td>
<td>0.09</td>
</tr>
<tr>
<td>Ox</td>
<td>1.05</td>
<td>0.43</td>
<td>0.84</td>
<td>2.32</td>
<td>0.02</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>BAC-SO3</td>
<td>0.34</td>
<td>0.29</td>
<td>0.90</td>
<td>1.53</td>
<td>0.21</td>
<td>1.47</td>
<td>0.46</td>
</tr>
<tr>
<td>Ox-SO3</td>
<td>1.16</td>
<td>0.67</td>
<td>1.72</td>
<td>3.55</td>
<td>0.01</td>
<td>1.47</td>
<td>0.46</td>
</tr>
</tbody>
</table>

* Carboxylic and/or more stronger acidic including sulfo group (–SO$_3$H)
value obtained by SEM-EDS analysis. The amount of sulfo group obtained by XPS analysis was 0.32 meq/g which was closed to the content of stronger acidic groups than carboxyl group determined by Boehm titration method. Therefore, the stronger acidic group than carboxyl group in the surface of BAC-SO₃ was expected as sulfo group.

3.5 Adsorption isotherm of DMDBT

Fig. 2 shows the adsorption isotherms of DMDBT on BAC, Ox, BAC-SO₃ and Ox-SO₃ in hexane solvent at 25 °C.

In order to characterize the DMDBT adsorption for each activated carbon, the Tri-Langmuir equation was used to fit the adsorption isotherms of DMDBT, and represented as:

\[
Q_e = \frac{K_{C\pi}C_e X_{C\pi} + K_{COOH}C_e X_{COOH} + K_{SO3H}C_e X_{SO3H}}{1 + K_{C\pi}C_e + K_{COOH}C_e + K_{SO3H}C_e}
\]

where \( Q_e \) is the equilibrium amount of adsorption (mmol/g), \( C_e \) is the equilibrium concentration of adsorbate (mmol/L), \( X_{C\pi} \), \( X_{COOH} \) and \( X_{SO3H} \) are, respectively, the maximum amount of adsorption (mmol/g) for \( C\pi \), COOH and SO₃H site, and \( K_{C\pi} \), \( K_{COOH} \) and \( K_{SO3H} \) are the equilibrium constant of adsorption for \( C\pi \), COOH and SO₃H site, respectively. \( C\pi \) site is related to the adsorption by \( \pi-\pi \) interaction between \( \pi \) electron of the graphite layer and aromatic ring of adsorbate, while COOH and SO₃H sites are concerned with the carboxyl group and sulfo group.

The parameters of Tri-Langmuir equation are presented in Table 4.

Having applied each parameter to the equation, the approximation curves for the Tri-Langmuir adsorption isotherms of DMDBT were represented in Fig. 2. The data in Table 4 indicated that the values of \( X_{COOH} \) and \( X_{SO3H} \) for Ox and BAC-SO₃ were 0.35 and 0.63 mmol/g, respectively. On the other hand, the amount of carboxyl and sulfo group for each activated carbon was 1.05 and 0.32 meq/g as shown in Table 2 and Table 3, respectively. Thus, the amount of DMDBT adsorption per one sulfo group showed 6 times greater than that of carboxyl group. However, the \( K_{SO3H} \) values of BAC-SO₃ represented 1.5 L/mmol, which was lower than 2.0 L/mmol of the \( K_{COOH} \) for Ox. These results suggest that sulfo group would be effective in a high DMDBT concentration level contrastive to the low concentration level.

3.6 Effect of inhibitory substance on the DMDBT adsorption

Fig. 3 shows the effect of 1 MN on the adsorption of DMDBT onto BAC, Ox, BAC-SO₃ and Ox-SO₃. The increase in 1 MN content to 0.9 and 2.2 wt% caused a decrease in the amount of DMDBT adsorption by approximately 45 and 60%, respectively, however, the differ-

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Table 3  Elemental composition and sulfur species contents of BAC and BAC-SO₃ obtained by XPS analysis.

<table>
<thead>
<tr>
<th>AC</th>
<th>Elemental composition</th>
<th>Sulfur group</th>
<th>R-SO₃H [meq/g]</th>
<th>R-SH [meq/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C [wt%]</td>
<td>O [wt%]</td>
<td>S [wt%]</td>
<td></td>
</tr>
<tr>
<td>BAC</td>
<td>95.67</td>
<td>4.33</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>BAC-SO₃</td>
<td>88.25</td>
<td>10.20</td>
<td>1.55</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Table 4  Tri-Langmuir parameters of DMDBT adsorption.

<table>
<thead>
<tr>
<th>AC</th>
<th>( X_{C\pi} ) [mmol/g]</th>
<th>( K_{C\pi} ) [L/mmol]</th>
<th>( X_{COOH} ) [mmol/g]</th>
<th>( K_{COOH} ) [L/mmol]</th>
<th>( X_{SO3H} ) [mmol/g]</th>
<th>( K_{SO3H} ) [L/mmol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAC</td>
<td>1.06</td>
<td>2.9</td>
<td>0.00</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Ox</td>
<td>0.90</td>
<td>2.9</td>
<td>0.35</td>
<td>2.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>BAC-SO₃</td>
<td>1.00</td>
<td>2.9</td>
<td>0.00</td>
<td>0.0</td>
<td>0.63</td>
<td>1.5</td>
</tr>
<tr>
<td>Ox-SO₃</td>
<td>0.88</td>
<td>2.9</td>
<td>0.35</td>
<td>2.0</td>
<td>0.63</td>
<td>1.5</td>
</tr>
</tbody>
</table>

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Fig. 2  Adsorption isotherms of DMDBT on BAC, Ox, BAC-SO₃ and Ox-SO₃ in hexane solvent at 25 °C.

Fig. 3  Adsorption capacity of DMDBT under various concentrations of 1 MN onto BAC, Ox, BAC-SO₃ and Ox-SO₃ in hexane solvent at 25 °C.
ences in the inhibition amount of DMDBT remained constant among each activated carbon. This implied that 1 MN affected the DMDBT adsorption onto the Cπ site contrastive to the adsorption onto the COOH and SO 3H sites. These results suggested that carboxyl and sulfo groups were effective for the selective adsorption of DMDBT. The selectivity could be attributed to dipole interaction between DMDBT and carboxyl and/or sulfo group. The dipole strengths of DMDBT and 1 MN are 0.77 and 0.27 D, respectively, which would cause the differences in the amount of DMDBT adsorption among BAC, Ox, BAC-SO₃ and Ox-SO₃ even the higher content of 1 MN.

3.7 Effect of solvent type on the adsorption

Fig. 4 shows the effect of solvent type on the DMDBT adsorption onto BAC, Ox, BAC-SO₃ and Ox-SO₃. In hexane solvent, the amount of DMDBT adsorption onto Ox, BAC-SO₃ and Ox-SO₃ was higher than that onto BAC. In methanol solvent, the amount of DMDBT adsorption onto Ox decreased compared to BAC, while BAC-SO₃ showed the opposite result. The dipole strength for methanol is 1.49 D, which is higher than 0.77 D for DMDBT. Therefore, it could be suggested that SO₃H site was effective for the DMDBT adsorption in methanol solvent compared to COOH site. Seredych and Bandosz showed that acidic functional groups had a positive effect on the oxidation of DMDBT to sulfoxide and/or sulfone as shown in Fig. 5. The products of DMDBT oxidation such as sulfone have higher boiling point, and also stronger polarity of 4.79 D than DMDBT. These results would reflect the increase in the amount of DMDBT adsorption onto BAC-SO₃ in methanol solvent.

3.8 Thermal analysis

DTG curves for Ox and BAC-SO₃ before and after DMDBT adsorption are presented in Figs. 6 and 7, respectively. The complex peaks for weight loss after adsorption related to the removals of solvent, adsorbate and surface functional groups. The peaks at the temperature of less than 100 °C attribute to the removal of moisture or n-hexane, of which the boiling points are known to be 100 and 69 °C, respectively. The peak at around 300 °C would be concerned with the removal of DMDBT (Boiling point: 340-350 °C). The gradual rise of the DTG curves at the temperature of more than 400 °C resulted from the decomposition of acidic functional groups. The peak at around
400 °C in Fig. 7 would indicate the removal of the products of DMDBT oxidation, whereas no peak in the DTG curve for Ox was detected. Accordingly, sulfo group could play an important role in the oxidation of DMDBT to sulfoxide and/or sulfone, although little effect for the oxidation was found out for carboxyl group.

4. Conclusions

This study is aimed to introduce sulfo group to activated carbon surface and also to examine the effect of sulfo group on the adsorptive removal of DMDBT. The main conclusions can be summarized as follows.

- After the SO$_3$ treatment of activated carbon surface, the acidic groups stronger than carboxyl group as well as sulfur content increased, implying the introduction of sulfo group on the activated carbon surface.
- The SO$_3$ treatment of activated carbon surface can obviously enhance the amount of DMDBT adsorption, and the amount of DMDBT adsorption per one sulfo group was 6 times greater than carboxyl group.
- Carboxyl and sulfo group could selectively adsorb DMDBT, and was effective for the DMDBT adsorption in the existence of inhibitory substance.
- Sulfo group could oxidize DMDBT to sulfoxide and/or sulfone, and enhanced the amount of DMDBT adsorption even in polar solvent.

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References