Plasma Modification of Activated Carbon Fibers for Adsorption of \( \text{SO}_2 \)

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Abstract
Viscose-based activated carbon fibers (VACFs) were treated by a dielectric-barrier discharge plasma under the feed gas of \( \text{N}_2 \). The surface functional groups of VACFs were modified to improve the adsorption and catalysis capacity for \( \text{SO}_2 \). The surface properties of the untreated and plasma-treated VACFs were diagnosed by SEM, BET, FTIR, and XPS, and the adsorption capacities of VACFs for \( \text{SO}_2 \) were also compared and discussed. The results show that after the plasma treatment, the external surface of VACFs was etched and became rougher, while the surface area and the total pore volume decreased. FTIR and XPS revealed that nitrogen atoms were introduced onto the VACFs surface and the distribution of functional groups on the VACFs surface was changed remarkably. The adsorption characteristic of \( \text{SO}_2 \) indicates that the plasma-treated VACFs have better adsorption capacity than the original VACFs due to the nitrogen functional groups and new functional groups formed in modification, which is beneficial to the adsorption of \( \text{SO}_2 \).

Keywords: cold plasma, surface modification, activated carbon fibers, adsorption, \( \text{SO}_2 \)

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1 Introduction

Pollutants such as \( \text{SO}_2 \), \( \text{NO}_2 \), etc. emitted from coal combustion processes harm the environment and human health. Many technologies have been developed to control the concentrations of these pollutants, such as fuel desulfurization, combustion process desulfurization, and flue gas desulfurization (FGD) which is one of the most widely used technologies. In view of the high cost and the complex systems for the removal of individual pollutants, research focuses on the new technologies that have higher desulfurization efficiency, lower investment and operating costs, and can remove \( \text{SO}_2 \), \( \text{NO}_2 \) and other pollutants simultaneously. Recently, the removal of \( \text{SO}_2 \) and \( \text{NO}_2 \) by using activated carbon fibers (ACFs) has been studied extensively due to its faster adsorption and desorption kinetics, significantly high specific surface areas, a uniform micropore structure, and cheap investment \(^{1\sim3}\).

The adsorption and catalytic properties of ACFs that affect the removal efficiency of \( \text{SO}_2 \) are closely related to their specific surface areas and surface chemical properties. For example, RAYMUNDO-PÍNERO et al. have demonstrated that the adsorption capacity of \( \text{SO}_2 \) depended on the pore size of ACFs, and the optimal pore size for the oxidation of \( \text{SO}_2 \) to \( \text{SO}_3 \) was around 7 Å \(^{4,5}\). LISOVSKII et al. have shown that concentrated nitric acid can increase the basicity of ACs and promote \( \text{SO}_2 \) adsorption \(^{6}\). Many methods have been devised to increase specific surface areas and strengthen the activities of surface functional groups. The method of loading metal ions to modify ACFs was used by WANG Jianying \(^{7}\). \( \text{NaOH} \) and KOH were also used to pretreat ACFs for the removal of \( \text{SO}_2 \) and NO \(^{8}\). Nitric acid, sulfuric acid, phosphoric acid and other oxidants for chemical treatment, and the oxidizers-gas for heat treatment of ACFs were all applied for the purpose of generating surface oxygen-containing functional groups \(^{9\sim12}\). In order to obtain nitrogen-containing functional groups, N-containing reactants, such as \( \text{NH}_3 \), urea, and \( \text{N}_2 \), were used to react with carbon at 1073 K \(^{4,5,13,14}\). Surface modification by discharge plasma is of great and increasing significance of industrial application because of its diversified advantages. For instance, it can uniformly modify the surface of the treated samples without changing their bulk properties significantly. It is also easy to create any ambiance for oxidation, reduction, or inactive reactions by changing the feed gas \(^{15\sim17}\).

In this work, VACFs were treated by dielectric-barrier discharge (DBD) plasma in nitrogen gas at atmosphere pressure to enhance their adsorption and catalysis capacities for \( \text{SO}_2 \), and the adsorption capacities of the untreated and treated VACFs for \( \text{SO}_2 \) were also compared and discussed.

2 Experiment

2.1 Materials

The VACFs used in this study were purchased from the Zichuan Carbon Fiber Co., Ltd. (Shan-
and down to change the discharge gap. 8 65 mm, and the grounded electrode can be adjusted up thin quartz foil with thickness of 1 mm and diameter of same at the multi-needle panel and the copper electrode are the by using a multi-needle-to-plate electrode. The size of polymethyl methacrylate (PMMA) is cylindrical with shown in Fig. 1. The DBD plasma reactor made of 2.2 Plasma treatment or sorbed moisture and organic molecules from air. 1048 the DBD reactor; \( V \): discharge voltage; \( T^a \): treatment time; \( V_\text{in} \): voltage in the DBD reactor; \( I^b \): electric current in the DBD reactor 2.3 Surface properties The surface morphologies of the untreated and treated VACFs were observed by using a scanning electron microscopy (SEM, scanning microscope type Quanta 200, FEI, Netherlands). The samples were examined and typical values of voltage and working distance of operation were 30 kV and 15 \( \mu \)m. The porous structure of VACFs was determined from the nitrogen adsorption isotherm at 77 K which was measured by using automatic gas adsorption apparatus (Micromeritics Gemini V2380, USA). The Brunauer-Emmett-Teller (BET) equation was used to obtain the specific surface areas (SBET) and the adsorption average pore width \( (W_p, 4 \text{ V} / \text{A}) \). The t-pot theory was employed to calculate the micropore surface area \( (S_m) \), the external surface area \( (S_{ex}) \), and micropore volumes \( (V_m) \). The mesopore surface area \( (S_{me}) \) and the mesopore volumes \( (V_{me}) \) have been determined by means of the Barrett-Joyner-Halenda (BJH) method.

The surface chemical compositions of the untreated and treated ACFs were determined by using a Kratos XSAM800 X-ray photoelectron spectroscopy (XPS). Prior to the analysis, the samples were dried at 393 K for 1 h. The analysis was performed under high-vacuum conditions using a Mg K\( \alpha \) X-ray source which produced photons at 1253.6 eV. The vacuum in the analysis chamber was always better than \( 5 \times 10^{-9} \) Pa. The analyser was operated in fixed-analyser transmission mode with step sizes of 0.25 eV and 0.1 eV for wide scans and region scans, respectively. After the base line was subtracted, the curve-fitting was performed using the non-linear least-squares algorithm assuming a Gaussian peak shape. This peak-fitting procedure was repeated until an acceptable fitting was obtained.

A Fourier transform infrared spectroscopy (FTIR, Nicolet 5700, Nicolet Instrument Co., USA) was also used for determining the surface functional groups of ACFs. The spectra were recorded from 4000 cm\(^{-1}\) to 400 cm\(^{-1}\) at a scan rate of 0.2 cm/s. Infrared spectra were recorded using KBr pellets. Before the spectrum of a sample was recorded, the background line obtained was arbitrarily and automatically subtracted.

2.4 Adsorption of \( \text{SO}_2 \) Adsorption of \( \text{SO}_2 \) by VACFs was carried out at atmospheric pressure in a fixed-bed reactor (20 mm\( \times \)20 mm\( \times \)250 mm). 8 pieces (about 1.0 g) of the untreated or the treated VACFs samples were closely packed into the reactor. The gas composition was \( \text{SO}_2 \) 1500 ppm, 9 vol\% \( \text{O}_2 \) and 8 vol\% \( \text{H}_2\text{O} \) balanced by \( \text{N}_2 \). The inlet \( \text{SO}_2 \) concentration \( (C_0) \) and the outlet \( \text{SO}_2 \) concentration \( (C) \) were analyzed by a flue gas analyser (Ecom J2KN, Germany). The adsorption condition was controlled at a gas speed of 0.8 L/min with temperature of 30\(^\circ\)C.

3 Results and discussion

3.1 Results and discussion

The SEM pictures of the untreated and treated VACFs are shown in Fig. 2. It is observed that the
surface of VACFs-8/10 (here, 8 denotes the discharge voltage, in kV; 10 denotes the treatment time, in minutes; the same hereafter) is as smooth as VACFs-0 after plasma modification. Meanwhile, the surfaces of VACFs-8/20 and VACFs-10/10 are etched to become much rougher with a few etch pits, but the surfaces are not destroyed significantly by plasma. This suggests clearly that the plasma treatment can affect the external fiber surface on the micron scale under a special circumstance.

![SEM pictures for (a) the untreated, (b) VACFs-8/10 (c) VACFs-8/20 and (d) VACFs-10/10](image)

Fig. 2

![Nitrogen adsorption isotherms of the VACFs before and after modification (color online)](image)

Fig. 3

The N$_2$ adsorption isotherms of VACFs-0, VACFs-8/10, VACFs-8/20 and VACFs-10/10 are shown in Fig. 3. These samples exhibit an adsorption isotherm of type I according to IUPAC, which indicates these samples are predominantly microporous materials. The surface pore structures of VACFs modified at different conditions are shown in Table 2. The results show that the surface area and total pore volume become smaller after plasma modification. This might be that the plasma generated in discharge acts on the VACFs surface and brings about some new functional groups which may be located at the entrance of pores and make the surface area and total pore volume decrease. Table 2 and Fig. 2 also show that although plasma treatment changes some of the properties to a certain extent, it does not greatly change the VACFs surface structure.

### 3.2 FTIR analysis

Fig. 4 shows the FTIR spectra for the VACFs treated at different voltages and time. The aliphatic hydrogen appears at 2920 cm$^{-1}$ and 2850 cm$^{-1}$. The C-O and C=O peaks of O-contained carbon ring groups (phenolic hydroxyl groups, quinonoid carbonyl groups) appeared at 1097 cm$^{-1}$. Compared with VACFs-0, some new peaks appear at 3734 cm$^{-1}$, 3671 cm$^{-1}$, 1456 cm$^{-1}$, and 1261 cm$^{-1}$ in the plasma-treated VACFs. Moreover, there are a number of overlapping bands appearing between 1610 cm$^{-1}$ and 1480 cm$^{-1}$. The peak at 3734 cm$^{-1}$ and 3671 cm$^{-1}$ should correspond to nitrogen functional groups [18]. The two correlative peaks at 1456 cm$^{-1}$ and 1384 cm$^{-1}$ indicate -C=O belonging to the carbonate groups [19]. The peak at 1261 cm$^{-1}$ corresponds to -COO symmetrical stretching vibration [20]. The bands appearing between 1610 cm$^{-1}$ and 1480 cm$^{-1}$ may be caused by the vibrations of pyridine-like structures or cyclic amides. Besides, a new peak appears at 1739 cm$^{-1}$ in VACFs-8/20, which can be attributed to the stretching vibrations of C=O moieties in carboxylic, ester, lactonic or anhydride groups [20].

![FTIR spectra of VACFs modified by plasma in N$_2$](image)

Fig. 4

<table>
<thead>
<tr>
<th>Samples</th>
<th>$S_{BET}$</th>
<th>$S_{mic}$</th>
<th>$S_{ext}$</th>
<th>$S_{mes}$</th>
<th>$V_{tr}$</th>
<th>$V_{mic}$</th>
<th>$V_{mes}$</th>
<th>$W_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(m$^2$/g)</td>
<td>(m$^2$/g)</td>
<td>(m$^2$/g)</td>
<td>(m$^2$/g)</td>
<td>(cm$^3$/g)</td>
<td>(cm$^3$/g)</td>
<td>(cm$^3$/g)</td>
<td>(Å)</td>
</tr>
<tr>
<td>VACFs-0</td>
<td>933.59</td>
<td>770.22</td>
<td>163.38</td>
<td>93.29</td>
<td>0.47</td>
<td>0.37</td>
<td>0.072</td>
<td>20.34</td>
</tr>
<tr>
<td>VACFs-8/10</td>
<td>888.15</td>
<td>726.40</td>
<td>161.75</td>
<td>88.97</td>
<td>0.45</td>
<td>0.35</td>
<td>0.066</td>
<td>20.24</td>
</tr>
<tr>
<td>VACFs-8/20</td>
<td>879.00</td>
<td>741.58</td>
<td>137.42</td>
<td>76.00</td>
<td>0.44</td>
<td>0.36</td>
<td>0.056</td>
<td>20.12</td>
</tr>
<tr>
<td>VACFs-10/10</td>
<td>909.64</td>
<td>756.05</td>
<td>153.59</td>
<td>84.20</td>
<td>0.46</td>
<td>0.37</td>
<td>0.062</td>
<td>20.16</td>
</tr>
</tbody>
</table>

Table 2. Pore structure parameters of VACFs

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3.3 XPS analysis

Fig. 5 shows the XPS survey spectra of VACFs-0 and VACFs-8/20. According to binding energy from low to high, there are three peaks assigned to C1s, N1s and O1s, respectively. It is observed that the original VACFs contained C and O atoms only but the nitrogen atoms were introduced onto the surface of VACFs after plasma treatment. The relative content of three elements in VACFs are shown in Table 3. It can be seen that the relative percentage of C atoms decreases greatly, while the relative percentage of O atoms increases remarkably from 7.1% to 17.8%, and N atoms are also introduced to VACFs. The higher O/C and N/C might suggest that a large amount of free radicals are formed in such conditions.

Table 3. XPS surface element analysis of VACFs

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relative concentration (%)</th>
<th>O/C</th>
<th>N/C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>O</td>
</tr>
<tr>
<td>VACFs-0</td>
<td>92.9</td>
<td>7.1</td>
<td>0</td>
</tr>
<tr>
<td>VACFs-8/20</td>
<td>80.0</td>
<td>17.8</td>
<td>2.2</td>
</tr>
</tbody>
</table>

In order to explore the surface functional groups and their relative content in VACFs-0 and VACFs-8/20, the high-resolution XPS spectra of C1s, O1s and N1s regions are illustrated in Fig. 6 to Fig. 8, respectively.

The high-resolution XPS spectra of the C1s region before and after modification are illustrated in Fig. 6. The spectra are asymmetric and have band tailing at high binding energy. However, the slope of the peaks at high bind energy is different before and after modification. This may result from differences in the structures of the oxygen-containing functional groups of VACFs and the surroundings of each oxygen-containing functional groups. The peak fitting and peak area are used to explore the form and content of surface functional groups of untreated and plasma-treated VACFs.

The binding energy of 284.5 eV, 285.5 eV, 287.0 eV, and 288.5 eV corresponds to C-C, C-O, C=O, and COOH/COOR, respectively [17]. The form and its relative content of functional groups before and after treatment are shown in Table 4. It can be seen that the content of C-C decreased greatly, while C-O, C=O and COOH/COOR (carboxyl, ester-based) increased after being treated by plasma, especially the increase of C=O (increased about 55 %) which is beneficial to the removal of acid gas.

The high-resolution XPS spectra of O1s region are illustrated in Fig. 7. Four different O functional groups and a contribution of chemisorbed water were identified, namely C=O groups at 529.5 eV, carbonyl oxygen atoms in esters, amides, anhydrides and oxygen atoms in hydroxyls or ethers at 531.7 eV, the ether oxygen atoms in esters and anhydrides at 532.7 eV, and the oxygen atoms in carboxyl groups at 533.6 eV [21]. As shown in Table 4, although the C=O (529.5 eV) group decreases slightly, the carbonyl (531.7 eV) and carboxyl (533.6 eV) groups that having C=O or -OH increase more after being treated, which is consistent with the increase of C=O (287.0 eV) in C1s.

Table 4. Functional groups and their content in VACFs-0 and VACFs-8/20

<table>
<thead>
<tr>
<th>Binding energy (eV)</th>
<th>Functionality</th>
<th>VACFs-0</th>
<th>VACFs-8/20</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s</td>
<td>C-C</td>
<td>62.06</td>
<td>48.75</td>
</tr>
<tr>
<td></td>
<td>C-O</td>
<td>19.43</td>
<td>24.32</td>
</tr>
<tr>
<td></td>
<td>C=O</td>
<td>8.19</td>
<td>12.72</td>
</tr>
<tr>
<td></td>
<td>COOH/COOR</td>
<td>10.32</td>
<td>14.21</td>
</tr>
<tr>
<td>O1s</td>
<td>Keto, quinone groups(C=O)</td>
<td>11.77</td>
<td>10.86</td>
</tr>
<tr>
<td></td>
<td>Carbonyl oxygen atoms in esters, amides, anhydrides and oxygen atoms in hydroxyls or ethers(carbonyl)</td>
<td>30.25</td>
<td>32.56</td>
</tr>
<tr>
<td></td>
<td>Ether oxygen atoms in esters and anhydride(ether)</td>
<td>25.63</td>
<td>26.39</td>
</tr>
<tr>
<td></td>
<td>Oxygen in carboxyl groups</td>
<td>18.69</td>
<td>19.56</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>13.66</td>
<td>10.63</td>
</tr>
<tr>
<td>N1s</td>
<td>Pyridine-like</td>
<td>24.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Amides</td>
<td>19.28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Aromatic amines, -NH2 aniline/imines C=NH</td>
<td>12.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Quaternary nitrogen</td>
<td>33.22</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Protonated amide-N</td>
<td>11.33</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 6 Representative C1s spectra of VACFs-0 and VACFs-8/20

Fig. 7 Representative O1s spectra of VACFs-0 and VACFs-8/20 (color online)

The high-resolution XPS spectra of the N1s region are illustrated in Fig. 8. Contrary to the C1s and O1s spectra, the N1s spectrum is relatively feeble. The binding energy of the N1s high-resolution spectra is acquired over 388∼408 eV which correspond to different types of pyridine, lactam, and pyrrole [22]. It is observed that the modified N1s spectrum shows no band tailings. It is indicated that the species of nitrogen functional groups belong to the same group of different structures. As shown in Table 4, the N1s spectrum is decomposed into five identified components: the peak at 398.4 eV is attributed to pyridine-like structures; the peak at 399.6 eV ascribed to amides; the peak at 400.4 eV attributed to the nitrogen atoms in aromatic amines, -NH2 aniline and/or imines C=NH; the peak at 401.6 eV ascribed to quaternary nitrogen; and the peak at 402.7 eV attributed to protonated amide-N [13]. There are two species of important functional N atoms on the surface of the treated VACFs: pyridine-N and quaternary nitrogen which make a difference in the adsorption of SO2.

Fig. 8 Representative N1s spectrum of VACFs-8/20 (color online)

3.4 Adsorption of SO2

The adsorption curves of SO2 on VACFs are shown in Fig. 9. It can be seen that plasma treatment can affect the adsorption capacity of VACFs for SO2, and all the plasma-treated VACFs show higher adsorption efficiency than the original VACFs. Compared to VACFs-0, VACFs-8/10 has an increase of 11% in adsorption efficiency at 30 min, while 19% for VACFs-8/20 and 21% for VACFs-10/10, respectively. The reason is probably that some basic functional groups, for instance, nitrogen-containing functional groups, were introduced onto the surface of VACFs, especially the pyridinic type groups which play a major role in the chemisorption of SO2 [18]. This is because the lone pair electrons of N atom in pyridinic type groups shows stronger alkalin- ity, so it has a strong adsorption affinity and capacity to acid gas [23]. Previous studies have shown that ACF surface area, the total pore volume, and surface functional groups were important factors for adsorption of SO2. Compared to the slight decrease of the surface area and total pore volume after treatment (Table 2), the adsorption capacity increases, which indicates that
the surface functional groups play more important role in the adsorption of SO$_2$.

![Fig.9 Breakthrough profiles of SO$_2$ over plasma-treated VACFs (color online)](image)

4 Conclusion

A multi-needle-to-plate DBD plasma has been used to modify VACFs with a feed gas of N$_2$. After being treated by plasma, the external surface of the treated VACFs was etched and became rougher while the surface area and the total pore volume decreased. The FTIR results show that some new functional groups like nitrogen functional groups are formed on the treated VACFs. The XPS obviously reveals that nitrogen atoms are introduced to the VACFs surface after plasma treatment and the distribution of functional groups on the VACFs surface are remarkably changed and more C=O groups are formed, which are beneficial to desulfurization. The results of SO$_2$ adsorption show that plasma-treated VACFs have higher adsorption capacities than the original VACFs, and the surface functional groups play a more important role than the surface area and the total pore volume in adsorption capacity of SO$_2$. Basically, an 11%×21% increment in adsorption efficiency has been achieved in this work.

References


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