Removal of target odorous molecules on to activated carbon cloths

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Abstract Activated carbon materials are adsorbents whose physico-chemical properties are interesting for the treatment of odorous compounds like hydrogen sulfide. Indeed, their structural parameters (pore structure) and surface chemistry (presence of heteroatoms such as oxygen, hydrogen, nitrogen, sulfur, phosphorus) play an important role in H₂S removal. The cloth texture of these adsorbents (activated carbon cloths) is particularly adapted for dealing with high flows, often found in the treatment of odor emissions. Thus, this paper first presents the influence of these parameters through adsorption isothermal curves performed on several materials. Secondly, tests in a dynamic system are described. They highlight the low critical thickness of the fabric compared to granular activated carbon.

Keywords Activated carbon cloths; adsorption; hydrogen sulfide; odor; oxidation

Introduction

Because of their adsorption properties, activated carbon cloths have become well known adsorbents in air and water treatment (Brasquet and Le Cloirec, 1997). Their major application is in the treatment of industrial volatile organic compound (VOC) emissions of relatively low flow (lower than 500 Nm³ h⁻¹) and relatively high concentration (1 to 10 g Nm⁻³) (Subrenat and Le Cloirec, 2000a). Their intrinsic properties also make them good candidates for the treatment of odorous emissions (such as H₂S), generally at low concentration and high flow. Indeed, their porous structure makes it possible to develop a large specific surface area for the mass transfer of the molecules, while their chemical properties (presence of oxygen-containing functional groups) enable H₂S oxidation (Adib et al., 2000). Moreover, the cloth texture of these materials makes it possible to design filters with high bypass sections in low reactor volumes (Subrenat et al., 2000b), allowing the treatment of high flows, with high resident times and acceptable pressure losses. Thus, activated carbon cloths offer a way of developing new treatment processes for odorous effluent.

This paper presents adsorption isotherm measurements and gives an overview of the oxidation reaction mechanisms in various activated carbon cloths. The influence of the surface chemical characteristics of the adsorbent and the quality of the gas phase (relative humidity) are discussed. The treatment capacities in a dynamic system are calculated from the breakthrough curves, and the critical thickness of these media is compared to the granular form.

Materials and methods

Adsorbents

Several commercial carbon adsorbent materials are selected for their different physico-chemical characteristics, and, more particularly, for their surface chemical properties that are of interest in the mechanisms of H₂S adsorption and oxidation. Thus, close attention is paid to this aspect through measurements of oxygenated surface functions (acidic and basic) using the Boehm method (Boehm, 1966), the point of zero charge (PZC) measured...
by potentiometric titration with various ionic strengths (Babic et al., 1999) and of the presence of ions on the carbon surface. The porous structure of each material is also characterized according to the BET method (Brunauer et al., 1938), as this also influences the phenomena of mass transfer. All these data are shown in Table 1. We can observe:

- differences in specific surface areas, which are higher for the cloths referred to as VS15 and the granules referred to as NC60 compared to the fabrics WWP3 and WWP3-V;
- the very microporous character of fabrics WWP3 and VS15;
- the greater concentration of oxygen functional groups for fabrics WWP3 and WWP3-V.

**Treatment in a batch reactor**

The samples of adsorbents are confined in glass reactors with an initial concentration of hydrogen sulfide ($C_0$) perfectly well determined and controlled. The relative humidity is controlled: 0% (dry air) and 30% (humid air).

The concentration of $H_2S$ in the gas phase of the reactor is measured by the Spectroquant® (Merck) method and based on the Caro–Fisher reaction (reaction between hydrogen sulfide with $N,N'$-dimethyl-1,4-phenylenediamine to form methylene blue). A gas sample of $H_2S$ is injected into a basic solution (pH 9–10). Then the reactant is added and mixed with the solution. The concentration is determined by analysis with a UV-spectrophotometer Shimadzu UV-1601 at 665 nm wavelength.

**Mass-transfer kinetics.** Kinetic curves are performed, following the decreasing concentration ($C_t$) in the gas phase versus time. The mass-transfer kinetics of $H_2S$ into carbon adsorbents result from complex combinations of diffusion phenomena and oxidation reactions of the molecules. Hence, the kinetic curves are modeled with a first pseudo-order equation:

$$q(t) = \frac{V}{M} \left( C_0 - C_e \left( 1 - e^{-\frac{t}{\tau}} \right) \right)$$

where $q(t)$ is the $H_2S$ quantity loaded on to the adsorbent porosity versus time $t$ (min), $V$ is the reactor volume (m$^3$), $M$ is the amount of adsorbent, $C_e$ is the equilibrium gas-phase concentration (mg m$^{-3}$) and $\tau$ the model constant (min$^{-1}$).

**Equilibrium isotherms.** Equilibrium isotherms are also studied using different amounts of adsorbents to reach different equilibrium concentrations ($C_e$) in the gas phase of the reactor. Mass balance is used to determine the $H_2S$ quantities loaded in the adsorbent ($q_e$). For each experimental point, the quantity of $S_0$ produced on the adsorbent surface is measured. The sulfur is extracted from the carbon adsorbents by dissolution in 10 ml of car-

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Characteristics of the studied carbon adsorbents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Texture</td>
<td>Woven</td>
</tr>
<tr>
<td>Precursor</td>
<td>Rayon</td>
</tr>
<tr>
<td>Specific weight (g.m$^{-2}$)</td>
<td>130</td>
</tr>
<tr>
<td>Thickness (mm)</td>
<td>0.47</td>
</tr>
<tr>
<td>Activation</td>
<td>CO$_2$</td>
</tr>
<tr>
<td>Specific surface area BET (m$^2$ g$^{-1}$)</td>
<td>976</td>
</tr>
<tr>
<td>Microporosity (% of the total volume)</td>
<td>&gt;96</td>
</tr>
<tr>
<td>Pore volume &lt; 20 Å (cm$^3$ g$^{-1}$)</td>
<td>0.335</td>
</tr>
<tr>
<td>2 nm &lt; pore volume &lt; 1,000 nm (cm$^3$ g$^{-1}$)</td>
<td>0.024</td>
</tr>
<tr>
<td>Acidic surface functional groups (meq g$^{-1}$)</td>
<td>1.10</td>
</tr>
<tr>
<td>Basic surface functional groups (meq g$^{-1}$)</td>
<td>0.75</td>
</tr>
<tr>
<td>pH$_{PZC}$</td>
<td>9.23</td>
</tr>
</tbody>
</table>
bon disulfide, with agitation, over 10 hours. After filtration, evaporation at room temperature and crystallization, the quantity of sulfur is determined by the gravimetric method.

**Treatment in a dynamic system**

The outlet H$_2$S concentration is continuously measured with a specific analyzer ONYX 5000, downstream of the cloth or granules filter (Figure 1). The inlet concentration is calculated by dilution of pure H$_2$S with dry or wet air (30% relative humidity) controlled with mass-flow regulators.

The critical thickness ($h_0$), defined as the minimal value when the breakthrough time equals 0, is given by the Adams–Bohart model:

\[ t_b = \frac{q_0}{U_0C_0} (h - h_0) \]

where $t_b$ is the breakthrough time (s), $q_0$ the maximal treatment capacity of the adsorbents (g m$^{-3}$), $U_0$ the flow velocity (m s$^{-1}$), and $h$ the thickness of the adsorbent material used (mm).

**Results and discussion**

**Adsorption in a batch reactor**

*Mass-transfer kinetics.* The experimental mass-transfer kinetics are presented in Figure 2, and the modeled parameters are summarized in Table 2.

It is difficult to establish a precise correlation between the mass-transfer velocity of the H$_2$S treatment and the physico-chemical characteristics of the adsorbent. This is due to the fact that the kinetics are more controlled by the reaction pathway of oxidation than by the diffusion phenomena. Nevertheless, we can observe that the presence of moisture (and oxygen in air) decreases the mass-transfer velocities but increases the treatment capacities (Marsteau, 2001). For all cases, equilibrium is reached in less than one hour. Thus, a three-hour delay is used for the isotherm equilibrium measurements.

![Experimental set-up used for dynamic studies](image)

**Figure 1** Experimental set-up used for dynamic studies

![Mass-transfer kinetics](image)

**Figure 2** Mass-transfer kinetics (a) Mass-transfer kinetics under dry air; (b) mass-transfer kinetics under wet air
The mass-transfer kinetics are more rapid under dry air (see constant-time reaction $\tau$ values in Table 2). This is due to the high velocity of the reaction pathway and the mechanisms in the liquid water film in the presence of oxygen. However, the quantities loaded in the adsorbents are greater under wet air (see $q_e$ values in Table 2).

**Equilibrium study.** The experimental isotherm equilibria are presented in Figure 3. They are Type I isotherms under wet air (Figure 3a) and Type IV isotherms under dry air (Figure 3b). Under dry air, the H$_2$S molecules are adsorbed in the presence of oxygen in air and at the adsorbent surface (functional groups) the molecule is mainly oxidized into the sulfur form S$_0$. The presence of sulfur autocatalyzes the oxidation mechanisms to convert H$_2$S into S$_0$. Hence, after a first step in the equilibrium concentration range of 500 to 2,500 mg m$^{-3}$, the treatment capacity of the adsorbents increases to a second step. Of course, these very high concentrations do not correspond to industrial applications where adsorption treatment could be carried out. Nevertheless, this concentration range allows the activity of the formed sulfur and the oxidation pathway to be observed. Hence, the results show that the sulfur activity depends on the amount of sulfur deposit at the surface of the adsorbent (Steijns et al., 1976a,b). This is observed for a quantity of sulfur of around 2 mmoles g$^{-1}$ (Figure 4b). Under wet air, the equilibrium isotherms reveal no autocatalytic role of the formed sulfur (Figure 4a). This is inhibited by the presence of a thin water film at the surface of the materials. Moreover, this liquid film allows high treatment capacities compared to dry air due to dissolution and support for the oxidation of the H$_2$S molecules into HS$^-$ or S$^{2-}$ as a function of the local pH.

**Adsorption in a dynamic system**

Some examples of breakthrough curves and critical thickness calculations are presented in Figure 5. The treatment capacity at the breakthrough point after saturation is given with the critical thickness in Table 3.

![Figure 3](https://iwaponline.com/wst/article-pdf/50/4/193/421747/193.pdf)

**Table 2** Kinetic mass-transfer parameters

<table>
<thead>
<tr>
<th>Name</th>
<th>$C_e/C_0$</th>
<th>$q_e$ (mg g$^{-1}$)</th>
<th>$\tau$ (min)</th>
<th>$R^2$</th>
<th>$C_e/C_0$</th>
<th>$q_e$ (mg g$^{-1}$)</th>
<th>$\tau$ (min)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>WWP3</td>
<td>0.34</td>
<td>26.01</td>
<td>5.06</td>
<td>0.986</td>
<td>0.05</td>
<td>29.95</td>
<td>5.76</td>
<td>0.987</td>
</tr>
<tr>
<td>WWP3-V</td>
<td>0.50</td>
<td>21.44</td>
<td>5.85</td>
<td>0.976</td>
<td>0.28</td>
<td>26.16</td>
<td>16.58</td>
<td>0.992</td>
</tr>
<tr>
<td>VS15</td>
<td>0.47</td>
<td>19.12</td>
<td>5.13</td>
<td>0.993</td>
<td>0.37</td>
<td>18.54</td>
<td>12.27</td>
<td>0.980</td>
</tr>
<tr>
<td>NC60</td>
<td>0.54</td>
<td>20.04</td>
<td>5.41</td>
<td>0.990</td>
<td>0.17</td>
<td>24.26</td>
<td>13.12</td>
<td>0.989</td>
</tr>
</tbody>
</table>

Figure 3 Amount of H$_2$S loaded in the carbon adsorbents. (a) Quantity of H$_2$S loaded under wet air; (b) quantity of H$_2$S loaded under dry air
The treatment capacities of the studied materials are in the same range as the capacities obtained in a batch reactor. The saturation capacities are very close to the isotherm data when $C_e$ (equilibrium concentration) equals $C_0$ (inlet concentration). The critical thicknesses for the activated carbon cloths are 10 to 100 times lower than for the granules (for a similar superficial velocity). This could be explained by the fibrous structure of the cloths presenting a higher external surface area to the flow than the granules. Hence, the residence time is higher for fabrics compared to a packed granule bed. This is an interesting aspect for the use of such an adsorbent in high flow rate applications.

Conclusions

This first approach in the study of the treatment of hydrogen sulfide using carbon adsorbents highlights the dependence of the H$_2$S oxidation mechanisms on the surface chemical properties of the adsorbents (the surface pH and the concentration of oxygenated functions) and the quality of the gas phase (relative humidity). Two reaction pathways are distinguished: with or without a water liquid film. The treated quantity increases with wet effluent compared to dry effluent, and mass-transfer velocity decreases. The catalytic role of the sulfur formed at the surface of the material is highlighted and quantified. This phenomenon occurs only under dry air conditions. Moreover, the critical thickness values, obtained in a
dynamic system, are lower with fibrous materials than with granules. Hence, activated carbon cloths can enable the treatment of high flow rates and low concentrations of odorous molecules in air.

References


