DYNAMIC ADSORPTION ON ACTIVATED CARBON OF SO₂ TRACES IN AIR

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Introduction

Sulfur dioxide is an atmospheric pollutant, the concentration of which has to be maintained at a very low value for environmental reasons. According to World Health Organization, for example, the upper limits of exposition are 500 µg m⁻³ for 15 minutes, 350 µg m⁻³ for 1 hour, 125 µg m⁻³ for 1 day and 50 µg m⁻³ for 1 year, corresponding respectively to 0.19, 0.13, 0.05 and 0.02 volumetric ppm [1].

On the other hand, it is well known that activated carbons are effective adsorbents for SO₂ at much higher concentrations, i.e., 1000 ppm or more [2-14], the industrial application being the abatement of SO₂ in flue gases. The mechanisms of adsorption proposed generally involve a physisorption and a chemisorption of SO₂, followed by a catalytic oxidation of SO₂ by oxygen.

This paper deals with the adsorption of SO₂ at much smaller SO₂ concentrations. This study is aimed to test whether an habitacle activated carbon filter, for example, is able to remove SO₂ from air. Experiments have been essentially carried out with a SO₂ concentration of about 30 ppm because this concentration is required by a German habitacle filter efficiency test [15].

The use of low SO₂ concentrations (<30 ppm) rises the following questions:
1. What is the amount of SO₂ adsorbed under an equilibrium pressure equal to or lower than 30 ppm? 2. Is this amount irreversibly adsorbed or does it leave carbon on removing SO₂ from the gas phase? 3. Do the mechanisms proposed for SO₂ adsorption at 2000 ppm hold if SO₂ is adsorbed at 30 ppm or less?

We tried to answer these questions by determining SO₂ breakthrough curves through activated carbon beds. Both up and down SO₂ concentration steps were used in order to evaluate the amounts of SO₂ irreversibly and reversibly adsorbed.

Experimental

Two carbon samples were used. The first one was a commercial extrudated activated carbon (Norit rox 0.8) termed “Carbon CN” in the following. The diameter of the cylindrical granules is 0.8 mm. The second one, termed “carbon CF” was an activated carbon felt. The nitrogen adsorption isotherms at 77K are shown in Figures 1 and 2. BET surface areas are 1110 and 607 m²/g for carbons CN and CF, respectively. Carbon CF presents an isotherm of type I and then it is essentially microporous. The isotherm for carbon CN shows the presence of both micro- and mesopores. The hysteresis loop for carbon CN is a typical Type H4 according to IUPAC classification [16]. This type is frequently associated with narrow slit-shaped pores with presence of microporosity.

A scheme of the experimental set-up employed is shown in Figure 3. A four-way valve (V1) allowed various gaseous mixtures to be sent to the adsorption chamber. Either synthetic air obtained by mixing a flow of N₂ (80 vol%) with a flow of O₂ (20 vol%), or nitrogen alone were used for heat treatments. The same gases loaded with 30 ppm SO₂ (unless otherwise indicated) were used to determine breakthrough curves. Nitrogen proceeded from a liquid nitrogen tank (L’Air Liquide). A second four-way valve (V2) was used to send the outlet gas to either the SO₂ analyzer or vent. A furnace around the adsorption chamber was used to heat the carbon samples up to 120°C under gas flow in order to eliminate most of the water initially present in activated carbon porosity. A thermocouple was located into the carbon bed to control the temperature of heat treatments. The total gas flow rate during breakthrough curve determinations was 242 dm³/hour.
**Figure 1.** Nitrogen isotherm at 77 K of carbon CN

**Figure 2.** Nitrogen isotherm at 77 K of carbon CF
All the SO$_2$ adsorption-desorption tests were carried out at room temperature.

Two adsorption chambers were used. They essentially differ by the material they were made of: the first one was constructed in stainless steel while the second one was a “Pyrex” glass tube. The diameter of carbon bed (d = 2.4 cm) was the same for both chambers. The carbon bed heights were in the range 0.2-2.5 cm.

Sulfur dioxide concentration at the outlet of adsorption cell was measured with a specific UV fluorescence analyzer (AF 21 M from Environment SA) equipped with a gas diluter because the maximum content allowed with this analyzer is 10 ppm.

The amounts of SO$_2$ reversibly and irreversibly adsorbed were determined as described below: Figure 4 shows breakthrough curves obtained with SO$_2$ concentration step from 0 to $C_0 = 31.2$ ppm followed by an opposite step from $C_0$ to 0 ppm. Blank responses obtained by the same procedure carried out without any adsorbent are also shown in this figure. The use of an inert solid was not necessary to obtain blank curves because the delay of the SO$_2$ response was checked to be only due to the diluter. The total amount of SO$_2$ adsorbed under $C_0$ is evaluated from the area between the blank curve and the response to the first SO$_2$ rising step. The amount of SO$_2$ reversibly adsorbed is obtained from the area between the blank curve and the SO$_2$ response to the subsequent falling step. The following steps only involve the reversibly adsorbed SO$_2$. The amount of SO$_2$ irreversibly adsorbed is calculated by difference between the total amount and the reversibly adsorbed amount.

Temperature-programmed experiments followed by mass spectrometry (TPD-MS) of the carbon samples before and after SO$_2$ adsorption were performed under an helium flow of 30 cm$^3$/min at a heating rate of 20°C/min. Sample masses were in the range 0.06-0.1 g.

**Results**

The breakthrough curves obtained with carbon CF are shown in Figure 5. The three curves shown correspond to different carbon masses, i.e., to different carbon bed heights, the bed density being constant. As expected, the total amount of SO$_2$ adsorbed is proportional to the mass of carbon. Nevertheless, the shapes of the breakthrough curves are different: for the smallest mass, the inflexion point is very low while it is located close to $C_0/2$ (symmetric curve) for the highest mass employed. This property is probably due to the fact that, for the lowest mass employed, the SO$_2$ front in carbon did not achieve a final stable shape. This final shape is achieved with the highest carbon mass.

The same features were found in breakthrough curves obtained with Carbon CN as shown in Figure 6. Nevertheless the amounts of SO$_2$ adsorbed per gram of carbon are smaller than for Carbon CF. Another difference is that the slopes of the curves at the inflexion point are smaller in this case than in the case of carbon CF.

Activated carbons exposed to ambient air contain water in their micropores. The influence of this water on the amounts of SO$_2$ adsorbed has been investigated by comparing the results obtained with Carbon CN “as received” with those obtained with the same carbon

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**Figure 3.** Scheme of the experimental set-up used to determine breakthrough curves.
previously heat-treated at 120°C for 14 hours. The results are shown in Figures 7 and 8 for irreversibly and reversibly adsorbed SO\textsubscript{2}, respectively. Besides, experiments have been carried out with air or nitrogen as carrier gas in order to investigate the influence of oxygen.

It is seen that physisorbed water has a positive effect on both types of adsorption. However the replacement of air by nitrogen has little influence on the amounts of SO\textsubscript{2} adsorbed. The slopes of the lines in figures 7 and 8 allow the evaluation of the amounts adsorbed per gram of carbon. These results are given in Table 1.

Finally, breakthrough curves were determined for SO\textsubscript{2} concentrations in air other than 30 ppm. Results are shown in Figure 9. Both amounts of reversibly and irreversibly adsorbed SO\textsubscript{2} decrease when the SO\textsubscript{2} content in the gas phase decreases. As expected, the curve for reversibly adsorbed SO\textsubscript{2} passes through the origin. Nevertheless, the amount of irreversibly adsorbed SO\textsubscript{2} remains relatively high for the lowest SO\textsubscript{2} concentration studied (2.5 ppm).

**Figure 4.** Successive steps of air and (air+SO\textsubscript{2}) to determine the total amount of SO\textsubscript{2} adsorbed and the amount of SO\textsubscript{2} reversibly adsorbed. Dashed line: blank experiment; continuous line: SO\textsubscript{2} response.

**Figure 5.** Breakthrough curves obtained with different amounts of Carbon CF. as received. a: 82 mg; b: 327 mg; c: 879 mg
Figure 6. Breakthrough curves obtained with different amounts of Carbon CN. as received. a: 771 mg; b: 1124 mg; c: 2013 mg

Figure 7. Amounts of SO$_2$ irreversibly adsorbed on Carbon CN as received or heat-treated at 120°C. SO$_2$ is diluted either in air or nitrogen
Figure 8. Amounts of $SO_2$ reversibly adsorbed on Carbon CN as received or heat-treated at 120°C. $SO_2$ is diluted either in air or nitrogen.

Table 1. Amounts of $SO_2$ reversibly and irreversibly adsorbed on Carbon CN under a gas flow (N2+SO2 or Air+SO2) containing 31.2 ppm of $SO_2$

<table>
<thead>
<tr>
<th>Total amount (mg/g)</th>
<th>reversible amount (mg/g)</th>
<th>irreversible amount (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN &quot;as received&quot; in $N_2+SO_2$</td>
<td>9.3</td>
<td>4.6</td>
</tr>
<tr>
<td>CN &quot;as received&quot; in Air+SO2</td>
<td>10.3</td>
<td>4.9</td>
</tr>
<tr>
<td>CN heat-treated in $N_2+SO_2$</td>
<td>5.0</td>
<td>3.5</td>
</tr>
<tr>
<td>CN heat-treated in Air+SO2</td>
<td>6.0</td>
<td>3.8</td>
</tr>
</tbody>
</table>
Figure 9. Variation of the amounts of SO\textsubscript{2} reversibly and irreversibly adsorbed per gram of Carbon CN as received versus SO\textsubscript{2} content in the gas phase

Discussion

It is well established that, at concentrations close to 2000 ppm, SO\textsubscript{2} adsorbs on activated carbons into two different states. These states are easily distinguished by TPD: SO\textsubscript{2} in the more loosely bonded state desorbs in a peak around 110°C, while SO\textsubscript{2} in the more strongly bonded state desorbs in a distinct peak around 325°C. The first state is generally assigned to physisorbed SO\textsubscript{2}. The second state has been assigned to either strongly physisorbed SO\textsubscript{2} in narrow microporosity or chemisorbed SO\textsubscript{2} or chemisorbed SO\textsubscript{3} or even physisorbed SO\textsubscript{3}. Besides, when SO\textsubscript{2} adsorption is performed in presence of humid air, sulfuric acid is formed. However, it is not obvious that these conclusions apply to our results obtained at low SO\textsubscript{2} concentrations in the gas phase, i.e., at very low SO\textsubscript{2} superficial concentration in the adsorbed phase.

In our case, it is also reasonable to associate the reversibly adsorbed SO\textsubscript{2} to physisorbed SO\textsubscript{2}. In order to get an insight into the state of SO\textsubscript{2} irreversibly adsorbed during our breakthrough experiments, we performed TPD-MS runs with samples before and after SO\textsubscript{2} adsorption, i.e., with carbons "as received" and after an adsorption-desorption cycle, respectively. The reversibly adsorbed SO\textsubscript{2} is not present on carbons after such a cycle. Results are shown in Figure 10. It appears clearly, by comparison of Figures 10(A) and 10(B), that some chemical reactions occur during heating. Thus, it is convenient to interpret these TPD results in terms of Temperature-Programmed Superficial Reaction (TPSR)[17]. The larger amounts of CO\textsubscript{2} and CO desorbed after SO\textsubscript{2} adsorption than before SO\textsubscript{2} adsorption show that there is an oxidation of some superficial entities SR (carbon or some oxygen group) during TPD. It is very likely that the oxidizing agent is SO\textsubscript{3} or H\textsubscript{2}SO\textsubscript{4}, as in the case of SO\textsubscript{2}-rich surfaces described in the literature. Then, it can be concluded that, even with oxygen contents as low as 30 ppm in the gas phase, a large part of the adsorbed SO\textsubscript{2} is oxidized into SO\textsubscript{3} at the surface of carbon.

In Figure 10, the only significant difference between CO\textsubscript{2} profiles before and after SO\textsubscript{2} adsorption is the conspicuous peak accompanying the peak of SO\textsubscript{2} at 325°C. The parallelism between the profiles of SO\textsubscript{2} and CO\textsubscript{2} strongly suggests the following formal TPSR mechanism:
\[ \text{SO}_3 \xrightarrow{k_1} \text{SO}_2 \xrightarrow{k_2} \text{CO}_2 \text{ (gas phase)} \]
\[ \text{SO}_3 + \text{SR} \rightarrow \text{SO}_2 + \text{CO}_2^- \text{G (adsorbed phase)} \]

where CO\(_2^-\)G is a superficial oxygen group that decomposes into CO\(_2\). The relative values of the rate constants are such that:

\[ k_1 << k_2 << k_3 \text{ and } k_4 \] (rate constants at 325°C)

This mechanism is termed "Type Ib" in a classical theory of TPSR [17]. The first inequality means that SO\(_3\) in unable to desorb before undergoing a reduction by SR. The second inequality traduces the fact that the

**Figure 10.** TPD for Carbon CF (as received) before (A) and after (B) adsorption of SO\(_3\) in air. m/e=28: CO + fragment of CO\(_2\); m/e = 44: CO\(_2\); m/e=64: SO\(_2\). In Figure (B) the peak 28 at 325°C is due to the fragmentation of CO\(_2\) in the MS source.
desorptions of SO$_2$ and CO$_2$ are fast, so that these compounds desorb as soon as they are formed by the superficial reaction.

This can be understood for SO$_2$ by assuming that SO$_2$ can only adsorb in its physical state. When it is initially present in this state at the surface of carbon, SO$_2$ desorbs in TPD runs around 110°C. In our TPD runs, SO$_2$ is formed by the superficial reaction at 325°C, consequently its desorption is very fast at this temperature.

In the case of CO$_2$, it is seen from Figure 10(A) that a large part of the CO$_2$-producing oxygen groups decompose under 300°C. Then, if the CO$_2$-producing oxygen group formed by the superficial reaction belongs to those groups, it is expected that its decomposition is fast at 325°C.

The case of CO is different. It is seen from the TPD spectrum before SO$_2$ adsorption that CO-producing oxygen groups mainly decompose above 400°C. Thus it is likely that the CO-producing oxygen groups formed by the superficial reaction remain on carbon surface until they reach their natural decomposition temperature. The corresponding TPSR mechanism (Type IIb for CO [17]) is:

\[
\begin{align*}
\text{SO}_3 & \xrightarrow{k_1} \text{SO}_2 \xrightarrow{k_3} \text{CO} \text{ (gas phase)} \\
\text{SO}_3 + \text{SR} & \xrightarrow{k_2} \xrightarrow{k_4} \text{SO}_2 + \text{CO-G} \text{ (adsorbed phase)}
\end{align*}
\]

with $k_1$ and $k_4$ << $k_2$ << $k_3$. CO-G is an oxygen group that decomposes into CO.

Thus, it is possible to understand the TPD results in terms of TPSR at the price of some reasonable assumptions. More work is needed to confirm these mechanisms. Nevertheless the above discussion shows that interpreting the TPD of SO$_2$ from carbons in terms of TPSR may be useful.

Numerous works described in the literature have reported SO$_2$ adsorption capacities for high sulfur dioxide contents in the gas phase at various temperatures. Some typical results are gathered in Table 2. It is not surprising that the amounts of adsorbed SO$_2$ reported in the present paper are much lower than those reported in the literature. This trend is in agreement with the fact that SO$_3$ isotherms rise when SO$_2$ concentration increases as shown by figure 9. Moreover, our samples have not been outgassed at high temperature before SO$_2$ adsorption and it has been recently shown that oxygen groups hinder the adsorption of SO$_2$ [14].

The positive effect of water on SO$_2$ adsorption, well established in the case of adsorption under 2000 ppm SO$_2$, is also observed in our experiments under 30 ppm SO$_2$. Thus our "as received" samples, which contain water in their microporosity, adsorbed a larger amount of SO$_2$ than samples outgassed at 120°C for 14 hours. It is worth noting that the positive effect of water is observed not only for the irreversibly adsorbed SO$_2$ but also for the reversibly adsorbed SO$_2$. In the first case, this effect might be explained by the formation of sulfuric acid from SO$_3$; however, it is more difficult to explain the latter case.

The very small influence, if any, of the presence of O$_2$ in the gas phase during adsorption on the amounts of SO$_2$ adsorbed is surprising. This observation is likely due to traces of oxygen in the nitrogen we used. Nevertheless, it is worth noting that, even at very low concentrations of SO$_2$ and O$_2$ in the gas phase, SO$_3$ is formed at the surface of carbon.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>SO$_3$ concentration (ppm)</th>
<th>Surface area (m$^2$/g)</th>
<th>Total amount adsorbed (mg SO$_2$/g C)</th>
<th>amount irreversibly adsorbed (mg SO$_2$/g C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>2700</td>
<td>1400</td>
<td>155</td>
<td>40</td>
<td>[2]</td>
</tr>
<tr>
<td>120</td>
<td>2500</td>
<td>1000</td>
<td>206</td>
<td>[5]</td>
<td></td>
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<tr>
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<td>20000</td>
<td>533</td>
<td>370</td>
<td>[10]</td>
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</tr>
<tr>
<td>25</td>
<td>2500</td>
<td>896</td>
<td>60</td>
<td>10</td>
<td>[11]</td>
</tr>
</tbody>
</table>
Conclusion

Activated carbons used "as received" are able to retain SO\textsubscript{2} in air at concentrations as low as 2.5 ppm. At this concentration, the adsorption of SO\textsubscript{2} is essentially irreversible. The fraction of reversibly adsorbed SO\textsubscript{2} increases when SO\textsubscript{2} content in air increases from 2.5 to 100 ppm. As expected, the amounts of SO\textsubscript{2} adsorbed per gram of carbon are much smaller than in the case of high SO\textsubscript{2} contents in air (>1000 ppm).

The presence of water in carbon micropores enhances both reversible and irreversible adsorption of SO\textsubscript{2}. The reversibly adsorbed part is physisorbed while the irreversibly adsorbed part results from an oxidation of SO\textsubscript{2} at carbon surface.

Then, it can be concluded that much of the well-established results for SO\textsubscript{2} adsorption at 1000 ppm, or more, hold for SO\textsubscript{2} concentrations lower than 30 ppm. This finding may be useful in applied researches aimed to select the most efficient carbon for the design of habitacle filters.

References

15. "Filtration Air Habitatle" DIN 71460