

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 $\mu\text{g m}^{-3}$ for 15 minutes, 350 $\mu\text{g m}^{-3}$ for 1 hour, 125 $\mu\text{g m}^{-3}$ for 1 day and 50 $\mu\text{g m}^{-3}$ 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.

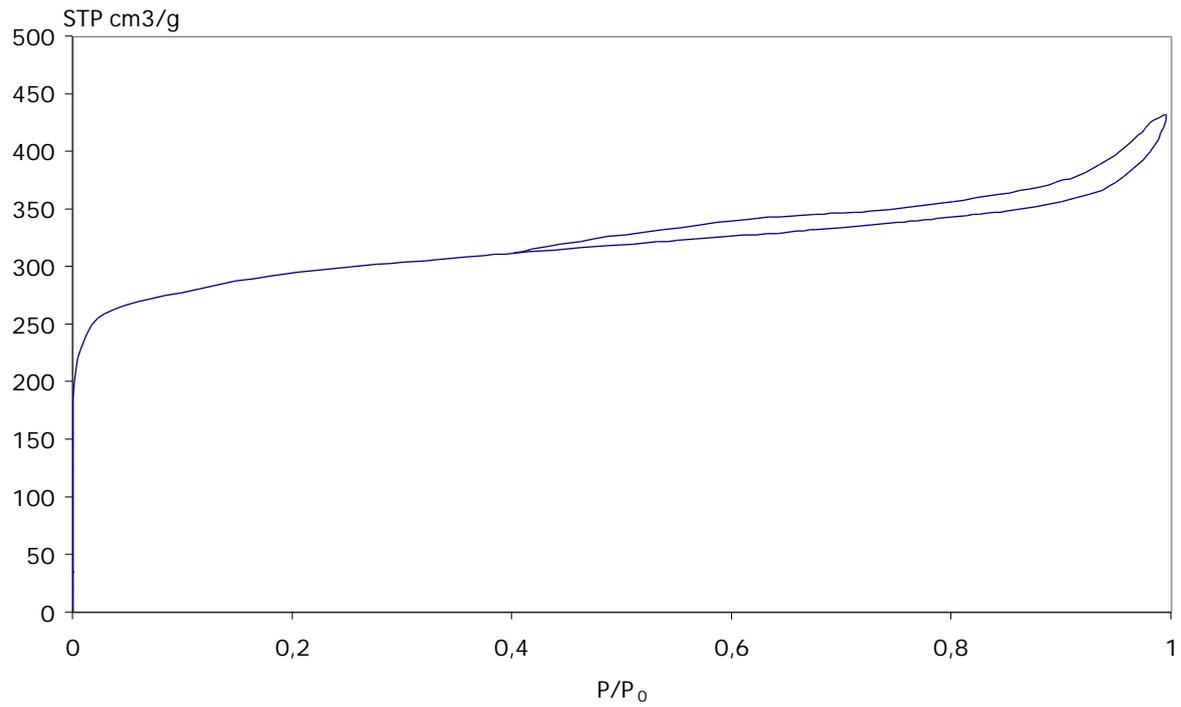


Figure 1. Nitrogen isotherm at 77 K of carbon CN

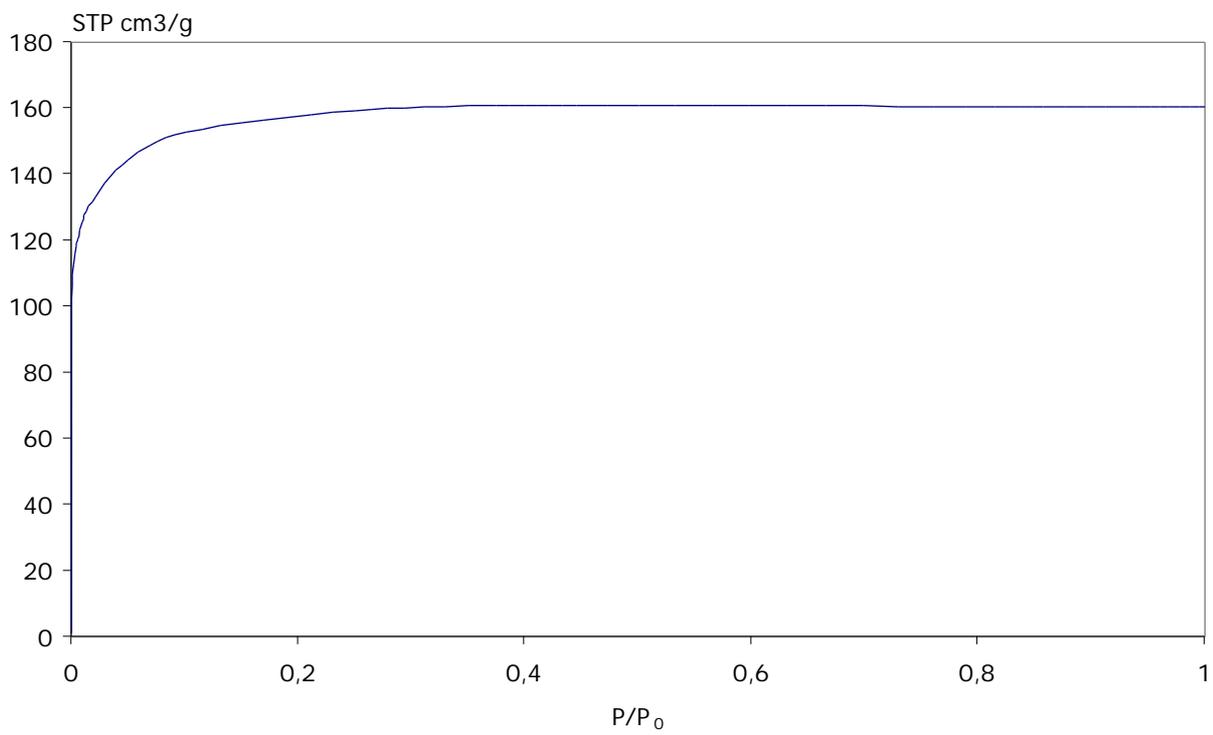


Figure 2. Nitrogen isotherm at 77 K of carbon CF

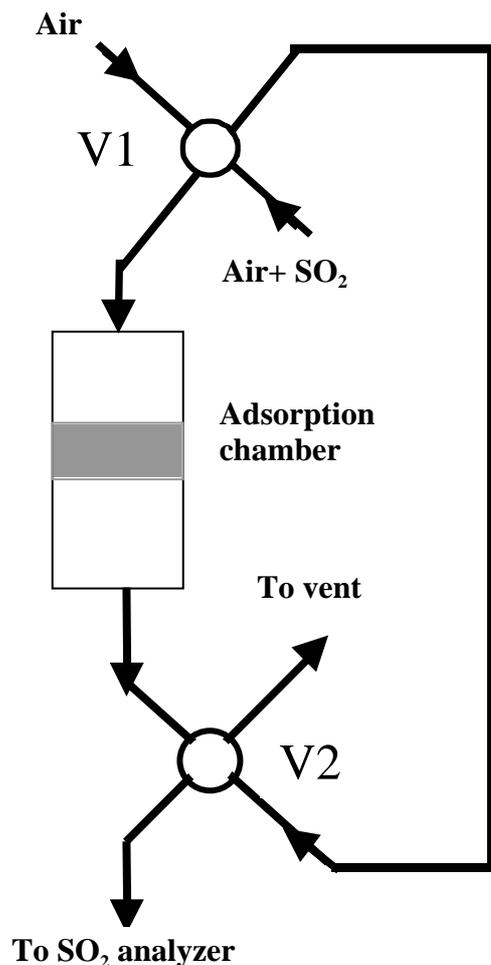


Figure 3. Scheme of the experimental set-up used to determine breakthrough curves.

All the SO₂ 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 SO₂ reversibly and irreversibly adsorbed were determined as described below: Figure 4 shows breakthrough curves obtained with SO₂ 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 SO₂ response was checked to be only due to the diluter. The total amount of SO₂ adsorbed under C_0 is evaluated from the area between the blank curve and the response to the first SO₂ rising step. The amount of SO₂ reversibly adsorbed is obtained from the area between the blank curve and the SO₂ response to the subsequent falling step. The following steps only involve the reversibly adsorbed SO₂. The amount of SO₂ 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 SO₂ adsorption were performed under an helium flow of 30 cm³/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 SO₂ 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 SO₂ 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 SO₂ 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 SO₂ adsorbed has been investigated by comparing the results obtained with Carbon CN "as received" with those obtained with the same carbon

previously heat-treated at 120°C for 14 hours. The results are shown in Figures 7 and 8 for irreversibly and reversibly adsorbed SO₂, 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 SO₂ 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 SO₂ concentrations in air other than 30 ppm. Results are shown in Figure 9. Both amounts of reversibly and irreversibly adsorbed SO₂ decrease when the SO₂ content in the gas phase decreases. As expected, the curve for reversibly adsorbed SO₂ passes through the origin. Nevertheless, the amount of irreversibly adsorbed SO₂ remains relatively high for the lowest SO₂ concentration studied (2,5 ppm).

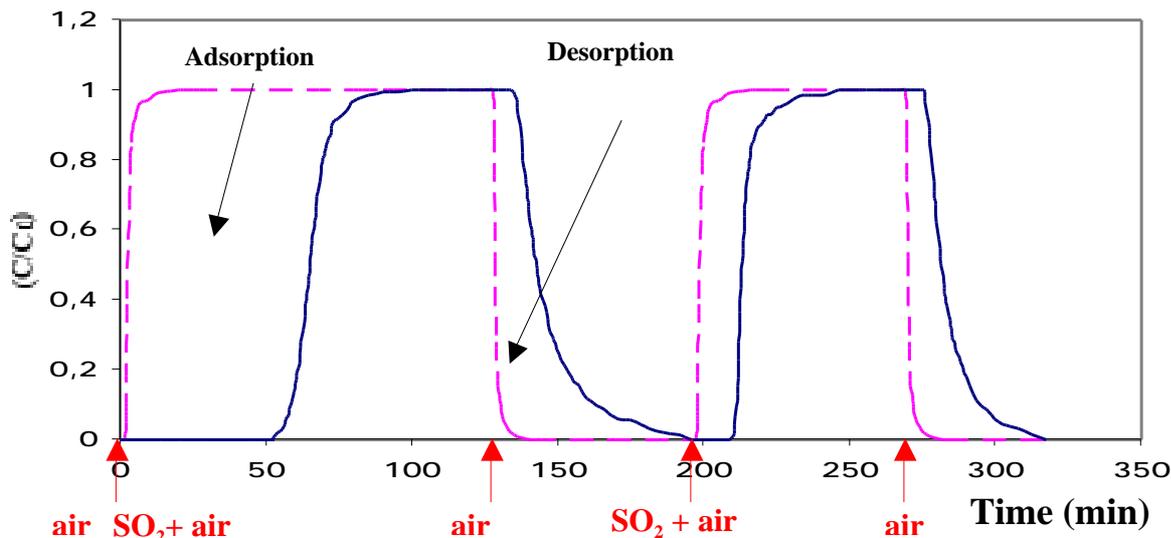


Figure 4. Successive steps of air and (air+SO₂) to determine the total amount of SO₂ adsorbed and the amount of SO₂ reversibly adsorbed. Dashed line: blank experiment; continuous line: SO₂ response.

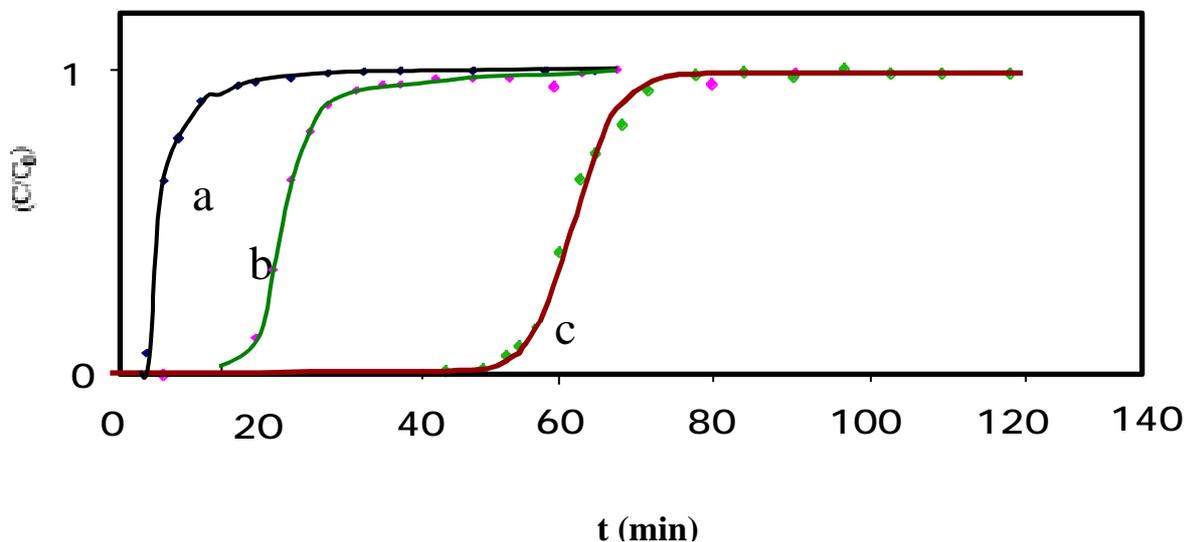


Figure 5. Breakthrough curves obtained with different amounts of Carbon CF. as received. a: 82 mg; b:327 mg; c: 879 mg

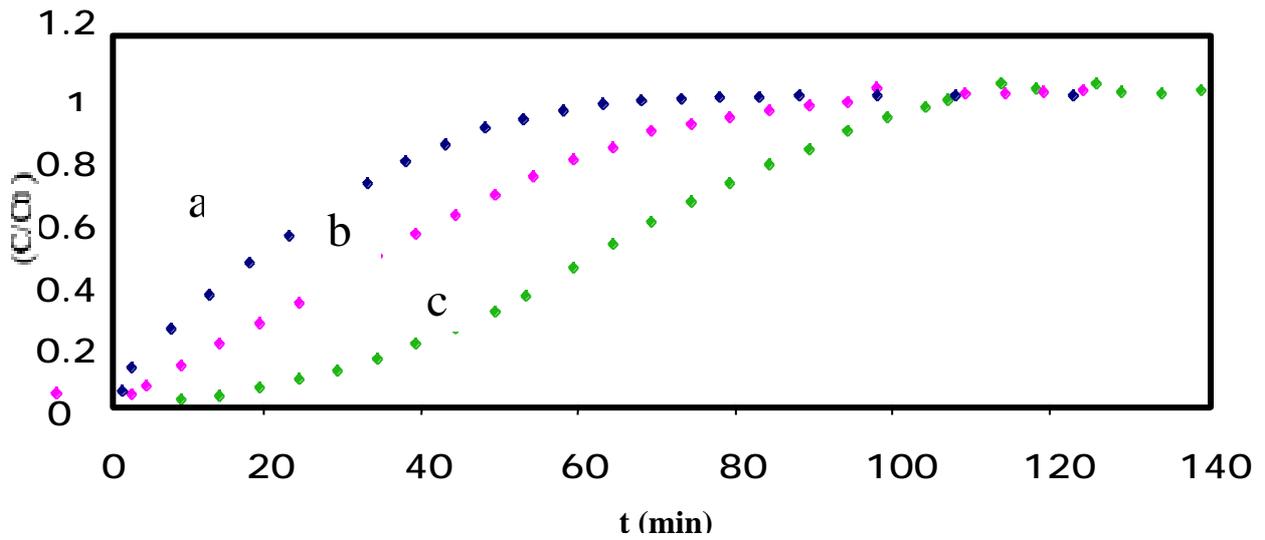


Figure 6. Breakthrough curves obtained with different amounts of Carbon CN. as received. a: 771 mg; b:1124 mg; c: 2013 mg

Mass of SO₂ adsorbed (mg)

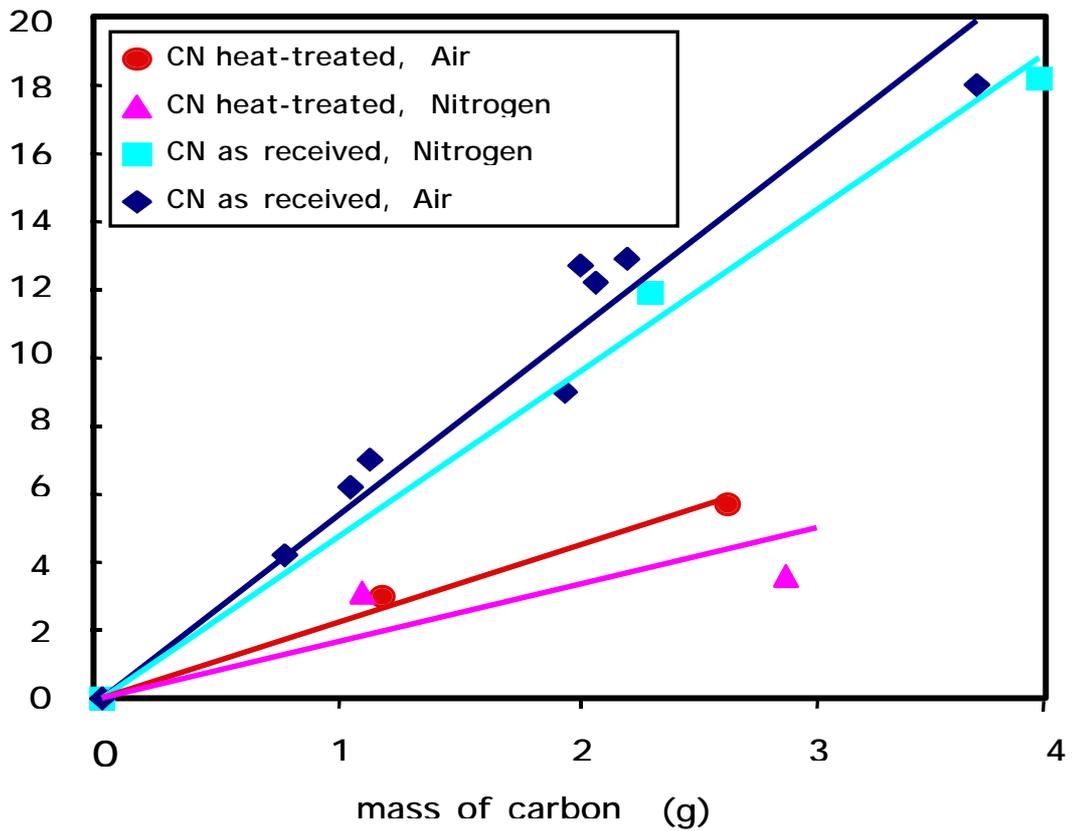


Figure 7. Amounts of SO₂ irreversibly adsorbed on Carbon CN as received or heat-treated at 120°C. SO₂ is diluted either in air or nitrogen

Mass of SO₂ adsorbed (mg)

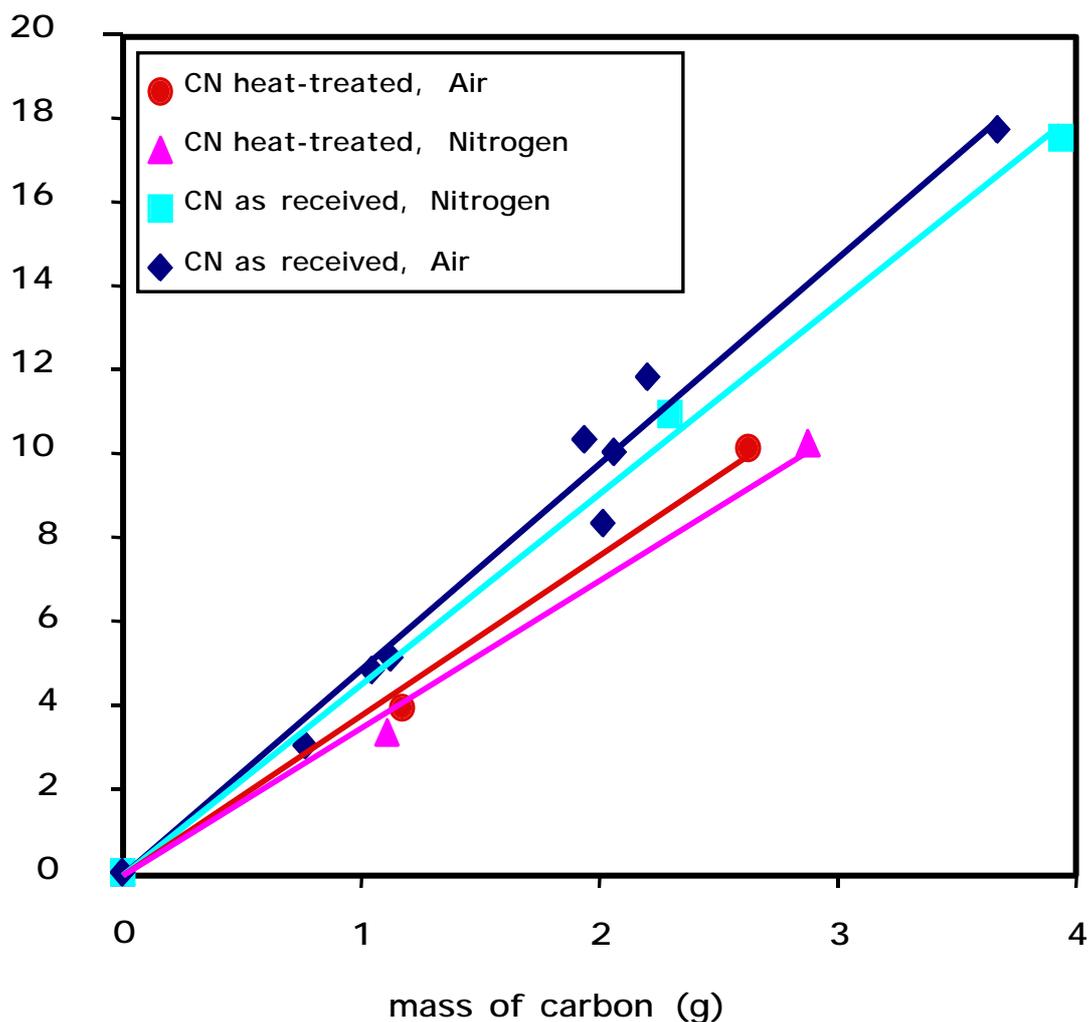


Figure 8. Amounts of SO₂ reversibly adsorbed on Carbon CN as received or heat-treated at 120°C. SO₂ is diluted either in air or nitrogen

Table 1. Amounts of SO₂ reversibly and irreversibly adsorbed on Carbon CN under a gas flow (N₂+SO₂ or Air+SO₂) containing 31,2 ppm of SO₂

| | Total amount (mg/g) | reversible amount (mg/g) | irreversible amount (mg/g) |
|---|---------------------|--------------------------|----------------------------|
| CN "as received" in N ₂ +SO ₂ | 9.3 | 4.6 | 4.8 |
| CN "as received" in Air+SO ₂ | 10.3 | 4.9 | 5.4 |
| CN heat-treated in N ₂ +SO ₂ | 5.0 | 3.5 | 1.5 |
| CN heat-treated in Air+SO ₂ | 6.0 | 3.8 | 2.2 |

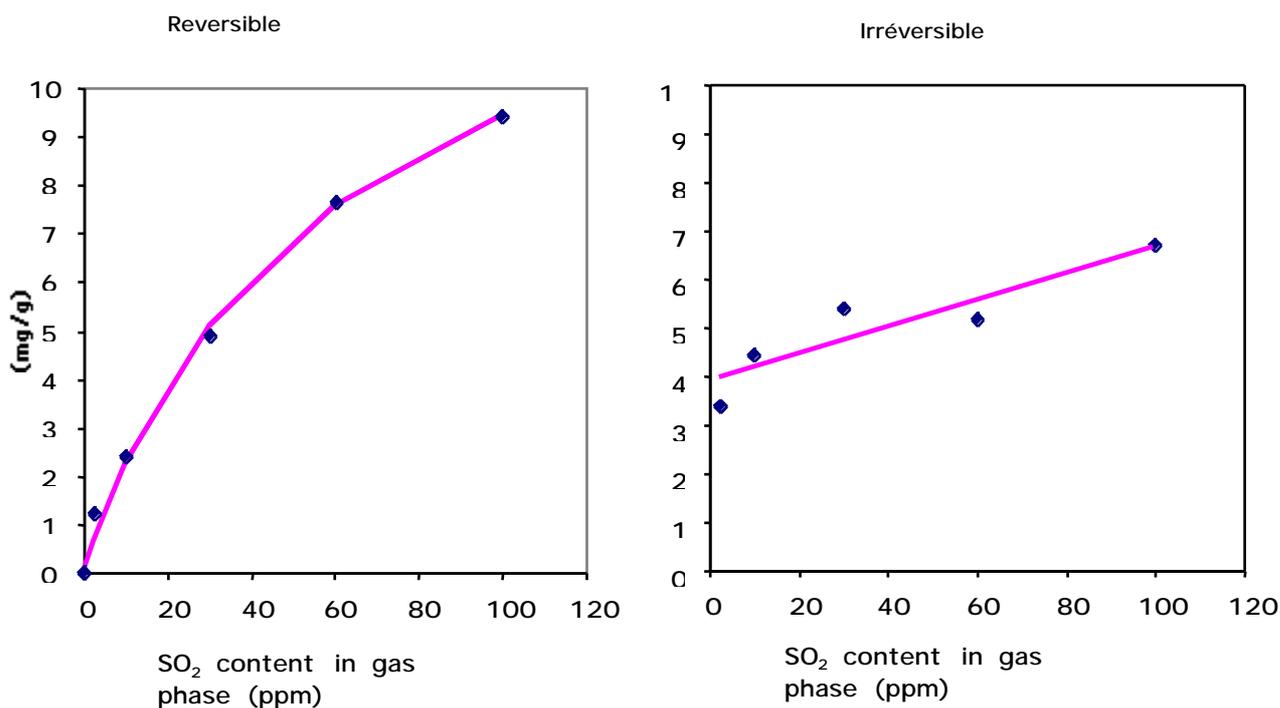


Figure 9. Variation of the amounts of SO₂ reversibly and irreversibly adsorbed per gram of Carbon CN as received versus SO₂ content in the gas phase

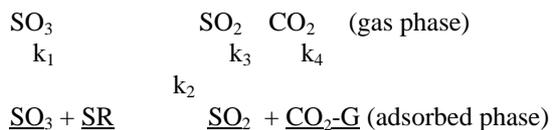
Discussion

It is well established that, at concentrations close to 2000 ppm, SO₂ adsorbs on activated carbons into two different states. These states are easily distinguished by TPD: SO₂ in the more loosely bonded state desorbs in a peak around 110°C, while SO₂ in the more strongly bonded state desorbs in a distinct peak around 325°C. The first state is generally assigned to physisorbed SO₂. The second state has been assigned to either strongly physisorbed SO₂ in narrow microporosity or chemisorbed SO₂ or chemisorbed SO₃ or even physisorbed SO₃. Besides, when SO₂ 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 SO₂ concentrations in the gas phase, i.e., at very low SO₂ superficial concentration in the adsorbed phase.

In our case, it is also reasonable to associate the reversibly adsorbed SO₂ to physisorbed SO₂. In order to get an insight into the state of SO₂ irreversibly adsorbed during our breakthrough experiments, we performed TPD-MS runs with samples before and after SO₂ adsorption, i.e., with carbons "as received"

and after an adsorption-desorption cycle, respectively. The reversibly adsorbed SO₂ 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 CO₂ and CO desorbed after SO₂ adsorption than before SO₂ 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 SO₃ (or H₂SO₄), as in the case of SO₂-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 SO₂ is oxidized into SO₃ at the surface of carbon.

In Figure 10, the only significant difference between CO₂ profiles before and after SO₂ adsorption is the conspicuous peak accompanying the peak of SO₂ at 325°C. The parallelism between the profiles of SO₂ and CO₂ strongly suggests the following formal TPSR mechanism:



$k_1 \ll k_2 \ll k_3$ 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 is unable to desorb before undergoing a reduction by SR. The second inequality traduces the fact that the

where $\text{CO}_2\text{-G}$ is a superficial oxygen group that decomposes into CO_2 . The relative values of the rate constants are such that:

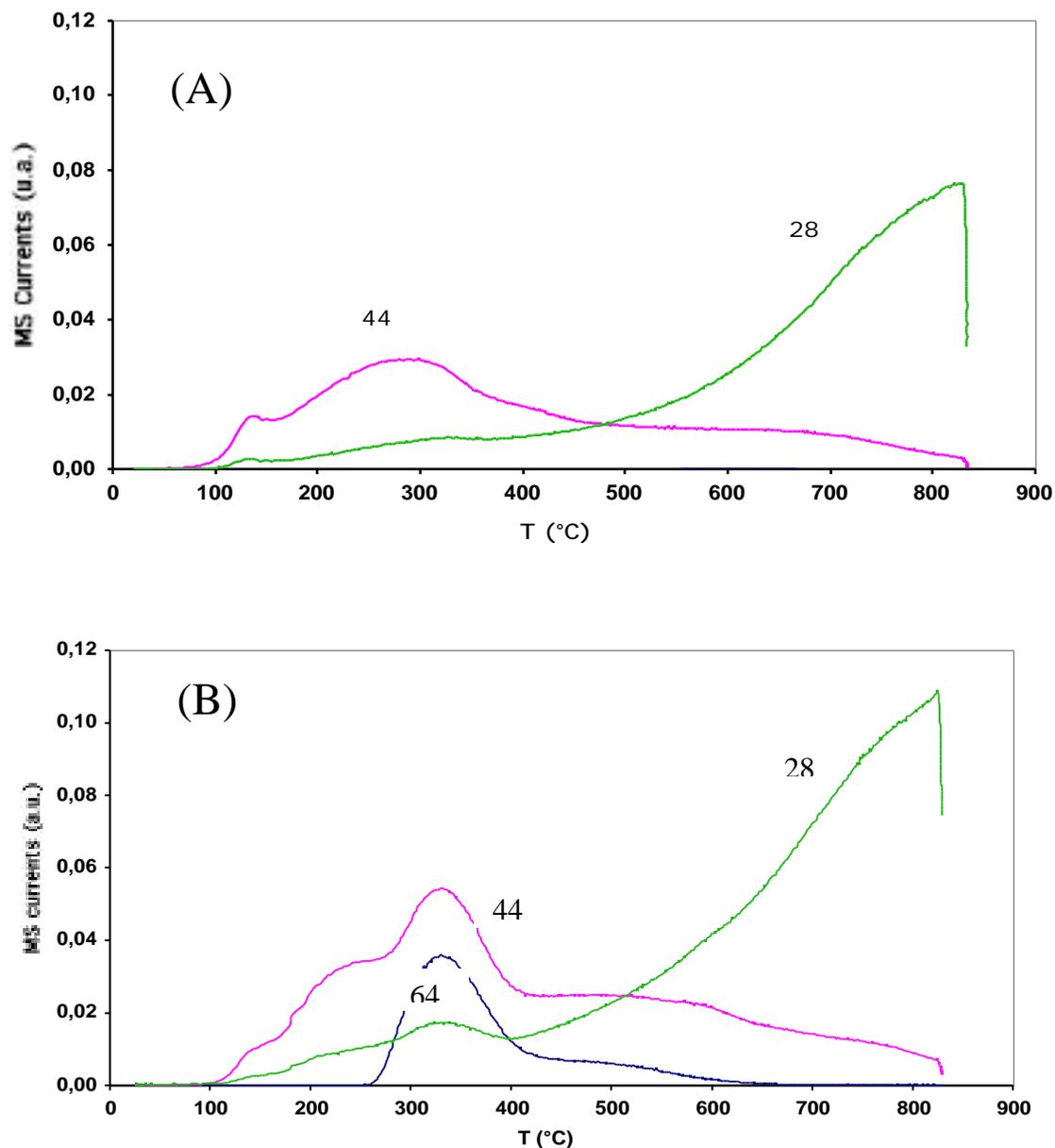


Figure 10. TPD for Carbon CF (as received) before (A) and after (B) adsorption of SO_2 in air. $m/e=28$: CO + fragment of CO_2 ; $m/e=44$: CO_2 ; $m/e=64$: SO_2 . In Figure (B) the peak 28 at 325°C is due to the fragmentation of CO_2 in the MS source.

Conclusion

Activated carbons used "as received" are able to retain SO₂ in air at concentrations as low as 2.5 ppm. At this concentration, the adsorption of SO₂ is essentially irreversible. The fraction of reversibly adsorbed SO₂ increases when SO₂ content in air increases from 2.5 to 100 ppm. As expected, the amounts of SO₂ adsorbed per gram of carbon are much smaller than in the case of high SO₂ contents in air (>1000 ppm).

The presence of water in carbon micropores enhances both reversible and irreversible adsorption of SO₂. The reversibly adsorbed part is physisorbed while the irreversibly adsorbed part results from an oxidation of SO₂ at carbon surface.

Then, it can be concluded that much of the well-established results for SO₂ adsorption at 1000 ppm, or more, hold for SO₂ 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.

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