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# Hydrogen Sulfide Adsorption and Oxidation onto Activated Carbon Cloths: Applications to Odorous Gaseous Emission Treatments

L. M. Le Leuch, A. Subrenat,\* and P. Le Cloirec

*Ecole des Mines de Nantes, GEPEA UMR CNRS 6144, 4 rue Alfred Kastler, BP 20722, 44307 Nantes Cedex 03, France*

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The objective of this study was to suggest mechanisms and to quantify activated carbon cloth capacities in the removal of hydrogen sulfide present in air. Several parameters affect the H<sub>2</sub>S treatment capacity of activated carbon. These include the physicochemical surface characteristics and the operating conditions. Four activated carbon cloths and a granular carbon were used in a batch reactor for their deodorization abilities toward hydrogen sulfide. Different parameters such as the level of humidity, the presence of oxygen in the gas phase, and the structural and chemical surface properties of the adsorbents have been studied. Kinetics and equilibrium isotherm curves were performed and modeled. The results showed that hydrogen sulfide loaded onto activated carbon develops chemical reactions. The different byproducts from the H<sub>2</sub>S oxidation have been identified and quantified. Mass balance of sulfur compounds has been performed. The hydrogen sulfide removal was found to be produced mainly by oxidation reactions on specific surfaces. An approach of the oxidation pathway has been determined and depended on the operating conditions and surface functional groups present on the intrafiber surface. The catalytic role in H<sub>2</sub>S treatment played by the sulfur S<sub>0</sub> byproduct from the oxidation reaction is shown. These results reveal the high treatment capacities of the activated carbon cloths in hydrogen sulfide removal.

## I. Introduction

Removal of the odorous substances from the atmosphere is of major interest to contemporary society. Odors are unpleasant and harmful to workers, and consequently, they cause public discontent. Some of these substances are hazardous to human health and are environmentally dangerous. A major odorous compound from industrial activity emission is hydrogen sulfide. The most important emission sources are from petrochemical industries, animal husbandry, and wastewater treatment plants.

Activated carbons have been used for a long time in numerous air treatment processes and wastewater purification.<sup>1</sup> Hence, the most widely used method for deodorization is adsorption onto granular activated carbons (GACs), which remove low-concentration odorous substance mixtures present in air. Numerous studies concerning hydrogen sulfide adsorption have been carried out over recent years as deodorization problems are increasing. Many papers published in the literature indicate a good efficiency of H<sub>2</sub>S removal onto GAC.<sup>2–4</sup> Activated carbon cloths (ACCs), recent adsorbents, seem to be an interesting material for odor control.<sup>5</sup> Their

application is especially important in the gas and trace vapor adsorption and industrial VOC emissions, due to their porous structure, large surface area, and high adsorption capacity.<sup>6</sup> The cloth texture enables the design of filters which develop low pressure drops and a low-velocity flow and high resident time in the adsorbent.<sup>7</sup> This characteristic associated with a high specific surface is particularly adapted to treat high flow rates and low concentrations, which correspond to the case of deodorization.

Sorption of odorous substances such as H<sub>2</sub>S onto activated carbons depends on the surface structural parameters and surface chemistry, which is governed by the presence of heteroatoms such as oxygen, hydrogen, nitrogen, sulfur, and phosphorus. The role of pore structure is not as well defined as the role of surface chemistry.<sup>8</sup> The treatment capacities are enhanced by the presence of oxygen groups. These oxygen-containing sites exist in the form of organic functional groups, which can be acidic, basic, or neutral, and are proposed as catalytic centers for H<sub>2</sub>S oxidation.<sup>9</sup>

Several studies have described the possible oxidation pathways.<sup>11–13</sup> Most of the results concerning the oxidation mechanism so far are based on an empirical analysis and

\* To whom correspondence may be addressed. E-mail: Albert.Subrenat@emn.fr. Phone: 33 2 51 85 82 95. Fax: 33 2 51 85 82 99.

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**Table 1. Production Parameters of Porous Material**

commercial name	origin	weave	temperature (°C)		
			carbonize	activate	activate
VS15	rayon	satin	1200	900	CO <sub>2</sub>
WWP3	rayon	woven	700–900	800	CO <sub>2</sub>
WWP3-V	rayon	woven	700–900	820	H <sub>2</sub> O
NC-60	coconut	granular	900	900	H <sub>2</sub> O

sometimes may be confusing. It is interesting to notice that the principal oxidation byproducts are elemental sulfur and, in the presence of humidity, sulfate ions.<sup>14</sup> The appearance of these compounds depends on the features of the carbon surface and the operating conditions. The role of oxidation byproducts in H<sub>2</sub>S adsorption/oxidation is not as well defined as the oxidation pathways.<sup>15,16</sup> The results published describe in detail the systems studied, the use of ACCs for H<sub>2</sub>S removal, the oxidation reaction, and the role of byproducts.

The present investigations attempt to provide a better understanding of the influence of the operating conditions and oxidation reactions on hydrogen sulfide removal. So far detailed investigations of the suitability for adsorption/oxidation of hydrogen sulfide have been performed onto activated carbon cloths in a batch reactor. So factors such as carbon surface area, porosity, H<sub>2</sub>S concentration, oxygen concentration, and moisture content were taken into consideration. The H<sub>2</sub>S sorption capacity was measured by spectroscopy. On the basis of the results obtained, the relationships between the H<sub>2</sub>S loaded onto the adsorbent and the major properties of the activated carbons were analyzed. The byproducts of oxidation reactions were identified and quantified. The data obtained support the hypothesis about the role of surface chemistry and the formed sulfur in the process of H<sub>2</sub>S adsorption and catalytic oxidation. The essential objective of this work is to study the H<sub>2</sub>S adsorption/oxidation mechanisms onto fibrous carbonaceous adsorbents by direct determination of sulfur byproducts. The influencing parameters such as the moisture and the adsorbent surface chemistry as well as the autocatalytic role of the formed sulfur are highlighted.

## II. Materials & Methods

### II.1. Characterization of the Studied Adsorbents.

To find the surface parameters governing the observed differences in the H<sub>2</sub>S sorption capacities of carbon adsorbents used, detailed analyses are performed on the studied materials (structural parameters and chemical surface properties). Three different activated carbon cloths, supplied by Actitex (Courbevoie, France), are used in this study, and a granular activated carbon supplied by Pica (Courbevoie, France) is used for comparison. The carbonization and activation processes of these materials and their macroscopic properties are given in Table 1. For each experiment, the materials are dried in an oven at 380 K in order to prevent any pollution or prehumidification.

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From a macroscopic point of view, the studied activated carbon cloths are presented in the form of traditional textiles (Figure 1) composed of multifiber threads. Microscopic electronic scanning images allow access to the macro- and microscopic parameters of the material. Typically, the diameter of the wire lies between 0.4 and 1 mm. These are composed of many fibers of a diameter ranging between 10 and 20  $\mu\text{m}$  (Figure 2). Hence, this fiber structure allow development of a very important external surface seen by the fluid.

The pore structure of the adsorbents is determined by nitrogen adsorption isotherms using an ASAP 2010 analyzer at 77 K. Before the experiment, the samples are degassed at 393 K to a constant pressure of  $10^{-5}$  Torr. These isotherms are used to calculate the micropore volume ( $V_{\text{micro}}$ ) and pore size distribution using density functional theory (DFT). The relative microporosity is calculated from the ratio of the micropore volume to the total pore volume. In addition specific surface area ( $S_{\text{BET}}$ ) using the BET method<sup>17</sup> and the total pore volume ( $V_t$ ) (evaluated from the last point of the isotherm) are calculated.

The number of oxygenated surface groups is determined according to Boehm's method.<sup>18</sup> One gram of activated carbon is placed in 50 mL of 0.1 mol·L<sup>-1</sup> solutions containing sodium bicarbonate, sodium carbonate, sodium hydroxide, sodium ethanolate, and hydrochloric acid. The vials are sealed and shaken for 24 h. Then 10 mL of each filtrate is pipetted, and the excess base or acid titrated with HCl or NaOH solutions. The titration is calculated under the assumption that NaOH neutralizes carboxylic, phenolic and lactonic groups, Na<sub>2</sub>CO<sub>3</sub> neutralizes carboxylic and lactonic groups, NaHCO<sub>3</sub> neutralizes only carboxylic groups, and NaOC<sub>2</sub>H<sub>5</sub> neutralizes carbonyls groups. The number of surface basic sites is evaluated from the amount of hydrochloric acid consumed by the carbon.

The surface pH is measured on active carbon samples of 0.4 g added to 20 mL of distilled water. The suspension is stirred overnight to reach equilibrium. Then the sample is filtered, and the pH of the solution was measured.

ACC points of zero charge are determined by potentiometric titration.<sup>19</sup> The titration started from the pH corresponding to the activated carbon surface pH. Two runs are carried out: one in the presence of activated carbon (0.4 g of ACC in 100 mL of 0.001, 0.01, or 0.1 mol·L<sup>-1</sup> NaCl), and one with the same electrolyte in the absence of activated carbon (blank). A 0.1 mol·L<sup>-1</sup> solution of HCl or NaOH is used as titrant respectively in the pH range below or above the initial pH of the solution. During the titration, solutions are stirred with bubbled nitrogen to prevent any CO<sub>2</sub> or O<sub>2</sub> absorption in the solution. The difference in acid or base quantities, used to reach the same solution pH with activated carbon and the blank, is used to represent the association or dissociation of H<sub>3</sub>O<sup>+</sup> ions from the activated carbon surface.

### II.2. Adsorption in a Batch Reactor.

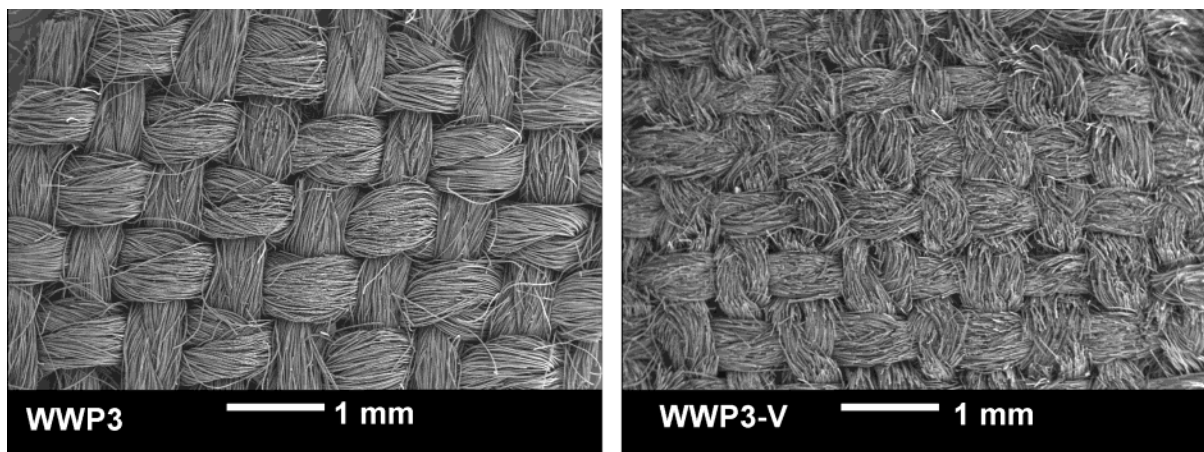
**II.2.1. Isothermal H<sub>2</sub>S Treatment Capacities.** A standard test is used to evaluate the performance of activated carbon H<sub>2</sub>S treatment. The sample is placed in a batch reactor before injection of gaseous H<sub>2</sub>S. The amount of loaded gas ( $q_e$ ) is determined from the mass balance

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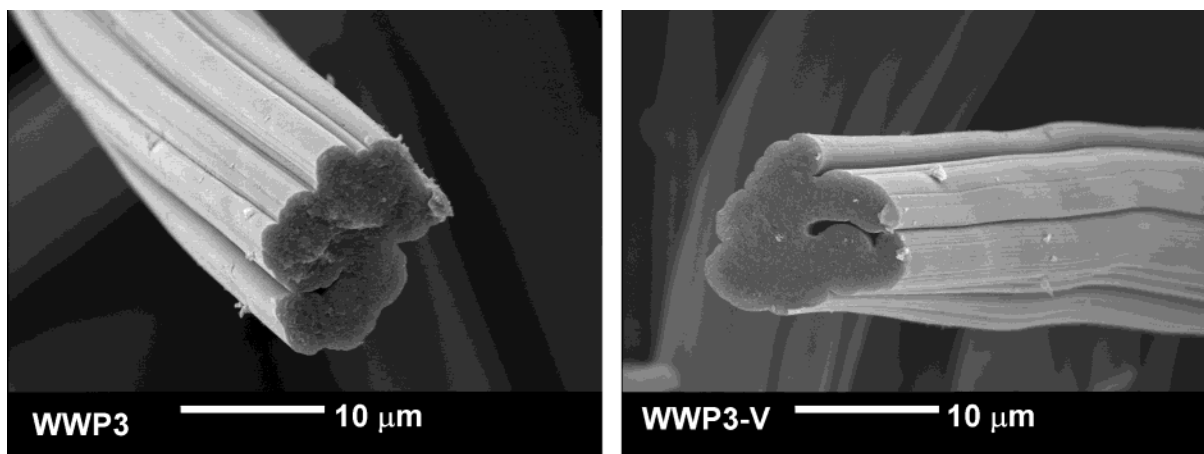
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**Figure 1.** Cloth texture, SEM observations.



**Figure 2.** Fibers, SEM observations.

between the gas injected into the reactor ( $C_0$ ) and that remaining in the gas phase ( $C_e$ ). All the experimental points  $q_e = f(C_e)$ , measured at the same temperature (298 K), constitute a capacity isotherm curve.

The concentration measurements of  $H_2S$  are performed with the Spectroquant (Merck) method, 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 in a basic solution (pH 9–10). Then, the reactant is added and mixed with the solution. So the concentration is measured by analysis with a UV spectrophotometer, Shimadzu UV-1601, at 665 nm wavelength.

For each adsorbent studied (see Table 1), the treatment capacity curves are performed with three different atmospheres: inert gas (nitrogen), dry air (RH equals 0%), and humid air (RH equals 30%). This allowed the influence of oxygen and moisture on  $H_2S$  elimination to be evaluated. Moreover, to determine influence of humidity, isotherm points are obtained at different relative humidity levels.

**II.2.2. Oxidation Byproduct Determination.** The  $H_2S$  capture onto activated carbon involves a competitive oxidation reaction which depends on the material characteristics and the operating conditions. The  $H_2S$  loaded onto the adsorbent is necessarily composed of  $H_2S$  physisorbate and the main different oxidation byproducts.

The  $S_0$  form is extracted from ACC by dissolution in 10 mL of carbon disulfide (the dissolution capacity of  $CS_2$  is 418 mg of  $S_0$  per gram of solvent) with agitation for 10 h. After filtration, evaporation at room temperature, and crystallization, the sulfur is determined by a gravimetric method.

The sulfate ions are measured by a nephelometric method. They are extracted from activated carbon by dissolution in 20 mL of concentrated HCl and stirred for 10 h. Then the materials are attacked by hot acid for 15 min. After filtration, the sulfate ions are precipitated on barium sulfate and stabilized with the surfactant Tween 20. The concentration measurements are performed with a UV spectrophotometer (Shimadzu UV-1601) at 690 nm wavelength.

The physisorbate hydrogen sulfide is obtained from the difference between the amount of loaded gas,  $q_e$ , in the adsorbent and the amount of the identified byproducts.

**II.2.3. Autocatalytic Role of the Sulfur Formed.** To highlight the catalytic role of the elemental sulfur byproduct, a first equilibrium point is performed in a batch reactor and a first treatment capacity is measured. Then, the sample is stripped at 333 K for 1 h with a nitrogen sweep to desorb the  $H_2S$  physisorbate. This sample, loaded with only elemental sulfur, is then used to perform another equilibrium point. The treatment capacity is then measured.

### III. Results and Discussion

**III.1. Adsorbent Characterizations.** The structural parameters calculated from nitrogen adsorption data are collected in Table 2. Analysis of the structural parameters along with the degree of microporosity reveals differences in porosity structure. The WWP3 and VS15 ACCs are predominantly microporous (Table 2), the WWP3-V ACC is partially mesoporous. This is due to the  $H_2O$  activation process which creates larger pores than  $CO_2$  activation.

**Table 2. Physicochemical Characterizations of the Studied Adsorbents**

	WWP3	WWP3-V	VS15	NC60
Structural Parameters				
BET surface (m <sup>2</sup> ·g <sup>-1</sup> )	976	871	1480	1058
mesoporous surface (m <sup>2</sup> ·g <sup>-1</sup> )	45	330	211	44
microporous volume (cm <sup>3</sup> ·g <sup>-1</sup> )	0.335	0.171	0.665	0.449
mesoporous volume (cm <sup>3</sup> ·g <sup>-1</sup> )	0.024	0.303	0.025	0.036
% microporous volume	96	68	96.4	91
median pore radius (Å)	1.67	2.49	2.31	2.77
Surface Functional Groups				
surface acidic groups (mequiv·g <sup>-1</sup> )				
carboxylic	0.35	0.35	0.25	0
lactonic	0.50	0.45	0.85	0
phenolic	0	0	0	0.45
carbonyl	0.25	0	0	0
total	1.10	0.80	1.10	0.45
surface basic groups (mequiv·g <sup>-1</sup> )	0.65	0.50	0.25	0.60
surface pH	10.24	9.60	7.80	8.43
point of zero charge	9.23	9.52	8.65	10.70

The highest surface area and micropore volume are observed for VS15. The lowest surface areas are obtained for WWP3-V and WWP3; the lowest micropore volume is obtained for WWP3.

The pH and point of zero charge (PZC) measurements are presented in Table 2. The highest pH value is obtained for WWP3, promoting the sorption of the acid gas H<sub>2</sub>S. The VS15 pH is the lowest. The WWP3 and WWP3-V PZCs are quite similar despite their activation process. The NC60 GAC has the highest PZC.

The differences in surface chemistry of the materials used are clearly seen from the Boehm titration results presented in Table 2. As expected, the WWP3 and WWP3-V samples are predominantly basic materials, whereas VS15 contains more acidic groups (lactonic). Concerning the NC60 GAC, the Boehm titration results correspond to its pH value (Table 2).

**III.2. Adsorption in a Batch Reactor.** For all atmospheres (Figures 3–6), the increasing order of treatment capacity is for the materials studied: WWP3 > WWP3-V ≈ NC60 > VS15. To discuss and explain this classification, both porosity and surface chemistry should be taken into consideration. Moreover the presence of humidity has a direct impact on the oxidation reactions, which play a major role in the treatment process. Then the discussion about the treatment capacities will be explained according to the presence or not of humidity inside the reactor.

For all experiments (Figures 3–6), at low concentrations ( $C_e < 1 \text{ g} \cdot \text{m}^{-3}$ ), the main sulfur form is elemental sulfur, which is greater than the physisorbate H<sub>2</sub>S. The minor products are sulfate ions due to the presence of water byproducts and adsorbed water. Indeed, gravimetric thermal analysis with dry samples reveals 2–5% in mass of water adsorbed according to the different materials.

**III.2.1. Under a Dry Atmosphere.** The H<sub>2</sub>S equilibrium curves in dry conditions, presented in Figures 3–6 (see only parts a and b), are type IV isotherms, which involve a first saturation step. Then, when equilibrium concentration increases ( $C_e > 2 \text{ g} \cdot \text{m}^{-3}$ ), a second step is obtained.

The specific surface area characterization of the material does not alone explain the classification of the treatment capacity. In fact, although H<sub>2</sub>S is a small molecule which suggests that small pores are favorable for physisorption, this classification does not follow the increase in microporous volume. Thus, it is interesting to note that although WWP3 has a smaller pore volume (93%) and specific surface area (976 m<sup>2</sup>·g<sup>-1</sup>) than VS15 (96% and 1480 m<sup>2</sup>·g<sup>-1</sup>, respectively), its H<sub>2</sub>S treatment capacity is

greater. However, the homogeneity in pore size enhances the dispersion of active centers where hydrogen sulfide can be oxidized. These results confirm that H<sub>2</sub>S treatment onto carbon adsorbents is not only physical adsorption but also oxidation reactions. Thus, the surface chemistry of the materials plays a significant role in H<sub>2</sub>S treatment. It is well-known that impregnation of carbons with chemical compounds promoting oxidation of hydrogen sulfide significantly enhances their performance.<sup>20</sup>

The differences in surface chemistry of the materials used are clearly seen from the Boehm titration results, the determination of pH, and the PZC presented in Table 2. The comparison of the material isotherm curves with the results of Boehm titration, pH, and PZC determinations shows the direct relation between oxygen-containing sites, in particular basic sites with H<sub>2</sub>S adsorption. Although the cloth WWP3 has a PZC lower than WWP3-V, its adsorption capacity is greater, due to its higher quantity of oxygen groups, in particular basic groups. The quantity of basic groups in the granular NC60 explains its higher efficiency for adsorbing H<sub>2</sub>S than the cloth VS15 which has the highest quantity of acidic groups and the lowest quantity of basic groups. So the results presented suggest that all oxygen groups present on the carbon surface act as catalysts for the oxidation reaction, but the basic groups contribute particularly in the process of hydrogen sulfide adsorption. H<sub>2</sub>S is an acidic gas and the presence of basic groups plays a significant role in the immobilization process. Thus the H<sub>2</sub>S adsorption/oxidation depends on the local pH in the pore structure.<sup>22</sup> All active carbons used in this study have a pH greater than 7, which ensures the effectiveness of removal of hydrogen sulfide from the gas phase.

Under nitrogen, the oxidative decomposition of H<sub>2</sub>S gas onto the ACC surface proceeds according to the equation

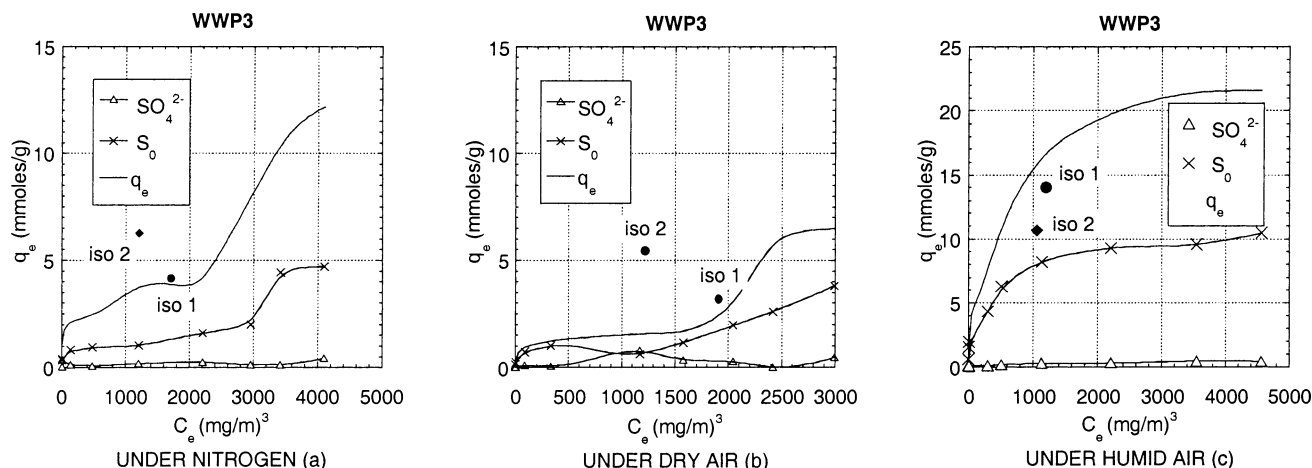


where C\* is an oxygen-containing site and/or radical C\* form at the carbon surface. Sulfur atoms react in a substitution reaction with the C(O) surface complex and

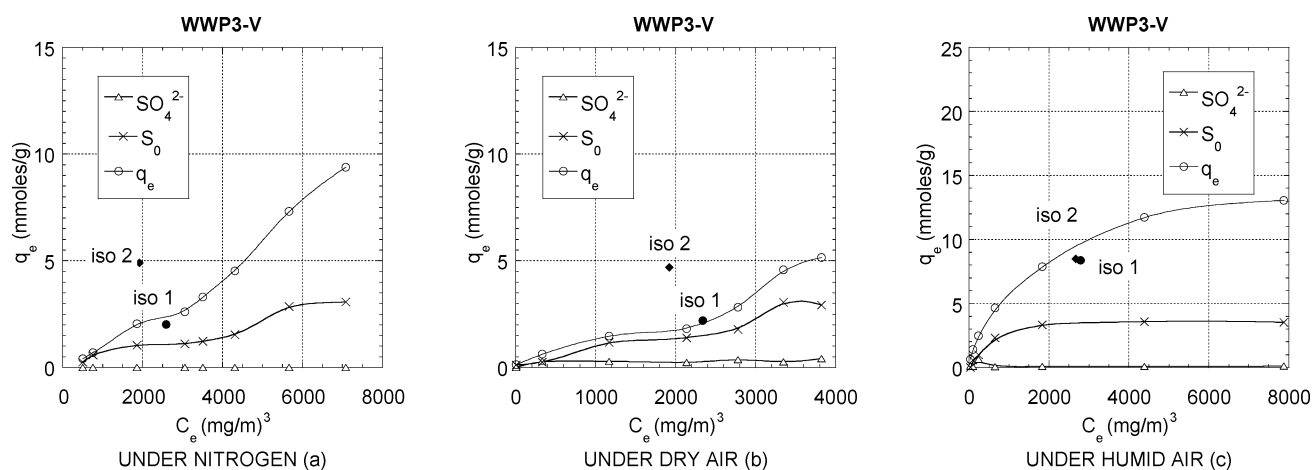
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**Figure 3.** Isotherms and sulfur byproduct determination after experiment, for WWP3 ACC under nitrogen (a), dry air (b), and humid air (c).



**Figure 4.** Isotherms and sulfur byproduct determination after experiment, for WWP3-V ACC under nitrogen (a), dry air (b), and humid air (c).

in an addition reaction with radical  $\text{C}^*$  to form  $\text{C-S}$  complexes until the formation of sulfur chains  $\text{S}_8$ .

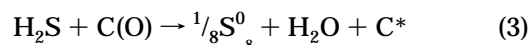
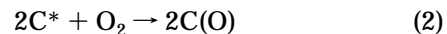
For each isotherm point, a mass balance of sulfur is performed. The byproduct determination under nitrogen for each material is presented in Figures 3–6 (see only part a). The sulfate ions represent only 5–10 mol % of the total  $\text{H}_2\text{S}$  loaded. The main byproduct is sulfur whose formation curves follow the quantity of  $\text{H}_2\text{S}$  loaded. So the curves obtained have two saturation steps. At low concentration ( $C_e < 1000 \text{ mg}\cdot\text{m}^{-3}$ ), in the first step, the average ratios between physisorbate  $\text{H}_2\text{S}$ , the sulfur formed, and sulfate ions is 30, 58, and 12 mol %, respectively. At high concentration, in the second saturation step, the same ratio is stabilized at 56, 40, and 4%, respectively. These ratios indicate a progressive sulfur saturation of activated carbon. Moreover, the presence of sulfate ions could be explained by the presence of water byproduct (see eq 3) which interferes in the reaction pathways.

The equilibrium curves under dry air, presented in Figures 3–6 (see only part b), reveal the same type as those obtained under dry nitrogen.

The classification of the treatment capacities of the adsorbents could be explained by the chemical properties and pore size, in the same way as under dry nitrogen. Equilibrium curves are again type IV isotherms. Compared to the nitrogen atmosphere, for all materials, lower treatment capacities are obtained. This indicates the role of oxygen in the  $\text{H}_2\text{S}$  adsorption/oxidation. The presence

of air oxygen decreases the quantity of  $\text{H}_2\text{S}$  physisorbate and also the quantity of sulfur formed by blocking access to active centers in a competitive adsorption.

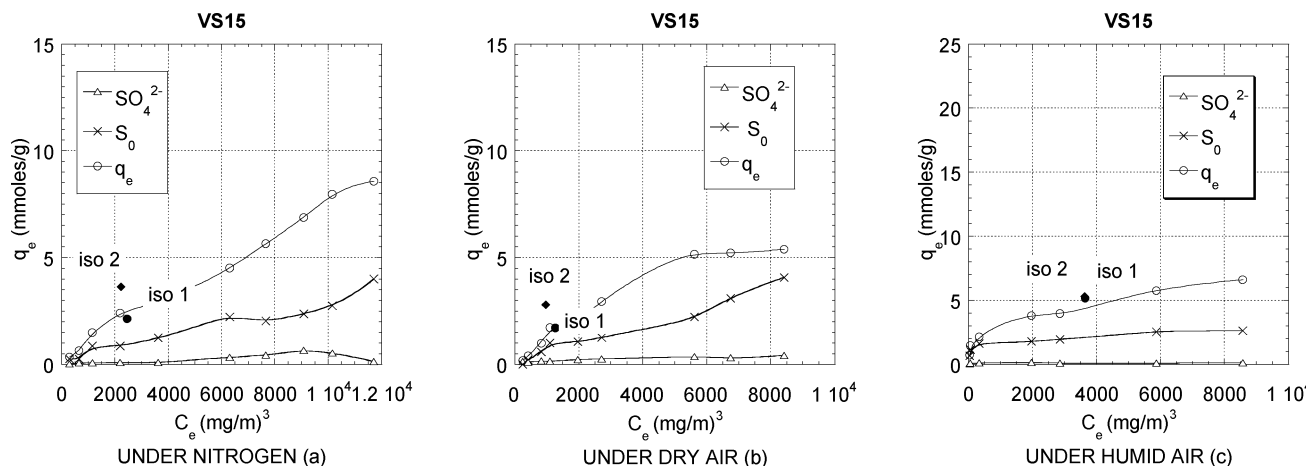
The first mechanism is quite similar to the mechanism proposed under nitrogen, but  $\text{C}^*$  is an oxygen-containing site where oxygen from air has been adsorbed by the carbon matrix



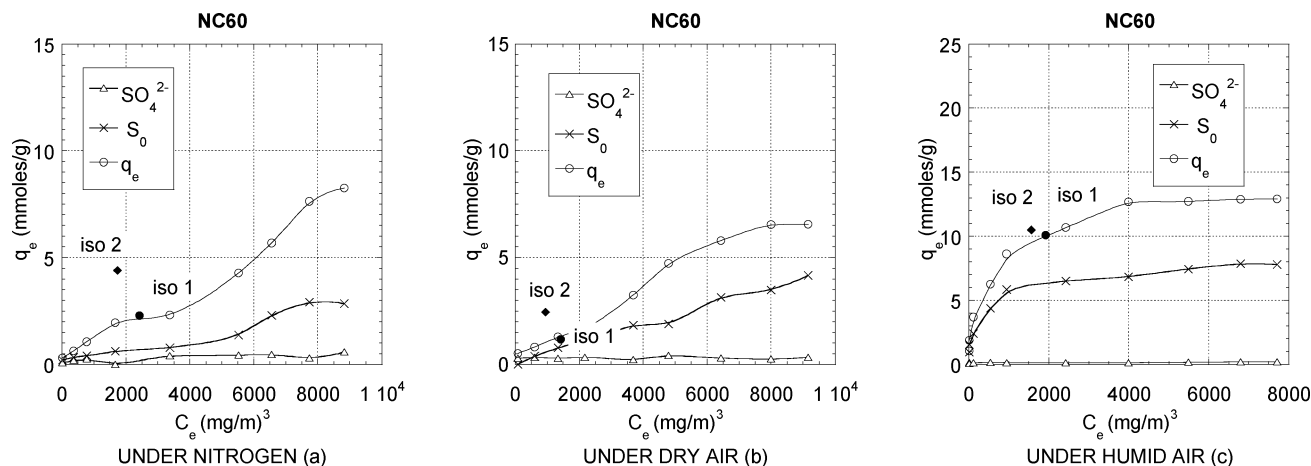
The sulfur byproduct quantification presented in Figures 3–6 (see only part b) reveals a higher ratio of sulfur formed than that obtained under nitrogen even through the absolute values are lower. The average ratios between physisorbate  $\text{H}_2\text{S}$ , the sulfur formed, and sulfate ions is 21, 53, and 26%, respectively. At high concentration, after the second saturation step, the same ratio is stabilized at 41, 52, and 7%, respectively.

The ratios for each studied material between physisorbate  $\text{H}_2\text{S}$ , the sulfur formed, and sulfate ions are presented in Figure 7. At first, the oxide products are very low (<10%) under both conditions and so are not presented in Figure 7. Then, the curves reveal a large conversion of  $\text{H}_2\text{S}$  to elemental sulfur at low concentration. At high concentration, after the second saturation step, the same ratios stabilized around 50%. The oxidation of  $\text{H}_2\text{S}$  is supported

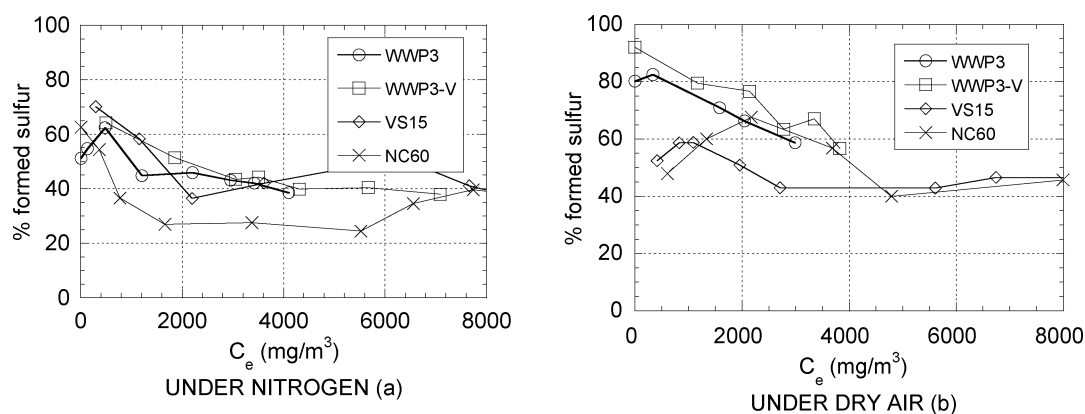




**Figure 5.** Isotherms and sulfur byproduct determination for VS15 ACC after experiment, under nitrogen (a), dry air (b), and humid air (c).



**Figure 6.** Isotherms and sulfur byproduct determination for NC60 after experiment, under nitrogen (a), dry air (b), and humid air (c).



**Figure 7.** Ratios (%) of formed sulfur for each adsorbent under nitrogen (a) and dry air (b).

in the presence of oxygen which participates in the oxidation reaction.

Under nitrogen, the sulfur formation is only due to the oxygen-containing site, but under dry air the oxygen contribution promotes the  $H_2S$  oxidation reaction. As under nitrogen, the sulfate ion formation is due to the presence of water byproduct. Thus, the presence of humidity in the porous material plays a significant role in the reaction pathways.

**III.2.2. Influence of Relative Humidity.** The  $H_2S$  isotherm curves in humid conditions (Figures 3c–6c) are type I isotherms. These isotherms seem to be controlled

by the presence of humidity, which inhibits the catalytic effect under dry conditions.

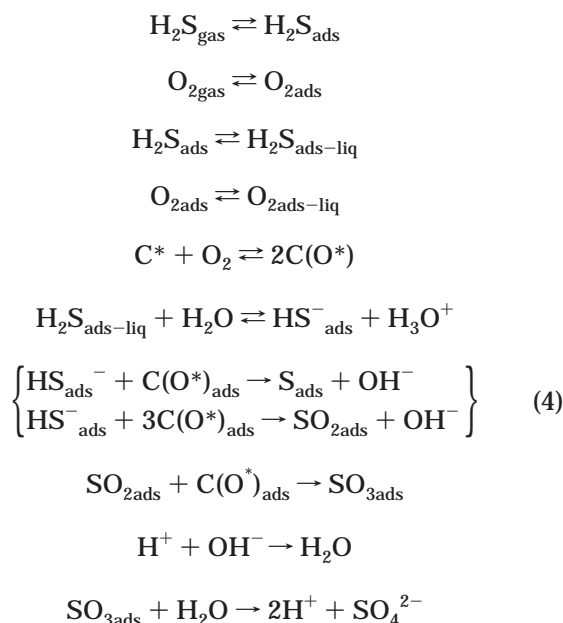
The  $H_2S$  equilibrium curves in humid conditions presented in Figures 3–6 (see only parts c) are classical type I isotherms. In contrast to the previous curves, only one saturation step appears, indicating a different mechanism to that in dry conditions.

A strong enhancing influence of humidity is explained by the condensation of water in the pore structure, favorable dissolution of  $O_2$  and  $H_2S$  gases into the preadsorbed water film, and then adsorption of the  $H_2S$  followed by oxidation of the latter.<sup>9</sup> The  $HS^-$  ions and  $O_2$



dissolved are presumed to diffuse inside the water film. The adsorption of water increases with the amount of polar groups present on the surface, which is due to the formation of hydrogen bonds between the polar species and adsorbed water. Single molecules of water (cross section of  $10.2 \text{ \AA}^2$ ) are adsorbed on the boundary surface. The dissolution of  $\text{H}_2\text{S}$  to  $\text{HS}^-$  is dependent not only on the amounts of preadsorbed water but also on the local pH. A moderately low average pH of the carbon surface suppresses the dissociation of  $\text{H}_2\text{S}$  to  $\text{HS}^-$  ions. On the other hand, a pH in the basic range promotes the dissociation of  $\text{H}_2\text{S}$  to  $\text{HS}^-$  ions. This results in a high concentration of  $\text{HS}^-$  ions, which are then oxidized to sulfur polymers having a chain or ringlike shape. The materials studied present a basic surface pH, but the differences in surface pH could explain the differences in adsorption capacities. So WWP3 has the highest surface pH and adsorption capacity and the lowest is attributed to VS15 ACC.

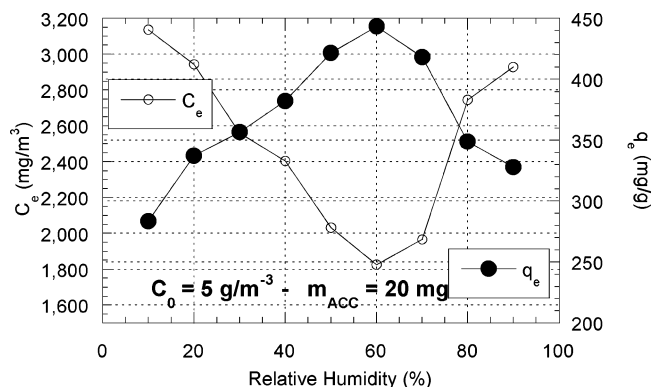
The oxidative decomposition of  $\text{H}_2\text{S}$  gas on the active carbon surface has been studied by Adib.<sup>4</sup> The authors suggest an oxidation pathway which proceeds according to the following equations



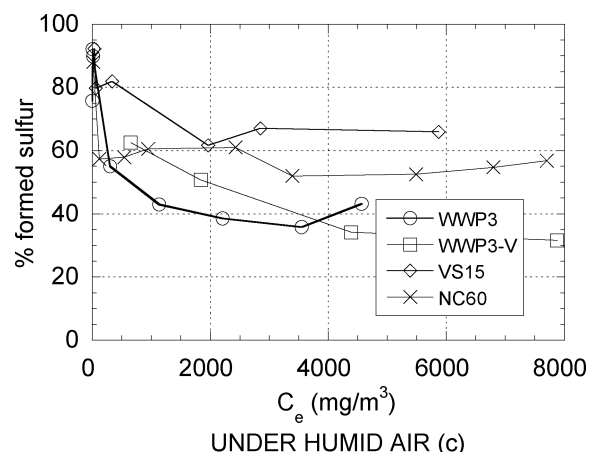
where "gas" and "ads" phases refer to the presence of reactants in the gas phase and the adsorbate phase.  $\text{C}^*$  represents a reduced site.

The presence of humidity increases strongly the loaded capacities of activated carbons compared to a dry atmosphere. This reaction occurs through an interaction between the dissociate adsorbed  $\text{H}_2\text{S}$  and the oxygen adsorbed on the active site of active carbon and is accelerated strongly with increasing humidity. So measurements of sorption capacities were carried out at various relative humidity rates. The obtained results (Figure 8) show that an excess of water flooding was reported as a factor decreasing adsorption from the gas phase onto active carbon. The optimal relative humidity rate was found to be around 60% with WWP3 ACC.

The  $\text{H}_2\text{S}$  byproduct determination under wet air is presented in Figures 3–6 (see only part c). Like under nitrogen and dry air, the sulfur formation curves follow the loaded  $\text{H}_2\text{S}$  curves. The single saturation step may be explained by the different mechanism due to the presence of water. The average ratios of different  $\text{H}_2\text{S}$  oxidized forms in wet condition are presented in Figure 9. The ratios of



**Figure 8.**  $\text{H}_2\text{S}$  adsorption on ACC as a function of relative humidity level with WWP3.



**Figure 9.** Ratios (%) of formed sulfur for each adsorbent under humid air.

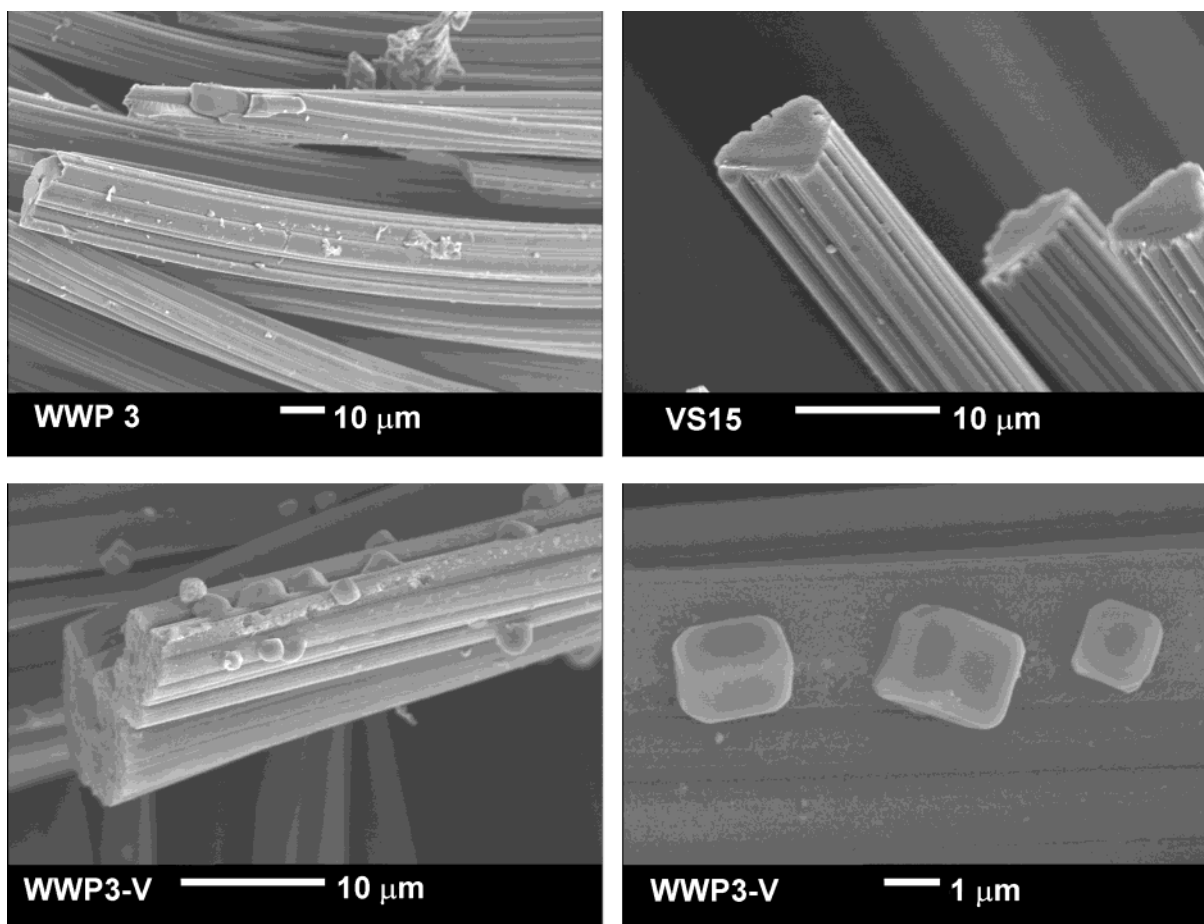
oxide forms are, like previously in dry condition, very low and not presented. The ratios of formed sulfur decrease for each material with the equilibrium concentration, as in dry conditions. But, it is necessary to note that these results are proportions and the real quantities of formed sulfur are more important under wet conditions than under dry conditions. Moreover, strong differences between materials concerning the conversion ratio of  $\text{H}_2\text{S}$  in elemental sulfur appears under wet conditions. These differences could be attributed to the affinity of each material with water which is implicated in the oxidation reaction under wet conditions.

In the  $\text{H}_2\text{S}$  treatment onto activated carbons, a catalytic effect, observed under dry conditions, is inhibited in the presence of water. The catalytic role of sulfur has been described by different authors.<sup>12,13,16,23</sup>

**III.2.3. The Role of Sulfur in the Adsorption/Oxidation Process.** As suggested in previous literature,<sup>13,15</sup> the oxidation byproducts are elemental sulfur in the  $\text{S}_8$  orthorhombic form and oxidized sulfur ( $\text{SO}_2$  and  $\text{SO}_3$ ). Since usually the process is carried out in the presence of moisture and oxygen,  $\text{SO}_2$  and  $\text{SO}_3$  are oxidized to sulfuric acid as a final product of the reaction ( $\text{SO}_4^{2-}$  form). Thus, for each experimental isotherm point, a molar balance sheet was performed with the different forms of sulfur.

Scanning electron microscopy (SEM) photographs presented in Figure 10 show fibers after  $\text{H}_2\text{S}$  sorption in a batch reactor. The photographs of WWP3 and VS15 ACC,

(23) Meeyoo, V.; Trimm, D. L.; Cant, N. W. Adsorption-reaction processes for the removal of hydrogen sulphide from gas streams. *J. Chem. Technol. Biotechnol.* **1997**, *68*, 411–416.

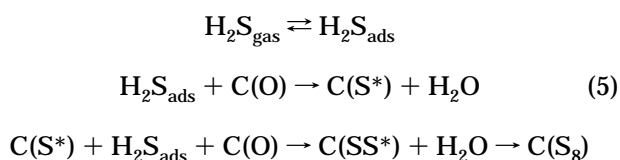


**Figure 10.** SEM observations on ACC fibers after H<sub>2</sub>S sorption in a batch reactor.

predominantly microporous, show small particles of mineral sulfur. This observation indicates that sulfur is formed mainly in microporous structures, in contrast to the mesoporous WWP3-V ACC where the photograph shows fibers covered with larger particles of sulfur at the external fiber surface. These sulfur particles have an orthorhombic form, characteristic of the S<sub>8</sub> crystalline structure.

To highlight the role of the sulfur formed in the oxidation process, for each equilibrium point, a molar determination of the principal oxidation byproducts was performed and is presented in Figures 3–6. It is interesting to note on the formed sulfur curves under dry atmosphere (see parts a and b of Figures 3–6), the presence of a first saturation step, followed by an acceleration of sulfur formation when its quantity reaches around 2 mmol/g. This value corresponds to the maximal sulfur catalytic activity described by Steinjs.<sup>12,13</sup> So the sulfur formed in a first step plays an autocatalytic role and promotes the oxidation reaction until sulfur saturation.

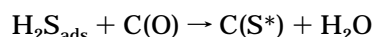
Under nitrogen, the catalytic role of sulfur probably interferes with active sites C(O) in a reaction as follows



The comparison of sulfur formation curves between the atmospheres shows a higher proportion of H<sub>2</sub>S byproducts under dry air. The excess of adsorbate oxygen promotes the formation of sulfur. A mechanism involving sulfur

and oxygen is proposed. Sulfur radicals as species play an important role in the chemisorption of oxygen on the carbon. The reaction in this case is as follows:

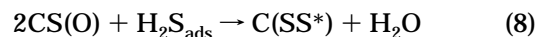
H<sub>2</sub>S dissociative adsorption:



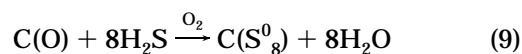
Oxidation: reaction between oxygen and adsorbate sulfur



Substitution reaction:



Finally



Moreover, some metals present at the surface of the adsorbent can also play the same role as sulfur, like a catalyst for the H<sub>2</sub>S oxidation.<sup>23</sup>

The second equilibrium isotherm points (see parts a and b of Figures 3–6), obtained as described in section 3.2.1, under a dry atmosphere, reveal a higher quantity of H<sub>2</sub>S loaded into the adsorbent than the initial equilibrium point. The increase of H<sub>2</sub>S loaded is obtained in

the same equilibrium concentration, in the first saturation step, and so is only due to the autocatalytic role of sulfur.

Under wet air (Figures 3c–6c), the results show quite similar treatment capacities for both equilibrium points. The sulfur formed in the first test does not play any role in catalyzing oxidation in contrast to tests under a dry atmosphere. The water film at the surface would prevent any catalytic sulfur reaction.

#### IV. Conclusion

The H<sub>2</sub>S sorption in a batch reactor reveals the good efficiency of activated carbon cloths as catalysts for H<sub>2</sub>S adsorption/oxidation in different atmosphere conditions at room temperature. These results, associated with the material characterization, highlight the influence of the surface chemical properties of the adsorbents. The H<sub>2</sub>S treatment occurs as a mass transfer from air to adsorbents which are the limiting factor. These are rather complex and also depend on the presence or not of moisture and oxygen in the treated atmosphere.

Between the different adsorbents (the  $S_{\text{BET}}$  surface ranged between 900 and 1500 m<sup>2</sup>·g<sup>-1</sup>), the differential parameter in H<sub>2</sub>S removal is the functional oxygen group concentration, and particularly the basic groups (included between 1.75 and 0.25 mequiv·g<sup>-1</sup>). Hence, we can observe that a basic surface ensures a good immobilization of H<sub>2</sub>S molecules, followed by their oxidation. It is important to emphasize here the significant role of water and oxygen in the capacities obtained and in the oxidation pathways.

Under dry air, after its adsorption, the hydrogen sulfide is oxidized in a substitution reaction by oxygen functional groups present close to the carbon surface. In the presence of water, the reaction pathway begins by the dissolution of hydrogen sulfide and oxygen in a thin water film on the adsorbent surface and is followed by a radical oxidation reaction. The best capacity is obtained in a wet air atmosphere with the most basic material WWP3.

In dry and humid conditions, oxidation byproduct quantification reveals that the major form is elemental sulfur and the minor forms are sulfur oxides. The differences in oxidation pathways indicate that the byproduct sulfur in dry conditions plays a catalytic role in its own oxidation reaction, in contrast to wet conditions where the water film at the surface prevents any catalytic sulfur reaction. This finding can be used as a new specification when the application of activated carbon cloths as hydrogen sulfide removers is taken into account.

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