

# POSTER

## CONTACT OF H<sub>2</sub>SO<sub>4</sub> SOLUTIONS WITH ACTIVATED CARBON. A STUDY OF THE SAMPLES

V. GOMEZ-SERRANO<sup>1</sup>, M. ACEDO-RAMOS<sup>1</sup> and A.J. LOPEZ-PEINADO<sup>2</sup>

<sup>1</sup>Departamento de Química Inorganica, Universidad de Extremadura  
Avda. Elvas s/n, 06071-Badajoz, Spain

<sup>2</sup>Departamento de Química Inorganica, Universidad Nacional de Educación a Distancia  
C/ Senda del Rey s/n, 28040-Madrid, Spain

### Introduction

Sulfuric acid is widely used in laboratory and in various branches of industry. In spite of the large amount of H<sub>2</sub>SO<sub>4</sub> which in a way or in another reaches the environment, investigations on a laboratory scale aimed at increasing the removal efficiency of H<sub>2</sub>SO<sub>4</sub> from contaminated media are rare, as deduced from a recent literature review. Since H<sub>2</sub>SO<sub>4</sub> is currently treated with granular activated carbon [1], a commercial product was used in this study. The main focus was to determine the influence of the method of preparation connected not only with the ability of activated carbon to remove H<sub>2</sub>SO<sub>4</sub> from aqueous solutions but also with the possible recovering of the H<sub>2</sub>SO<sub>4</sub>-exhausted activated carbon could be obtained.

### Experimental

Activated carbon from Merck (AC) and a commercial sulfuric acid from Carlo Erba (96 wt%, 1.833 g·cm<sup>-3</sup>) were used in this work. Samples were prepared by using H<sub>2</sub>SO<sub>4</sub> solutions of varying concentration, which were brought into contact with AC after outgassing the material. The contact between the phases and the outgassing of the carbon was carried out under controlled temperature and time conditions. The experimental conditions were described previously [2]. Codes and specific conditions of preparation of the

samples are: D, dilution of H<sub>2</sub>SO<sub>4</sub>; O, outgassing; T (°C), temperature; t (h), time; and, C, contact. The H<sub>2</sub>SO<sub>4</sub> solution used in the preparation of D-0 was sulfuric acid as such, whereas for D-2 and D-4 the solutions were prepared by mixing 25 cm<sup>3</sup> and 12.5 cm<sup>3</sup> of H<sub>2</sub>SO<sub>4</sub> with 25 cm<sup>3</sup> and 37.5 cm<sup>3</sup> of water, respectively.

FT-IR spectroscopy was carried out in a Perkin Elmer, model 1720, spectrometer by using KBr pellets and being the sample:KBr ratio of 1:500 by weight.

The thermal behavior of samples was studied in a thermobalance, Mettler TA3000, heating about 100 mg of sample from 303 to 1073 K at a heating rate of 5 K·min<sup>-1</sup> and a nitrogen flow of 200 cm<sup>3</sup>·min<sup>-1</sup>.

The samples were texturally characterized by gas adsorption of N<sub>2</sub> at 77 K, mercury porosimetry and helium and mercury density measurements. The adsorption data of nitrogen were obtained in a Micromeritics ASAP 2000 analyzer using about 2 g of sample and a outgassing temperature of 393 K.

### Results and Discussion

It is observed a significant weight increase of the activated carbon treated with H<sub>2</sub>SO<sub>4</sub>, this

increase varies between 17.8 and 70.1% of the original weight, which depended strongly on the method of preparation of the samples. The former points at the uptake by AC of a large amount of components of the H<sub>2</sub>SO<sub>4</sub> solution, especially H<sub>2</sub>SO<sub>4</sub>, which were not removed from the wet samples when these were oven-dried at 333 K. It was likely due to the low vapor pressure of the H<sub>2</sub>SO<sub>4</sub> solutions. The high density of sulfuric acid will also contribute to the mass increase.

A significant decrease in the mass increase is observed with increasing the concentration of the H<sub>2</sub>SO<sub>4</sub> solution, this fact is compatible with an unfavorable influence of the viscosity increase in the same direction of concentration variation of diffusion of the H<sub>2</sub>SO<sub>4</sub> solution in AC pores.

The FT-IR spectrum of AC sample shows the corresponding absorption bands due to hydroxyl, carbonyl, carboxilate or iono-radical, and ether groups, which have been described elsewhere [2]. The samples treated with H<sub>2</sub>SO<sub>4</sub> show different bands due mainly to S=O and S-O stretching in species HSO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>.

Thermal stability of activated carbon samples has been studied by thermogravimetric analysis. The corresponding DTG curves showed two maxima of weight loss centered at about 373 and 573 K. The first weak effect has been associated to removing the remaining water after oven-drying the samples. The stronger effect at higher temperatures is attributable to the loss of H<sub>2</sub>SO<sub>4</sub>. In fact, this effect occurs in the neighborhood of the boiling point of H<sub>2</sub>SO<sub>4</sub> (≈ 573 K for anhydrous H<sub>2</sub>SO<sub>4</sub>, which decomposes).

The results of the thermogravimetric analysis of the samples suggest that a feasible method of recovering of activated carbon which contains

H<sub>2</sub>SO<sub>4</sub> could be based on the heat treatment of the samples at temperatures not too high.

Adsorption isotherms of activated carbon samples belong to the type I of the classification of Brunauer, Demming, Demming, and Teller (BDDT). These isotherms are characteristics of essentially microporous solids since in small size pores the adsorption occurs largely at low P/P<sub>0</sub> values.

The corresponding nitrogen surface area (S<sub>BET</sub>) of samples decreased greatly with respect to AC. In the various series of samples, the variation of S<sub>BET</sub> is in line with that of percentage of mass variation. The greater mass increase originated the larger surface area loss.

The mercury density is markedly higher for the samples prepared with H<sub>2</sub>SO<sub>4</sub> solutions than for AC. This is consistent with the great amount of H<sub>2</sub>SO<sub>4</sub> uptaken. In the instance of helium density, its value appears to be strongly dependent on the porosity of the samples which is accessible to helium at room temperature.

From the N<sub>2</sub> adsorption data, the micropore volume W<sub>0</sub> was estimated by applying the Dubinin-Radushkevich equation. The W<sub>0</sub> values show the introduction of H<sub>2</sub>SO<sub>4</sub> solution in Ac caused a drastic decrease in the micropore volume of the samples.

### References

- 1.-W.G. Schuliger, in P.N. Cherimisinoff and F. Ellerbusch (eds.) *Carbon Adsorption Handbook*, Ann Arbor Sci., MI, p. 82, 1980.
- 2.-V. Gomez-Serrano, M. Acedo-Ramos, A.J. Lopez-Peinado and C. Valenzuela-Calahorro, *Fuel*, **73** (1994) 387.