

ADSORPTION FROM AQUEOUS SOLUTIONS IN RELATION WITH THE SURFACE PROPERTIES OF ACTIVATED CARBONS

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Introduction

The activated carbons are profusely used as adsorbents for depollution processes because of their extended surface area, high adsorption capacity, porous structure and special surface reactivity [1]. Their physical or porous structure, the adsorption capacity and the adsorption kinetic is strongly influenced by the chemical nature of the surface. Very frequently the water is contaminated with phenol and related compounds [2]. The effects of the treatments with HCl, H₂F₂ and HNO₃ on the surface area and porosity, on the surface functional groups of four microporous commercial carbons and on the phenol adsorption behavior from aqueous solutions are studied.

Experimental

Materials. Four types of commercial microporous activated carbons were used. A carbon R1 from Norit N. V. (The Netherlands) (N); a carbon from CECA (France) (C); and two activated carbons prepared from olive stones ICASA (Spain) (S1 and S2).

Surface treatments. All the samples were washed with HCl (10%) to eliminate inorganic impurities. The carbons resulting of this treatment were denoted as NC, CC, S1C and S2C. Subsequently NC and CC carbons were washed with concentrated H₂F₂ to eliminate silica impurities, the obtained samples were called NF and CF. The carbon S1C, NF and CF were also treated with HNO₃ (10%) given the S1N, NN and CN samples. This treatment is well known to be very efficient for the production of oxygen surface groups [3].

Specific surface areas and pore-size distribution. The specific surface areas were determined by nitrogen adsorption at 77 K by B.E.T. method. Micromeritics ASAP 2000 volumetric system was used to obtain the corresponding gas adsorption isotherms. The pore-size distributions of the samples were also obtained.

Determination of ash content. All the samples were burned in a air furnace at 973 K during 16 h. The ash content was determined by weighting the residue inorganic components.

Phenol adsorption isotherms. The phenol adsorption isotherms from water solutions were obtained by the immersion method [3]. The adsorbed amount was calculated on basis of the concentration change, determined by UV (Varian Cary 1 Spectrophotometer) at 269.5 nm before and after phenol adsorption on active carbons.

Temperature programmed desorption. The TPD experiments were performed in a quartz vessel with a vacuum of 10⁻⁶ Torr. A mass spectrometer (Baltzers, QMG 421) allow to measure in the gas phase the concentration of species desorbed from the active carbons during the experiments.

Kinetic of phenol adsorption. The measurements of the remanent amounts of phenol in the solutions were analyzed using the method above described. After, the values were adjusted to an empirical equation.

Results and discussion

On Table 1 specific surface areas, volume in pores, ash content, adsorbed amount (Γ) of phenol at isotherm "plateau" and the empirical kinetic constant are given.

The carbons S1 and S2 present as main impurities inorganic carbonates, which can be removed by treatment with HCl solutions. Carbon N exhibit as principal impurity silica, while carbon C presents both types of inorganic. It appears that these kind of impurities do not affect significantly the adsorbed amounts of phenol (Table 1). On the other hand, the treatment with HNO₃ decreases the surface area and the micropore volume of carbons been this behavior explained because the introduced oxygen surface groups are located on pores entrances. The adsorbed amount of phenol on HNO₃ treated samples and specially for S1N carbon, diminishes because the new oxygen groups are predominantly acidic whereas

Table 1. Physical characteristics of active carbons , adsorbed amount (Γ) and kinetic constant of phenol

| Sample | Area (m ² /g) | Volume in pores (cm ³ /g) | | | %Ash content | Γ $\mu\text{mol}/\text{m}^2$ | $k \cdot 10^6$ l/ $\mu\text{mol} \cdot \text{min}$ |
|--------|--------------------------|--------------------------------------|-------|--------|--------------|-------------------------------------|--|
| | | Total | 0-2nm | 2-50nm | | | |
| N | 1175 | 0.51 | 0.40 | 0.11 | 3.12 | 3.30 | 4.0 |
| NC | 1202 | 0.45 | 0.40 | 0.05 | 3.12 | 3.20 | 3.5 |
| NF | 1319 | 0.51 | 0.43 | 0.08 | 0 | 3.11 | 3.7 |
| NN | 523 | 0.18 | 0.01 | 0.17 | - | 1.25 | 8.0 |
| C | 1367 | 0.60 | 0.43 | 0.17 | 7.00 | 2.70 | 2.5 |
| CC | 1443 | 0.65 | 0.45 | 0.20 | 2.35 | 2.57 | 3.0 |
| CF | 1654 | 0.79 | 0.52 | 0.27 | 0 | - | 3.5 |
| CN | 857 | 0.37 | 0.27 | 0.10 | - | 2.07 | 3.0 |
| S1 | 1145 | 0.50 | 0.36 | 0.14 | 8.66 | 2.85 | 4.5 |
| S1C | 1223 | 0.51 | 0.38 | 0.13 | 0.20 | 2.95 | 4.5 |
| S1N | 832 | 0.36 | 0.12 | 0.24 | - | 0.34 | 70 |
| S2 | 1182 | 0.51 | 0.38 | 0.13 | 7.50 | 3.32 | 3.5 |
| S2C | 1687 | 0.72 | 0.54 | 0.18 | 0.28 | - | 4.0 |

the phenol forms electron donor-acceptor complexes with basic surface oxygen groups.

Figure 1 shows the CO and CO₂ profiles from TPD experiments of carbon S1 series. The peaks

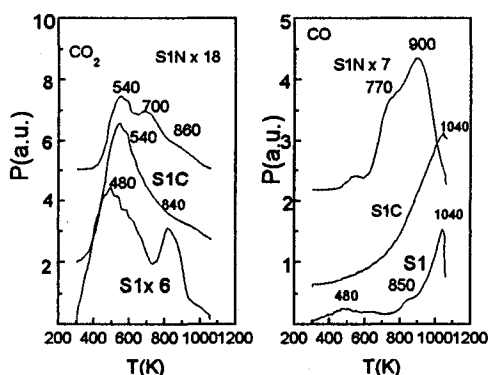


Figure 1. TPD profiles of carbon S1 series

at 840 K on CO₂ profile and at 400 and 850 K on CO profile of sample S1 disappear on sample S1C (treated with HCl). It means that these peaks may be probably assigned to carbonates. The CO₂ peaks of S1N carbon are tentatively assigned : 540 K to carboxyl groups, 700 K to anhydride groups and 860 K to lactones. The CO peaks of S1N are proposed: 770 K to anhydride groups and 900 to phenol groups[4].

The kinetic dates may be reproduced by the empirical expression $-d\Gamma'/dt=kC(\Gamma_e-\Gamma')$. Where Γ' is the adsorbed amount at time t ($\mu\text{mol}/\text{g}$), k is a proportional constant, C is the liquid phase concentration at time t ($\mu\text{mol}/\text{g}$) and Γ_e ($\mu\text{mol}/\text{g}$) is the adsorbed amount if the equilibrium was reached with each C. The adsorption kinetic is similar for each carbon serie (considering the original carbon and its treatments with HC and H₂F₂). This is in accord with

adsorbed amounts at the "plateau" and with the textural characteristics (Table 1).

As it has been said above, when the samples are oxidized, the created groups are placed on pores entrances diminishing the adsorption capacity. In all samples, the amount of micropores decreases indicated that the new groups are placed, mainly, on micropores. However, in the cases of samples S1N and NN at the same time, the amount of mesopores increases (Table 1) due to that part of the pore walls are destroyed by the HNO₃ treatments. As the available pores are wider, the effective diffusion of carbon increases and thus, its kinetic constant.

Acknowledgments

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