VARIATION OF SURFACE PROPERTIES OF AN ACTIVATED CARBON WITH THE ADSORPTION OF HUMIC SUBSTANCES. INFLUENCE ON THE Cr(III) IONS ADSORPTION

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Introduction

In a previous paper [1] the adsorption process of Cr ions on activated carbons was studied and it was detected that the presence of humic acid in the solutions decreased Cr(III) uptake mainly when humic acid is in low concentrations. As a hypothesis, this decrease was explained as due to a blockage effect of the adsorbed humic acid on the surface of the carbon. The aim of the present paper is to go insight the effect of the humic compounds on the adsorption of Cr(III) by activated carbons, studying the changes of the activated carbon surface (charge and porous texture) owing to the adsorption of humic substances such as gallic, tannic and humic acids. The capacity of the activated carbon to adsorb these acids both in the absence and in the presence of Cr(III) will be also studied.

Experimental

An activated carbon suplied by Merck (sample M) was used in this study. This carbon was characterized by N_2 and CO_2 adsorption at 77 and 273 K respectively, mercury porosimetry up to 4200 $Kg.cm^{-2}$, mercury and water densities, pH measurements and ash content and elemental analysis determination. Details about the experimental procedure followed in all these experiments are given elsewhere [1].

The adsorption of the different humic substances: gallic acid (GA), tannic acid (TA) and humic acid (HA) on the activated carbons were carried out at 298 K. The samples obtained after saturating the activated carbon M with GA, TA and HA will be denominated in the text as to M-GA, M-TA and M-HA, respectively. The adsorption isotherms of the above acids were also obtained in the presence of Cr(III) ions from $Cr(NO_3)_3.9H_2O$. The concentration of Cr ions in the solutions was 40 $mg.L^{-1}$; which was adequate to saturate the adsorption capacity of the activated carbon, according to the results reported in a previous paper [1].

In order to study the textural changes produced by the adsorption of the different acids when they are adsorbed on the activated carbon surface, the N_2 adsorption isotherms at 77 K were obtained on the saturated carbon (samples M-GA, M-TA, M-HA).

The effect of GA, TA and HA on the Cr(III) uptake by the activated carbon was tested as follows: solutions containing different concentrations of these acids, between 5 and 100 $mg.L^{-1}$, activated carbon (0.1 g) and Cr(III) ions (concentration = 40 $mg.L^{-1}$) were prepared and kept in a thermostat shaker bath at 298 K for seven days and then the Cr(III) concentration was measured and the amounts of Cr adsorbed by the carbon calculated and plotted as a function of the acid concentration. Electrophoretic measurements of the above systems both in the presence and absence of Cr(III) were carried out with a Zeta-Sizer IIc (from Malvern Instruments).

Results and Discussion

Adsorption isotherms of GA, TA and HA were very well fitted by the Langmuir equation. From it the adsorption capacity, Xm, the constant, B, and the relative affinity of the adsorption process, XmB, were obtained. All these data are listed in Table 1. The adsorption capacity of this carbon increases in the orden HA < TA << GA, reaching a value of 342.8 $mg.g^{-1}$ for GA. This variation in Xm is mainly due to the molecular size of these acids. Therefore, since adsorption on a porous substance such as activated carbon may take place in pores of a diameter similar to that of the adsorbing species, the micropores of the activated carbon (less than 2nm in diameter) should be mostly inaccessible to HA; hence, only that suface area corresponding to mesopores (diameter 2-50 nm) and macropores (>50 nm) is effective to remove HA from aqueous solutions. According with data in Table 2, this fraction of surface area is very small comparing with the total surface area (including that corresponding to

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micropores) which is practically accessible to the GA molecules.

Table 1. Results obtained from the Langmuir equation applied to the adsorption isotherms of GA, TA and HA on activated carbon M, both in the absence and the presence of Cr(III) ions.

Adsorbate	Xm mg.g^{-1}	B L.mg^{-1}	BXm L.g^{-1}
GA	342.8	0.125	42.85
TA	21.0	0.056	1.18
HA	6.9	0.012	0.08
GA+Cr(III)	366.3	0.327	120.10
TA+Cr(III)	22.2	0.036	0.80

Other factor favoring the adsorption process of GA againts TA and HA is the higher degree of ionization per weight unit of the former. Thus, at the pH values used to carry out the isotherms (lower than 7) the surface charge of the carbon was positive and, therefore, the adsorption process should be favored with the ionization degree of the adsorbates. The greater B value found for GA compared with those for TA and HA (Table 1) indicates stronger interactions between GA and the carbon surface than for the other two acids. These stronger interactions in the case of GA should be due to both its adsorption in the micropores and its higher degree of ionization.

Table 2. Characteristcs of the activated carbon samples obtained from the N$_2$ isotherms.

Sample	SN$_2$(m^2.g^{-1})	W$_o$(cm^3.g^{-1})	S$_{mesop}$.(m^2.g^{-1})
M	1086	0.491	50.6
M-GA	643	0.297	20.6
M-TA	1110	0.495	49.1
M-HA	1089	0.490	31.3

The adsorption isotherms of GA and TA in the presence of Cr(III) were also obtained. The capacity of this carbon to adsorb GA and TA in the presence of Cr(III) is slightly higher than in the absence of this metal. It is noteworthy the high increase in the B constant corresponding to the adsorption of GA in the presence of Cr(III) which indicates that, in this case, the adsorbent-adsorbate interactions are very strong. The relative affinity of this process is also very high (Table 1).

Data in Table 2 point out that the adsorbed GA caused pore blockage in a great extent which limits the accessibility of the N$_2$ molecules, in such a manner that the total surface area (SN$_2$), the micropore volume (W$_o$) and the mesopore surface area (S$_{mesop}$) were halved by the adsorption of GA. The greater extent in the pore

blockage when adsorbing GA should be due to the higher amounts of this acid adsorbed on the carbon due to its easier accessibility to the carbon porous structure because of its lower size.

With regard to the changes in the carbon surface charge caused by the adsorption of the three acids, the pH drift tests indicate that the negative surface charge of the carbon enhanced when adsorbing these acids, and this increase varied in the order M-HA< M-TA<< M-GA.

Figure 1 shows the variation in the relative amount of Cr(III) adsorbed as a function of the amount of GA, TA and HA added to the solution. X is the amount of chromium adsorbed per gram of carbon when each of the above acids is present in the solution at the indicated concentration, and Xm the adsorption capacity of the activated carbon for Cr(III) in the absence of these acids. There is a large decrease (more than 50%) in the X/Xm value when these acids are present at low concentrations, this decrease is enhanced following the orden HA < TA < GA, and should be due to the pore blockage effect of the adsorbed acid on the surface of the carbon mentioned above. Thus, the highest decrease corresponds to GA, which blocks the pore structure of the carbon in a larger extent.

In the three cases, when the acid concentration increases X/Xm also increases due to the interactions of the cations Cr(III) with the negatively charged unbound functional groups of the adsorbed acids.
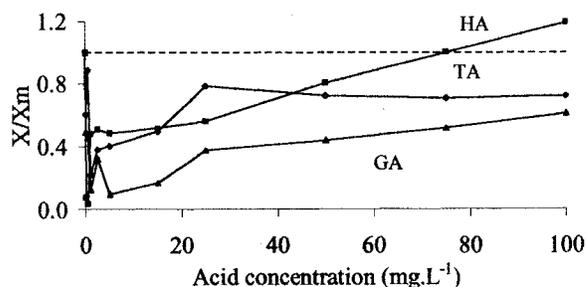

Figure 1. Relative Cr(III) uptake as a function of the GA, TA and HA concentration.

References

1. Bautista-Toledo, I., Rivera-Utrilla, J., Ferro-García, M.A. and Moreno-Castilla, C., Carbon 1994, 1, 93.