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Effect of the surface chemical groups of activated carbons on their surface adsorptivity to aromatic adsorbates based on π-π interactions

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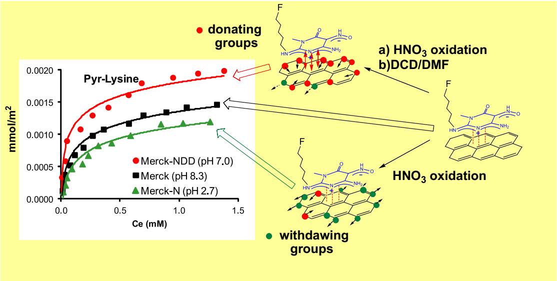
HIGHLIGHTS

- A graphitic AC was provided with π-donor or π-withdrawing surface chemical functions.
- The nature of the surface functions influences the basicity of graphite sheets.
- Highly polar pyrimidine ligands are adsorbed on the AC through π-π interactions.
- Adsorption of pyrimidine ligands do not relate with the amount of surface functions.
- Adsorption of pyrimidine ligands is affected by the basicity of the graphite sheets.

GRAPHICAL ABSTRACT



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ABSTRACT

Three activated carbons with different surface chemical groups were used to analyse the influence of these groups on their adsorption capacities towards aromatic-type molecules whose adsorption is based on π-π interactions with surface arene centres. The three activated carbons studied were a low-functionalized carbon (Merck), an oxygen-rich carbon obtained by HNO_3 oxidation of Merck, and a nitrogen-rich carbon also prepared from Merck by mild HNO_3 oxidation followed by treatment with a dicyanodiamide/dimethyl formamide mixture at 300 °C. The nature of the surface chemical groups of the three activated carbons was investigated by both physical and chemical techniques (TPD, XPS, Boehm analysis and pH potentiometric titration). A systematic study of the adsorptions of a series of analogous aromatic adsorbates on the three activated carbons was carried out to study the adsorption mechanisms. In all cases the adsorption mechanism is based on π-π interactions between the aromatic moiety of the adsorbates and the arene centres of the graphite sheets. The differences in the normalized adsorption capacities of the adsorbents for a set of adsorbates indicate that the π-donor or π-withdrawing character of the functional groups have a clear influence on the basicity of the arene centres.

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1. Introduction

Besides the textural properties (porosity and surface area), the surface chemistry of the activated carbons (ACs), has a strong effect on their adsorption properties [1]. Thus, the surface functionalization of these materials becomes an important task to improve the advantages derived from their uses in different fields. Although there is an extensive literature describing methods for chemical surface functionalization of ACs, most of them are based on classical chemical reactions which are rather unspecific [2]. More specific methods, based on the covalent attachment to the carbons of functionalized molecules, *via* their reactions with the oxygen containing groups on the AC surface, have been successfully used to prepare hybrid catalysts. Nevertheless, these methods have limited efficiency on the functionalization control of the materials [3–8].

The development of new functionalization methodologies allowing an adequate control of both the type of functions and of their distribution on the AC surface, remains a subject of great interest. With this aim, we have reported the adsorption of a series of molecular receptors derived from the 2-amino-5-nitroso pyrimidine compound, **1**, (Fig. 1) [9–16], on a low-functionalized AC, (hereafter Merck). The receptors consist of a heteroaromatic (pyrimidine) residue, Ar, that contains a substituent at $C(2)_{ring}$ position consisting of a non-conjugated polymethylene residue, S, which has a function, **F**. It has been established that the adsorption of these Ar-S-F receptors on Merck, takes place by a plane to plane interaction between the pyrimidine plane of the receptors and the arene centres of the AC [9–11]. The high strength of this interaction is evidenced by the highly irreversible adsorption character of the receptors and by the XPS data of the Merck-receptor hybrid materials. Recent studies and some calculations based on molecular models of both the Merck AC and the receptors indicate that not only dispersive forces between the π rings contribute to the adsorbate-adsorbent interactions but also some π-orbital interactions [17]. The last interactions are likely favoured by the strong polarization of the heteroaromatic moieties of the receptors whose positive charge is almost delocalized on the pyrimidine ring [18–20]. Thus, as a consequence of this type of interaction the anchorage of the receptors onto the carbon surface results in the blockage of all the functional groups of the Ar moiety, while the F functions remain fully operatives. Besides, the original features of the graphite moieties of the adsorbents are preserved, thus rendering a quite homogeneously F-functionalized hybrid material, whose surface properties are controlled by those of the F function. Merck/Ar-S-F stable hybrid materials obtained by this procedure, have shown increased adsorption capacities to different metal ions and anions compared to the original Merck. Furthermore, it has been shown that those adsorption capacities are related to the complexation properties of the F functions.

The design and preparation of efficient AC/Ar-S-F hybrid materials, involve the proper selection of the receptors and the knowledge of the factors determining the stability and properties of such hybrid materials. It is assumed that one of these factors is the surface chemical groups of the AC as they can influence the adsorption processes of the receptors [21–23]. So, it is expected that the π-electron donor groups in the borders of the graphite sheets increase the π electron-density of the layer favouring both orbital and dispersive interactions with the electron-deficient pyrimidine moiety of the receptors. This might results in an increase of the amount of receptor adsorbed by the AC. Conversely, the prevalence of surface groups with π-electron acceptor character will decrease the π electron-density, which will result in a decrease of the adsorption capacity of the AC to the receptors.

With the aim of checking this hypothesis, two activated carbons with different π electron-densities have been prepared from a low functionalized activated carbon(Merck): a first one (Merck-N) with π-electron withdrawing chemical functions, and a second (Merck-NDD) with a majority of π-electron donor groups. The work has been focused in three aspects: i) analysis of the textural and chemical characteristics of the ACs ii) checking if the receptor adsorption on the new functionalized ACs occurred through a similar mechanism to that observed on non-functionalized AC (Merck) and iii) analysis of the influence of the π electron-density of the graphite planes on the amounts of the receptors adsorbed by the ACs.

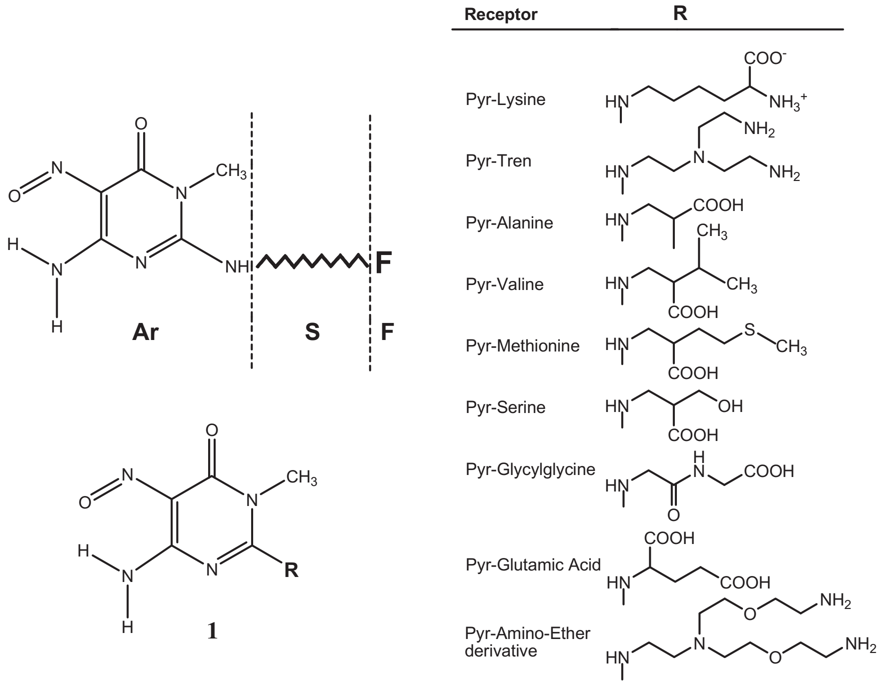

Fig. 1. Structures of the receptors (see text).