

Carbon Materials Research in Évora

La Investigación en Materiales de Carbono en Évora

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Abstract

An overview is presented of the work involving carbon materials which has been carried out in Évora by the Surface and Materials Chemistry Group. Current active interests related to the synthesis or preparation and surface modification of carbon materials, studies of gas phase and liquid phase applications and fundamental studies of adsorption, are highlighted.

Resumen

Este trabajo presenta una visión general del trabajo que se ha llevado a cabo en Évora por el Grupo de Química de Superficies y Materiales con materiales de carbono. Entre los intereses actuales del Grupo son de destacar la síntesis o preparación de nuevos materiales, la modificación de la química superficial de los materiales de carbono, el estudio de sus aplicaciones en las fases gaseosa y líquida, y los estudios fundamentales de adsorción.

1. Introduction

Research in adsorption and materials chemistry began in Évora in 1991 with a study financed by the Portuguese National Environmental Agency on the use of activated carbons for the removal of pollutants from water. Subsequently, what is now the Surface and Materials Chemistry Group of the Évora Chemistry Centre, concentrated most of its research activity in three major areas. On the one hand, the synthesis or preparation and surface modification of carbon and silica based porous materials. Although the latter will not be discussed here it is of interest to point out that the group have always maintained a strong and active interest in the synthesis and applications of pure and surface modified mesostructured mesoporous silicas. The second major area is gas phase and liquid phase applications of the materials developed, with emphasis on environmental control, gas separations and certain health related issues, as well as some catalytic studies. The third major area is related to fundamental studies of adsorption. Silica based materials, because of their more uniform and ordered mesoporous structure, have proven to be particularly useful for this type of study. However, some interesting results have also been obtained using carbon materials.

Besides the three major areas, the Surface and Materials Chemistry Group, usually in collaboration with other research groups, has also studied other materials, including zeolites, clays, polymer aerogels and molecularly imprinted polymers, as well as non-porous materials, including carbon blacks and non-porous polymers. With regard to the latter, it is of interest to mention that the group is currently participating in an EC Workgroup developing European Standards for the characterization of End-of-Life Tyres. Taking this together with the work on porous materials, this means that the group now has first-hand practical experience of measuring surface

areas over 3 orders of magnitude from $< 1 \text{ m}^2 \text{ g}^{-1}$ to $> 1000 \text{ m}^2 \text{ g}^{-1}$, as well as porosity over 4 orders of magnitude from $< 1 \text{ nm}$ (by adsorption of N_2 at 77 K) up to $53 \text{ }\mu\text{m}$ (by mercury porosimetry).

Over the years, the Surface and Materials Chemistry Group has collaborated with a large number of other research groups around the world. It is especially relevant to highlight here the long standing "carbon contacts" with two Spanish institutions, namely, the Universidad de Extremadura, which is actually the closest other university to the University of Évora, and the Instituto Nacional del Carbón (INCAR) in Oviedo. As well as various publications, joint patents between these institutions and the University of Évora have been obtained.

In the following sections, we will present an overview of some of the work involving carbon materials which the Surface and Materials Chemistry Group has carried out with current active interests highlighted. Only a few references, which can be considered a representative selection of the group's carbon work, are given [1-31].

2. Synthesis, preparation and surface modification of carbon materials

2.1. Bioresources

A recurring theme in the Surface and Materials Chemistry Group's work has been the valorization of residues arising from agricultural or industrial activities. Évora is situated in the Alentejo, which is the world's largest cork producing region, and it was natural therefore that we should be the first to study the transformation of cork into activated carbon [1, 2]. The Alentejo is also the home of Delta Cafés, which is one of the largest coffee roasting companies in Europe, and hence coffee manufacturing residues have also been used as activated carbon precursors [3, 4]. A significant research effort, with EC and national funding, was also put into the production of activated carbons from different types of lignin [5, 6]. Other bioresources which the group have investigated include almond shell [7], vine shoots [8], esparto grass [9], sunflower stems and olive stones. Work which is currently in progress is using chitosan, sacarose, fructose and different types of wood from the Benguela region of Angola and from the Dili region of Timor-Leste.

Both physical and chemical activation have been used. One of the novel features of the work, originally carried out with cork, was the use of "dry" chemical activation, which was found to have some advantages over the more usual "wet" chemical activation [2]. Similarly, hydrothermal carbonization is presently being developed as an interesting higher yield, and hence precursor and energy efficient, alternative to the traditional thermal carbonization [10, 11]. In conjunction with subsequent chemical activation, very high surface area ($\sim 2000 \text{ m}^2 \text{ g}^{-1}$) materials with

controllable porosity are being obtained.

2.2. Polymer precursors

Members of the Surface and Materials Chemistry Group were working with activated carbon fibres, more specifically viscose rayon based activated carbon cloths, before moving to Évora and this interest in microporous carbon fibres was continued using acrylic textile fibres and cloths as precursors [12-15]. Some work has also been carried out using cloths made from lyocell rayon. A particularly interesting feature of this work, carried out in collaboration with INCAR, was that it was found that microwave heating could be used as a rapid and clean method to modify the activated carbon fibres and to introduce molecular sieve properties [14, 15].

The principal centre for recycling of PET in Portugal is located in the Alentejo, which led us to study the use of recycled PET for producing activated carbons [16] and this line of work is still being actively developed. Following the same theme of valorization of residues, ongoing work, under a R&D Project supported by the FCT, is related to the conversion of MDF and PB composites, which are becoming available in increasingly large amounts, and lend themselves naturally to the formation of monolithic adsorbents. Low density carbon aerogels are another ongoing interest of the group and these have been prepared from both the usual resorcinol-formaldehyde (RF) polymer aerogels [17, 18] as well as from 2,4-dihydroxybenzoic acid-formaldehyde (DHBAF) polymer aerogels [19, 20]. One of the reasons for studying DHBAF aerogels is that the carboxyl hydrogens can be exchanged with metal ions which, after carbonization of the polymer, are converted into metallic nanoparticles, uniformly deposited on a mesoporous carbon support.

3. Gas phase and liquid phase applications of carbon materials

3.1. Gas phase applications

Gas phase applications, excluding fundamental adsorption and characterization studies, referred to below, have been directed towards the separation of gases, namely, N_2 , O_2 , CH_4 and CO_2 [14-16], CO_2 capture [20], VOC reduction and some catalytic processes. In the first case, various methods, including CVD, γ -irradiation and microwave treatment, have been used to induce molecular sieve properties in activated carbons prepared from different precursors and, under certain conditions, it has been possible to achieve selectivities for O_2/N_2 separation, for example, superior to those given by the widely used commercial Takeda carbon molecular sieves.

Studies of CO_2 capture have been based on surface modification of carbon aerogels by deposition of amines. Other alternative methods of modification, as well as non-carbon adsorbents, are currently being investigated. A novel aspect of this work, for the group, is the development of thermogravimetric analysis as a convenient and versatile technique for studying the equilibrium and kinetics of gas phase adsorption.

A long standing and ongoing characteristic of the Surface and Materials Chemistry Group is related to studies of the adsorption of hydrocarbons and alcohols and water vapour. It might be mentioned

that many visiting PhD students have come to Évora specifically to carry out equilibrium and kinetic studies of adsorption with our equipment, as gravimetric adsorption equipment is not available in all laboratories. The adsorption of organic vapours is of some relevance in the context of VOC pollution, although the main focus of our own work is generally directed more towards characterization and fundamental studies of adsorption and is referred to below.

3.2. Liquid phase applications

The early studies carried out by the Surface and Materials Chemistry Group were related to the adsorption of metal ions [21, 22]. Subsequently, attention was switched to the adsorption of phenolic compounds [23-27] and then to pharmaceuticals and pesticides [28]. Environmental Persistent Pharmaceutical Pollutants (EPPPs) have been classified as "priority substances" by the EU, while both pharmaceuticals and pesticides are classified as Persistent Organic Pollutants (POPs). Hence, they are highly relevant to us as, on the one hand, agriculture and forestry based industries are amongst the principal economic motors of the Alentejo and, on the other, a number of Portugal's major water resources, including the Rivers Guadiana and Tagus (*Tejo*) and the Alqueva Reservoir, are, wholly or partially, in the Alentejo.

Studies of the adsorption of solutes from the liquid phase are generally carried out in batch mode. On the other hand, for our work currently in progress with MDF and PB based activated carbons, it was considered important to compliment these studies by developing procedures for carrying out adsorption studies in a flow system as well. Hence, kinetic and equilibrium adsorption studies of specific probe molecules, considered pollutants, such as phenolic compounds (including phenol) and dyes (including Neutral Red), by MDF and PB based activated carbons in both monolithic and powder form, has been studied in both batch and dynamic modes.

Studies related to health are one of the most recent areas of interest of the group, in particular the adsorption of metformin, a drug to treat diabetes, and fluoxetine, the active ingredient of many antidepressant drugs, in simulated gastric and intestinal fluids and very interesting results are being obtained. The group has produced carbon materials with the potential to treat intoxications, assuming the usual dose of activated carbon slurry to treat overdoses at hospital level and that the person had ingested a full box of pills. Recently, the adsorption of glucose using hybrid materials was also studied.

4. Fundamental studies of adsorption by carbon materials

4.1. Adsorption from the gas phase

One of the standard methods for analyzing vapour adsorption isotherms is the α_s method. In order to apply the method a standard or reference adsorption isotherm is needed and, with the exception of N_2 at 77K, these are rarely available. Part of our work is to evaluate the possibility of using adsorptives other than N_2 at 77 K and to publish standard data whenever possible. The adsorptives studied in most detail so far include benzene, methanol, ethanol and dichloromethane [29, 30].

Carbon aerogels are simultaneously micro and mesoporous and this leads to errors in the estimation of micropore volume when the α_s (underestimated) and DR (overestimated) methods are used. Initially, we resolved the problem by recurring to the nonane preadsorption method, which proved to be ideally suited for these materials [17, 18]. Subsequently, we were then able to validate the applicability of the QSDFT method, as opposed to the more common NLDFT method, for the characterization of the microporosity of carbon aerogels [19].

Ordered mesoporous materials are of great interest as model adsorbents. In this context, the Surface and Materials Chemistry Group have also carried out detailed studies of adsorption-desorption isotherms of aromatic and aliphatic hydrocarbons on various ordered mesoporous materials, including CMK-3 type mesoporous carbon [31]. This work is of particular interest, on the one hand, as it combines our experience with mesostructured silica and carbon adsorbents and, on the other, as it allowed us to evaluate the effect of adsorbent characteristics, such as surface chemistry, pore size and shape and pore opening size, on the adsorption behavior of different hydrocarbons of different size and polarity.

4.2. Adsorption from the liquid phase

Here, we will mention just two aspects of our work with carbon materials.

Adsorption from aqueous solutions is more complex than gas phase adsorption as i) there is competition between solute and solvent for adsorption space, ii) the solute will usually be present in different, frequently charged, forms, in proportions which vary according to the conditions and iii) the adsorbent surface may also have a charge which will also vary according to the conditions. In our work on the adsorption of metal species we developed a simple surface ionization / adsorption model and this was subsequently adapted for adsorption of organic solutes [21, 22, 26]. By a combination of solute adsorption at different concentrations and solution pH values, acid/base titrations, mass titrations and simulation of the model, it was possible to make estimates of surface ionization constants and, in the case of the metal species, adsorption equilibrium constants.

A more commonly used empirical equation for adsorption of organic solutes, which is also an integral feature of ASTM standard D3860 for the determination of the adsorptive capacity of activated carbon, is the Freundlich Equation. We presented an analysis of a solute solubility normalized form of the equation and its application to adsorption isotherms of various phenolic solutes indicated that two regimes of adsorption, characterized by an adsorption energy, E_{ads} , greater than or less than a critical value, E_{ca} , could be distinguished. When $E_{ads} > E_{ca}$, the shape of the adsorption isotherm is determined by solute-solid interactions. On the other hand, when $E_{ads} < E_{ca}$, solute-solution interactions become more important [25].

5. Acknowledgements

The work carried out by the Surface and Materials Chemistry Group has been supported by the Portuguese Science & Technology Foundation

(FCT) and National Environmental Agency (DGA), the Alentejo Regional Development Coordination Commission (CCDRA), the Council of Rectors of the Portuguese Universities (CRUP), The British Council and the European Commission, under various programmes with national and FEDER funding. We are also grateful to all the visiting scientists from various parts of the world who have made invaluable contributions to the progress achieved.

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