

# New Strategies for the Selective Functionalization of Carbon Materials

## Nuevas Estrategias para la Funcionalización Selectiva de Materiales Carbonosos

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### Abstract

Selectively surface-modified solids can play a crucial role in the development of new materials devised to give effective answers to the new technology demands of the more sustainable 21<sup>st</sup>-century industry. This has brought about a concentration of research efforts on the elaboration of specific chemical functionality on solid surfaces. Nevertheless, the introduction of specific surface functionalization on carbon materials has not yet realized the degree of sophistication and control that other solid materials have reached. This article reviews the latest research developed under the CARB-NANOMETAL project (at the Universities of Granada and Jaén) towards the designing of new strategies for the selective functionalization of carbon materials.

### Resumen

Los materiales sólidos funcionalizados superficialmente de forma selectiva pueden jugar un papel fundamental en el desarrollo de nuevos materiales que den respuestas a las nuevas demandas tecnológicas de las, cada vez más sostenibles, industrias del siglo XXI. No obstante, la funcionalización selectiva de materiales carbonosos no ha alcanzado todavía el nivel de sofisticación y control que sí se ha conseguido en otros materiales. Este artículo hace una revisión de las últimas investigaciones llevadas a cabo en las Universidades de Granada y Jaén, en el marco del proyecto CARB-NANOMETAL.

### 1. Introduction

The functionalization of carbon materials has become a key issue for materials science researchers in the latest years. It is well known that the behaviour of carbon materials can vary from side to side depending on their surface chemistry. Therefore to control the introduction of functionalities onto carbon surfaces, in a selective and homogeneous way, can be the doorway to find new applications for carbon materials and to tackle some of the targets set by industry.

This is even more relevant for carbon nanotubes, where the surface chemistry can condition the solubility in different media, the electronic behaviour and the mechanical properties, and where the external surface area/bulk ratio is higher than in other carbon materials. For example, the capability of the tubes to be dispersed in aqueous media is crucial for their use in bio-applications like drug delivery or biomaterials. Another large field of potential application for selective-functionalized carbon materials is their use as chemical sensors and complexants for selective ion recovery.

Last years, at the Department of Inorganic Chemistry of the University of Granada and at the Department of Inorganic and Organic Chemistry of the University of Jaén, we have been developing new strategies to selectively functionalize different type of carbon materials (active carbons, carbon nanotubes and carbon blacks) by selectively fixing organic functions to their surface. The aim is preparing hybrid materials that can act as good and selective metal ion scavengers in aqueous solutions, susceptible of being subsequently reduced to obtain metal nanoparticles. The selective metal ion retention is achieved by introducing selective metal ligands centres in the anchored organic functions.

Two different approaches to produce a selective and homogeneous functionalization have been explored. The first one is based on creating a  $\pi$ - $\pi$  interaction between the arene centres existing on the graphite microcrystals of the carbon material and a conveniently functionalized pyrimidine ring bonded to the metal receptor part of the organic function (Figure 1). The second one is based on establishing covalent bonds between a dendritic organic molecule, with metal complexing units, and the carbon surface. This is achieved through previously introduced reactive heteroatoms or functions at the surface, i.e., using reactive functionalities as primary groups to subsequent anchoring of complex organic functions as secondary functionalization (Figure 2). In this communication, we review our latest results on both

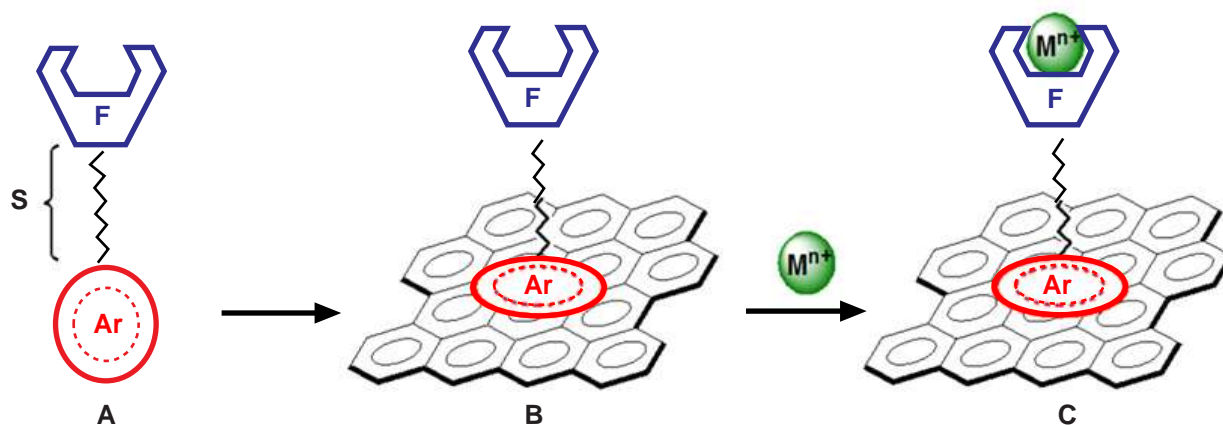
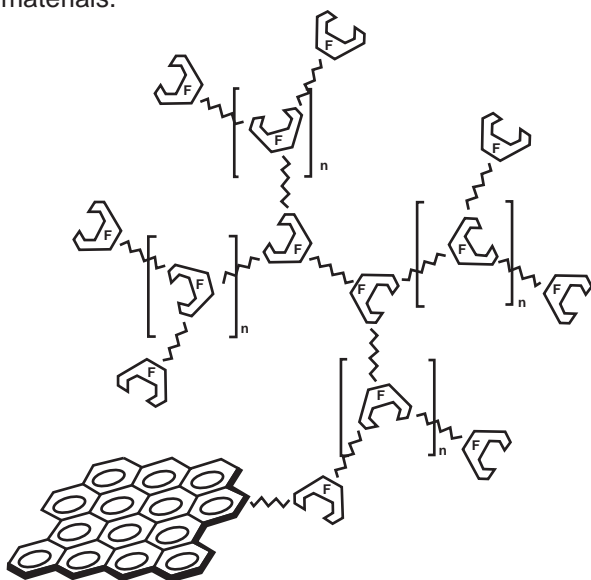


Figure 1. Functionalization using a selective molecular receptor.

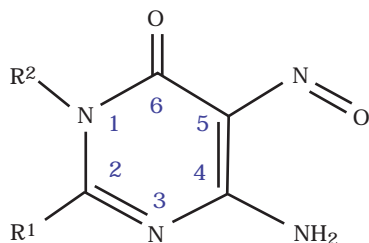
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methodologies, which can be easily extrapolated to other organic functions and other type of carbon materials.



**Figure 2.** Functionalization using a polyfunctional molecular receptor.

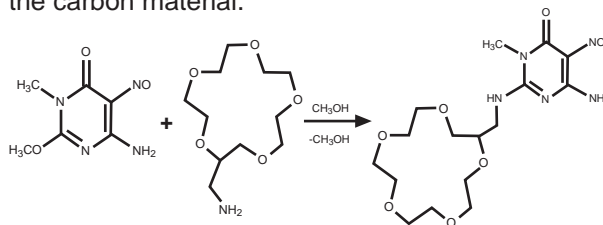
## 2. Functionalization with molecular receptors by $\pi$ - $\pi$ stacking interaction



**Figure 3.** Structure of the pyrimidine moiety.

As mentioned in the introduction section this approach, originally developed at the Department of Inorganic and Organic Chemistry of the University of Jaén, is based on the anchorage of organic molecules to the graphite sheets of the carbon surface. These organic molecules (from now on, receptors) are based on a pyrimidine moiety that has in C2 a polymethylene chain with different functions (F), which can behave as selective metal ligands (Figure 3). The anchorage takes place by, among others,  $\pi$ - $\pi$  interaction (stacking) between the pyrimidine moiety of the chemical receptor and the arene centres of the graphite planes. Thus, it

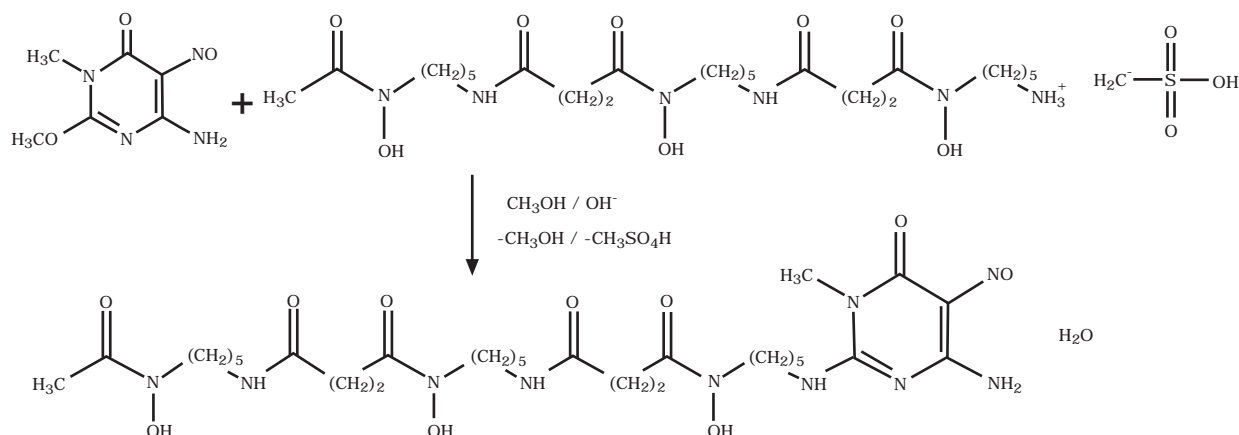
was proposed that not only dispersive forces, but also electrostatic and these  $\pi$  interactions contribute to the adsorbate-adsorbent interaction.[1,2]. The electrostatic contribution is the result of negative charge of the quadrupole moment of the arene centres and the positive charge of the aromatic moiety of the receptors, while the  $\pi$ - $\pi$  stacking is an electronic donor-acceptor interaction. This interaction has been corroborated by XPS analysis of the molecular receptors before and after adsorption, showing a shift in the N 1s band towards lower binding energies. The result of these relatively strong interactions is that the adsorption of the receptors on the carbon surface is highly irreversible [3]. Therefore, this procedure allows obtaining very stable carbon/receptor hybrid materials. Moreover, these hybrid materials have two additional advantages: i) a rather specific and selective functionalization of the surface, provided by the F functions, and ii) a very homogeneous functionalization evenly dispersed through the whole surface. It is worth mentioning that this procedure does not require a primary introduction of chemical groups on the surface of the carbon material.



**Figure 4.** Preparation of the 15-crown-5 molecular receptor.

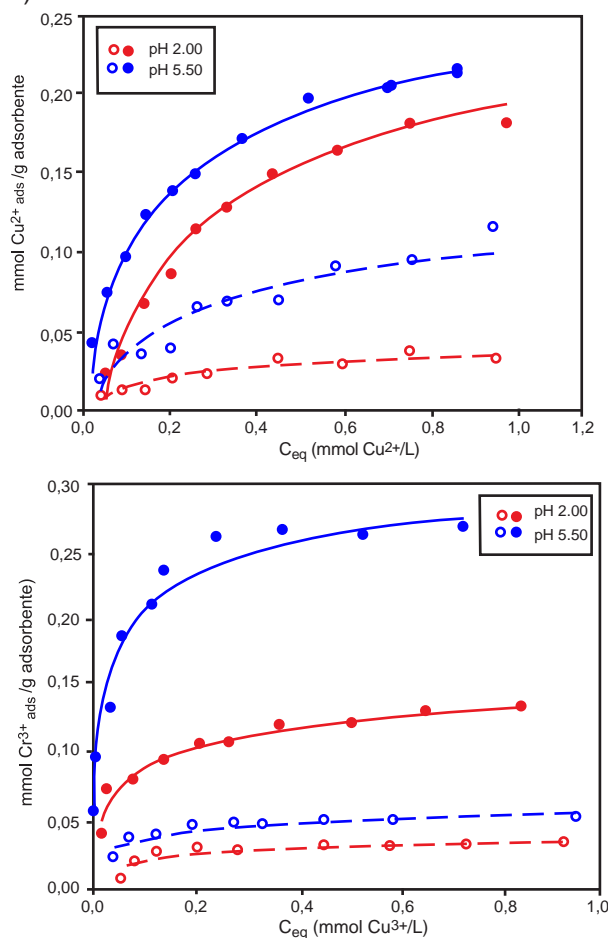
The C2 position of the pyrimidine moiety (Figure 3) presents a very remarked low electron density, which facilitates nucleophilic attacks by amines or other similar nucleophiles. Therefore, it is relatively easy to attach different organic functions with a hydrophilic character to the C2 position of the pyrimidine ring. This allows us to design and prepare selective molecular receptors for targeted metal ions depending on the complexing properties of the functional units (F) of the organic fragments [4]. An aliphatic chain (S) is used as a separator. The charge variation in F can give the receptor great versatility regarding the type of ion we want to adsorb.

In previous works, good adsorption capacity for metallic ions was achieved by using aminoacidic fragments as F, and supporting the organic function on the surface of a commercial activated carbon [4,5]. Those works clearly evidenced that the metal ion adsorption was taking place at the F function and that the capacity was substantially improved



**Figure 5.** Preparation of the desferrioxamine-b (DFB) molecular receptor.

with regard to the original active carbon. Following the same methodology [6,7], new more selective functional units have been designed recently in order to prepare hybrid materials with improved selectivity. For example, we obtained a receptor with a crown ether function in the C2 position (Figure 4) due to the selectivity that the crown ether macrocycle can offer depending on the size of the metal ion [8,9]. The crown ethers are also very flexible molecules, capable to adapt to different coordination environments and reaction media. Another receptor prepared is based on the desferrioxamine-B (DFB) (Figure 5), due to its high affinity for metal ions with acid Pearson character, like iron, aluminium or gallium [10,11]. Both receptors have been irreversibly anchored to the surface of two different activated carbons. The amount of receptor fixed can be tuned by varying the concentration of the receptor and the pH of the solution [4,12]. In all cases, the hybrid materials prepared resulted very stable and with a remarkable improved adsorption capacity for metal ions compared to the original carbon material (Figure 6).



**Figure 6.** a)  $\text{Cu}^{2+}$  adsorption isotherms on Merck-15-crown-5 hybrid material (solid symbols) and carbon Merck (empty symbols); b)  $\text{Cr}^{3+}$  adsorption isotherms on F-DFB hybrid material (solid symbols) and carbon F (empty symbols).

Nevertheless, the most remarkable result of such work is that the metal adsorption is directly related to the ion affinity of the free receptors in solution [4,12]. For a defined ligand and at a fixed pH, the adsorption capacity  $X_m$  increases linearly with the effective constant,  $K_{\text{eff}}$ , which is related to the thermodynamic nature of the metal-ion receptor interaction. Thus, a higher selectivity of the receptor for a certain metal ion (higher value of  $K_{\text{eff}}$ ) results in a larger maximum adsorption capacity for that ion

of a hybrid material with that supported receptor. This means that we are succeeding in transferring the complexing properties of the functional centres to the carbon surface. Such result can have important implications in the design of new selective hybrid materials, as it is feasible to predict the metal ion adsorption capacity based on the affinity constants of the receptors in solution.

Another relevant result of this work relates to the effect of the porosity. Although this factor is less important in carbon nanotubes and carbon blacks, it turns crucial when the support is an active carbon with a well-developed porous texture. The results found using activated carbons with different textural characteristics point out that the existence of a wide range of porous sizes, with wide mesopores and a significant amount of macropores, increases the efficiency of the functionalization, even for carbon materials with lower total pore volumes and lower surface areas. The functions fixed in the narrow microporosity block the access to inner pores, resulting in hybrid materials with lower amounts of supported molecular receptors. Moreover, the porous texture has also critical importance in the complexation capability of the organic functions. For example, results for  $\text{Cu}^{2+}$  adsorption allow us to conclude that a considerable amount of the molecular receptors adsorbed in narrow micropores are forced to adopt conformations that are not adequate for the coordination with the metal ions. In the case of the hybrid materials based on an activated carbon with mainly narrow micropores, this results in lower  $\text{Cu}^{2+}$  adsorption capacities than the parent AC material. Therefore, a well-developed network of pores, with large pores and good accessibility, is more important for the efficiency of the functionalization and the performance of the hybrid materials than higher specific surface areas and micropore volumes.

### 3. Functionalization with polyalkylamines by covalent bonding to the carbon surface

The second approach considers the preparation of new effective and stable metal-scavenging hybrid materials based on rigid, non-swelling and chemically inert carbon supports, which can range from active carbons to carbon nanotubes. In particular, we have focused in  $\text{Pd}^{2+}$  recovery. The scarcity of palladium in the earth crust and the location of its sources in a very few territories have made palladium recovery and recycling a highly strategic and economic issue tackled in the general policies of developed countries [13]. Palladium scavenging, apart from being a valuable strategy for recovery, has become an important subject since the transference of a large collection of advantageous palladium catalyzed synthetic procedures from laboratory to the large-scale industrial production depends on the availability of efficient palladium scavengers capable of removing metal traces from the final products. A significant instance of this situation is the fabrication of active pharmaceutical ingredients (API), for which the strict regulation relative to their content in transition metals hampers the use of more efficient metalcatalyzed synthetic procedures [14,15]. Then, large-scale application of transition metal-catalyzed synthetic processes in APIs production requires efficient methods to remove metal residues, especially palladium [16]. Different scavenging techniques have been applied to particular cases [17,18], but retention with solid sorbents constitutes the preferred approach to the problem [16,19]. Among them, chelant resins and surface modified silicas (some currently



commercialized for such purpose) seem to offer the best behaviour in terms of stability and loading capacity, while classical adsorbents as activated carbons have rendered much poorer results [20].

For this purpose, a flexible, water compatible, stable, organic complexant was covalently linked to the carbon surface. Hyperbranched polyethyleneimine (HBPEI) was chosen as the complexant component due to the excellent  $\text{Pd}^{2+}$  complexing properties. These properties were tested by characterising the system HBPEI/ $\text{Pd}^{2+}$  in aqueous solution by potentiometric titration methods. The results revealed the formation of very stable complex species between  $\text{Pd}^{2+}$  and HBPEI, where the effective complexing units were the ethyleneimine trimers,  $(-\text{CH}_2-\text{CH}_2-\text{N}-)_3$  (L in the following) into which the polymer can be divided [21]. The predominant species in the pH range from 1 to 9 were  $[\text{PdL}]^{2+}$  and  $[\text{Pd}_2\text{L}_2\text{H}]^{5+}$ , for which  $\log K_{st}$  values of 31.8 and 28.5, respectively, were measured. Even if this complexing behavior is referred to free HBPEI in aqueous solution, our previous experience on ion retention by carbon-supported complexing agents indicates that the complexation behavior after anchorage onto the solid support is closely parallel that observed for the same free complexing agents in solution [2,22], as already commented in the previous section.

The preparation of the new hybrid materials (Figure 7) consisted in a three-stepped procedure: i) oxidation, ii) esterification and iii) grafting of the polychelator HBPEI to the carbon material surface through a carboxamide bond with the ester intermediate. In the oxidation step, it is necessary to introduce a considerable amount of carboxylic functionalities on the surface to be subsequently transformed into methyl esters. For this purpose, we have used classical oxidation methods, like  $\text{HNO}_3$  oxidation, but also other oxidising techniques like ozonisation and oxygen plasma treatment. The three treatments succeeded in increasing the amount of carboxylic functions on the surface. Particularly, ozonisation treatments, both in solution and in gas phase, rendered good results with oxygen surface concentrations over 8%. It is worthy to note that the

procedures to prepare the new material follow a good observance of the green chemistry practices, since only preferred solvents [23], namely water and methanol, are employed, and a direct transformation of esters into amides is conducted.

Several factors influencing the efficiency of the grafting reaction were analyzed, including reaction solvent, temperature, HBPEI/carbon-material mass ratio, reaction time and HBPEI average molecular weight. When a commercial activated carbon F (Filtracarb-SKI 8X30) is used as support, a very efficient grafting of low molecular weight HBPEI ( $M_n = 600$ ) was achieved, so giving a hybrid material, F-HBPEI, with an 8.4% of nitrogen (measured after thoroughly washing with boiling methanol for 24 h in a Soxhlet extractor), i.e. it is constituted by a 26% (w/w) of HBPEI and a 74% of carbon structural support. Extraction for 24 h in a Soxhlet with boiling water only reduced its nitrogen content to 7.1% what gives an idea of the good stability of this material. The precursors, intermediates and polyamine-grafted materials were characterized by elemental analysis, XPS and solid state DP-MAS  $^{13}\text{C}$  NMR. The XPS data afforded, in the case of F-HBPEI hybrid sample, an amine/amide nitrogen atoms ratio of 83:17, i.e. almost half of the terminal amine groups of HBPEI (41% according to quantitative  $^{13}\text{C}$  NMR) formed carboxamide linkages with the carbon support. Thus, considering "typical" HBPEI molecules with  $MW = 600$ , so containing 14 N atoms in their structures, they should be linked to the surface through 2-3 amide bonds as average. This result is important as, increasing the anchorage points of the polyamine, we are increasing the stability of the organic functionalities on the carbon surface. Such stability is crucial when applying these functional materials in certain applications like selective metal-ion complexation.

The interest of this new materials derives from the variety of capabilities that its surface functionalization offers since (a) it changes the carbon surface into water-compatible, (b) provides the carbon surface with reactive primary and secondary amino groups for further elaboration of the surface functionality,

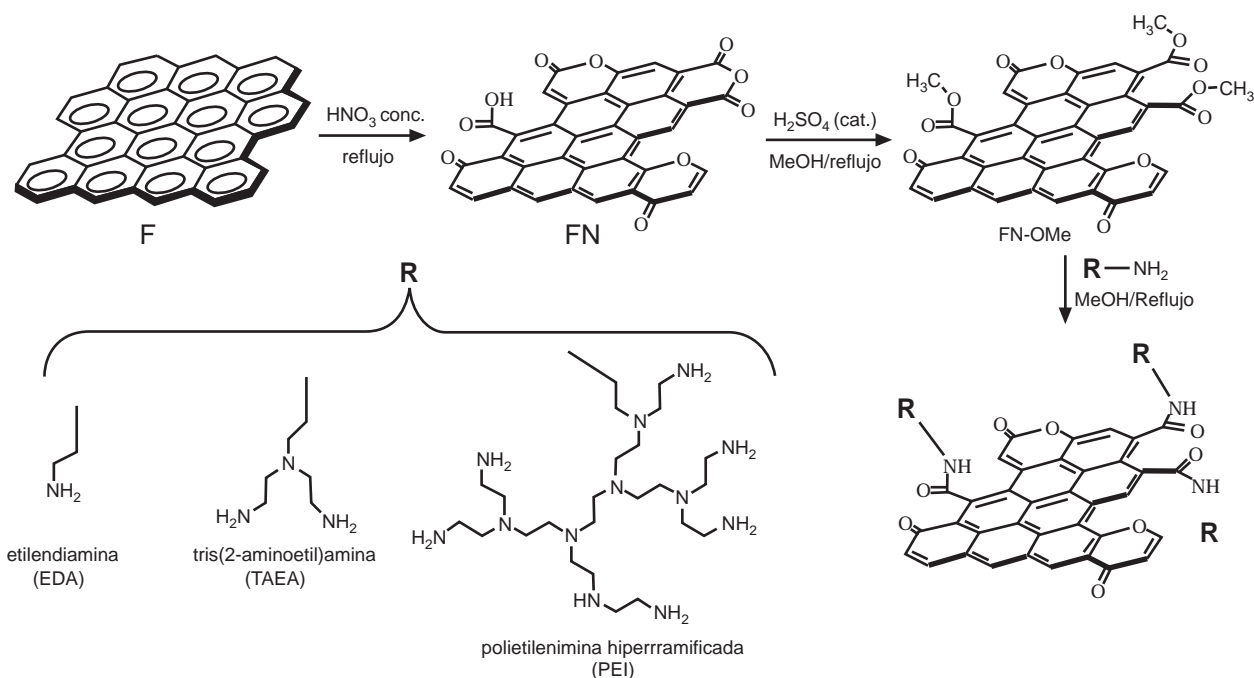


Figure 7. Scheme for the synthesis of carbon-polyamines hybrids.

(c) transforms the carbon into a strong heterogeneous base, (d) provides the carbon surface with an excellent metal-complexing layer because the alkylamino groups are all in relative 1,4 positions placed in a flexible network capable to form stable chelates with transition metal ions, and (e) its easy preparation and scale-up (batches of up to 12.0 g were prepared in our lab) makes it suitable for large-scale applications.

To test the adsorption capacity of the hybrid material based on an active carbon support (F-HBPEI), adsorption experiments of Pd<sup>2+</sup> solutions (298 K, [Cl<sub>4</sub>Pd]<sup>2-</sup> aqueous solutions at pH 5 and 0.1 M in KCl) were conducted. The isotherms fitted quite well (R<sup>2</sup>=0.97) to the Langmuir model with a maximum loading capacity of 1.72 mmol×g<sup>-1</sup>, which is superior to most of the commercial Pd<sup>2+</sup> sorbents and comparable with the highest levels retained by some thiol-based scavenging resins<sup>20</sup>. Leaching tests performed in water at pH 5 and pH 1 showed that the full loaded material (1.72 mmol×g<sup>-1</sup>) losses a minor fraction of metal (4.5% at pH 5 and 13.0% at pH 1), and that there is a loading threshold at 1.33 mmol×g<sup>-1</sup> under which no leaching was detected even after 7 days at pH 1 and an ion strength of 0.1 M in KCl. Thus, F-HBPEI is an exceptional scavenger that outperforms previously described materials used for Pd<sup>2+</sup> removal from aqueous solutions.

In summary, an exceptionally large proportion of a functionality that is very rich in aliphatic polyamines can be efficiently introduced onto carbon surfaces through reliable HBPEI grafting achieved through a straightforward, sustainable and easily scalable procedure. This surface functionality is quite stable and opens a wide variety of interesting applications to the so modified materials due to the versatility of the amine groups. One of such applications is the capture of transition metal ions, which is exemplified by the outstanding performance of F HBPEI as Pd<sup>2+</sup> scavenger from water solutions.

Different methodologies for the grafting of the polyalkylamines on the surface of different type of carbon materials are also under investigation at present. One possibility to avoid the esterification step and bond the polyamine function directly to the surface is the use of halogen atoms as primary functions. Halogens are well known good leaving groups, which can facilitate the formation of covalent C-N bonds between the nucleophilic attacking amino-group and the carbon surface. Studies using interhalogen compounds in different solvents as halogenating surface agents are being carried out with promising results that reach halogen atomic concentrations over 10% in the surface of carbon nanotubes. Similarly, plasma treatments with halogen derivatives are another way to halogenate carbon surfaces that we are currently exploring. Remarkable halogen surface concentrations have been achieved in the preliminary tests. Similarly, non-destructive reduction methods to transform the captured metal ions into supported nanoparticles are also under study. This would add interesting new possibilities for the already mentioned hybrid materials.

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