UiO-66 derived etched carbon/polymer membranes: High-performance supports for the extraction of organic pollutants from water

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HIGHLIGHTS

- MOF derived etched carbon/polymer membranes for the extraction of organic pollutants.
- Acidic etching treatment to enhance the adsorption capacity of the material.
- Fast adsorption kinetics and an outstanding maximum adsorption capacity.
- High performance for removal of different phenolic compounds.

GRAPHICAL ABSTRACT
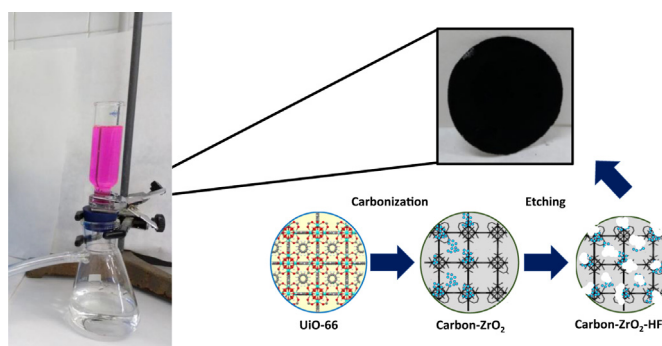
ABSTRACT

Herein we report the use of the zirconium metal–organic framework (UiO-66) as precursor to prepare porous carbons by a direct carbonization step (carbon-ZrO$_2$). By applying a post-carbonization acidic etching treatment with hydrofluoric acid (HF), the initial surface area of the carbon-ZrO$_2$ sample increased from $270\,m^2\,g^{-1}$ to $1550\,m^2\,g^{-1}$ (carbon-ZrO$_2$-HF). This increase is attributed to the partial removal of the ZrO$_2$ present in the UiO-66-derived carbon. Carbon-ZrO$_2$-HF exhibited fast adsorption kinetics and an outstanding maximum adsorption capacity of $510\,mg\,g^{-1}$ for the dye rhodamine B. For practical applications, the obtained porous carbon-ZrO$_2$-HF material was used to fabricate a carbon composite membrane using polyvinylidene fluoride. The prepared membranes were applied as water filtration supports for the extraction of toxic phenols from water, including an endocrine disrupting phenol with widespread exposure: bisphenol A. High efficiency for the simultaneous extraction of phenolic pollutants, and an excellent reusability with a variation of a 2% for 10 consecutive bisphenol A extraction cycles, were obtained. Due to their high and accessible porosity, small particles size, and facile processability into membranes, the UiO-66 derived etched carbons are promising materials for environmental applications, such as the extraction of organic toxic pollutants.

1. Introduction

Metal-organic frameworks (MOFs) have gained particular attention as a novel class of nanoporous materials due to their varied architectures, built from metal ion (or clusters) with bridging organic ligands, high surface areas, adjustable pore sizes from the microporous to the mesoporous scale, and tailored chemical functionalities [1,2]. Due to these properties, MOFs have been widely studied as materials for

catalysis [3], gas storage [4], sensing [5], drug delivery [6], and, more recently, for the adsorptive removal of different pollutants, such as heavy metals, dyes, or phenols [7,8]. In this field, one of the most important barriers in the applicability of MOFs as sorbents is their limited stability in aqueous or complex mediums. In this regard, MOFs have recently shown to be useful precursors for the synthesis of other materials, such as metal oxides, metal carbides, or porous carbons [9–11]. Specifically, MOFs-derived porous carbons have attracted much attention because the periodic porous and hybrid structure of MOFs provides unique features for the fabrication of porous carbons with uniform pores of different sizes and with novel structures and properties. In addition, considering the large carbon content of organic components in MOFs, highly porous carbons can be achieved by a very simple, one-step pathway, without the need of any additional carbon precursor, avoiding tedious, costly and environmentally harmful synthetic procedures [12,13]. Thermal carbonization of MOFs is carried out in an inert atmosphere in which the organic linkers and metal ions are transformed into carbonaceous structures and metal or metal oxide nanoparticles, respectively. The direct MOF carbonization process results, in this way, in the formation of metal- or metal oxide–carbon composite materials, where the precursor MOFs has a dual function acting as a sacrificial template and carbon precursor.

Thus far, several types of MOFs have been used as precursors to yield porous carbons for a wide range of applications, such as gas adsorption [14], catalysis [15], and electrochemical energy storage [10]. In addition to these applications, MOF-derived porous carbons, due to their remarkable high surface area, thermal and chemical stability, and their tendency to interact with aromatic compounds, have acquired great significance as sorbents for the removal of chemical pollutants. For instance, ZIF-67 is an excellent precursor to obtain nanoporous carbons because their direct carbonization yields a magnetic porous carbon, which has been applied to the extraction of methylene blue dye [16], phenylurea herbicides [17] and benzoylurea insecticides [18]. The potential of ZIF-8-derived nanoporous carbon as sorbent has also been studied and demonstrated for the extraction of herbicides by Sarker et al. [19]. Other examples of the application of MOFs-derived carbons as pollutant sorbents are the use of bimetallic ZIF-derived carbons, containing both Zn(II) and Co(II), for the extraction of chlorophenols in water samples [20] and the application of porous carbon derived from metal azolate framework-6 for removal of different pharmaceuticals and personal care products in water [21]. Very recently, the first examples of the use of a porous carbon prepared from Zr-based MOF as sorbent of organic pollutants have been reported [22,23]. Among the different types of Zr-based MOFs synthesized so far, UiO-66, which is a cubic rigid porous MOF based on a $Zr_6O_4(OH)_4$ clusters linked by 1,4-benzenedicarboxylate [24], has received much attention because of its thermal stability, tunable pore size, and high specific surface area [25–27], being a promising precursor for the synthesis of nanoporous carbons.

A critical step in the direct application of porous materials for pollutant extraction is the post-extraction retrieval of the sorbent from the sample medium, which requires laborious and, in most cases, incomplete filtration and centrifugation steps. An interesting alternative to solve this limitation is the integration of the porous materials into functional extraction devices, such as beads [28], fibers [23], monoliths [29], and membranes [30,31], facilitating their use as sorbents for the extraction of pollutants from water with environmental or monitoring purposes. Among them, the preparation of nanoporous membranes is a desirable approach for wastewater treatment due to their reusability and excellent flow-through properties achieving high extraction yields, and the easy automation of the process, increasing the extraction throughput and reproducibility. To achieve an efficient water purification, it is desirable to develop nanoporous membranes with high adsorption capacity, fast kinetics, high water flux, mechanically and chemically stable and easily regenerable [31,32].

Bearing these in mind, we report the first example of the application

of MOF-derived porous carbon/polymer membranes as sorbents for the extraction of environmental organic pollutants from water. As a proof of concept, UiO-66 was used as a precursor and a template for the easy preparation of porous carbon/ZrO$_2$ composite material (carbon-ZrO$_2$) by one-step direct carbonization process. A post-carbonization acidic etching treatment was carried out to increase the porosity of the material. The resulting porous carbon (carbon-ZrO$_2$-HF) was then immobilized in a Nylon filter using polyvinylidene fluoride as binder, obtaining a highly robust and mechanically stable and efficient flow-through support for pollutant extraction. Rhodamine B, one of the most commonly used xanthene dyes and dye pollutants from the textile and paper industry, was selected as model adsorption analyte to evaluate the performance of the prepared MOF-derived carbon/polymer membranes. Additionally, we used these composite membranes for the flow-through extraction of four substituted phenols (1-naphthol (NPh), 2,4-dimethylphenol (2,4-DMP), 2,4-dichlorophenol (2,4-DCP) and bisphenol A (BPA)), with representative structures of the vast family of phenols catalogued as environmental pollutants due to their widespread use as pharmaceuticals, personal care products, or as by-products from massively used plastics [33].

2. Experimental

2.1. Chemicals

Methanol ($\geq 99.8\%$), ethanol (96%), N,N-dimethylformamide (DMF, 99.5%), terephthalic acid (99%), hydrofluoric acid (HF, 40%), acetone ($\geq 99.8\%$), 1-naphthol (NPh, 99%), and charcoal activated powder (reagent grade ref, Ca0352, $930\,m^2\,g^{-1}$), were obtained from Scharlau. Zirconium (IV) chloride (ZrCl$_4$, 98%), and rhodamine B ($\geq 98\%$) were acquired from ACROS. Polyvinylidene difluoride (PVDF, MW $\sim$ 180,000), 2,4-dimethylphenol (2,4-DMP, 98%), 2,4-dichlorophenol (2,4-DCP, 98%), and bisphenol A (BPA, 97%) were obtained from Sigma & Aldrich. As starting support, GVS Maine Magna 0.45 μm Nylon membrane filters (25 mm diameter and 80 μm thickness) were used.

A stock standard solution of each selected phenol ($2000\,mg\,L^{-1}$) was prepared in methanol. A working solution with a concentration of $10\,mg\,L^{-1}$ of each phenol was prepared daily by diluting the stock standard solution in water. A mixture of phenols ($10\,mg\,L^{-1}$, each) was prepared in water. All solutions were prepared using Milli-Q water (Direct-8 purification system, resistivity > 18 MΩ cm, Millipore Iberica, Spain).

2.2. Characterization

Powder X-ray diffraction (XRD) data were collected using CuKα (λ = 1.5418 Å) radiation on a Bruker D8 Advance diffractometer. The morphology and elemental distribution of the prepared materials were analyzed by using a scanning electron microscope (Hitachi S-3400N), equipped with a Bruker AXS Xflash 4010 EDS system to enable multielemental mapping, and transmission electron microscope (Hitachi ABS) operated at 100 kV. Nitrogen adsorption–desorption isotherms were measured at 77 K using a TriStar II (Micromeritics) gas adsorption analyzer. The samples were previously outgassed at 393 K overnight. Data were analyzed by using the Brunauer-Emmett-Teller model (BET) to determine the specific surface area. The pore volume and pore size distribution were calculated using the two dimensional non local density functional theory model (2D-NLDFT). Thermogravimetric analysis (TGA) was carried out in an air atmosphere using a TA Instrument SDT 2960 simultaneous DSC-TGA.

2.3. Preparation of carbon-ZrO$_2$ sample

Zirconium-based metal–organic framework (UiO-66) was prepared by solvothermal reaction according to a procedure reported in the