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Magnetic solid-phase extraction using metal-organic frameworks (MOFs) and their derived carbons

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ABSTRACT

Magnetic solid-phase extraction (MSPE) is a useful sample preparation technique, enabling the dispersion of solid sorbents in liquid sample matrices followed by the magnetic retrieval of the sorbent. MSPE can be implemented using any kind of magnetic materials independently of their size and shape, and is a powerful tool for the application of micro/nanomaterials for analytical sample preparation. Metal-organic frameworks (MOFs) have emerged recently as highly valuable sorbents for solid-phase extraction (SPE) due to their large surface area, chemical selectivity, and versatility for tuning their chemical composition and pore size. For MSPE applications, MOFs can be magnetized, or used as precursors for the preparation of MOF-derived magnetic porous carbons (MPCs).

In this review, we outline and discuss the different approaches for the preparation of magnetic MOFs and their conversion to MPCs. The applications of magnetic MOFs and MPCs as sorbents for MSPE are critically discussed and oriented to the type of MOF used and the extracted analytes. Recent efforts on the automation of MSPE procedures using magnetic MOFs and MPCs are also described.

1. Introduction

In the analysis of complex samples (biological, food, environmental, …), sample preparation plays a crucial role in the overall analytical process. An appropriate sample pretreatment ensures an adequate sensitivity by enriching the analytes to detectable limits, and simultaneously increases the selectivity of the method by removing potential interferences present in the matrix of the sample. Among the different extraction techniques, solid-phase extraction (SPE) has gained widespread recognition [1,2], due to its simplicity, high analyte preconcentration factors, the reusability of SPE sorbents, and the use of small volumes of organic solvents. In addition, SPE can be automated, increasing the extraction throughput and reproducibility, and enabling the miniaturization of the overall analytical methodology [3,4]. The typical SPE format relies in the preparation of bead packings of the desired sorbents. However, the applicability of sorbents with small particle size and non-spherical shape in packed format contributes to high back pressures, hindering the SPE process. Magnetic solid-phase extraction (MSPE) is an interesting alternative to typical SPE [5–7]. MSPE is based on the use of a magnetic sorbent, enabling the dispersion of the sorbent in a large sample volume, followed by the efficient sorbent retrieval facilitated by an external magnetic field. Using MSPE, problems related with sorbent packing, high back pressures, or packed bed clogging are non-existent. A number of magnetic sorbents for MSPE have been already reported in the scientific literature, including the direct use of magnetic nanoparticles (NPs) after surface functionalization [5,8], or the use of

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Abbreviations: ACN, acetonitrile; CVAAS, cold vapor atomic absorption spectrometry; EDTA, ethylenediaminetetraacetic acid; ETAAS, electrothermal atomic absorption spectrometry; FA, formic acid; FAAS, flame atomic absorption spectroscopy; FPD, flame photometric detection; GAs, gibberellin acids; GC, gas chromatography; HG-AFS, hydride generation atomic fluorescence spectrometry; HKUST, Hong Kong University of Science and Technology; HPLC, high performance liquid chromatography; IRMOF, isoreticular metal-organic framework; LbL, layer-by-layer; MAA, mercaptoacetic acid; MIL, Materials Institut Lavoisier; MOF, metal-organic frameworks; MPC, magnetic porous carbons; MS, mass spectrometry; MSPE, magnetic solid-phase extraction; NPs, nanoparticles; PAHs, polycyclic aromatic hydrocarbons; PCBs, polychlorinated biphenyls; PNIPAM, Poly(N-isopropylacrylamide); RP, reversed phase; SAED, selected area electron diffraction; SEM, scanning electron microscopy; SPE, solid-phase extraction; TEM, transmission electron microscopy; UHPLC, ultra-high performance liquid chromatography; UiO, Universitetet i Oslo; XRD, X-ray diffraction; ZIF, zeolitic imidazolate framework.

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composite/hybrid materials containing magnetic NPs combined with molecularly imprinted polymers [9], carbon nanotubes [10], or graphene [11], to name a few examples.

Among the different materials used as SPE sorbents, the use of metal-organic frameworks (MOFs) [12–14] for analytical extractions is gaining interest [15–18]. MOFs are based on the coordination of metal ions or clusters with bi- or multidentate organic linkers, shaping extended porous crystalline structures. The variety of metals and organic linkers suitable to build MOFs, and the different strategies for their magnetization, open almost endless possibilities for their use as MSPE sorbents [19]. A number of different MOF magnetization procedures and applications for MSPE have been developed within the last 5 years. Furthermore, MOFs have been used as precursors to obtain other unprecedented materials, such as MOF-derived magnetic porous carbons (MPCs) [20,21]. After carbonization of some MOFs, the metallic component of the MOF aggregates shaping magnetic NPs, while the organic linker is converted to a porous carbon structure embedding the magnetic NPs. MOF-derived MPCs have high stability and retain part of the initial porosity of the precursor MOF, making them good candidates as sorbents for MSPE.

In this work, the potential of magnetic MOFs and MOF-derived MPCs as sorbents for MSPE is discussed. The different approaches to prepare magnetic MOFs and MOF-derived MPCs are described with focus to their use as sorbents for MSPE. Recently developed applications of these materials as MSPE sorbents are overviewed. In addition, different strategies for the automation of MSPE using magnetic MOFs and MOF-derived MPCs are described. Future research directions for batch and automated MSPE using this type of magnetic materials are also identified.

2. Fundamentals of magnetic solid-phase extraction using MOFs

In the past years a considerable number of novel materials with interesting features for their use in analytical applications have been developed [22,23]. Among them, MOFs have attracted significant interest. MOFs are prepared by joining metal ions (or clusters) with bi- or multidentate organic linkers, although multivariated MOFs (MTV-MOFs) containing multiple metals [24], or organic linkers have been also described [25]. Due to the large variety of inorganic and organic precursors suitable to build MOFs, more than 20.000 different MOFs have been reported to date [14]. An important factor to bear in mind when using MOFs for certain applications is their potential toxicity. However, many typical MOFs are built from metals with a low toxicity, as well as non-toxic organic ligands or biomolecules [69,70]. Nevertheless, the final MOF toxicity will depend not only on the precursors used, but also on the resulting MOF stability and MOF particle size. MOFs are highly porous, with surface areas exceeding 1000 $m^2\ g^{-1}$, and reaching values of up to 10,000 $m^2\ g^{-1}$ [14]. The high porosity, together with their versatile chemical composition and pore surface tunability, make them promising sorbents for SPE applications. However, small particle size or non-spherical morphology of MOFs hinders their applicability in typical SPE formats based on packed sorbents. The direct use of micro/nanomaterials for SPE can be carried out by dispersing the sorbent in the sample medium. Nevertheless, the recovery of sorbents based on very small particles dispersed in a liquid phase can be a very hard task, and typical filtration or centrifugation procedures can be inefficient. An interesting alternative to solve this limitation is the use of magnetic sorbents, which can be easily retrieved from the different liquid phases involved in the SPE method (sample, washing solution, eluent) by simply applying an external magnetic field.

Typical sorbents for MSPE are based on magnetite (Fe_3O_4) NPs coated with silica, polymers, or carbon nanostructures. These materials usually have a low surface area, requiring long extraction times due to the low mass transfer of analytes in solution to the dispersed solid phase. In this sense, the synergies between highly porous MOFs and magnetic NPs could be exploited to develop high performance sorbents for MSPE applications. In addition, the use of MOFs for extraction applications is not limited to the use of the MOF itself. MOFs can be used as porous precursors to obtain other interesting materials such as porous carbons, metal oxides, or layered double hydroxides.

A small number of MOFs are commercially available, and no magnetic MOFs or magnetic MOF derived materials have been commercialized to date. The preparation of the desired MOF for MSPE requires an additional magnetization step (Fig. 1a). A variety of different MOF magnetization approaches are possible, which are discussed in detail in the next section.

Once the desired magnetic MOF has been prepared, the classic steps of a MSPE procedure are applied (Fig. 1b), which are as it follows:

- Add magnetic sorbent to the sample and allow sufficient contact time to ensure a quantitative extraction.
- Retrieve magnetic sorbent using an external magnet, and discard the sample.

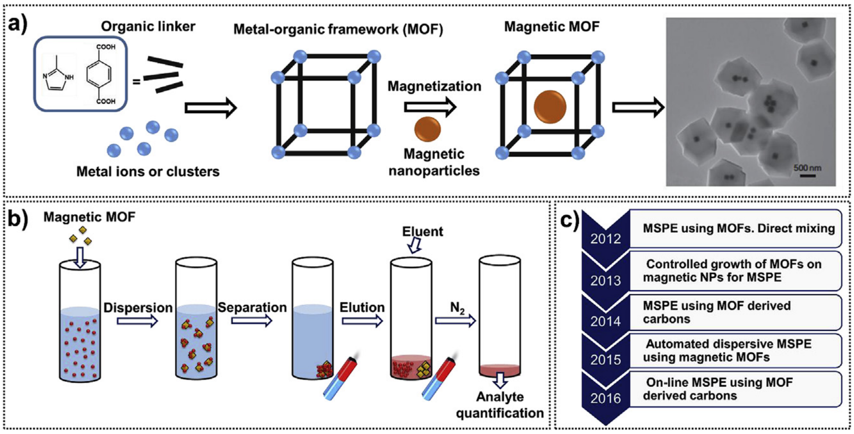

Fig. 1. a) Schematic representation of the preparation of a magnetic MOF. b) Scheme of the general procedure of magnetic solid-phase extraction using MOFs. c) Milestones on the use of MOFs for MSPE. Transmission electron microscopy image reproduced with permission from Ref. [19], Copyright 2012, Nature Publishing Group.