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Recent advances in the adsorbents for isolation of polycyclic aromatic hydrocarbons (PAHs) from environmental sample solutions

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ABSTRACT

This article offers a critical review on the materials that have been applied as adsorbents in the isolation of polycyclic aromatic hydrocarbons from matrix solutions. The review looks at adsorbents that have been used during the clean-up stage to isolate polycyclic aromatic hydrocarbons from aqueous samples and organic solvent extracts from treatment of solid samples. Articles that report the application of adsorbents for solid phase extraction and solid phase microextraction of PAHs in the past decade stretching from 2007 were considered. The review focussed mainly on recent advances that have been done to enhance the applicability of both traditional adsorbents like silica, and modern ones like molecularly imprinted polymers and nanoparticles. The application of adsorbents modified with functional organic groups is critically evaluated with areas for possible improvement suggested. Finally, the authors offer areas of exploration that can allow the analysis of polycyclic aromatic hydrocarbons to reach new heights.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds that consist of fused benzene rings. These compounds have low solubility and tend to adsorb on solid and carbonaceous materials in the environment. PAHs are ubiquitous in the environment with several studies reporting their presence in both aqueous (mainly surface water, plant oils and petroleum products), air and solid samples that include sediments, soils and wastewater sludge [1,2]. Several studies have also reported the presence of PAHs in food samples [3–7]. For analysis of PAHs in solid samples, the PAHs firstly need to be transferred into a solvent. Most of the extraction techniques, both conventional and modern, are non-selective and result in an extract with a large amount of matrix effects. A further clean-up step is therefore needed in which the PAHs are isolated from the matrix effects and finally preconcentrated for detectability in quantitation instruments. Analysis of water samples also requires that the PAHs be isolated first before introduction into the chromatographic instrument for quantitation. Solid phase extraction (SPE) and gel permeation chromatography (GPC) are commonly used during the isolation stage. Isolation is achieved by binding on various adsorbent phases that are packed on the SPE and GPC systems. For analysis of water samples, the adsorbent may also be dropped directly into the solution. Suitable organic solvents are then used to elute the PAHs from the sorbent followed by chromatographic determination. Another important isolation technique in the analysis of PAHs that uses adsorbents is solid phase microextraction (SPME).

Challenges in the application of adsorbents for PAHs are related to lack of functional groups on PAHs that can be targeted for binding. They are hydrophobic and tend to co-extract with large amounts of matrix effects. In addition, they have a very low charge, exist in the environment as mixtures and in trace amounts. Mass spectrometry is arguably the best detection technique yet it exhibits low sensitivity towards PAHs due to lack of soft spots that can easily be fragmented. These undesirably characteristics have made the search for adsorbents that can effectively isolate PAHs from

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Abbreviations: C_{18}, octadecyl; CNP, carbon nanoparticle; EGDMA, ethylene glycol dimethacrylate; Fe_3O_4, magnetite; GPC, gel permeation chromatograph; LOD, limits of detection; MIL-101(Cr), Cr-doped Material of Institute Lavoisier no. 101; MIL-100(Fe), Fe-doped Material of Institute Lavoisier no. 100; MCM-41, mobil composition of matter or mobil crystalline material no. 41; MIP, molecularly imprinted polymer; MOF, metal or metal oxide organic framework; MWCNT, multiwalled carbon nanotube; NP, nanoparticle; PAH, polycyclic aromatic hydrocarbon; PMO, periodic mesoporous organic silica; SBA-15, santa barbara amorphous no. 15; SPE, solid phase extraction; SPME, solid phase microextraction; TBCD, 1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane.

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environmental samples a priority. In this regard, several potential adsorbents have been investigated. These include traditional adsorbents such as the synthetic silica and alumina while molecular imprinting and nanoparticles (NPs) have been tried as modernized adsorbents. This review discusses the impact of each adsorbent type in the analysis of PAHs.

2. Silica gel and alumina adsorbents

The traditional silica gel and alumina are still reported as effective clean-up adsorbents in the isolation of PAHs from matrix effects [8–12]. Silica and alumina are micro-powdered synthetic adsorbents with a nano-porous structure made of silicon dioxide and aluminium oxide, respectively. These classical adsorbents are still common during the clean-up step after PAHs had been extracted from solid samples using organic solvents. They have been used for sample clean-up and pre-concentration of PAHs after Soxhlet extraction [13], ultrasound assisted solvent extraction (ultra-sonication) [4,14], saponification [15,16] and microwave assisted extraction [11,17,18]. The SW-846 US-EPA 3630C silica gel clean-up approved by the US-EPA has been used by Cai et al. (2007) while Bojes and Pope (2007) have used a modified SW-846 US-EPA Method 3611B that uses alumina as an adsorbent [19,20]. Other researchers have combined alumina and silica as SPE sorbents [14,21,22] or GPC column gels [11,23]. Fromberg and Højgård (2007) have combined GPC using commercial Bio-Beads S-X3 and the silica based SPE for cleaning PAHs while Hossain and Salehuddin (2012) have used silica as both the fractionating GPC column and the SPE adsorbent for isolation of PAHs from oil samples [24,25]. Comparative studies have shown that better selectivity and reproducibility are achieved with activated silica gel. Generally, the applicability of silica in the adsorption of PAHs is restricted by the presence of –OH groups on the surface. These groups interact with water molecules that result in formation of a hydration film around silica particles. The interaction of the silica surface and a PAH molecule therefore has to suppress this water phase. As such, focus has shifted to modifications of the silica surface using organic functional monomers mainly the ringed organic groups that can complement the structure of PAHs. Attempts have also focussed on down-scaling the particle size to the nano scale for the purposes of improving surface area. Herein we discuss the applications of functionalized silica and silica NPs in the analysis of PAHs in environmental samples.

2.1. Mesoporous organic silica

One of the major advances in the application of functionalized silica is the use of periodic mesoporous organic silica (PMO). This is silica that has been functionalized with organic derivatives to provide mesoporosity on its surface. PMOs are characterized by periodically ordered pores of 2–50 nm sizes and large surface areas of up to 1884 $m^2\ g^{-1}$ recorded by Xia et al., 2005. This PMO had a pore size distribution of 2.2–2.6 nm [26]. However, the highest surface area recorded for any silica-based PMO is 2370 $m^2\ g^{-1}$ which was reported by Wei et al., 2016 for PMO nanocubes with a 200 nm pore size [27]. Functionalization occurs by covalently linking the organic functional groups with siloxane domains.

Several studies have reported the application of PMOs. Cyclodextrin-functionalized PMOs are very common as sorbents for extracting PAHs. β-cyclodextrin, a doughnut-shaped oligosaccharide consisting of 7 D-glucopyranoside units, is documented as the functional coating agent of choice. Its cyclic structure in addition to the cyclic repeating units makes it a better choice for targeting cyclic hydrophobic molecules like PAHs. A β-cyclodextrin-functionalized PMO has been used by Mauri-Aucejo et al. (2016) for analysis of trace levels of 8 PAHs in different water samples with limits of detection (LOD) values of 3–800 ng L^{-1} and efficiency levels of 54–145% [28]. The observed spread in the efficiency values was attributed to matrix influences. The authors further suggested that a standard addition calibration approach can be used to counteract these matrix effects using the proposed method. This is an indication that there is still need for improvement in the synthesis of cyclodextrin-based PMOs to produce a sorbent with a selective affinity for priority PAHs. Topuz et al. (2017) used a similar PMO based on silica NPs to isolate 5 PAHs in aqueous samples. The adsorption capacities ranged from 0.3 to 1.65 mg g^{-1} [29]. Soler-Segui et al. (2016) gave LODs of 1.2–38 ng L^{-1} for 7 PAHs in water samples using a dextrin–silica hybrid composite [30]. Pentynyl β-cyclodextrin as the organic moiety for a PMO adsorbent for phenanthrene has recently been reported with extraction efficiencies above 95% [31].

Other organic coating agents for silica include an aminopropyl imidazole-modified silica sorbent reported by Wang et al. (2014) in water samples with LODs of 6.5–500 ng L^{-1} and efficiencies of 63.2–112.3% [32]. Zhao et al. (2016) have used a macrocyclic tetraazacalix[2]arene[2]triazine functional agent with efficiencies of 94.3–102.4% and LODs of 0.4–3.1 ng L^{-1} in the analysis of 5 PAHs in water samples [33]. Vidal et al. (2011) have functionalized silica with phenyl groups for extraction of 5 PAHs in aqueous solutions with removal efficiencies of 40–70% and adsorption capacity of 0.72–1.69 mg g^{-1} [34]. Haemoglobin-coated mesoporous silica by Laveille et al. (2010) yielded removal efficiency of above 82% for 11 PAHs in water samples [35].

A novel approach has been reported by Liu et al. (2014) in which a macrocyclic polyamine functionalized with an ionic liquid, 1,3-dibutylimidazolium bis[(trifluoromethyl)sulfonyl]imide with LOD values of 2–100 ng L^{-1} and efficiencies of 80.9–120.1% was used in the determination of 5 PAHs in water samples [36]. Other improvements in the application of silica include doping the PMO with magnetite (Fe_3O_4). Li et al. (2017) have magnetized silica coated with polydopamine with LOD values recorded at 0.185–0.367 mg g^{-1} for PAHs in water samples [37]. Tetraethyl orthosilicate magnetized with maghemite (Fe_2O_3) NPs with a binding capacity of 0.39 mg g^{-1} has been applied by Huang et al. (2016) for the isolation of acenaphthene with removal efficiencies reported at 85% [38].

2.2. Mesoporous silica nanoparticles

Mesoporous silica NPs have also been reported as adsorbents for isolation of PAHs from aqueous solutions and environmental water samples. An Si-MCM-41 (Silica-functionalized Mobil Composition of Matter or Mobil Crystalline Material No. 41) has been reported in the analysis of PAHs in aqueous samples [39,40]. This is a silica-based mesoporous molecular sieve prepared from a silica source in the presence of a surfactant. Once the surfactant is washed out, a hexagonal framework with a high surface area and specific pore size is formed. Dodecylamine and tetramethylammonium have been reported as the surfactants with adsorption capacity values of 18.35–18.78 μg g^{-1} and 0.69–1.09 mmol g^{-1} respectively [39,40]. An NH_2-SBA-15 (amine-functionalized Santa Barbara Amorphous No. 15) hybrid with an adsorption capacity range of 0.76–1.92 mg g^{-1} towards PAHs has been reported by Balati et al. (2015). SBA-15 differs from MCM-41 in that its pores are round and pluronic acid is used as a surfactant [41]. Studies by Li et al. (2017) have shown that the geometric framework of SBA-15 renders it a better adsorbent for PAHs than MCM-41 [42]. Zhang et al. (2017) have recently reported a magnetized form of a mesoporous silica NP called Fe-SBA-15 for adsorption of pyrene [43]. Magnetized silica NPs using cholesterol as a functionalizing agent for the