Development of a single format membrane assisted solvent extraction-molecularly imprinted polymer technique for extraction of polycyclic aromatic hydrocarbons in wastewater followed by gas chromatography mass spectrometry determination

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ABSTRACT

A technique that combines membrane assisted solvent extraction and molecularly imprinted polymer into a single step format has been successfully developed and evaluated for the extraction of the 16 US-EPA priority polycyclic aromatic hydrocarbons in wastewater samples followed by determination using gas chromatography coupled with time of flight mass spectrometry. The technique involves placing the polymer particles into a hydrophobic polypropylene membrane bag which is in contact with an aqueous donor phase. The technique was optimized for various parameters that include presence of an organic modifier in the donor phase, stirring rate and extraction time. The optimum conditions were 25% of dimethyl sulfoxide as an organic modifier and stirring at 1000 rpm for 120 min. The limits of detection using the technique were in the 0.01–0.45 ng mL^{-1} range. Linearity values determined in the 10–1 000 ng mL^{-1} calibration range were all above 0.9972. Extraction efficiencies of the sixt analytes calculated as averages for three spiking concentrations ranged from 62.8 to 96.8% (RSD = 3.1–12.3%). The optimized method was tested for the extraction of polycyclic aromatic hydrocarbons in wastewater samples in the presence of surrogate standards. The developed method showed great reproducibility with inter day repeatability values ranging from 0.6 to 24.9%. The analytes were quantified in the nanogram level showing that the developed technique is a viable alternative in the analysis of trace organic compounds in complex aqueous samples.

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1. Introduction

The analysis of complex samples still offers researchers a challenge due to the presence of various forms of matrix effects which eventually affect extraction efficiency of sample preparation techniques especially if the target analytes exist in trace amounts and have physicochemical properties similar to their matrix counterparts. One such group of pollutants with unfavourable properties are the polycyclic aromatic hydrocarbons. These compounds are ubiquitous in the environment with several studies reporting quantitation in solid and aqueous environmental samples, as well as in air and food samples [1–4].

Liquid-solid approaches are commonly used in the extraction of organics in aqueous samples. This involves passing an aqueous sample through an adsorbent material packed in solid phase extraction (SPE) cartridges. The target analytes become isolated from matrix effects by binding on the adsorbent. For the analysis of PAHs in environmental samples, several adsorbents have been used as packing material for SPE cartridges [5]. Among these adsorbents are molecularly imprinted polymers (MIPs). These are synthetic polymers with cavities that bind specific compounds. They have been reported as better adsorbents in the analysis of organics compared to C18, silica and nanoparticle-based sorbents [5,6].

Attempts to eliminate matrix effects in the analysis of complex samples has led to introduction of microporous membrane-based liquid-liquid extraction. These include the membrane assisted solvent extraction (MASE), a technique first used by Hauser and Popp [7–10] and the supported liquid membranes (SLMs) such as the

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miniaturized hollow fibre liquid phase micro-extraction (HF-LPME) first reported by Jönsson and Mathiasson [11–14] while emulsion liquid membranes [15] and ionic liquid membranes [16] have also been reported. The hydrophobic and size-exclusive properties of the micromembranes used during these techniques are responsible for eliminating both hydrophilic compounds and higher molecular weight (HMW) hydrophobic matrix compounds. Other advantages include high enrichment power and the potential for automation through online interfacing with chromatographic instruments [13,17–19]. The main drawback of membrane-assisted extraction techniques is that extraction is not exhaustive [18]. Membrane memory effects are also possible due to clogging of the surface and the pores of the membrane by HMW and other hydrophobic compounds [20].

Recent advances in the application of membranes has been to incorporate nanosorbents and immunoassays on the SLM in order to enhance further selectivity [15,21,22]. Electro-membranes have also been reported as a way of facilitating transfer across SLMs [23–28]. Other studies have reported a non-porous polymeric membrane in combination with pressurized liquid extraction [29,30]. Another strategy has been to follow up the membrane technique with isolating the target analytes on a solid adsorbent. This is common with the MASE technique where the sorbent material can be placed in the lumen of the membrane or used as an SPE packing material [17,31–34].

The MASE technique for PAHs from aqueous samples has been reported before [8,35–38]. This technique alone is not a favourable approach in the analysis of PAHs with March et al. recording recoveries of 12.5–23% for 7 PAHs from sea water [37], Zuin et al. recording 13.6% for benzo[a]pyrene in sugarcane solution samples [35] while Alcudia-Leon et al. did not report recoveries for their analysis of 5 PAHs in water samples [36]. However, Rodil et al. recorded recoveries above 65% for all the 16 US-EPA priority PAHs using the MASE method coupled with large volume injection programmed temperature vaporisation [8]. The same technique was reported by Prieto et al. and obtained recoveries of 81–116% in the analysis of the same PAHs in estuarine water samples [38]. Amdany et al. have used a semipermeable membrane device as a passive sampler for PAHs in dam water with recoveries of 55–123% [39]. The HF-LPME technique has been reported by Charalabaki et al. for the extraction of PAHs from wastewater effluent samples [40]. An adsorbent-assisted MASE technique in the analysis of six PAHs from water samples has been reported by Ge and Lee with recoveries recorded at 88.1–110.9% [41].

The MIP-assisted membrane approaches have been reported within our research group for the analysis of triazines and 17β-estradiol in aqueous solutions. Both membrane bags [31] and flat membranes [42,43] in combination with MIPs were investigated. A membrane bag containing MIPs has been recently reported in combination with Soxhlet extraction for analysis of PAHs in wastewater sludge samples [44]. Other studies that have reported membranes and MIPs include Barahona et al. who used an HF-LPME coated with MIPs for extraction of triazines from aqueous samples [45]. Takeda et al. used a molecularly imprinted nylon membrane for enhanced selective extraction of L-phenylalanine [46].

This study aimed at investigating the potential of combining membrane assisted solvent extraction and a molecularly imprinted adsorbent into a single step format for analysis of PAHs in wastewater. The approach is herein referred to as the membrane assisted solvent extraction-molecularly imprinted polymer (MASE-MIP) technique. The premise is that when the analytes cross the membrane, they are selectively isolated by binding onto the MIP cavities. The bound PAHs can then be eluted using an appropriate solvent. MIPs were preferred as the adsorbent because of their specificity towards target analytes and the easy of synthesis under laboratory conditions. Further, MIPs work best in non-polar organic solvents

where their selectivity is retained. The single entity MASE-MIP technique eliminates the need for a separate clean-up of the membrane extract and forms part of the search for modern technologies aimed at giving high selectivity and minimizing the number of steps during analysis.

2. Materials and methods

2.1. Chemicals and reagents

A 10 μg mL^{-1} PAH calibration mix in acetonitrile (CRM 47940) with 99.0% purity was obtained from Supelco (Bellefonte, PA, USA). HPLC-grade dimethyl sulfoxide, acetonitrile, methanol and dichloromethane were purchased from Sigma-Aldrich (Johannesburg, South Africa). All chemicals used in preparation of the polymer were purchased from Sigma Aldrich (Johannesburg, South Africa).

2.2. Instrumentation and apparatus

Quantitation of PAHs was done on a Pegasus 4D gas chromatograph in one-dimensional mode and time-of-flight mass spectrometer (GC-TOF/MS) (LECO Corp., St. Joseph, MI, USA) with a 7683B Series auto-injector (Agilent Technologies, DE, USA). The PAHs were separated on a 30 m $\times$ 0.32 mm ID $\times$ 0.25 μm RXI-5SIL MS capillary column by Restek Corporation (Bellefonte, PA, USA). The temperature program was increased from 50 to 310 °C over 32 min. Data processing was done using ChromaTOF software version 4.5.1. (LECO Corp, St. Joseph, MI, USA). An MS-MP8 magnetic stirrer by Daihan Scientific Co.,Ltd, Seoul, South Korea was used for stirring. Microporous polypropylene membrane bags of dimensions 4 cm long, 6 mm internal diameter, 0.22 μm pore size and 160 μm thickness were from Gerstel GmbH & Co. KG (Mülheim, Germany).

2.3. Synthesis of the molecularly imprinted polymer

The MIP used in this study was prepared using the method reported by Ncube et al. [47]. The adsorbent consisted of a benzo[k]fluoranthene and an indeno[1 2 3-cd]pyrene-imprinted polymer prepared separately and then mixed at 1:1 (w/w). This polymer combination is reported to have a high cross selectivity towards the 16 US-EPA priority PAHs. It has a binding capacity of 5.188 mg g^{-1} with only 2.9% loss in selectivity when re-used [47].

2.4. General extraction procedure

The MASE-MIP system was set up as shown in Fig. 1. The membrane extraction cell consisted of a 20 mL headspace vial filled with deionized water spiked with PAHs. The deionized water was spiked at 0.5 μg mL^{-1} individual PAH concentration. The membrane bag was attached to a metal funnel and fixed with a PTFE ring. The membrane bag was filled with 80 mg of the MIP particles and 1 mL of an organic acceptor phase. The membrane bag with MIP particles dispersed in the acceptor phase was placed inside the extraction cell containing the donor solution and stirred for pre-set times. After extraction, the acceptor content (MIP and the acceptor solvent) was transferred into a 3 mL empty cartridge with a 10 μm frit at the bottom and mounted onto an SPE unit. A steady vacuum pump was then applied for 1 min to dry off the MIP particles completely. The PAHs were eluted from the MIP cavities using 3 $\times$ 1 mL of an organic solvent. The solvent extract would then be reduced to 1 mL before being injected directly by GC-TOF/MS for identification and quantitation of PAHs.