DEVELOPMENT OF MINIATURIZED EXTRACTION METHODS WITH ADVANCES OF NOVEL SORBENT MATERIALS FOR ENVIRONMENTAL ANALYSIS

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DECLARATION

I hereby declare that this thesis is my original work and it has been written by me in its entirety, under the supervision of Professor Lee Hian Kee, (in the Microextraction, Separation Science and Enviroanalytics Laboratory), Chemistry Department, National University of Singapore, between January 2011 and January 2015.

I have duly acknowledged all the sources of information which have been used in the thesis.

This thesis has also not been submitted for any degree in any university previously.

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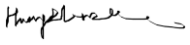
Huang Zhenzhen		4th November 2015
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SUMMARY

Sample preparation remains a critical component of the workflow for an analytical protocol and thus deserves a lot of attention. Featuring the reduction or complete elimination of solvents, and using small-scale devices, miniaturized extraction techniques have been considered a key trend in the analytical science field. This research work aimed at exploration of novel materials as the sorbent for the development of fast, simple and sensitive microextraction approaches. Two solid-phase based microextraction methods were reported, making use of one type of metal-organic framework (MOF), MIL-101. A new solid-phase microextraction (SPME) device was fabricated with the advantages of bio-inspired polydopamine (PDA). Magnetic nanoparticles with polymer and carbonaceous shell were synthesized and compared in magnetic solid-phase extraction (MSPE).

Firstly, MIL-101 was synthesized and used as a micro-solid-phase extraction (μ-SPE) sorbent for efficient enrichment of organochlorine pesticides (OCPs) from water samples, followed by gas chromatography-mass spectrometry (GC-MS). This study demonstrated a new application of MIL-101 using μ-SPE. Its stability in water and various solvents allowed MIL-101 to be used in the sample preparation of aqueous samples. The large pore size and high surface area allowed the material with the capacity to extract OCPs. The limits of detection (LODs) yielded were between 0.0025 and 0.016 ng/mL.

Secondly, MIL-101 crystals were modified with the nonionic surfactant, Triton X-114, and the resulting material was applied to dispersive micro-solid-phase extraction (dSPE) of estrogens from environmental water samples. Triton X-114 molecules adhered onto the hydrophobic surface of the MIL-101 crystals and therefore improved the dispersibility of MIL-101 in aqueous solution by serving as protective layer-like micelles. The cloud point phase separation effect of Triton X-114 accelerated the separation of extracts from the aqueous matrix. Post-extraction derivatization using N-methyl-N-(trimethylsilyl) trifluoroacetamide was employed to facilitate the quantitative determination of the analytes by GC-MS. The surface modified MIL-101 showed improved extraction performance compared to the unmodified MIL-101. The main factors affecting the construction of modified MIL-101 and extraction of the analytes, were investigated in detail. Under the optimized conditions, the present method yielded low LODs (0.006-0.023 ng/mL).

Thirdly, a facile preparation route for surface coating on a stainless steel fiber with carbon material derived from PDA was evaluated for SPME. The robust adhesion of dopamine to metal oxides ensured sufficient stability of the polymer coating. Carbonization treatment of the polymer coating resulted in a layer of carbonaceous coating on the fiber. The obtained carbon coated fiber was utilized for SPME and exhibited effectiveness in the extraction of OCPs from aqueous solution. Most of the analytes could be detected efficiently in the presence of humic aicd at a concentration of 20 mg/L. Enrichment factors of 102 to 757 were obtained for the selected OCPs in aqueous solution. Moreover, in the experiment, the prepared fiber could be reused for more than 150 times.

Lastly, magnetic nanoparticles with polymer (Fe_3O_4@PDA) and carbonaceous (Fe_3O_4@C) shell were prepared by self-oxidization of dopamine and carbonization of the PDA coating. The performance of the two magnetic sorbents in MSPE of estrogens from environmental water samples was studied. Orthogonal array design was adopted to facilitate the optimization of this sorbent based extraction approach. Fe_3O_4@PDA was shown to be superior to Fe_3O_4@C in the enrichment of estrogens. Owing to the high magnetic response of the two sorbents, the collection of sorbents was simplified. Analysis of the extracts was conducted by high-performance liquid chromatography coupled with ultraviolet and fluorescence detection. The LODs achieved were in the range of 0.072 to 0.15 ng/mL for E1 and DES, and 0.0017 to 0.0062 ng/mL for E2 and E3.

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LIST OF ABBREVIATIONS

ACN	Acetonitrile
BET	Brunauer-Emmett-Teller
BJH	Barrett–Joyner–Halenda
CAR/PDMS	Carboxen/ Polydimethylsiloxane
C-PDA	Carbonized polydopamine
CPE	Cloud point extraction
DAD	Diode array detection
DES	Diethylstilbestrol
DI	Direct immersion
DLLME	Dispersive liquid-liquid microextraction
DMF	Dimethylformamide
DMIP	Dummy molecularly imprinted polymer
DSPE	Dispersive solid-phase extraction
dSPE	Dispersive micro-solid-phase extraction
E1	Estrone
E2	Estradiol
E3	Estriol
ECD	Electrochemical detection
EC-SPME	Electrochemically-controlled SPME
EDC	Endocrine disrupting chemical
EE2	17α-ethynylestradiol

EE-SPME	Electrochemically-enhanced SPME
EF	Enrichment factor
FD	Fluorescence detection
FPSE	Fabric phase sorptive extraction
FT-IR	Fourier transform infrared
GC	Gas chromatography
GCB	Graphitized carbon black
GC-MS	Gas chromatography-mass spectrometry
HF	Hollow fiber
HFM	Hollow fiber membrane
HF-LLLME	Hollow fiber liquid-liquid-liquid microextraction
HF-LPME	Hollow fiber-LPME
HPLC	High-performance liquid chromatography
HPLC-UV/FD	High performance liquid chromatography coupled with ultraviolet and fluorescence detection
HS	Headspace
IL	Ionic liquid
ITMS-MS	Ion trap tandem mass spectrometry
LC	Liquid chromatography
LC-MS	Liquid phase chromatography-mass spectrometry
LC-MS/MS	Liquid phase chromatography tandem mass spectrometry
LLE	Liquid-liquid extraction

LOD	Limit of detection
LOQ	Limit of quantitation
LPME	Liquid-phase microextraction
MALDI-MS	Matrix-assisted laser desorption/ionization-mass spectrometry
MALDI-TOF MS	Matrix-assisted laser desorption/ionization time of flight mass spectrometry
MDGC	Multi-dimensional gas chromatography
MeOH	Methanol
MEKC	Micellar electrokinetic chromatography
MEPS	Microextraction in packed syringe
MFCNT	Magnetic cobalt ferrite filled carbon nanotubes
MIP	Molecularly imprinted polymer
MMIP	Magnetic molecular imprinted polymer
MNP	Magnetic nanoparticle
MOF	Metal-organic framework
MSTFA	Methyl-N-(trimethylsilyl)trifluoroacetamide
MSPE	Magnetic solid-phase extraction
m-μSPE	Magnetic-micro solid-phase extraction
MWCNT-OH	Hydroxyl-terminated multi-walled carbon nanotube
OAD	Orthogonal array design
OCP	Organochlorine pesticide
PAH	Polycyclic aromatic hydrocarbon

PC	Percentage contribution
PDA	Polydopamine
PDMS	Polydimethylsiloxane
PDMS-MOF	Polydimethylsiloxane-metal organic framework
PIL	Polymeric ionic liquid
PMAA-DVB-EDMA	Poly(methyacrylic acid-divinylbenzene-ethyleneglycol dimethacrylate)
RSD	Relative standard deviation
S/N	Signal-to-noise
SBME	Sorbent-bar microextraction
SBSE	Stir bar sorptive extraction
SDME	Single-drop microextraction
SEM	Scanning electron microscopy
SIM	Selective ion monitoring
SPE	Solid-phase extraction
μ-SPE	Micro-solid-phase extraction
μ-SPEE	Micro-solid-phase equilibrium extraction
SPME	Solid-phase microextraction
SUPRA	Supramolecular solvent
TEM	Transmission electron microscopy
THF	tetrahydrofuran
Tris	Tris(hydroxymethyl) aminomethane
UHPLC-MS/MS	Ultrahigh pressure liquid chromatography-tandem

	mass spectroscopy
UV	Ultraviolet detection
UACPE	Ultrasound-assisted cloud point extraction
VOC	Volatile organic compound
XRD	X-ray diffraction

CHAPTER 1 INTRODUCTION

1.1 Sample preparation in environmental analysis

Over the past few decades, numerous concerns have been raised worldwide over economic growth and environmental sustainability. Accompanying the rapid expansion of industrialization and urbanization, environmental pollution is becoming a critical issue, as various severe adverse impacts across environment, biota and human health [1-3]. More data about the presence and the possible impact of pollutants are essential for assessment studies of risk and toxicological potential [4, 5]. Hence, fast and accurate analytical techniques to identify, quantify and regulate of the pollutants in the environment, particularly of emerging chemical compounds are needed [6-8].

With advances of instrumentation achieved so far such as chromatography and spectroscopy, chemical analysis based methods can reach high accuracy and low detection limits [9]. Sample preparation in most cases means the isolation and/or concentration of components of interest from various matrices and, if necessary, derivatization, putting them in a suitable form for subsequent separation and detection by instruments. In general, it is the sample preparation of a complete analytical task process, which is most prone to error and loss [10]. Therefore, the importance and stature of sample preparation cannot be underestimated in establishing efficient analytical methods.

The release of chemical pollutants by anthropogenic activities could end up in various matrices, such as indoor or ambient air, surface and ground water, soil and sediment, and aerosols. Accordingly, sample preparation methods are different depending on the matrix and physiochemical properties of the target analytes. For air samples, collection relies on solvent absorption or sorbent adsorption [11]. The concentrated analytes in the latter case could be recovered with either thermal desorption or liquid extraction prior to instrumental analysis. Though it might seem that gases can be analyzed directly by some instruments, e.g., gas chromatography (GC), the concentration of the analytes in real samples may be too low to be effectively detected. For soil samples, solvent extraction and digestion are often required in the sample preparation procedure. There are several well established sample preparation approaches for this purpose, including continuous extraction with a solvent (Soxhlet), ultrasound-assisted extraction, pressurized liquid extraction, microwave-assisted extraction and supercritical fluid extraction [12]. For aqueous samples, the classical and widely used sample preparation methods are liquid-liquid extraction (LLE) and solid-phase extraction (SPE). Some shortcomings of traditional sample preparation procedures are obvious, such as the consumption of a large amount of organic solvents, long extraction time, and multiple operating steps.

As the concept of green chemistry becomes an overarching concern in analytical chemistry [13], environmental friendly sample preparation has been an aspiring goal for almost every chemist when devising new analytical techniques. In this respect, extraction methods which use less harmful solvents or no solvent have been

put forward, among which the typical examples are cloud point extraction (CPE), solid-phase microextraction (SPME), stir bar sorptive extraction (SBSE), single-drop microextraction (SDME), liquid-phase microextraction (LPME) and so on. The so-called miniaturized techniques feature the reduction of no or much reduced volume of solvents, and the use of microscale devices. Apart from the environmentally benign feature of miniaturized sample preparation techniques, they are more cost-effective and less laborious compared to traditional methods.

In this chapter, the basic concepts and applications of different miniaturized sample preparation strategies for the analysis of organic pollutants in environment are be reviewed based on their extraction mechanisms: solvent-based sorption or sorbent-based adsorption, with a focus on the latter. Subsequently, a range of procedures involving extraction by novel materials is discussed. In the last part of this section, the research objectives and scope of the thesis are presented.

1.2 Liquid-phase microextraction (LPME) techniques

The preliminary mode of LPME was introduced by in 1996 as a novel alternative sample preparation approach to conventional LLE, using negligible volumes of extraction solvent (a few microliters) and reduced steps in the procedure [14, 15]. Later, with the use of a microsyringe, a drop of organic solvent could be successfully suspended at the tip of the microsyringe and extraction would take place through the dissolution of analytes of interest from the aqueous matrix into the solvent drop. Based on such design of the extraction setup, two similar modes were proposed, direct immersion (DI)-SDME [16] and headspace (HS)-SDME [17],

opening up a new direction for microscale sample preparation. The distinct merits of SDME include the integration of extraction and injection using the same apparatus, simplicity of operation and low cost. To improve the extraction efficiency, dynamic SDME [18], continuous-flow microextraction [19] and automated SDME [20] were developed. On the other hand, based on the principle of the SDME technique, different variants of SDME, for example directly-suspended droplet microextraction [21] and solidified floating organic drop microextraction [22] were also proposed.

In order to improve the stability and reliability of SDME technique, hollow fiber-LPME (HF-LPME) was first investigated in 1999 [23]. For HF-LPME, the extraction medium is trapped inside the pores of a polypropylene hollow fiber that is attached to the needle of a syringe. The syringe could facilitate extract injection after extraction. Due to the protection of hollow fiber, the sample solution can be stirred vigorously to increase extraction efficiency without loss of extracting phase. Moreover, the matrix interference can be minimized. The development of HF-LPME has been mainly focused on the selection of suitable extraction media and the regulation of the mass transfer by utilization of either a two phase or three phase system. The modified versions of HF-LPME include solvent bar microextraction [24] and electromembrane extraction with the aid of applied electrical field as the extraction driving force [25].

Dispersive liquid-liquid microextraction (DLLME) has been reported in 2006 as a mode of LPME [26]. It has a similar extraction principle as classical LLE for mass

transfer between aqueous matrix and water immiscible solvent. However, a dispenser solvent which is highly miscible with both of the aqueous solution and the extracting solvent is required. Since instantaneous mixing of the sample solution and the extractant can be achieved in the extraction process and high contact area will be formed between them, DLLME is a relatively fast and highly efficient sample preparation approach. Ultrasound [27] and vortex agitation [28] have been widely employed to enhance the dispersion/emulsification process so as to improve the enrichment performance in less time.

It is obvious that the extraction performance of these LPME techniques as mentioned above are determined to a large extent by the characteristics and extraction capability of the solvent used. One of the important tasks in developing novel LPME methods is to focus on non-toxic extraction media. Ionic liquids and surfactant-based coacervates have been employed as alternatives to conventional solvents. Nevertheless, some issues associated with their compatibility with analytical instruments, handling and disposal, and available green solvents deserve more attention with regard to performance and also amenability to potential automation.

1.3 Sorbent based microextraction

SPE was the first, and hitherto probably still the most successful extraction procedure that involves the utilization of sorbent materials in the sample preparation field. The principle of SPE is similar to LLE in that extraction depends on the partitioning of analytes between two phases. However, for SPE, it is between

a liquid phase (aqueous sample or solvent matrix) and a solid phase (sorbent). Generally, in the most basic SPE format, during extraction an aqueous sample is preloaded in an immobilized sorbent phase. Subsequently, analytes are eluted by a suitable solvent. Though much effort has been expended to improve SPE during the past 45 or more years, it does not conform strictly to green chemistry principles, because relatively moderate amounts of solvent are needed for activation of the sorbent and desorption of the extracted analytes. To address these disadvantages, while retaining the advantages of SPE, a variety of novel sorbent based sample preparation techniques have been developed since 1978, beginning with the introduction of SPME, the first miniaturized sorbent phase based extraction mode. The solvent-minimized nature (in some cases, solventless) of such an adsorptive sample preparation technique is the attractive feature of SPME.

1.3.1 Solid-phase microextraction (SPME)

SPME was introduced in 1990 by Arthur and Pawliszyn [29] and became commercially available in 1993. The basic SPME device consists of an extracting phase (normally of 5-100 μm thickness) immobilized on a substrate fiber (fused silica [29] or stainless steel [30]), and a syringe-like holder for the fiber. This technique is based on the analyte partitioning between the extracting phase and the sample matrix that can be water, air etc. The extraction efficiency depends on the distribution coefficient and the thickness of the coating phase. The absorbed target compounds can be thermally desorbed by exposing the fiber in the GC injector, or

eluted and dissolved in an appropriate solvent, if high-performance liquid chromatography (HPLC) used for determination of the target compounds [31].

One of the requirements of the design of a fiber coating is to ensure it has high hydrophobicity and good extraction capacity. SPME can be carried out in DI-SPME [29] or HS-SPME [32], depending on the polarity and volatility of the compounds of interest. DI-SPME is usually applied for polar or nonvolatile compounds, whereas HS-SPME is advantageous in sampling gases or volatile molecules. The range of SPME application is wide, e.g. in the environmental [33-35], biological [36, 37], and food [38, 39] areas, as long as a proper extracting phase and sampling mode are selected. SPME is a generally solventless versatile sample preparation technique. Automation of SPME with the help of an autosampler is available currently, allowing for improved precision and better repeatability and saving the labor in routine analysis as well.

SPME does suffer from some problems, such as short lifespan of the fused silica fiber, potential of stripped coatings, and commercial fibers are expensive. The instability and swelling of the coating phase in organic solvent or water hampers SPME in diverse applications. In addition, the limited types of commercial SPME fiber could not often meet expectations in practical analysis. However, since the innate merits of SPME are sufficiently attractive, much interest has been paid to the development of in-house coating phases to expand its application range.

1.3.2 Various configurations of SPME

1.3.2.1 In-tube SPME

In-tube SPME is a dynamic extraction configuration of SPME [40]. This technique uses an open tube capillary column with the extracting phase coated on its inner wall as the extraction device. Extraction occurs when aqueous sample is passed in one direction through the capillary and the preconcentration efficiency could be enhanced by repeating this aspirate-and-dispense step. The analytes extracted by the stationary phase of the capillary can be desorbed by introducing a flow elution solvent or a static solvent. This extraction device can be easily coupled to a conventional HPLC autosampler for on-line sample preparation, separation and quantitative analysis. So far, fiber-packed [41, 42], particle-sorbent packed [43, 44] and rod-monolith [45, 46] capillary have been developed to increase sample loading volume and adsorptive capacity, thus improving the extraction sensitivity and specificity. Conventional SPME is suitable at extracting volatile or semi-volatile organic compounds; in contrast, in-tube SPME is better suited for the analysis of semi-volatile or nonvolatile, thermal labile and/or very polar compounds.

A novel in-tube SPME taking advantage of a magnetic microfluid to preconcentrate analytes was proposed in 2012 [47]. Application of magnetic field to a SiO_2-supported Fe_3O_4 nanoparticles packed capillary column created different magnetic gradients, so the diamagnetic analytes were trapped in the regions where the field gradient was minimal, resulting in the adsorption of the analytes inside the SiO_2 phase. For desorption, the magnetization of the sorbent needed to be inverted. This

approach was demonstrated to enhance the extraction efficiency of in-tube SPME system from 10-30% to 70-100%.

The ease of automation for in-tube SPME would facilitate the hyphenation of on-line sample preparation and instrument analysis and provide a fast, sensitive, and high-throughput analytical method. Nonetheless, in-tube SPME is applicable for very clean samples, because the capillary can be easily blocked. Sample pretreatment such like filtration or centrifugation may be necessary before in-tube SPME is applied.

1.3.2.2 Microextraction in packed syringe (MEPS)

MEPS is a minimized SPE technique using an extraction procedure similar to in-tube SPME. The preliminary applications of MEPS were reported in 2004 [48, 49]. It is commercially available due to the innovative design that makes simple, fast and less expensive sample preparation possible. In a typical MEPS device, a very small amount (~1 mg) of sorbent is packed inside a microsyringe barrel as a plug, or loaded between the barrel and the needle. Such a miniaturized extraction cartridge is suited to handling low sample volumes, e.g., 10 μL, while a large volume of 1000 μL is also acceptable. Similar to SPE, a variety of sorbents including conventional silica materials and laboratory made sorbents is equally suitable for MEPS [50-52]. The MEPS procedures do not differ from conventional SPME, except that the sample solution can be passed through the sorbent more than once, which benefits the extraction recovery. The syringe format of MEPS can be connected on-line to GC or HPLC without further modification.

The MEPS cartridge is claimed to be reusable for approximately 100 times depending on the sample type. However, possible carryover effects should be reduced or eliminated prior to reuse. Although MEPS is overall a straightforward technique, some additional experimental factors, such as the number of extraction cycles and loading speed have to be optimized in order to achieve high extraction efficiency in a minimum extraction time.

1.3.2.3 Electrochemically-enhanced SPME (EE-SPME)

Inspired by the preparation of SPME coating phase through an electrochemical method, Wu and Pawliszyn proposed an electrochemically-controlled SPME (EC-SPME) method [53]. It was suggested that extraction and desorption of ionic analytes could be facilitated by cycling the potential applied to the conductive polypyrrole coating on a platinum wire for SPME. The redox and anion exchange properties of polypyrrole played an important role in this method, for the charge of the polymer would be tuned by the potential applied. It showed clear advantages for the extraction of polar, aromatic and charged chemical species. Nevertheless, a desorption step under electric field control was required for EC-SPME and thus the procedure could not be coupled directly to chromatography. To overcome this shortcoming, electrosorption-enhanced SPME (EE-SPME) was then developed that used activated carbon coated SPME fiber as the working electrode in a three-electrode system [54]. EE-SPME depends mainly on changing the molecular properties of analytes under an electric field which places them in a favorable state for extraction. In these techniques, much shorter time consumption for the

extraction process could be expected and selective extraction for analyes with different polarities and charges is achieved. The challenges that remain in this area may be the fabrication of stable and robust SPME fibers. Besides, the practical application of this technique is not convenient, because of the requirement of an electrochemical setup, which makes it difficult to automate.

1.3.2.4 Stir bar sorptive extraction (SBSE)

SBSE is a variant of static equilibrium SPME technique**.** Like the latter, it also avoids the use of solvent and is easy operated and time efficient, fulfilling the requirements of green chemistry. Most notably, the SBSE technique succeeds at overcoming the limit capacity of SPME fibers. Since the first implementation of SBSE in 1999 [55], it has been increasingly studied and applied for the determination of organic contaminants in aqueous matrices [56-58]. The initial version of SBSE was composed of a magnetic stirrer bar (10 and 40 mm of the length) coated with polydimethylsiloxane (PDMS) (with a volume of 55 and 219 μL), a thermal stable and high viscous liquid, as the sorptive coating, and a glass tube as the protector. Obviously, the extracting phase in SBSE was at much higher volume than in SPME [55]. The SBSE device can be immersed in, or suspended in the headspace above, sample solutions or other matrices for extraction. The analytes retained in the coating can be desorbed through thermal desorption or liquid desorption. With a commercial autosampler, the SBSE technique can be hyphenated to GC or HPLC. If the extraction takes place in HS mode, fully automated SBSE can be achieved with the aid of thermal desorption, as

demonstrated by Loconto [59]. Yu and Hu made use of a flow injection analyzer to realize automated SBSE-HPLC [60]. Comparatively, it takes a longer extraction time for SBSE than for SPME resulting from the larger volume of the coating phase in SBSE.

1.3.3 Dispersive solid-phase extraction (DSPE)

DSPE was originally introduced in 2003 as an innovation of SPE [61]. It was later patented with the name of "QuEChERS". In this approach, samples are preliminarily extracted by a small volume of organic solvent and then the solvent phase with extracted compounds was dehydrated and mixed with sorbent. The extraction takes place based on a liquid-liquid partitioning with solvent followed by a clean-up by dispersive SPE. Apart from its characteristics such as the simplicity, quickness, and low cost, it has been proven to be highly flexible so that it has a wide range of applications, including plants and food, biological fluids and various environmental matrices [62]. However, several factors affecting the extraction recovery such as the sample type, components, extraction solvent, type and amount of salt, pH and extraction time should be carefully studied in advance. On the other hand, research on this approach has seen many modifications to the original demonstrated procedure, e.g., combination of ultrasonic assisted extraction and DSPE [63] and DSPE with magnetic separation [64].

1.3.4 Micro-solid-phase extraction (μ-SPE)

Although the advantages of polymeric hollow fiber membrane had been unequivocally demonstrated in the HF-LPME, there have been reports on HF applications in relation to sorbent-based extractions. In 2006, a porous polymeric membrane-protected SPE approach, termed μ-SPE**,** was developed [65]. For preparation of a typical μ-SPE device, a specific amount (a few milligrams) of sorbent is packed inside an envelope made of porous HF membrane (HFM). The hydrophobic property and durability of the HFM ensure that the μ-SPE could maintain integrity in aqueous solutions [65] or soil slurry [66] for extraction under magnetic stirring and desorbed in organic solvents with the aid of ultrasonication. In 2011, Bagheri et al. proposed a new μ-SPE format [67]. They fabricated a polypyrrole-polyamide composite nanofiber sheet and used it directly as an extraction device with no need of additional sorbent. The extraction process was conducted in headspace mode. In general, membrane-protected extraction such as μ-SPE is more efficiently at reducing interferences in more complex sample matrices. However, if the sorbent is coated on the membrane, such protection may be weakened or compromised. Compared to conventional SPE, particularly when dealing with in-house sorbents, the μ-SPE approach is simpler in preparation, operation and is of higher time-efficiency.

1.4 Materials for miniaturized sample preparation techniques

Since the introduction of the leading sorbent-based extraction techniques as discussed above, method development and selection of the most appropriate

sorbent materials represent the two key issues related to the application of adsorption based analytical sample preparation. During the past few years, many of the research contributions to the area have been related to the discovery and application of novel materials as sorbents for the determination of persistent organic pollutants as well as emerging chemical contaminants and pollutants [68-70]. Rapid and more selective extraction and high enrichment of analyte have been the desired objectives that can be achieved with the use of appropriate sorbents, especially in SPME and SBSE (for which currently, only PDMS and PDMS/Ethylene glycol are available), and relevant approaches. For instance, these new sorbents serve to address some of the limitations of the commercial ones mentioned in the preceding paragraph concerning their adsorption capacity and reusability. In the following paragraphs, some recent achievements in novel materials based approaches to sample preparation are reviewed.

1.4.1 Graphene materials

Carbonaceous nanomaterial has always played an essential role in sorbent-based sample preparation technique [71, 72]. Carbon exists in a number of allotropic forms; however, in recent years much of the attention has been focused on graphene related materials.

Research on graphene, an isolated single atom plane of graphite, has seen a tremendous boost in its application to analytical chemistry since 2004 when an easy method to provide high quality graphene was devised [73]. Compared to traditional carbonaceous materials such like graphite or carbon nanotubes, graphene continues

to attract more and more attention. Due to its unique two-dimensional planar monolayer structure, graphene has demonstrated remarkable properties including high electron and thermal conductivity, superior mechanical strength and ultrahigh specific surface area (2630 m^2/g). Various simple and facile synthetic approaches of graphene and chemical modified graphene have been put forward in recent years. Consequently, advances in graphene chemistry have roused much research interest in analytical chemistry, e.g., in sensing systems like sensors and biosensors [74, 75]. However, the exceptional high surface area, hydrophobic and electrical properties and possibility of multifarious chemical modifications also allow this novel material to be a good candidate as sorbents or adsorbents. Other desirable features that make graphene suitable as sorbents have been reported. The planar geometry of graphene nanosheets allow them to be in close contact with the surrounding environment which is important in sorptive processes [76]. The wrinkly graphene surface can interlock well with the adsorbed targets [77].

The first application of graphene powder as SPE sorbent was presented by Liu et al. [78], who employed cartridges packed with graphene powder to extract eight chlorophenols from water prior to determination by HPLC with ultraviolet (UV) detection. The method showed promising results with high sensitivity and repeatability. Comparative studies demonstrated that graphene was superior to other sorbents including C18 silica, graphitic carbon, single- and multi-walled carbon nanotubes (SWCNTs and MWCNTs) in terms of adsorption capacity, facility of elution and recovery for the extraction of the analytes considered.

Graphene is hydrophobic; in contrast, graphene oxide contains additional hydroxyl, epoxy and carboxy polar moieties and is thus more polar and hydrophilic [79]. Graphene oxide is conceivably more effective for the adsorption of compounds with polar moieties. High surface-volume ratio and distinctive electronic transfer properties render them suitable as substrates to trap, preconcentrate and ionize analytes for matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS). Dong et al. for the first time investigated graphene as a novel matrix for small molecules in MALDI-TOF MS [80]. Their results showed that all the target molecules could be detected without apparent background noise. Graphene can be used as the SPE sorbent for extraction of target compounds which could be directly analyzed after enrichment. Graphene oxide also performed well in this application [81, 82].

Hybrid graphene sorbents have also been specially tailored for specific applications. Gulbakan et al. prepared aptamer-modified graphene oxide as a selective enrichment and detection platform for cocaine and adenosine from plasma samples [83]. A novel poly(ethylene glycol dimethacrylate)-graphene composite material was synthesized and applied as the extraction coating to a stir rod [84]. By stir rod sorptive extraction, 16 polycyclic aromatic hydrocarbons (PAHs) from water were preconcentrated. Notwithstanding the fact that graphene and graphene oxide can be used in a directly dispersed manner for extraction, and then collected by centrifugation, the process is tedious and possible irreversible aggregation of the graphene monolayer may reduce its effective contact area with the analytes. In view of this problem, a facile technique of retrieving magnetized graphene used as

sorbent to extract sulfonamide antibiotics from an aqueous dispersion was proposed [85]. The authors had graphene sheets immobilized onto silica-coated magnetic microspheres by simple adsorption with the aid of ultrasonication. In another study, a chemical precipitation method was adopted in the synthesis of a graphene incorporated magnetic nanocomposite [86]. The prepared sorbent could achieve EFs in the range of between 474 and 868 for five carbamate pesticides from an environmental water sample. Tan et al. prepared a disk using a three-dimensional nanocomposite consisting of graphene oxide as the precursor and gold nanoparticles that acted as building blocks [87]. The disk embedded into a stainless steel filter and assembled on the six-port divert valve of a HPLC system and served as an extraction unit. It displayed excellent extraction capability for heterocyclic aromatic amines due to the high specific surface and polar groups on the surface. Very recently, Zhang et al. proposed an approach to immobilize graphene layers onto the plastic microtube of poly(tetrafluoroethylene) with the use of polydopamine (PDA) as molecular linker of and layer-by-layer assembly of graphene [88]. The modified microtube was successfully used for in-tube SPME analysis of PAHs with low detection limits.

The high thermal and chemical stability and high mechanical strength of graphene are advantageous when used as an SPME coating phase. The main approaches used in the construction of graphene based SPME fibers are based on two considerations: physical deposition and chemical binding. The first application of graphene-based materials as SPME fiber coatings was reported in 2010 [89]. In this investigation, graphene was immobilized onto a stainless steel wire by repetitive immersions of a

stainless steel wire into the graphene sediment obtained by centrifugation of graphene ethanol solution. Later, the fabrication of graphene modified SPME fiber via sol-gel approach was reported for the first time [90]. Graphene oxide dispersion, tetraethoxysilane and hydroxyl terminated polydimethylsiloxane were used to prepare the sol-gel network. With a stainless steel as the substrate, the obtained graphene coated fiber displayed higher extraction efficiency and selectivity for polybrominated diphenyl ethers than several commercial SPME fibers. Graphene oxide has also been reported to be bonded to the surface of the silica with cross-linking agent 3-aminopropyltriethoxysilane layer-by-layer [91]. Electrochemical polymerization could also be a liable approach for immobilizing a composite coating made of conducting polymer and graphene on a metal wire as the substrate, as shown in some reports [92-94]. Similarly, electrochemical reduction of graphene oxide on a copper wire was reported, for the fabrication of an SPME fiber, and for the analysis of tricyclic antidepressants [95]. Such prepared SPME fibers possessed a long life time due to the strong adhesion of the coating onto the surface of the metal wire. Good extraction performance was reported.

1.4.2 Molecular imprinted polymers (MIPs)

Inspired by the creation of highly selective extraction methodologies in biological processes, researchers have taken advantage of the specific binding concept and developed a variety of sample separation approaches with the help of MIPs. MIPs can be described as the formulation of a polymer network with specific recognition and binding sites that are designed to be complementary to a template, which may

be either a biomolecule or a synthetic molecule [96]. In the manner of mimicking the function of an antibody, MIPs have been widely regarded as highly efficient and goal-targeted sorbents, e.g., as sensors [97, 98] and as chromatographic stationary phases [99, 100]. For sample preparation, MIP has mostly been used for SPE application, but also increasingly for SPME and its other various modes.

An MIP is normally obtained by polymerizing a functional monomer with the aid of a cross-linking agent in the presence of a template molecule which serves as an analogue of the eventual target analyte, and which is subsequently washed away from the polymeric network by an appropriate solvent. Normally, an MIP sorbent is designed to exhibit very strong, almost exclusive, selectivity towards a single target analyte [101]. However, occasionally, group selectivity and group enrichment are necessary for the analysis of a particular class of compounds. A recent report described the synthesis of a MIP with cypermethrin as template, and demonstrated the simultaneous determination of six pyrethroid insecticides from aquaculture seawater [102]. Group selective extraction by SPE was also exploited for the clean-up and pre-concentration of estrogens from aqueous sample with the help of a commercial AFFINIMIP sorbent [103]. In comparison with C18, the proposed MISPE method showed higher recoveries, demonstrating the suitability of MIP sorbents for extraction of a class of structurally related analytes.

Magnetic nanoparticles serve as good substrates for the preparation of small molecularly imprinted materials that combine the ability to recognize target molecules with magnetic responsiveness. Magnetic MIPs represent an important

sorbent in the area of magnetic sorptive extraction. The advances with development of polymerization technique have promoted the emergence of diverse magnetic MIPs for the purpose of sample preparation [104-107].

In-house SPME approaches with selective sorbents based on MIPs continue to contribute to the expansion of the application range of SPME. Since MIPs must be coated on suitable fibers for SPME, judicious design and skillful synthesis for surface activation and chemical modification are required. Hu et al. prepared a 17β-estradiol-MIP coated silica fiber by a multiple copolymerization method [108]. The silica fiber was activated by silylation and then immersed in the pre-polymerization solution for a fixed time. To obtain enough thickness of the MIP coating, the immersion was repeated several times. In DI-SPME mode coupled with HPLC detection, the home-made fiber showed specific selectivity for structural analogues of 17β-estradiol from hexane. When steel supports are used instead of silica fiber, silylation is still a prerequisite step to establish chemical bonding between the steel fiber and the MIP. MIP coated stainless steel fibers showed excellent lifespans of up to more than 200 times in some studies [109, 110].

MIPs can also be generated in the form of monoliths which may be used as alternative SPME fibers. MIP monoliths synthesized in situ in a capillary or column molds via the bulk polymerization method have been demonstrated to be useful sorbents [111-113]. To demonstrate integration of a MIP monolith with an SPME device, a novel thiamphenicol-MIP was prepared in a micropipette which could be directly fitted to a microsyringe tip for the extraction process [114]. A syringe

infusion pump was employed for facilitating sample loading and analyte elution. The eluent was transferred by a microsyringe to an HPLC system for analysis. This semi-automated MIP-SPME approach showed high recoveries of more than 90% and good reproducibility when extracting thiamphenicol from milk and honey samples. Zian et al. developed a facile approach for the preparation of glycoprotein-imprinted monolithic columns by combining a boronate-functionalized monolithic column with surface imprinting of dopamine, addressing the problems with protein imprinting, such as huge molecular size, poor mass transfer and so on [115]. Based on it, they prepared a horseradish peroxidase imprinted MIP column and used it in in-tube SPME. The resultant MIP column showed selective enrichment of horseradish peroxidase.

At present, only two extraction phases (PDMS and PDMS/Ethylene glycol) are commercially available for SBSE which greatly restrict wider applicability of the technique. In this regard, Zhu et al. incorporated MIP in an SBSE approach by the use of a phase inversion method to precipitate a MIP film on the surface of a commercial stir bar [116, 117]. The MIP film was Nylon 6 imprinted with monocrotophos [116] or L-glutamine [117]. The resultant stir bars had a thickness of 180 μm and 160 μm of the MIP coating, respectively. Compared to the original PDMS stir bar, the MIP device displayed specific extraction of template molecules and their structural analogues over a shorter equilibrium time. In the two studies, the MIP coated stir bars could be used for up to 100 times, although swelling in certain organic solvents was observed. MIP can be chemically bonded to the silylated substrate (glass capillary) surface through a copolymerization reaction

[118-120]. However, this approach gave a much thinner coating (about 20 μm). The resultant MIP stir bars were durable enough to be used for 40 to 50 times. They also exhibited relatively strong chemical resistance towards several conventional organic solvents. Generally, the operational procedure for preparing MIP coated stir bars seems to be universally applicable and easily performed, similar to the preparation of MIP coated SPME fibers.

1.4.3 Ionic liquids (ILs) and polymeric ionic liquids (PILs)

ILs are a special class of molten salts which are usually composed of an organic cation (quaternary ammonium or phosphonium, imidazolium, pyridinium, pyrolidinium, etc.) and relatively weak coordinating anions (halides, acetates, tetrafloroborate, hexafluorophosphate, etc.) [121]. The melting points of ILs are normally below 100 ^{o}C and some of them, like imidazolium cations based ILs, exist in the liquid phase at room temperature. ILs have emerged as a new group of coatings in the application of SPME because of their unique physicochemical properties which conventional solvents are lacking in, such as negligible vapor pressure, elevated thermal stability, tunable viscosity and miscibility with other solvents [122]. Depending on appropriate tuning of the structural component of the cations and anions, enhanced thermal stability of ILs is achievable, e.g., functionalization of the imidazolium cations such as with alkyl substitution can enhance the thermal stability of these liquids. Compared to conventional organic solvents, ILs have much higher viscosities. Some ILs are immiscible with water and instead are compatible with various organic species. These features make them

promising for sorptive extraction. In utilizing ILs as sorbent coatings, π-π interaction, dipolarity, hydrogen bonding formation and other types of interactions are usually considered as possible tunable characteristics.

The initial attempt to incorporate ILs in SPME was made in 2005 by Liu et al. [123]. The selected IL was physically adsorbed on a fiber which was used for HS-SPME. Washing out the used IL, and then recoating the fiber were necessary but tedious steps, after every extraction in this approach. Hsieh et al. adopted the Nafion membrane as a support to increase the IL amount immobilized on the fiber [124]. A notable improvement in sensitivity was obtained. Notwithstanding, matrix interferences from liquid samples can have negative influence on the integrity and extraction capacity of the IL coatings for DI-SPME.

An SPME approach based on direct incorporation of ILs onto a fused silica fiber through chemical bonding was presented later [125]. In this study, the researchers synthesized an IL containing Si-O groups, which assisted in linking IL to the modified silica fiber surface. Although the chemically IL-modified fiber had thermal stability of 220 ^{o}C and some durability (up to 16 extractions), it was not a very satisfactory choice for SPME. Liu et al. anchored two allyl functionalized ILs, 1-allyl-3-methylimidazolium hexafluorophosphate and 1-allyl-3-methylimidazolium bis(trifluoromethanesulphonyl)imide, onto a fused silica fiber via sol-gel and free radical cross-linking reactions [126]. The prepared fibers exhibited excellent acidic and basic stability indicating promising applications in the extraction of polar compounds. The two modified fibers were also thermally

stable at up to 290 ^{o}C and 380 ^{o}C, respectively. In the extraction of phenolic environmental estrogens and aromatic amines from water samples, these IL-coated fibers showed higher extraction efficiency than non-IL-coated fibers due to the strong electrostatic interaction, hydrogen bonding and π-π interactions provided by the special molecular structure of the ILs.

PILs are synthesized from IL monomers and, as expected, present some of the unique properties of ILs together with intrinsic polymeric characteristics [127]. Commonly, PILs are superior to ILs in the realm of thermal and chemical stability, so SPME fibers made from PILs have longer lifespan and higher reproducibility in practice. Anderson and co-workers initiated research on PILs in the application of SPME technology and their contributions demonstrated that PIL-based fiber coatings could be used in both HS and DI modes [128-132]. To achieve efficient and selective extraction, careful tuning of the polarity, hydrogen bonding ability, chirality and molecular configuration of the PILs are quite important. The routine approach for the construction of SPME fiber coatings is to keep the modified fibers immersed in the PIL solution for a fixed period of time. Feng et al. adopted an alternative surface radical chain-transfer polymerization technique and grafted poly(1-vinyl-3-octylimidazolium hexafluorophosphate) coating in situ onto a modified stainless steel wire [133]. The fabricated fiber had the advantage of relatively high stability that can be operated at 250 ^{o}C and good durability, indicated by the fact that it could be reused for 56 times. Not surprisingly, the polymerization process controlled the thickness of the prepared fiber. Thus the obtained thickness was only 5 μm, much thinner than the fibers made by the immersion or dipping

process. The extraction performance for benzene, toluene, ethylbenzene and xylenes in the HS mode, and phenols and PAHs in the DI mode demonstrated wide linear ranges, and low LODs.

So far, there are very few contributions with regard to the ILs in other SPME modes, for example in-tube SPME, implying the challenges in preparing ILs based coating phase in a capillary column. Earlier reports of ILs in in-tube SPME were related to their solvent and porogen roles in the sol-gel technique [134, 135]. Recently, Wang et al. prepared an IL-modified organic-polymer-based monolithic column by chemical grafting of the IL of 1-aminopropyl-3- methylimidazolium chloride onto the surface of the monolithic column [136]. The IL-monolith-based in-tube SPME was used for the extraction of acidic additives from soft drinks. Due to the presence of hydrophobic and anion-exchange groups on the sorbent, high extraction efficiency was yielded.

The use of ILs and PILs has made an important contribution in sample preparation. However, the availability of pure ILs including task specific ILs and their potential toxicity should be taken into account in preparing for the future advancement of ILs in routine analysis.

1.4.4 Metal-organic frameworks (MOFs)

MOFs are a new type of hybrid materials formed by the self-assembly of metal ions of clusters and polydentate bridging ligands, typically under mild conditions [137]. MOFs possess high surface area and porosity, as well as thermal and chemical

stability that making them promising for applications in catalysis [138], separation [139], chemical sensing [140], and so on. The virtually limitless combination of metals and ligands is advantageous for MOFs to address specific applications. Particularly, MOFs have been used for analyte pre-concentration and separation science for a few years.

The first example of utilization of MOFs as an SPME fiber coating was reported in 2009 [141]. In this work, the SPME fiber was fabricated by in situ hydrothermal growth of MOF-199 films on the etched surface of a stainless steel fiber. The fiber was applied to enrich benzene homologues in HS-SPME. Due to its unique structure, especially the pores and open metal sites and also the large surface area, the MOF-199 coated fiber achieved high enrichment factors (EFs) of up to 19613 after 20 min of extraction. However, the material was less efficient in humid atmosphere as a result of the water induced inactivation of the MOF-199. Besides, the application of the material was restricted to volatile compounds, which restricted its range of utility and applicability.

Later, MOF-5 was packed in tubes for in-field sampling and pre-concentration of the predominantly indoor air contaminant, formaldehyde [142]. With the aid of thermal desorption and GC-MS determination, the MOF-5 material showed excellent performance compared to other commercial sorbents for air analysis. However, it was noted that a relative humidity of more than 45% would decrease the adsorption efficiency of the material for formaldehyde significantly. In yet another study on MOF, both the SPME fiber and GC column were coated with ZIF-

8, for the extraction and subsequent separation of n-alkanes in environmental and biological fluid samples [143]. The molecular sieving effect due to the ZIF-8 pore size was exploited in the selective enrichment and chromatographic separation of the analytes. In any case, the size specific extraction feature suggested that for other kinds of compounds, MOFs with particular pore sizes and ligand and ionic properties, (such as polarity, basicity and coordinative saturation of the metal), may prove to be a versatile material for analytical applications.

Most MOFs are moisture sensitive and they can lose extraction activity and even the integrity of the crystal structure, due to the presence of water, as mentioned earlier. This is conceivably why many applications of MOFs in separation science field currently are focused on gas samples. ZIF-8 on the other hand is an interesting species amongst MOFs due to its exceptional thermal and chemical stability including in the presence of water from aqueous samples. Thus, ZIF-8 was used for the membrane-protected μ-SPE of PAHs in water samples [144]. Another water stable MOF, MIL-101 was fabricated in a polyetheretherketone tube and coupled to HPLC for the in-tube sorptive extraction of several drugs [145].

Hybrid MOF composites retain the advantages of MOFs, while endowing MOFs with additional features so as to facilitate their wider applicability. PDMS/MOFs have been prepared with the sol-gel technique and successfully coated on stainless steel wires [146] or stir bars [147] for SPME and SBSE applications, respectively.

Though the reported contributions has exploited the merits of MOFs that favor the adsorption process very well, some issues associated with MOFs such as lack of

diverse functional groups in their framework and difficulties of integrating them into various extraction devices or the durability of prepared extraction devices need to be resolved to improve their performance and facilitate the development of more novel sample preparation approaches.

1.5 Research objective and thesis organization

Achieving high sensitivity with a simple, easy and environmental friendly sample preparation approach is the goal of analytical chemistry, especially for the monitoring and control of environment pollution in which the compounds of interest are at trace concentrations. To this purpose, miniaturized sample preparation technique is proposed. It is an essential part of the current state-of-the-art of analytical science. Solventless microextraction is an important trend for future prospects of sample preparation technique. However, it is closely related to the innovation of extraction approaches and smart utilization of robust and efficient sorbents.

The objective of this research was to explore novel materials for the development of miniaturized sample preparation methods. The preparation and characterization of one MOF, MIL-101, and PDA derived materials were conducted, and the feasibility of their applications in adsorption based microextraction methods for the efficient determination of endocrine disrupting compounds in environmental water samples was investigated.

This dissertation is organized and structured into six chapters. Chapter One provides a general introduction of sample preparation techniques in environmental analysis, and then gives a brief overview of the microextraction techniques with a focus on sorbent based techniques. The innovative materials that show great potential in sample preparation field are also discussed in this chapter.

In Chapter Two, the preparation of MIL-101 and its use as a μ-SPE sorbent is reported. Owing to its high stability in water and organic solvents, MIL-101 was successfully exploited for determination of organochlorine pesticides (OCPs) from aqueous samples. The large pore size and high surface area endowed the material with good extraction capacity of the target analytes.

Chapter Three presents the use of nonionic surfactant, Triton X-114, as a surface modifier for MIL-101 crystal particles. The resultant MIL-101 was explored in dispersive micro-solid-phase extraction (dSPE) for the preconcentration of estrogens. The presence of Triton X-114 enhanced the stability and dispersion of MIL-101 particles in water and facilitated the collection of the sorbent along with the extracted analytes because of its cloud point phase separation effect.

In Chapter Four, a facile preparation route for surface coating on a stainless steel fiber with carbonaceous materials derived from PDA is described. The robust adhesion of dopamine to metal oxides ensured sufficient stability of the polymer coating. Carbonization treatment of the polymer coating resulted in a carbonaceous layer deposited on the fiber. The obtained carbon coated fiber was utilized for SPME and exhibited effectiveness in the extraction of OCPs from aqueous samples.

In Chapter Five, the preparation of magnetic nanoparticles with polymer (Fe_3O_4@PDA) and carbon shell (Fe_3O_4@C) based on self-oxidation of dopamine and carbonization of the PDA coating, is reported. The performance of the two magnetic sorbents in the extraction and determination of estrogens from environmental water samples in the form of magnetic solid-phase extraction was studied. Orthogonal array design was utilized to facilitate the optimization of the proposed sample preparation approach.

General conclusions drawn from this research study are summarized in Chapter Six. Also, some recommendations or suggestions for future research are included in this chapter.

CHAPTER 2. MICRO-SOLID-PHASE EXTRACTION OF ORGANOCHLORINE PESTICIDES USING POROUS METAL ORGANIC FRAMEWORK MIL-101 AS SORBENT

2.1 Introduction

Organochlorine pesticides (OCPs) belong to a primary subcategory of chemical pesticides. The use of these pesticides was very popular in agriculture, industry and domestic households. Due to the persistence and accumulation properties of these OCPs, many regulations and policies require them to be removed from the market. Indeed, some environmental monitoring studies demonstrated that the use of OCPs had decreased during the past decade [148, 149]. However, the wide presence of OCPs and their degradation products in various circumstances of human activities, such as the air [150, 151], water [152, 153], soil [154-156], aquatic organisms [157, 158] and food products [159], can still be observed.

For many years now, great efforts have been expanded to develop reliable, sensitive and convenient techniques to monitor trace OCPs with high accuracy. The sample pretreatment process is critical to analytical efficiency and analyte recovery, especially for those target compounds which exist at trace levels in various matrices. Apart from conventional liquid-liquid extraction, SPE and microwave-assisted solvent extraction, various microextraction methods have been innovatively employed for effective concentration of OCPs in aqueous samples before

instrumental analysis. These include emulsification microextraction [160], SDME [161], DLLME [162-164], SPME [165], SBSE followed by thermal desorption [166], magnetic solid-phase extraction [167] and so on.

As initially proposed as a variant of sorbent-phase extraction in 2006 [65], μ-SPE included the encapsulation of sorbents in a polypropylene membrane bag. The hydrophobic character of the membrane greatly reduces the loss of the sorbent and eliminates matrix interference to a larger extent than many other sampling approaches, in which the sorbents are normally unprotected. Thus, μ-SPE is suitable for processing relatively complex matrices. The development and application of effective materials that can fulfill extraction requirements is an important trend in the field of sample preparation [168, 169]. Since the invention of μ-SPE, different types of sorbents have been applied with this extraction approach for diverse applications, for example carbon nanotubes [65], commercial C18 bonded silica [170], graphite fiber [171] and activated carbon [172]. In previous research on the determination of OCP residues, the mostly used sorbents included silica [173], Florisil [174], graphene [175], and graphitized carbon black (GCB) [176]. As the demand for higher sensitivity and reuse of the sorbents become increasingly important, the exploitation of new useful materials deserves more attention.

MOFs have emerged as a new class of advanced hybrid crystalline materials with metal ions and organic ligands. Their promising properties of tunable tropology and porosity, structure flexibility, luminosity and high loading capacity have led to their

utilization in chemical detection and separation [177], catalysis [178], sensing and biomedical therapy [137] fields. Early explorations of MOFs in sampling and sample preparation demonstrated their potential for in-filed sampling and adsorption of volatile organic compounds (VOCs) from polluted air [141, 179]. However, the intrinsic shortcomings, e.g. moisture instability, of some MOFs limited their practical applicability range. Since the application of a copper(II) isonicotinate in 2006 [180], there hass been growing interest on the exploration of water- and solvent-stable MOFs for the development of efficient SPE [144, 145, 181-183], in combination with various analytical techniques. Hence the role of MOFs in the adsorption of emerging contaminants in aqueous solution, especially those with complex molecular configurations and low volatilities than VOCs could be studied. Moreover, the fabrication of homemade SPME fibers using MOFs [184-186] and hybrid MOF composites have also been reported [146, 187]. The application of MOFs in membrane-protected μ-SPE was initially attempted using Zeolite Imidazolate Framework 8 by Ge et al. [144]. This procedure was explored with copper(II) isonicotinate by Zhou et al. [188].

This work focused on the investigation of one type of MOF material which is highly stable in water and organic solvents, MIL-101 (Cr), for an efficient μ-SPE coupled with GC-MS method towards the trace analysis of OCP residues in environmental water samples. In previous research, Yang et al. studied the adsorption behavior of MIL-101 of fullerenes dissolved in toluene [189], extending the applications of MOFs from the consideration of small organic molecules to a wider range of analytes. Huang et al. reported the performance of Fe_3O_4@MIL-101 in removing

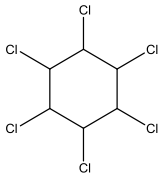
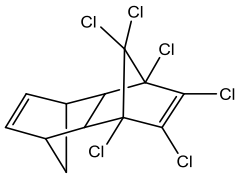
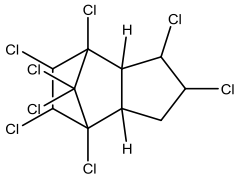
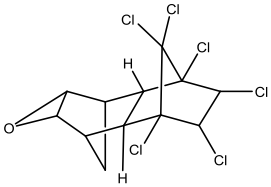
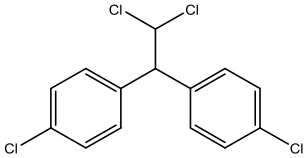
textile dyes from water [190]. MIL-101 was also used as a sorbent in dispersive SPE mode for detection of hormones in liquid cosmetics [191]. In another study, a hollow fiber based extraction device was prepared by the injection of dispersed MIL-101 into the fiber, and used for the extraction of polychlorinated biphenyls [192]. However, desorption of the hollow fiber consumed much more solvent (ca. 5 mL) than that for the membrane-protected μ-SPE (typically, μL range). Thus, we explored MIL-101 as the sorbent of the latter extraction format and used it for the determination of pesticides at trace levels in the environment. Factors related to the sample preparation performance were studied in order to establish its feasibility for real water analysis.

2.2 Experimental

2.2.1 Chemicals and materials

Analytical grade chromium nitrate nonahydrate and terephthalic acid were purchased from Alfa Aesar (Heysham, UK). Analytical grade sodium acetate was bought from Sigma Aldrich (St. Louis, MO, USA). HPLC grade ethanol, N,N-dimethylformamide (DMF), hexane, ethyl acetate, methanol, acetonitrile were obtained from Fisher (Loughborough, UK). The OCPs, aldrin, dieldrin, α-1,2,3,4,5,6-hexachlorocyclohexane (α-HCH), α-chlordane and p,p'-DDD (1 mg/mL each in methanol) were supplied by SPEX CertiPrep (Stanmore, UK). Commercial C8 and C18 (3 μm, 80 Å) silica sorbents were from Alltech (Deerfield, IL, USA) and Waters (Milford, MA, USA) respectively. Q3/2 Accurel 2E HF (R/P)

Table 2- 1 Physicochemical properties and characteristic ions of OCPs for their quantitative and quantitative analysis

Analyte	Structure	Mw	Log K_{ow}*	Characteristic ion (m/z)
α-HCH		290.83	3.8	181, 219
Aldrin		364.92	6.5	263, 265
α-Chlordane		409.78	6.1	373, 375
Dieldrin		380.91	5.4	263, 265
p,p'-DDD		320.04	6.02	235, 237

* log K_{ow} data are obtained from Syracuse Research Corporation's PHYSPROP database.

polypropylene (PP) sheet (157-µm thickness, 0.2-µm pore size) was purchased from Membrana (Wuppertal, Germany). Ultrapure water for the study was generated on an ELGA Purelab Option-Q system (High Wycombe, UK). A

MR3001K (Heidolph, Kelheim, Germany) magnetic stirrer was used to control the stirring rate during extraction.

2.2.2 GC-MS analysis

Analysis was performed on a Shimadzu (Kyoto, Japan) QP2010 GC-MS system equipped with a Shimadzu AOC-20i autosampler. A DB-5 (Agilent Technologies, Santa Clara, CA, USA) fused silica capillary column (30 m length x 0.25 mm internal diameter x 0.25 mm film thickness) was used for separation with helium as carrier gas at a flow rate of 1 mL/min. Chromatographic data were recorded and processed with GCMS Solution software (Shimadzu). The GC conditions were as follows: the injector temperature, 250 ^{o}C; the initial oven temperature was 80 ^{o}C (held for 1 min), increased to 240 ^{o}C at 20 ^{o}C/min (held for 5 min), then further increased to 270 ^{o}C at 5 ^{o}C/min, and a final increase to 300 ^{o}C at 20 ^{o}C/min (held for 3.5 min). The GC-MS interface was maintained at 250 ^{o}C. Splitless injection was adopted throughout the whole experiment. Data acquisition was performed firstly in full scanning mode from 50 to 500 m/z to confirm the retention times for the analytes. All standards and sample extracts were analyzed in selective ion monitoring (SIM). The selected ions for each analyte were as follows: m/z 181, 219 (α-HCH); m/z 263, 265 (aldrin); m/z 373, 375 (α-chlordane); m/z 263, 265 (dieldrin); m/z 235, 237 (p,p'-DDD).

2.2.3 Synthesis and characterization of MIL-101

MIL-101 crystals were synthesized according to the method reported by Guo et al. [193], with minor modification. Chromium nitrate nonahydrate (2 g), terephthalic acid (820 mg) and sodium acetate (102.5 mg) were added to 25 mL of ultrapure water and mixed homogeneously before being transferred to a Teflon-lined bomb. The Teflon-lined bomb was then sealed and put in an oven set at 200 ^{o}C for 12 h. The resulting fine green crystals were obtained by filtration and washed thoroughly with ultrapure water and DMF first. Then, the primary product was further treated by soaking in 100 mL ethanol in the Teflon-lined bomb and left at 100 ^{o}C for 10 h. The final product was filtered, washed by ultrapure water and dried at 80 ^{o}C for 24 h.

The as-synthesized MIL-101 was characterized as follows: powder XRD was conducted on a Siemens D5005 XRD instrument (Siemens AG, Karlsruhe, Germany) using Cu Kα=1.5418 Å radiation to investigate the XRD pattern of the MIL-101 crystals; Fourier transform infrared (FT-IR) spectrum of MIL-101 was conducted on a Varian 3100 system (Santa Clara, CA, USA). Sample was mixed and ground with KBr for FT-IR measurement in the wavenumber range of 4000-400 cm^{-1}. Nitrogen adsorption/desorption experiments were carried out at 77K using a Micromeritics ASAP 2020 surface area and porosity analyzer (Norcross, GA, USA) to determine the surface area, pore volume and pore size. The MIL-101 crystals were activated by evacuating in vacuum and heating to 523 K for 8 h to remove any physically adsorbed substances before measurement. The samples were

also characterized on a JSM-6701F field emission scanning electron microscopy (SEM) instrument (JEOL, Tokyo, Japan).

2.2.4 Preparation of the μ-SPE device

The μ-SPE device with sorbent materials enclosed was fabricated as reported previously [65]. Briefly, a clean PP sheet was folded and two of its open edges were heat-sealed. The sorbent (4 mg) was introduced to the envelope through the remaining open end that was then heat-sealed to secure the contents. The dimensions of the final envelope were 1.0 cm × 0.5 cm. The home-made μ-SPE devices were used directly without preconditioning in the subsequent extraction experiments.

2.2.5 Sample preparation

Separate stock solutions of each OCP compound in methanol (1 mg/mL) were prepared. Water samples were prepared by spiking ultrapure water with the respective stock solutions of OCPs to the desired concentrations of each analyte. The optimization of extraction parameters was conducted using the prepared working solutions. To evaluate the proposed method, unspiked and spiked genuine water samples collected from the Singapore River were analyzed.

2.2.6 Extraction procedures

A typical extraction process for optimizing the μ-SPE conditions was as follows: the μ-SPE device was first immersed in a glass vial with 10 mL water sample

(spiked at 10 ng/mL of each analyte), which was magnetically stirred at a rate of 1000 rpm for a prescribed time under ambient temperature. After extraction, the μ-SPE device was removed, washed with ultrapure water twice and then dabbed dry using lint-free tissue paper. Finally, the device was placed in 100 μL of elution solvent for desorption of the extracts with the aid of ultrasonication (Soniclean, Thebarton, SA, Australia). The process of desorption was assisted by sonication for a prescribed time. The used device was regenerated by washing with 200 μL elution solvent after each desorption to ensure that there were no residual analytes. The extracts (ca. 1 μL) were injected directly into the GC-MS system for analysis.

2.3 Results and discussion

2.3.1 Preparation and characterization of MIL-101

The original method of synthesis of MIL-101 was reported by Férey et al. [194]. For this method, hydrofluoric acid is normally a necessary additive that is critical in the coordination framework. There are alternatives, however. Recently, some researchers proposed the use of other mineralization agents instead of hydrofluoric acid [193, 195]. Their results showed that the new methods could be more efficient in removing the recrystallized terephthalic acid in the pores of the MIL-101.

MIL-101 was successfully synthesized using sodium acetate as additive [193] in the present work. The XRD pattern of the synthesized MIL-101 (Figure 2-1 (a)) is in accordance with the reported in the literature [194]. The simulated XRD pattern from the Cambridge Crystallographic Database Centre is shown in Figure 2-1 (b).

After extraction, the sorbent was also characterized by XRD (Figure 2-1 (c)). The relative intensity difference of the peaks at small angle might be due to residues of analytes or solvent molecules occupying the pores of the crystalline structure after the MIL-101 had been used for 20 times. The consistency of the peak positions in the XRD pattern by comparison with the original MIL-101 confirmed the retention of the crystalline structure. The crystalline morphologies of the prepared MIL-101 before and after utilization for twenty times were recorded by SEM (Figure 2-2) indicating no obvious difference between them. Also, the MIL-101 octahedral particle size was shown to be small (with diameter of 100-300 nm), which can facilitate the adsorption of analytes. The FT-IR spectrum of MIL-101 is shown in Figure 2-3. The band at 1400 cm^{-1} from the symmetric vibration of O-C-O indicated the presence of dicarboxylate linker within the MIL-101. The bands at 1016 and 750 cm^{-1} were due to the deformation vibration of C-H in benzene, while the band of 1510 cm^{-1} showed the stretching vibration of C=C bonds in benzene. The band of 590 cm^{-1} could be identified as the plane bending of COO- groups from dicarboxylate linker. The nitrogen adsorption isotherm of the synthesized MIL-101 is depicted in Figure 2-4. The specific surface area calculated according to the Brunauer-Emmett-Teller (BET) method [196] was 3278 m^2/g and the total pore volume was 1.66 cm^3/g. The pore size distribution estimated by the Barrett-Joyner-Halenda (BJH) method [197] was 3.5 nm, slightly larger than the large pores (3.4 nm) of the MIL-101 obtained from its crystalline structure [194].

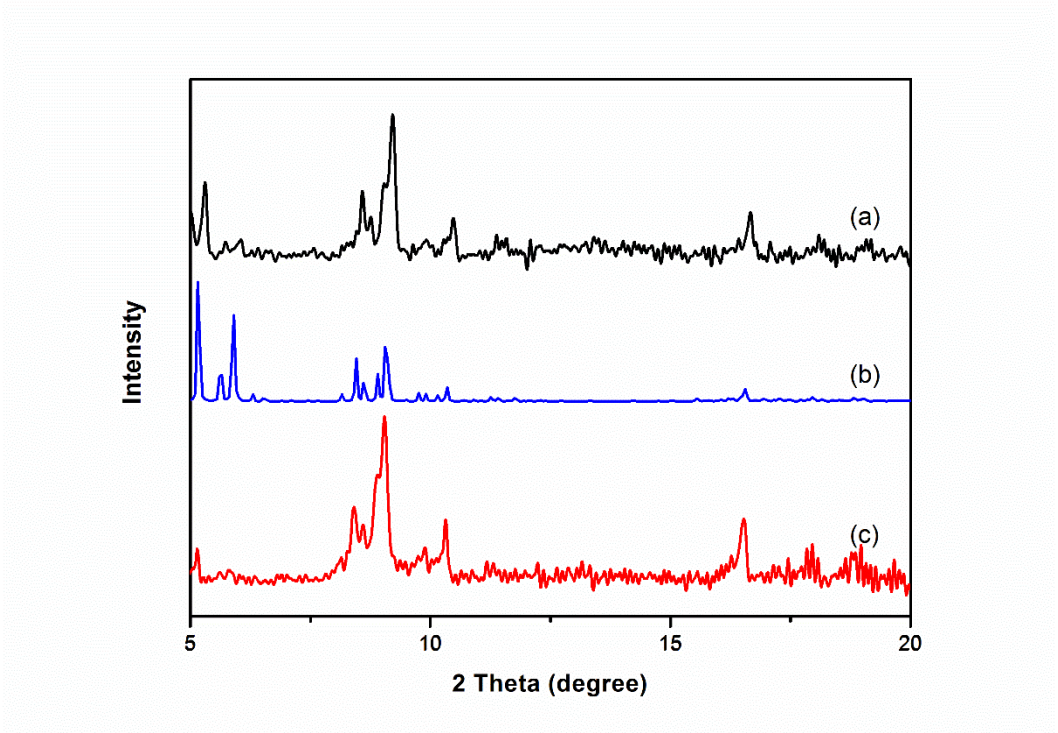


Figure 2- 1 X-ray powder diffraction patterns for (a) synthesized MIL-101, (b) simulated MIL-101 and (c) MIL-101 after twenty extraction/desorption cycles.

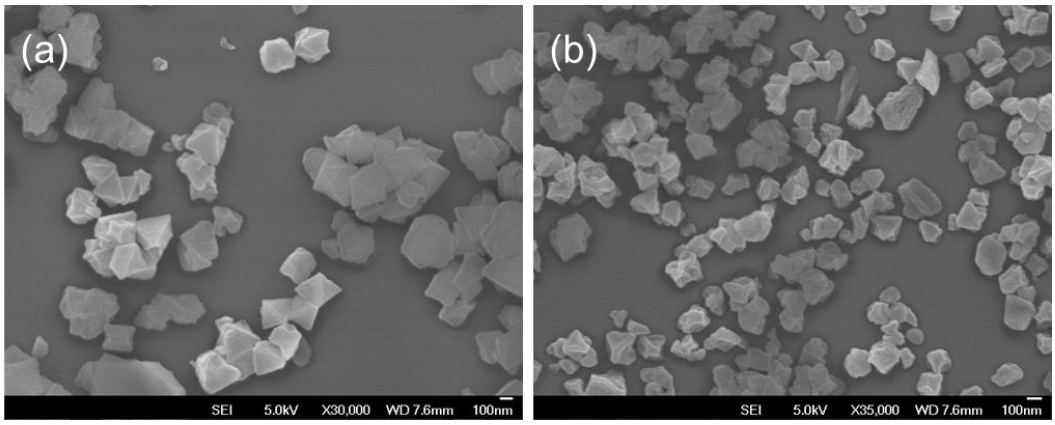


Figure 2- 2 SEM images of MIL-101 before (a) and after (b) utilization for about twenty times.

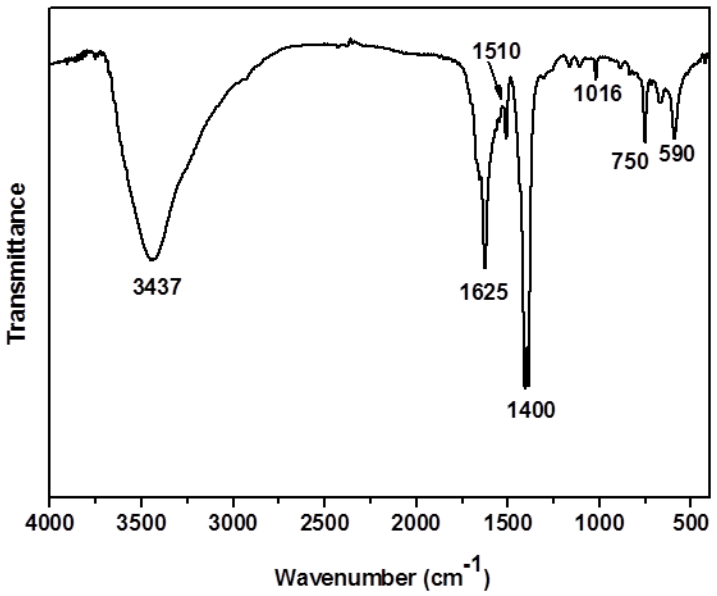


Figure 2- 3 FT-IR spectrum of MIL-101.

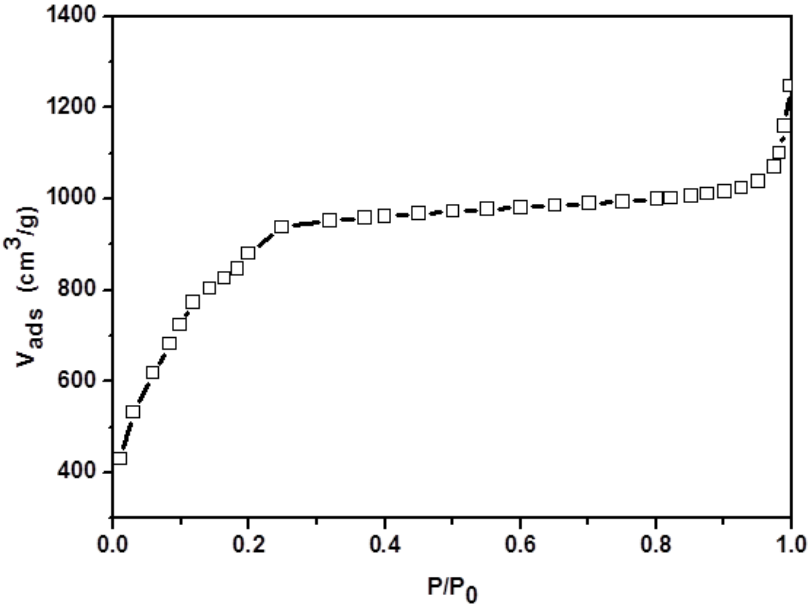


Figure 2- 4 Nitrogen adsorption isotherm at 77K for MIL-101. P/P_0 is the ratio of gas pressure (P) to the saturation pressure (P_0).

2.3.2. Optimization of extraction performance

The performance of μ-SPE is influenced by various factors, such as the amount of sorbent, sample matrix conditions, extraction time, desorption solvent and time, agitation speed and so on. The pH and salt concentration were not tested in detail here for several reasons. OCPs are non-ionizable compounds, and in aqueous medium their molecular volatilities and polarities will not be significantly affected by changing the pH of the sample matrix [198, 199]. In general, adding salt into sample phase could change the ionic strength of the sample matrix solution thereby increasing the partition of analytes onto the sorbent phase. Nevertheless, the salt effect does not lead to any enhancement of the extraction efficiency towards OCPs [200]. For α-HCH with a lower log K_{ow} of 3.8, enrichment could possibly become better, whereas the other OCPs in the study having higher log K_{ow} values of between 5.4 and 6.5 would result in negligible or even negative effects with salt addition, according to the observations made in previous reports [199, 201]. Besides, the addition of salt might cause increased viscosity and complexity of the sample matrix that would hamper the transfer of the analytes to the sorbent.

2.3.2.1. Desorption solvent

It has been proved that MIL-101 could remain stable when treated with various organic solvents [202]. In the perspective of the principle of like dissolves like, several solvents covering a wide range of polarity including hexane, ethyl acetate, hexane-ethyl acetate (9:1, v/v) and acetonitrile were tested to select the one giving the highest analyte recovery of the μ-SPE. The results for desorption are shown in

Figure 2-5, from which it can be seen that ethyl acetate performed better than the others. Ethyl acetate has medium polarity compared to the relatively polar acetonitrile and non-polar hexane, affording a more favorable performance in desorbing the analytes from MIL-101. Acetonitrile gave the lowest desorption efficiency due to its lower compatibility in terms of polarity with the hydrophobic OCPs. Although hexane is normally a good solvent for OCPs and is often used to avoid interference of polar substances in the sample matrix, it did not appear to be the optimal choice in the experiments. This might be ascribed to that MIL-101 has lower affinity for hexane and the polar open metal sites of MIL-101 exposed to the solvent environment have a greater affinity for polar solvents [203], than for the non-polar hexane which could not approach the adsorbed analytes, especially those inside the pores. Ethyl acetate was consequently considered to be the most suitable desorption solvent for further experiments.

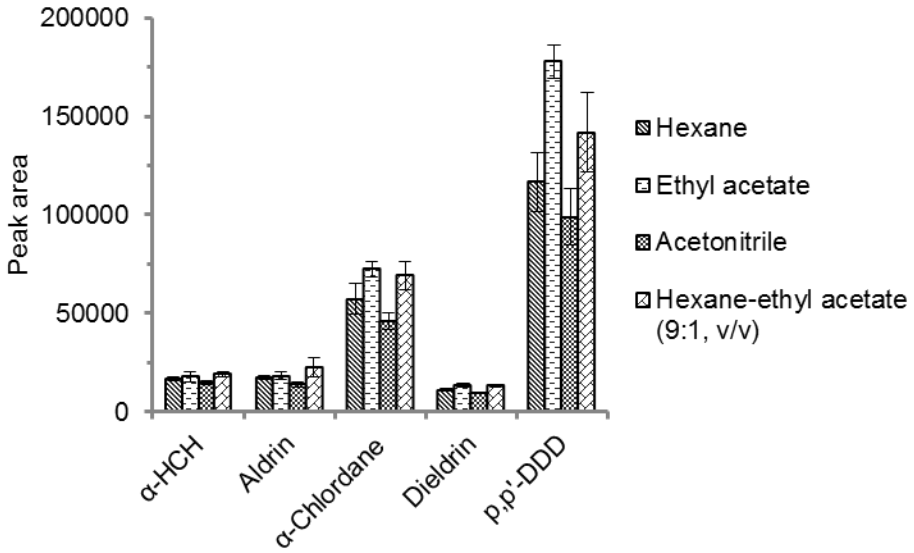


Figure 2- 5 Influence of desorption solvent on extraction of OCPs under the following conditions: Extraction time of 20 min and desorption time of 10 min.

2.3.2.2. Desorption time

The use of ultrasonication has been investigated as an efficient means to improve the desorption process [204]. The efficiency of ultrasound-assisted desorption depends on the parameters affecting the acoustic cavitation induced in the process [205]. Apart from the ultrasound power, the time taken also affects the total amount of analytes eluted. According to the literature and our previous experience [65], the influence of desorption time in the range of 5 to 30 min was investigated.

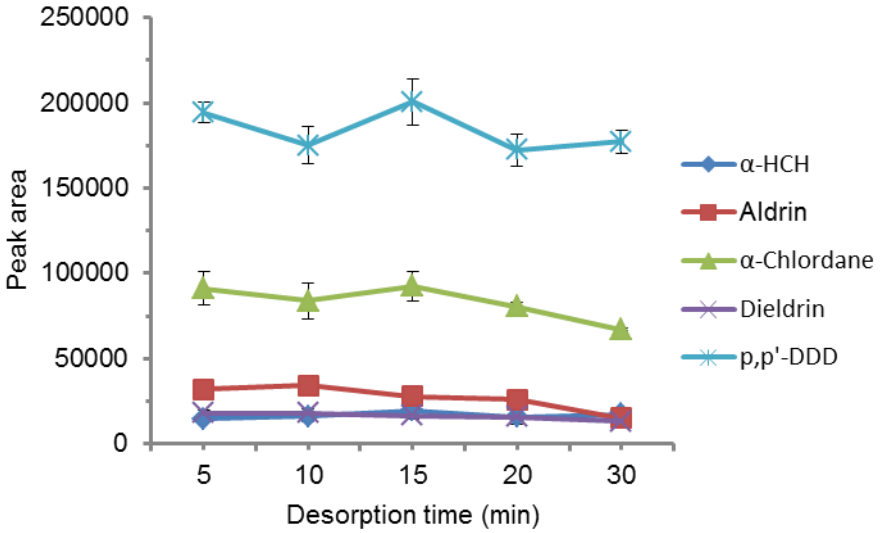


Figure 2- 6 Influence of ultrasonication time on extraction of OCPs under the following conditions: Ethyl acetate as desorption solvent and extraction time of 20 min.

As Figure 2-6 shows, there were only marginal differences in desorption efficiency for the various durations of ultrasonication. Yet a little enhanced desorption for α-HCH, α-Chlordane, Dieldrin and p,p′-DDD with the ultrasonic time increasing from 5 to 15 min could be observed. This was then followed by a slight decrease. For aldrin, the extended ultrasonication led to a lower desorption efficiency. The

result may be attributed to the relatively high hydrophobicity of aldrin among these analytes, indicating preference of the analyte to diffuse into the hydrophobic pores of MIL-101. It has been reported that ultrasonication could promote desorption of adsorbed molecules as well as enhance pore diffusion in the sorption process [205]. To ensure complete desorption within a reasonable duration in the overall context of analysis time, 15 min was selected as the most favorable.

2.3.2.3 Extraction time

In μ-SPE format, the sorbent is enclosed in a membrane bag; therefore its sorption behavior is based on the equilibrium of mass transfer between sample matrix and sorbent rather than exhaustive extraction like conventional cartridge- or disc-based SPE.

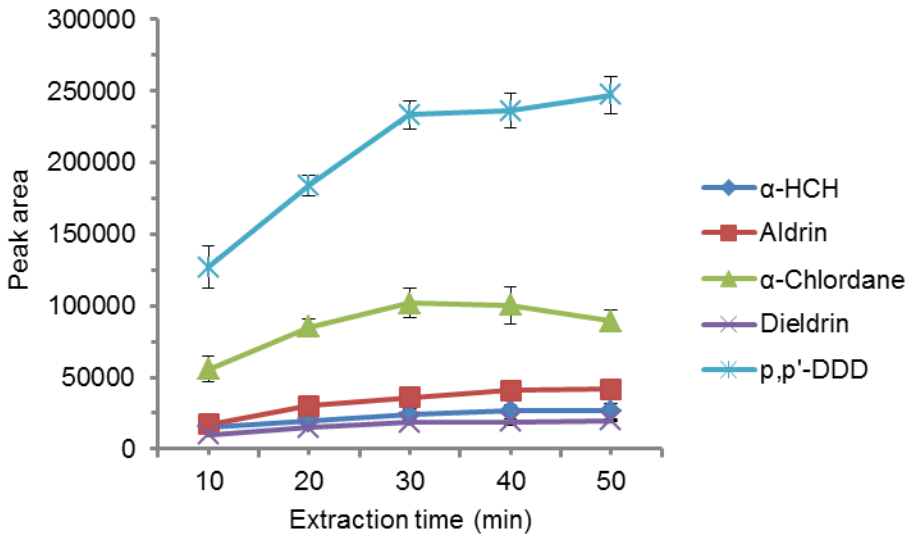


Figure 2- 7 Influence of extraction time on extraction of OCPs. Conditions: Ethyl acetate as desorption solvent, and desorption time of 15 min.

The extraction time profile is shown in Figure 2-7. It can be seen that equilibration for the analytes were approached at approximately 30 min under constant magnetic stirring. Only a slight impact on the peak areas were observed as the extraction time was extended beyond 30 min. This type of behavior has been observed previously in our laboratory [65]. Since it is not practical to carry out extraction for too long, 40 min was chosen as a reasonable compromise to ensure satisfactory results.

2.3.2.4 Sorbent comparison

The present study aimed to take full advantage of the MIL-101 sorbent to gain favorable extraction and preconcentration performance for the trace analysis of OCPs in water samples. Carbon materials have been widely used in the determination of OCPs in various real samples. For instance, GCB and commercial C18 cartridges have previously been used as sorbents for OCP extraction by SPE and matrix solid phase dispersion extraction [176, 206]. Here in the study, C8 and C18 silica sorbents were selected for direct comparison to evaluate the extraction performance of MIL-101 under identical conditions. The extraction devices with C8 and C18 sorbents were prepared in the same way as for the MIL-101. C8 and C18 sorbents (4 mg each) were packed in membrane bags and tested for the extraction of OCPs under the optimized conditions obtained above. The results in Figure 2-8 indicate that MIL-101 performed better than the other two sorbents. For MIL-101, its enrichment capacity could lie in two kinds of adsorption: pore encapsulation, and surface adsorption by the coordinatively unsaturated site and π-π interaction. The large pores (~3 nm) of MIL-101 are conceivably able to

accommodate or partially accommodate OCP molecules, according to the previous observation of adsorption affinity shown by cyclodextrin functionalized silica sorbent towards certain OCP compounds as a result of geometry fit [207]. It is noted that MIL-101 displayed relatively higher adsorption recovery of α-chlordane, dieldrin and p,p′-DDD, than aldrin and α-HCH. It could be speculated that better size fitting of the analytes and the pore structure of MIL-101 would result in higher adsorption efficiency, while bulky steric configurations would impede molecular diffusion. On the other hand, the unsaturated sites of Cr(III) in MIL-101 have adsorption affinity with electron rich analytes, for example, those with aromatic rings or double bonds. For C8 and C18, the adsorption primarily depends only on van der Waals' interactions between the sorbents and the analytes, and may be relatively less efficient.

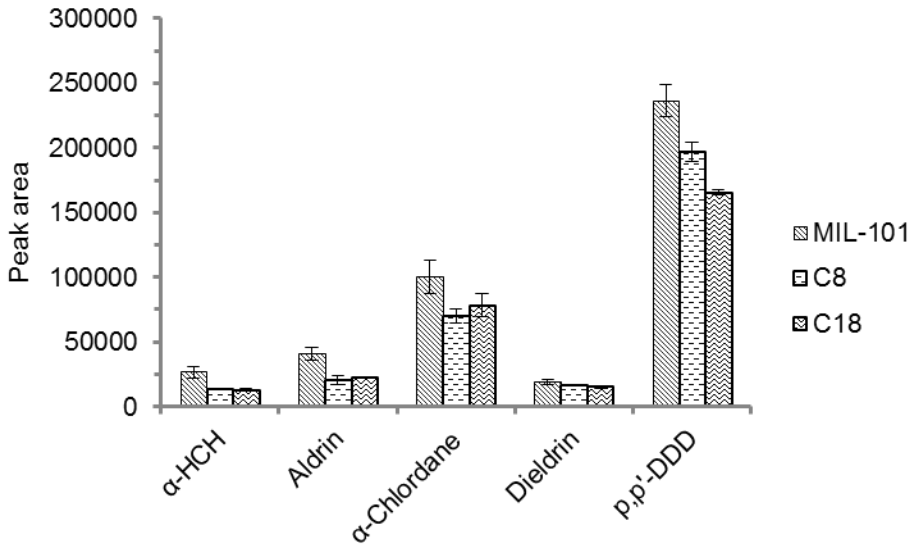


Figure 2- 8 Comparison of the extraction efficiency of MIL-101 with C8 and C18 sorbents for OCPs.

2.3.3 Method evaluation

Spiked water samples were repetitively (n=3) analyzed to determine the linearity, LODs, EFs, limits of quantitation (LOQs) and precision (relative standard deviations, RSDs) under the optimized extraction conditions (Table 2-2). The linearity was studied over a concentration range of 0.05 and 50 ng/mL for α-HCH and 0.1 and 50 ng/mL for aldrin, α-chlordane, dieldrin and p,p′-DDD with coefficients of determination (r^2) ≥ 0.9946. The LODs for these analytes calculated at a signal-to-noise (S/N) ratio of 3 by gradually decreasing the spiked concentrations were from 0.008 to 0.016 ng/mL and LOQs obtained from the lowest concentration of linearity, at S/N=10, ranged from 0.010 to 0.074 ng/mL. The precision of this method was determined to be 4.2-11% for three replicate experiments of working samples at a concentration of 10 ng/mL.

Table 2- 2 Linearity, coefficients of determination, LODs, LOQs of the proposed method for OCPs

Analyte	Linear range (ng/mL)	r^2	EF	LOQ (ng/mL)	LOD (ng/mL)	RSD[a] % (n=3)
α-HCH	0.05-50	0.9997	16	0.026	0.008	11
Aldrin	0.1-50	0.9954	22	0.032	0.0075	10
α-Chlordane	0.1-50	0.9950	59	0.017	0.0025	4.2
Dieldrin	0.1-50	0.9946	50	0.074	0.016	11
p,p'-DDD	0.05-50	0.9988	59	0.010	0.003	6.7

[a] Calculated from working samples with spiked concentrations of 10 ng/mL of each OCP.

Table 2-3 summarizes the analytical characteristics of some reported analytical methods along with this study for the extraction and determination of OCPs. Compared to SBSE [208], SPE [176, 209-211] and SPME [165] methods, the proposed method showed good or comparable analytical characteristics, and consumed a relatively small amount of sorbent. The results suggest that the μ-SPE method with MIL-101 coupled to GC-MS is reliable and sensitive for trace analysis of OCPs in environmental samples. μ-SPE also allows the tailoring of sorbents to specific analytes or classes of analytes.

2.3.4 Real sample analysis

Real water samples collected from the Singapore River which had been stored at 4 ^{o}C in the dark were analyzed by the present method without any prior treatment. Experimental parameters were as follows: 10 mL water, extraction time 40 min, desorption time 15 min, stirring rate of 1000 rpm and no adjustment of pH and ionic strength. The relevant results are summarized in Table 2-4. However, the chromatogram for genuine river water sample showed no apparent peaks of the selected analytes indicating their probable absence, or presence below the LODs established in this work. After spiking the river water at a concentration level of 5 ng/mL of each analyte, subsequent extraction and analysis clearly showed five peaks (Figure 2-9), as expected. Relative recoveries (defined as the ratios of the GC peak areas of the respective spiked river water sample extracts to spiked ultrapure

water extracts) were calculated to be between 87.6 and 98.6%, implying very low matrix interferences when dealing with water samples, indicating that the membrane of the μ-SPE device afforded significant protection of the sorbent. Satisfactory RSD values of < 10% were obtained.

2.4 Conclusions

The present work investigated the mesoporous metal-organic framework, MIL-101, as a sorbent in the application in μ-SPE of five OCPs. Its stability in water and various solvents allowed MIL-101 to be used in the sample preparation of aqueous samples. The large pore size and high surface area allowed the material with the capacity to extract OCPs from water samples. Combined with GC-MS detection, satisfactorily low limits of detection of 0.0025 to 0.016 ng/mL for the five OCPs were achieved when 4 mg of MIL-101 was used to extract from 10 mL sample solution. The extraction device could be reused for about twenty times with acceptable RSDs of between 4.2 to 11%. This study explored the successful application of MIL-101 for the trace analysis of OCPs present in relatively complex water samples. Conceivably, the same material may be used for the extraction of other relatively nonvolatile analytes from aqueous samples.

Table 2- 3 Comparison of the proposed method with other analytical methods for OCPs.

Analytical method	Sample	Sorbent material	Eluent	LOD (ng/mL)	RSD %	Ref.
HS-SBSE/GC-MS	water	PDMS (35 μL)	Toluene/acetonitrile (1.5 mL)	0.02-0.38	4.9-12.5	[208]
Magnetic SPE/GC-ECD	honey and tea	MFCNT (10 mg)	Ethyl acetate (200 μL)	0.0013-0.0026	3.7-5.5	[209]
SPE/MDGC/GC-MS	water, rice, tea	DMIP (150 mg)	Dichloromethane (12 mL)	0.021	0.37	[210]
SPE/GC-ECD	sediment	GCB (0.5 g)	Acetone/acetonitrile (4 mL)	0.002	1.2-3.4	[176]
μ-SPEE/GC-ECD	water	TiO_2 nanotube (-)	Dichloromethane (-)	0.0097-0.1	7.0-9.12	[211]
SPME/GC-MS	water	Graphene	-	0.00169-0.0083	4.7-10.6	[165]
μ-SPE	water	MIL-101 (4 mg)	Ethyl acetate (100 μL)	0.0025-0.016	4.2-11	This work

Table 2- 4 Analytical results for extraction of OCPs in real water sample

Analyte	Unspiked river water	Spiked river water at 5 ng/mL	
	Concentration detected	Relative recovery (%)	RSD (%) n=3
α-HCH	N.D.[a]	97.8	1.3
Aldrin	N.D.	98.6	9.2
α-Chlordane	N.D.	88.0	2.8
Dieldrin	N.D.	87.6	3.5
p,p'-DDD	N.D.	95.3	9.0

[a] Not detected.

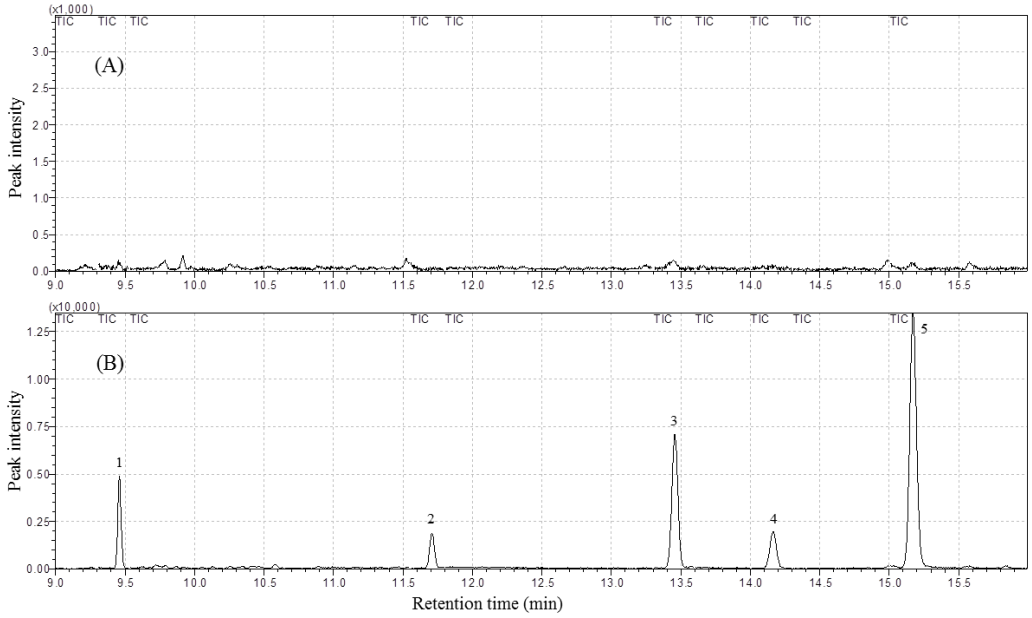


Figure 2- 9 GC-MS-SIM traces of (A) extract of river water sample; (B) extract of water sample spiked with OCPs at concentration levels of 5 ng/mL of each. Peak identities: (1) α-HCH, (2) aldrin, (3) α-chlordane, (4) dieldrin, (5) p,p'-DDD.

CHAPTER 3. PERFORMANCE OF MIL-101 AFTER SURFACTANT MODIFICATION IN THE EXTRACTION OF ENDOCRINE DISRUPTING CHEMICALS FROM ENVIRONMENTAL WATER SAMPLES

3.1 Introduction

In the past few years, MOFs have received huge attention in various fields, such as gas storage or separation, catalysis, biomedical therapy and electrochemistry [212-215], owing to their high surface-to-volume ratios and unrivalled degree of tenability. Explorations of MOFs in the analytical chemistry field show interesting potentials as SPE sorbents, MALDI-MS matrice, chromatographic stationary phases, and as biosensors [143, 216-219]. Certain types of MOFs have properties which endow them with humidity or chemical stability, so that they can be easily utilized in practice. However, processing or formulation of MOFs for more diverse purposes has emerged as a new focus of research interest. For instance, MOFs based core-shell nanostructures or hybrid materials have demonstrated promising applications [220-222]. These materials can be obtained by post-modification or incorporating additional functionalities during synthesis.

Research on the use of MOFs in analytical chemistry, particularly sample preparation, has involved different types of MOFs. These MOFs have the common advantages of large surface area and well defined internal pores. Moreover, almost

all of them possess high hydrophobicity, which is an advantage when they are utilized for aqueous samples and could ensure efficient trapping of nonpolar analytes, such as PAHs. So far, water stable ZIFs have been explored in μ-SPE [144, 223]; besides, magnetic assisted extraction approaches using functionalized MOF-5 and MIL-101 have also been reported [182, 221]. It is well known that the MOFs with aromatic organic linkers in the frame structure have strong affinity to the analytes with carbon-carbon double bonds and condensed rings. For polar analyte enrichment, it has been suggested that hydrogen bonding contributed to the extraction performance in the study of Fe_3O_4 nanoparticles decorated MOF-5 sorbent [221]. In spite of some successful examples of enrichment of polar compounds, more work on MOFs in this area is still needed. Specifically, the hydrophobic characteristic of the MOFs may impede their full dispersibility in solution, and thus their contact with the analytes of higher solubility in water. Hence it could be desirable to improve the dispersibility of MOFs without decrease their stability in water and extraction capability.

Surface modification is a common strategy to strengthen water dispersibility and reduce protein binding of the nano-MOFs designed for biomedical applications [224]. Lin et al. initially described a general method of coating nano-MOFs with silica shell via a sol-gel approach [225]. In this case, a pre-modifying polyvinylpyrrolidone layer on the surface of the MOF crystals was necessary for the success of silica shell modification. In another report, Cai et al. reported the preparation of chitosan coated magnetic nanoparticles sorbent. It was found that the positively charged chitosan coating not only contributed to the extraction of

perfluorinated compounds but also helped with the dispersibility and anti-interference ability of the sorbent [226]. Because of these merits, introducing suitable modifiers, for example, a polymer shell to the surface of selected MOFs would ameliorate their dispersion behavior and slow down their aggregation. In this work, we explore the potential of surface modification of MIL-101 with surfactant molecules to improve its enrichment performance toward EDCs in environmental water samples.

Recently, the noncovalent interactions between MIL-101-NH_2 (Fe) and florescent dyes, and the surface modification strategy of the material with comb-shaped copolymers were studied [227]. Their results suggested that the dye molecules could effectively bind and assemble on the surface of MIL-101-NH_2 (Fe) through electrostatic attraction and hydrophobic interaction; the latter was evidently significant by the cooperative binding behavior and the formation of surface hydrophobic assemblies. Moreover, such interactions played crucial roles in the binding and grafting process of the polymers. Triton X-114 is non-ionic surfactant and exhibits phase separation in solution above a certain temperature (ca. 23-24 ^{o}C) called the cloud point. Extraction based on the enhanced solubility of targets in the surfactant phase referred to as CPE has been exploited intensively [228]. Triton X-114 has also been exploited to improve the dispersibility of nanomaterials, e.g., carbon nanotubes [229]. It was found that the surfactant was adsorbed on the carbon nanotube surface with a monolayer coverage, and hydrophobic and π-π interactions were revealed to be the dominant mechanism. Considering that MIL-101 mainly displays hydrophobicity on the outer walls of its framework and Triton X-114 has

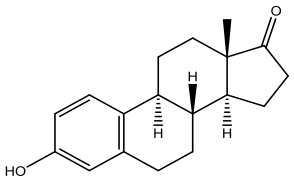
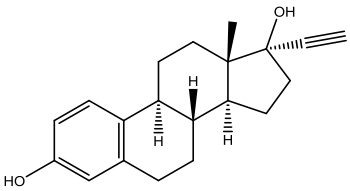
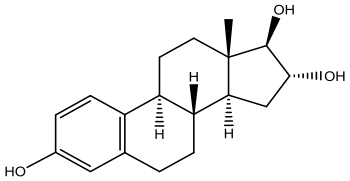
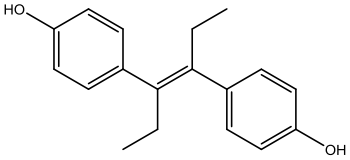
strong affinity with the aqueous environment, Triton X-114 molecules may adsorb on its surface with their nonpolar tail groups while the hydrophilic head groups face outward into the solution, thereby increasing the dispersiblity of MIL-101 in aqueous solutions. In addition, CPE could provide the potential of enhanced extraction of the analytes due to the micelle structure, which favors the latter's interaction with hydrophobic compounds, and improves analyte retrieval driven by temperature induced phase separation.

This work aimed to develop an effective sample preparation method based on Triton X-114 modified MIL-101 as sorbent for dSPE. Firstly, the use of nanomaterials in dSPE is advantageous taking into account their desirable properties. Moreover, a synergistic enhancement in the extraction performance is expected to occur due to the CPE process that takes place simultaneously. Four EDCs, estrone (E1), 17α-ethynylestradiol (EE2), estriol (E3) and diethylstilbestrol (DES) were selected as model analytes to examine the feasibility of the proposed method, because of their carcinogenicity, potential interfering effects of the endocrine system of human and wildlife [230, 231]. With the combination of the proposed preconcentration approach and GC-MS, the performance of the proposed method was evaluated.

3.2 Experimental

3.2.1 Chemicals and materials

Table 3- 1 Structures and relevant physicochemical properties of analytes

Analyte	Structure	Mw	Log K_{ow}*	Characteristic ion (m/z)
E1		270.37	3.13	218, 257, 342
EE2		296.41	3.67	285, 300, 425
E3		288.39	2.45	345, 386, 504
DES		268.36	5.07	383, 412, 413

* log K_{ow} data are obtained from Syracuse Research Corporation's PHYSPROP database.

E1, EE2, E3 and DES were all purchased from Sigma Aldrich (St. Louis, MO, USA) with purity of ≥ 99%. N-methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA) (≥ 98.5%) and Triton X-114 were also purchased from Sigma Aldrich. Pyridine (≥ 99%) was bought from Merck (Darmstadt, Germany). Other chemicals used in this chapter were the same as those described in Chapter 2.

3.2.2 GC-MS analysis

Separation and analysis of the EDCs were performed using a Shimadzu (Kyoto, Japan) QP 2010 Ultra GC-MS system coupled with a Shimadzu AOC-5000 auto sampler. A DB-5MS (Agilent Technologies, Santa Clara, CA, USA) fused silica capillary column (30 m length × 0.25 mm i.d. × 0.25 μm film thickness) was used for separation with ultrapure helium as carrier gas. Chromatographic data was recorded and processed with GCMS Solution software (Shimadzu). All the sample injections were conducted in splitless mode. In a typical GC-MS run, the instrumental conditions were set as follows: the injector temperature was 300 ^{o}C and the detector was kept at 250 ^{o}C with a helium gas flow rate of 1.1 mL/min. The column temperature program run was started at an initial oven temperature of 50 ^{o}C (1 min hold time), increased to 150 ^{o}C at a rate of 20 ^{o}C/min, and further increased to 280 ^{o}C (3 min hold time) at a rate of 10 ^{o}C/min. Finally, the temperature was raised to 300 ^{o}C at a temperature ramp of 10 ^{o}C/min and held for 7 min. The GC-MS interface was maintained at 300 ^{o}C. Full MS scanning mode was exploited across a mass range of between 50 and 500 m/z to confirm the retention times for target compounds. In consequent runs, the MS was operated in SIM mode. The selected ions for each analyte were as follows: m/z 218, 257, 342 (E1); m/z 285, 300, 425 (EE2); m/z 345, 386, 504 (E3); m/z 383, 412, 413 (DES).

3.2.3 Synthesis of MIL-101

The synthesis procedures of MIL-101 were the same as described in Chapter 2.

3.2.4 Characterization

Powder XRD, FT-IR and SEM characterization of the prepared MIL-101 was performed on the instruments used in Chapter 2.

3.2.5 Procedures of dSPE

Giving the participation of Triton X-114 molecules in dSPE, the extraction process combines the advantages of dSPE and cloud point induced phase separation simultaneously. First, 1 mg of MIL-101 was added into the 10 ml water sample that was spiked at 9 ng/mL of each analyte and adjusted in advance to have a prescribed concentration of Triton X-114. Subsequently, the solution was ultrasonicated for a certain period in the course of which manual shaking was applied to assist the formation of a homogenous solution and the water bath temperature was maintained around 18 ^{o}C to 20 ^{o}C. The solution was then subjected to vortex mixing for a prescribed time to ensure sufficient contact between the analytes and the resultant hybrid sorbent. Subsequently, it was immersed in a water bath set at 35 ^{o}C for 10 min. After centrifugation for 5 min at 4000 rpm, the sorbent was separated from the aqueous matrix. The sorbent with adsorbed analytes was eluted with 150 μL solvent ultrasonically and centrifuged at 4000 rpm for another 5 min. One hundred and twenty-five microliter of the supernatant was collected in a glass insert.

The eluate obtained was dried with a gentle stream of nitrogen gas. After that, 25 μL pyridine and 25 μL MSTFA were added and the mixture conditioned at 70 ^{o}C

for 30 min to derivatize the analytes. Finally, 1 μL of the solution was injected into the GC-MS system for analysis. Figure 3-1 illustrates the extraction process.

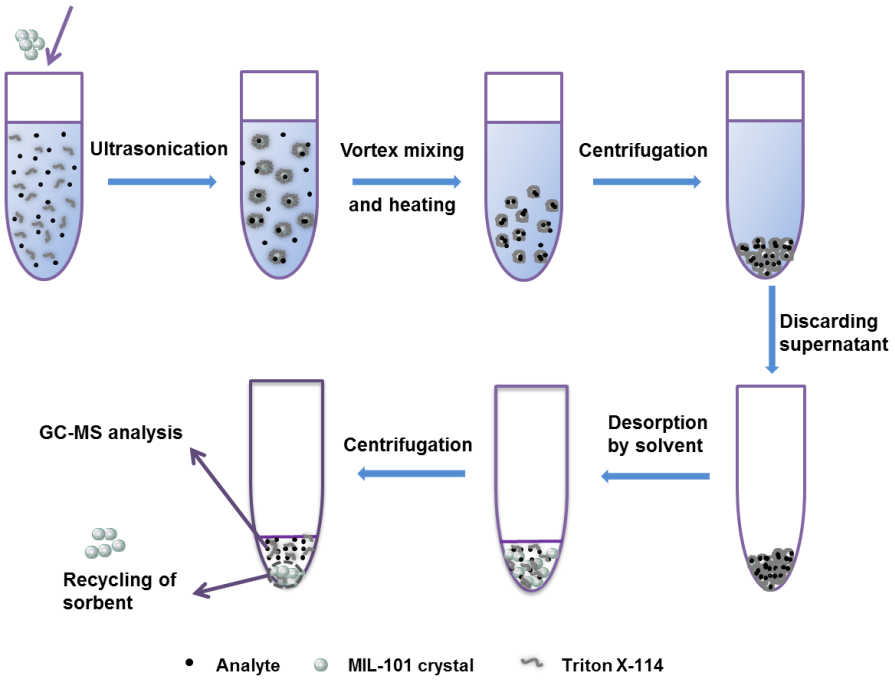


Figure 3- 1 Schematic of the extraction process.

3.2.6 Sample preparation

Stock solutions of individual EDCs were prepared at a concentration of 1 mg/mL in methanol and stored at 4 ^{o}C in the dark. The working solutions were prepared daily by appropriate dilution of the stock solutions with ultrapure water to desired concentrations. The pH of sample solutions was adjusted with 1 mol/L HCl or NaOH solutions. Tap water in our laboratory and the domestic water from Singapore River were collected in clean bottle and stored in the dark at 4 ^{o}C until

use. The river water containing many suspending particles was filtered through 3 μm filter papers (Whatman, Maidstone, Kent, UK).

3.3 Results and discussion

3.3.1 Synthesis and characterization of MIL-101

Powder XRD pattern of the synthesized MIL-101 was in good agreement with the result in the literature [194], suggesting successful synthesis of the material. The XRD pattern of the MIL-101 after being used in the extraction procedure is also displayed in Figure 3-2. In addition, FT-IR spectra of MIL-101 pre- and post-extraction are shown in Figure 3-3. Both of them matched well and thus revealed good stability of MIL-101 through the proposed extraction process. The crystal size and morphology were examined by SEM (Figure 3-4). It clearly showed that MIL-101 had octahedral structures with an average size of about 200 nm. The TEM images of MIL-101 without and with surfactant modification were recorded (Figure 3-5). The framework morphology of MIL-101 was not significantly changed after the adsorption of Triton X-114. However, it can be observed that the MIL-101 crystals after modification became slightly rounded and appeared to be covered by a thin film.

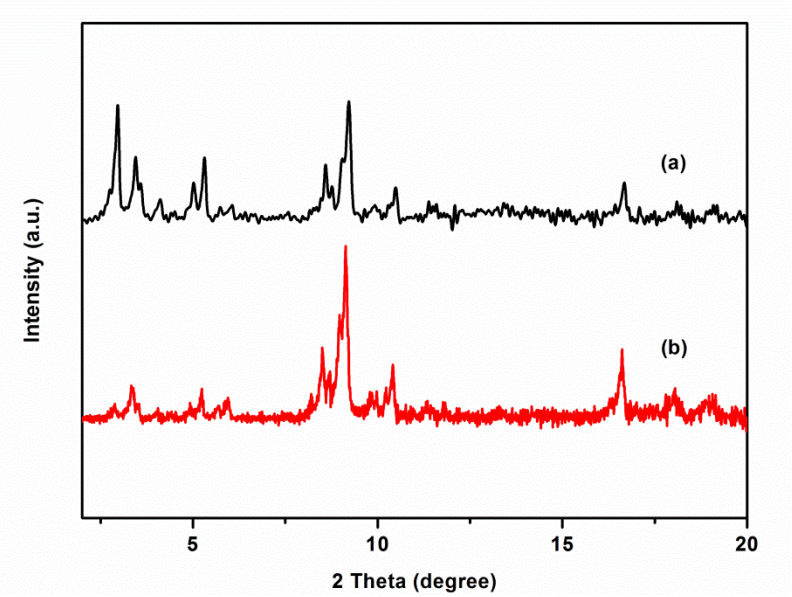


Figure 3- 2 X-ray diffraction patterns of synthesized MIL-101(a) and MIL-101 after extraction (b).

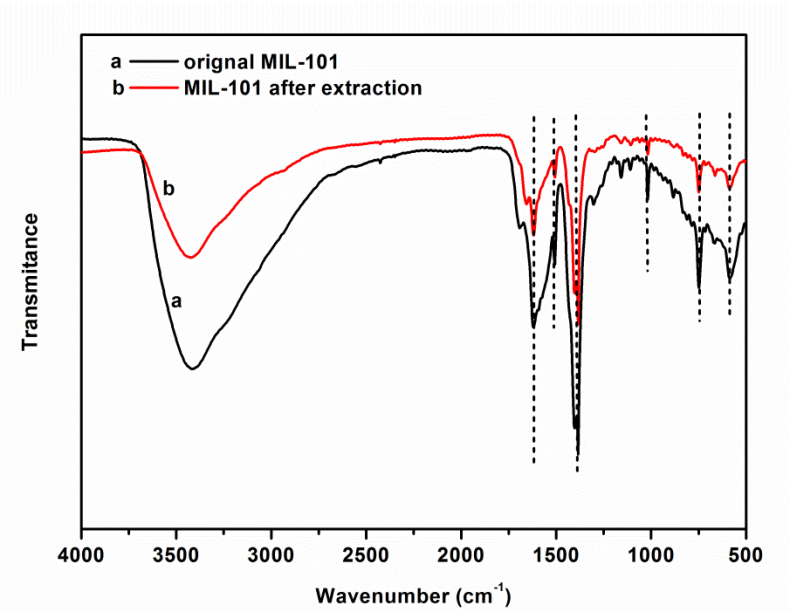


Figure 3- 3 FT-IR spectra of original MIL-101 (a) and MIL-101 after extraction (b).

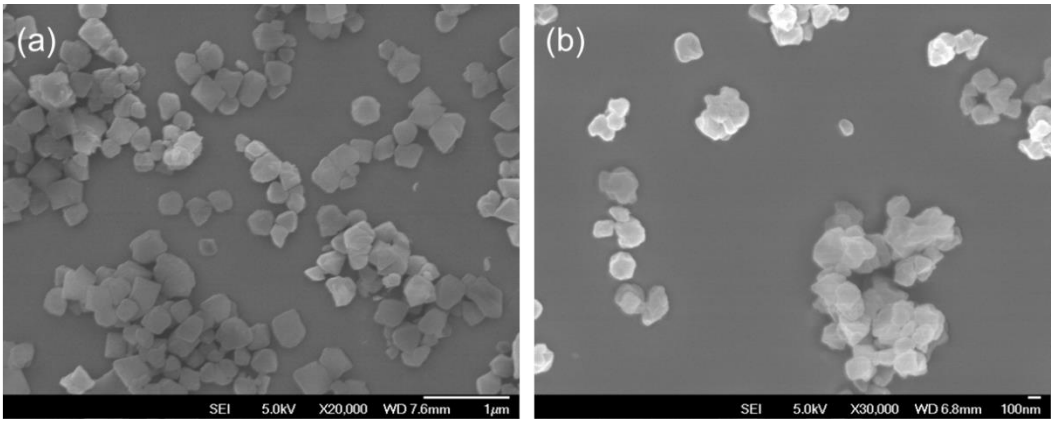


Figure 3- 4 SEM images of original MIL-101(a) and used MIL-101(b).

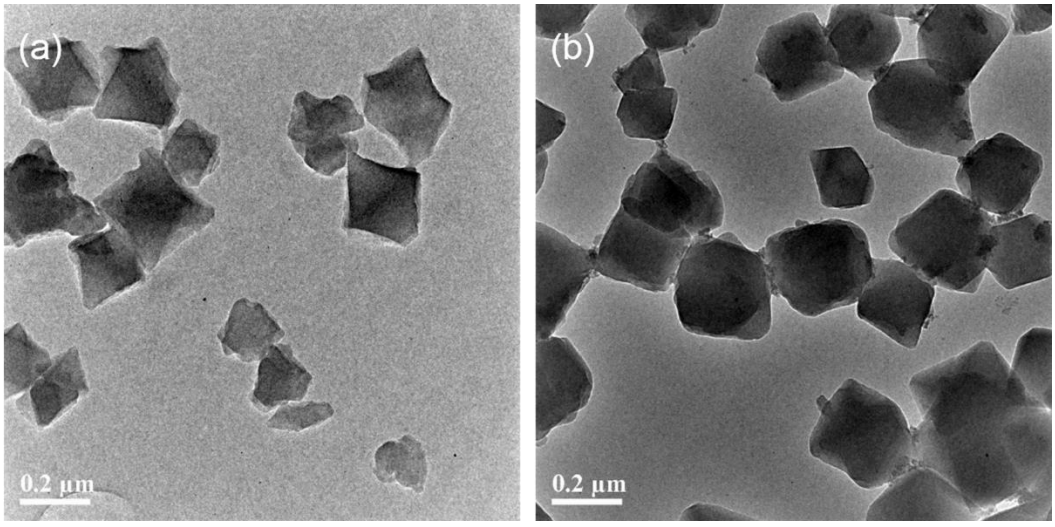


Figure 3- 5 TEM images of MIL-101 without (a) and with (b) surfactant (Triton X-114) modification.

3.3.2 Optimization of dSPE

Experimental parameters that influence extraction efficiency of the EDCs, such as concentration of the modifier-Triton X-114, time of ultrasound assisted mixing step, vortex time, pH of the sample solution and desorption time were studied to obtain the optimal extraction conditions.

3.3.2.1 Influence of surfactant concentration

Amphiphilic polyvinylpyrrolidone has been used to modify nanoparticles or MOF crystals in previous reports [225, 232]. The present study relied on using Triton X-114 as polymer modifier. Such a selection allows the stabilization of the MIL-101 in solution, and might also induce a synergistic enrichment due to the CPE phenomenon. The critical micelle concentration of Triton X-114 is 0.2 mM at room temperature (20-25 ^{o}C). However, the amount of Triton X-114 that was sufficient to enhance the dispersibility of MIL-101 was unknown. Thus, the effect of the concentration of Triton X-114 in the working solution was examined to seek satisfactory extraction efficiency (Figure 3-6).

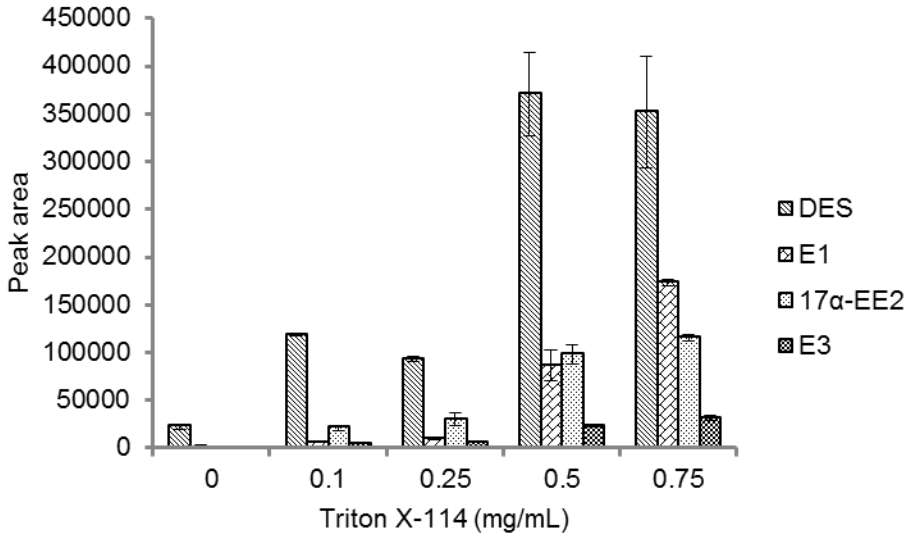


Figure 3- 6 Influence of the concentration of Triton X-114 on the extraction efficiency. Conditions: ultrasonic mixing for 10 min, vortex for 0.5 min, desorption for 10 min in methanol.

It was found that an obvious increase in the extraction efficiency for the four analytes occurred, when the concentration of Triton X-114 was raised to 0.5 mg/mL.

If no or only a little amount of surfactant was present in the sample solution, the MIL-101 crystals were observed to agglomerate quickly at the conical bottom of the containers. External applied ultrasonic field could not prevent such agglomeration effectively.

In addition, it could be observed that there was no significant difference between the two concentrations of 0.1 and 0.25 mg/mL. The results might indicate that the surfactant molecules were mainly present in the bulk solution in this concentration range. In a previous study, enrichment of estrogen compounds through CPE with the assistance of Triton X-114 was reported [233]. It was found that when the concentration of surfactant was below 0.25% (w/v), it was always suspended in the solution and was difficult to separate into two phases, the surfactant rich phase and the aqueous solution phase. The concentration studied in the present work was lower, ranging from 0 to 0.075% (w/v); however, the surfactant could be separated at the presence of MIL-101, indicating the existence of interactions between them. On the other hand, with the addition of Triton X-114 at 0.75 mg/mL, the extraction efficiencies for E1 and E3 were increased, but those for DES and E2 were only slightly, probably due to the micelle based extraction because of the presence of extra surfactant molecules suspended in solution. Nevertheless, such a high concentration of surfactant would cause chromatographic peak tailing and high background noise as the temperature of the capillary column increased. Although post-extraction derivatization, which would allow extractant phase with surfactant to be directly analyzed by GC-MS [234], was adopted in the study, it could not completely avoid the adverse effects from high concentration of surfactant.

Therefore, 0.5 mg/mL was regarded to be the most suitable concentration of Triton X-114.

3.3.2.2 Influence of ultrasonication time

Ultrasonication was applied to facilitate the assembling of surfactant molecules with the MIL-101 crystals in order to obtain a homogeneous solution of MIL-101 with hydrophilic coating. Time intervals varying from 2.5 to 15 min for this step were investigated.

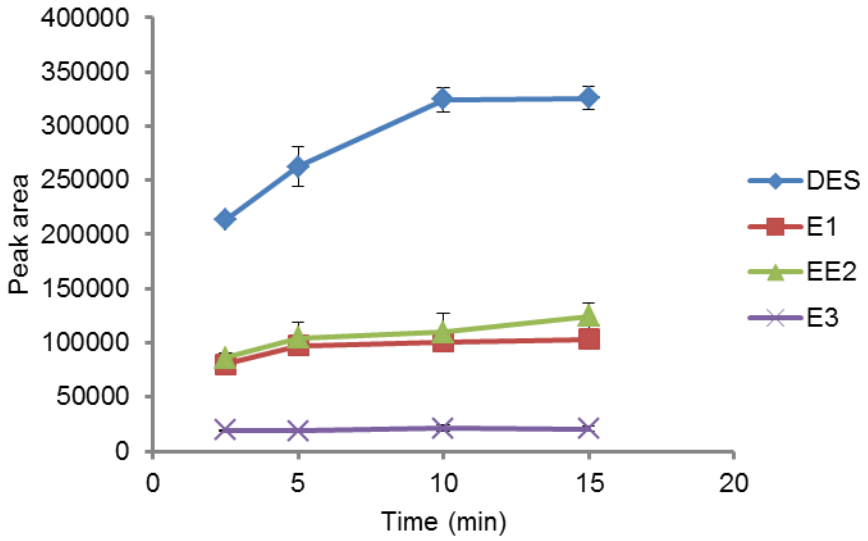


Figure 3- 7 Influence of the ultrasonication time for mixing of Trion X-114 and MIL-101 on the extraction efficiency Conditions: Triton X-114 at 0.5 mg/mL in sample solution, vortex for 0.5 min, desorption in methanol for 10 min.

Figure 3-7 shows the intensities of the chromatographic peaks as a result of different ultrasonic durations, and indicates that the partition equilibrium of surfactant molecules between the solution phase and the surface of the MIL-101 crystals could be reached in 15 min. According to the discussions relating to the

adsorption of polyvinylpyrrolidone-modified nanoparticles [232], the adsorption of amphiphilic Triton X-114 on the MIL-101 crystals surfaces in solution is possibly driven by two interactions: weak coordination interactions between ethoxyl groups (-C-C-O-) and chromium ions in MIL-101, and hydrophobic interactions between tert-octylphenoxyl groups of Triton X-114 and organic linkers of MIL-101. Considering the aqueous matrix, the latter interactions may be dominant, leaving the hydrophilic head groups of Triton X-114 stretched in water. Thus, the surfactant molecules are expected to form a self-assembled micelle layer around MIL-101 crystals, stabilizing them in dispersion fashion. No additional significant improvement in adsorption was obtained for DES when the time span was longer than 10 min. The peak areas for the other EDCs increased very slightly. The extraction of E3 with a log K_{ow} value of 2.45, having a greater polarity than the other analytes, did not improve significantly. This observation might indicate that the dominant adsorption means is hydrophobic interaction. We speculate that despite of the hydrophilic feature of the head of Triton X-114, the limited chain length of the surfactant molecule cannot provide sufficient affinity and retention capacity for the target molecules in an aqueous environment. Thus, although the longer ultrasonication time could ensure a higher degree of surface modification and help to attract more analytes by increased stability, it would only lead to prominent improvement in the extraction performances for EDCs with relatively larger log K_{ow} values which are easier to be adsorbed. An ultrasonication time of 15 min was finally assigned to subsequent experiments to guarantee complete

functionalization of MIL-101 crystals via ultrasonication assisted mixing and assembling processes.

3.3.2.3 Influence of vortex time for dSPE step

The ultrasonication applied in the earlier step was to accelerate the formation of surfactant molecules protected MIL-101 sorbent; thus it might not be sufficient to facilitate the homogenous interaction between the sorbent particles and the analytes, as indicated in one published report [235]. Hence, vortex was employed to enhance the extraction efficiency by vigorously mixing the sample solution with the sorbent. The intensities of the chromatographic signals as the vortex time increased from 0 to 4 min are shown in Figure 3-8.

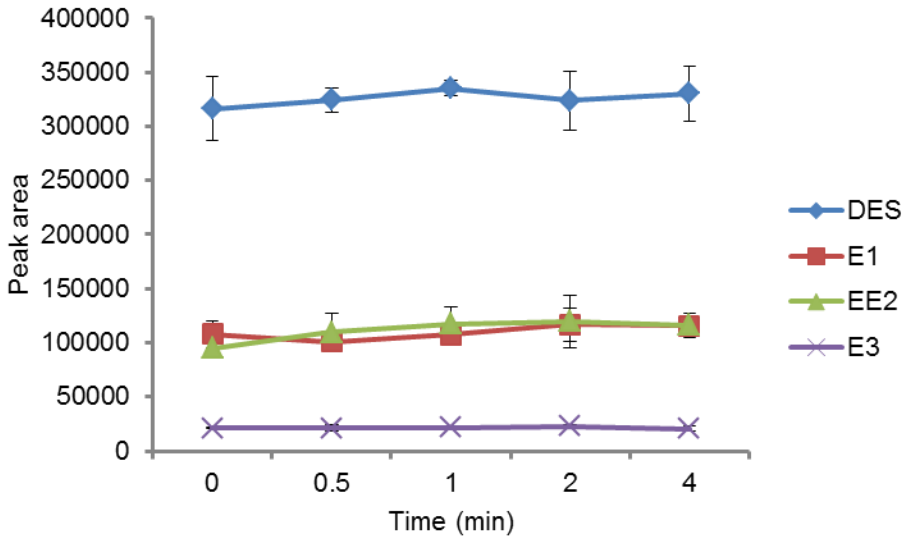


Figure 3- 8 Influence of the vortex time for dispersive-SPE on the extraction efficiency. Conditions: Triton X-114 at 0.5 mg/mL in sample solution, ultrasonication for mixing for 15 min, desorption in methanol for 10 min.

For E1 and EE2, extraction equilibria were reached when vortex time was extended to 2 min. However, it was not the same case for DES and E3, which had no apparent

difference in extraction efficiencies. These results imply that vortex mixing could be a supplementary step to assist the adsorption of analytes in this approach, but the ultrasonication had a dominant role in determination of total extraction performance. On the basis of the foregoing, 2 min was considered necessary to benefit the extraction of the EDCs.

3.3.2.4 Selection of desorption solvent

The recovery efficiency is highly dependent on the property of desorption solvent. First, the target analytes should be highly soluble in it. Additionally, the solvent-analyte interaction should be stronger than the analyte-sorbent interaction. The desorption efficiency in relation to the analytes and the sorbent was examined using four different organic solvents. All the solvent candidates are compatible with the sorbent, while they vary in polarity. Triton X-114 is also soluble in them.

From the desorption profile in Figure 3-9, it is seen that these solvents exhibited comparable desorption efficiencies. Ethyl acetate exhibited better desorption efficiencies of DES and EE2 without compromising too much of the results for E1 and E3. The moderate polarity of ethyl acetate may contribute to its superior elution ability to other solvents. Drawing on this observation, ethyl acetate was determined to be the optimal elution solvent.

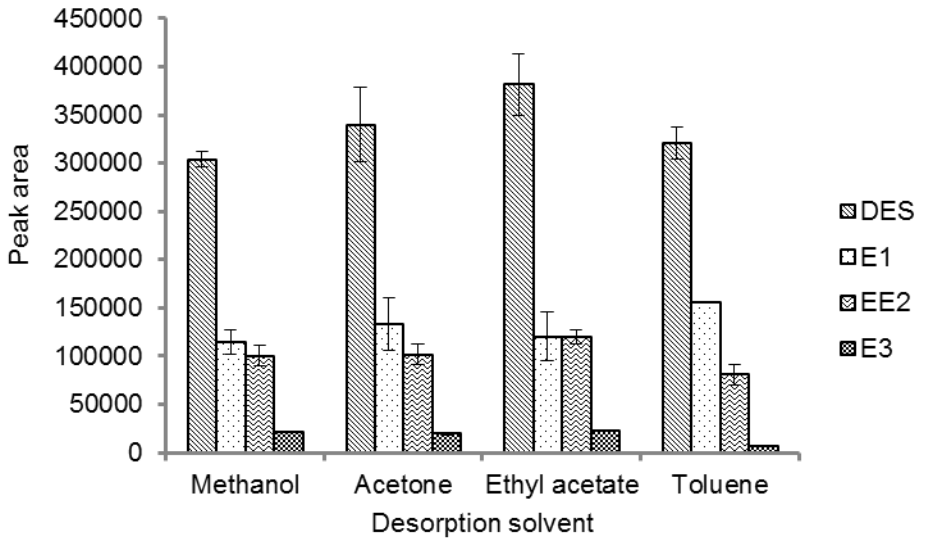


Figure 3- 9 Influence of the desorption solvent on the extraction efficiency. Conditions: Triton X-114 at 0.5 mg/mL in sample solution, ultrasonication for mixing for 15 min, vortex for 2 min, desorption for 10 min.

3.3.2.5 Influence of pH of sample solution

The potential advantages from adjusting the pH of sample solution on extraction efficiency were studied. Generally, the four EDC analytes have weak acidities with their pK_a values i of ca. 10.25 [236]. For MIL-101, the coordinatively unsaturated chromium(III) ion sites on the framework are Lewis acidic sites. Thus the pH environment can influence the protonation and deprotonation of the analytes and the sorbent. The interactions between the analytes and sorbent mainly account for the extraction behavior under different conditions of the aqueous phase. Figure 3-9 depicts the influence on adsorption performance when regulating the pH of sample solutions from 2 to 10. The profiles in Figure 3-10 reveal that an acidic aqueous phase benefited the extraction, with the highest efficiency being obtained at pH 3. As the pH was increased from 3 to neutral, the recoveries of the analytes decreased gradually. When the pH approached the range of basicity, the extraction of DES

declined dramatically, while the influences on the other analytes were not as significant. It may be due to that DES has a relatively lower pK_a of 10.18 compared to the others; thus it was affected to a higher extent when changing the pH of solution toward the basicity range. These observations suggest that target molecules are favorably extracted when they are fully protonated. The net charge of the molecules would render them highly dissolvable in aqueous phase instead of adsorption by the sorbent. Since the interaction between the nonpolar group of Triton X-114 and the terephthalic acid ligand in MIL-101, and the π-d interaction between the aromatic ring of Triton X-114 and the metal can facilitate the coating of the surfactant on MIL-101's surface, it is reasonable to surmise that the extraction of the analytes, which relied mainly on the hydrophobic interactions, was assisted by the amelioration of MIL-101's dispersibility in water, and the synergistic effect of CPE enabled by the Triton X-114.

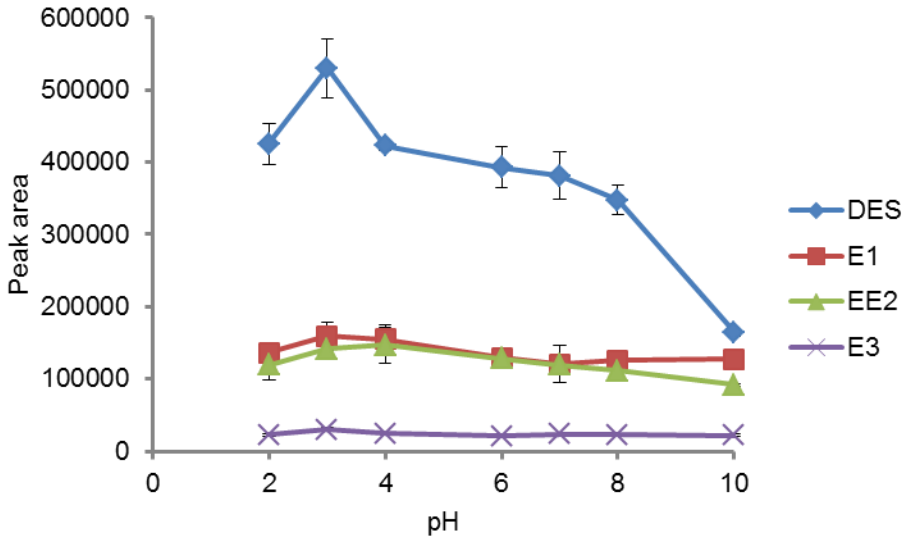


Figure 3- 10 Influence of the pH of the sample solution on the extraction efficiency. Conditions: Triton X-114 at 0.5 mg/mL in sample solution, ultrasonication for 15 min, vortex for 2 min, desorption in ethyl acetate for 10 min.

3.3.2.6 Influence of desorption time

Retrieval of the analytes extracted by the Triton X-114 modified MIL-101 was realized using a small volume of organic solvent with assistance of ultrasonication. The time for desorption should be sufficient to ensure complete desorption, not only of the analytes but also of the surfactant in order to regenerate the sorbent. From the profile presented in Figure 3-11, it could be seen that 5 min or less time was unable to secure satisfactory recovery of the analytes. This suggests that the interactions between the surfactant and the sorbent particles were strong. Energy was needed to overcome such interaction and allow the analytes absorbed to be released into the solvent. By comparing the chromatographic signals obtained from different desorption durations, 10 min seems to be an appropriate desorption time. After desorption, the used sorbent was further washed with 50 μL methanol for cleaning. No obvious characteristic peaks of Triton X-114 were seen in the FT-IR spectrum of the regenerated sorbent (see Figure 3-3), suggesting successful removal of surfactant modifier so that the sorbent could be reused.

3.3.3 Method evaluation

Calibration plots were prepared for the determination of the four EDCs by using 10 mL ultrapure water spiked with varying concentrations of the analytes, over the range of 0.09 to 45 ng/mL. Under the optimized experiment conditions, calibration curves and the figures of merit for the proposed extraction method combined with GC-MS analysis were obtained, and are listed in Table 3-2. All the analytes exhibited good linearity with coefficients of determination (r^2) above 0.9980. The

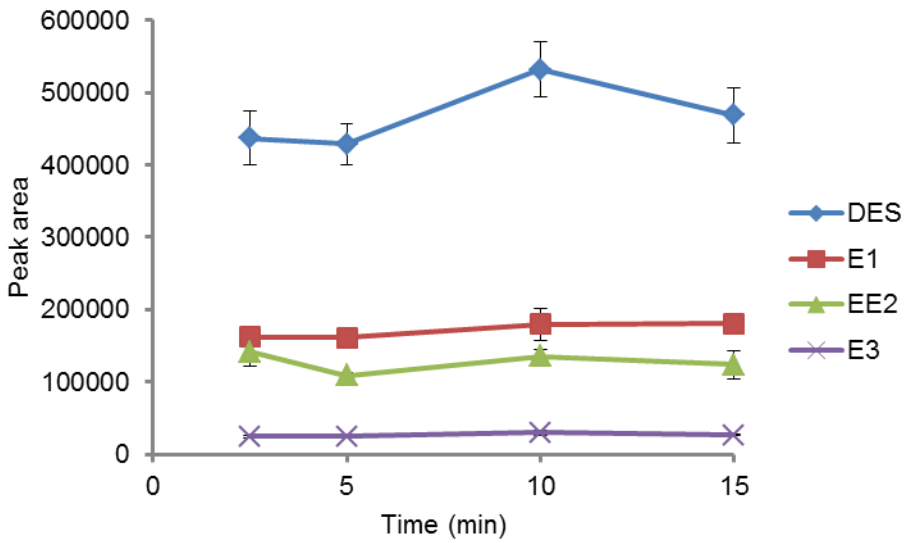


Figure 3- 11 Influence of desorption time on the extraction efficiency. Conditions: Triton X-114 at 0.5 mg/mL in sample solution, ultrasonication for 15 min, vortex for 2 min, desorption in ethyl acetate, pH of sample solution=3.

LODs calculated at a S/N of 3, ranged between 0.006 and 0.023 ng/mL. As shown in Table 3-3, the LODs obtained in the study were lower than some other the CPE [233, 237] and solvent based extraction [238, 239] methods. Micro-SPE extraction methods relying on home-made devices have also been developed in the determination of these EDCs from environmental samples, but they exhibited 2-100-fold higher LODs relative to those of the present study [240, 241]. Compared with the results achieved by SPE, the LODs of the proposed method ranging from 0.006 to 0.023 ng/mL are higher than those obtained with commercial Strata X [242] and tandem ENVI-18/Florisil cartridges [243], yet comparable to and even lower than the others [103, 244] (Table 3-3). However, the sample amount required in the present study was only 10 mL, while for the SPE method, relatively large volumes (a few hundred milliliters to 1 L) of sample solution were necessary to ensure

sufficient sensitivity. Thus, the proposed method is an effective and sensitive extraction method for the analysis of trace EDCs in water.

3.3.4 Analysis of environmental samples

The feasibility of the proposed method for analysis of environmental samples was evaluated. Extractions of EDCs from tap water in the laboratory and seawater taken from the Singapore River were carried out under the optimal conditions. No EDCs were detected, however. The results of the determination of the targeted compounds in genuine water samples and recoveries of spiked samples are summarized in Table 3-4. Relative recoveries (defined as ratios of chromatographic peak areas of extracts of spiked real water to that of spiked ultrapure water) ranged from 70.8 to 118.8% for tap water and 70.7 to 113.7 % for Singapore River, where indicating no distinct difference. A chromatogram of an extract of Singapore River water sample spiked with 4.5 ng/mL of each of the analytes is shown in Figure 3-12.

Table 3- 2 Comparison of the proposed method and other methods for the determination of EDCs in real samples

Analytical method	Sample	Sample volume (mL)	Sorbent/Solvent	LOD (ng/mL)				Ref.
				DES	E1	EE2	E3	
CPE/HPLC-UV	water	10	Triton X-114	-	0.25	-	0.23	[233]
UACPE/HPLC-DAD	urine	10	Tergitol TMN-6	0.1	0.2	-	-	[237]
HF-LLLME/ HPLC-UV	water	6	Toluene/n-octanol	0.20	0.51	0.66	0.11	[238]
SUPRA microextraction/ LC-MS/MS	sediment	-	Decanol based SUPRA	-	0.07	0.94	0.53	[239]
Magnetic extraction/MEKC	water	10	Magnetic MWCNT-OH	0.9	1.7	-	1.0	[240]
Micro-SPE/LC-MS/MS	water	20	ZIF-8	-	0.1	0.05	0.05	[241]
SPE/GC-MS	water	1000	Strata-X cartridge	0.0005	-	0.0005	0.0005	[242]
SPE-SPE/LC-MS	water	250	ENVI-18/Florisil cartridge	0.003	0.018	0.005	0.009	[243]
MIP-SPE/HPLC-ECD	water	25	P(MAA-DVB-EDMA) MIP	-	0.0710	0.0798	0.1930	[244]
MIP-SPE/LC-MS/MS	water	100	AFFINIMIP	0.0085	0.0057	0.0061	0.0061	[103]
Dispersive-SPE/GC-MS	water	10	MIL-101 modified with Triton X-114	0.015	0.015	0.006	0.023	This work

Table 3- 3 Analytical results for the determination of EDCs in water samples

Water sample	Analyte	Concentration detected (ng/mL)	Spiked concentration (ng/mL)	Relative recovery (%, n=3)
Tap water	DES	N.D.[a]	4.5	70.8
	E1	N.D.	4.5	118.8
	EE2	N.D.	4.5	72.0
	E3	N.D.	4.5	93.9
Singapore River	DES	N.D.	4.5	70.7
	E1	N.D.	4.5	113.7
	EE2	N.D.	4.5	72.3
	E3	N.D.	4.5	83.6

[a] Not detected.

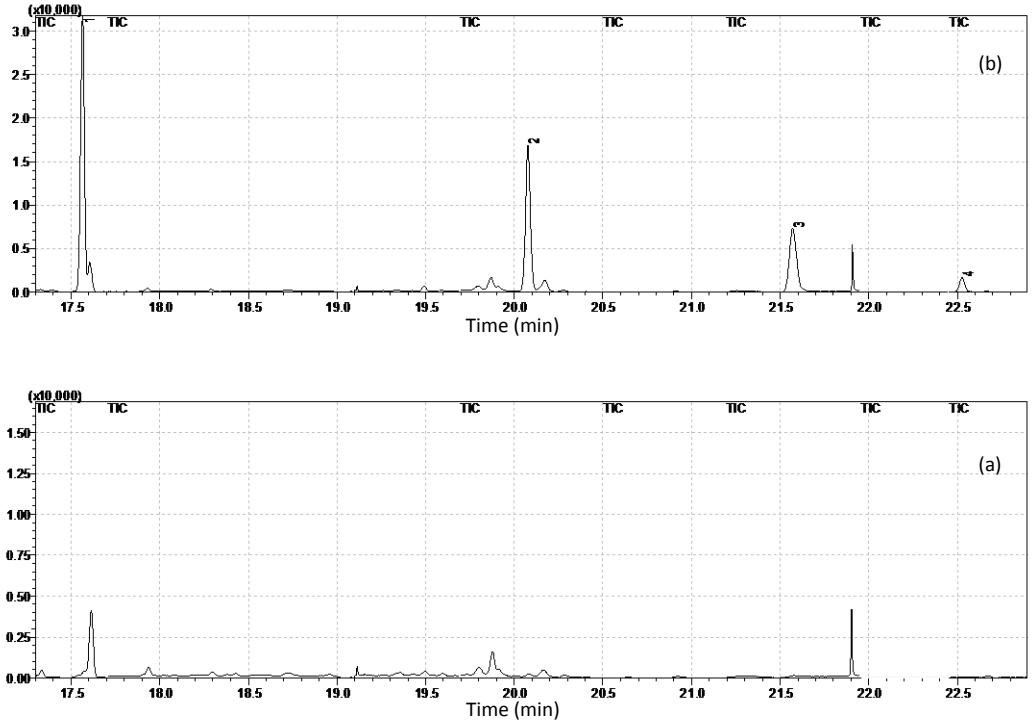


Figure 3- 12 GC-MS-SIM traces of extracts of a genuine Singapore River sample. (a) unspiked water; (b) water spiked with 4.5 ng/mL of each analyte. Peak identities: (1) DES; (2) E1; (3) EE2; (4) E3.

3.4 Conclusions

In the present work, Triton X-114 was used of to serve as a modifier of MIL-101 crystals with the aim to improve the dispersibility of MIL-101 in aqueous phase. The amphiphilic nature allows Triton X-114 to be adsorbed by MIL-101, with the resulting composite behaved like a hybrid sorbent with a hydrophilic protective layer. The modification endowed MIL-101 with good extraction capabilities as sorbent for the trace analysis of EDCs from environmental water samples, as the external hydrophilic coating of surfactant molecules increased the contact probability of the target analytes and the sorbent. Moreover, the separation and collection of the entrapped analytes were assisted by the cloud point phase separation involving the Triton X-114. Therefore, the extraction process occurred synergistically with the combination of dSPE extraction and cloud point extraction. The developed method was environmentally friendly in that only a small amount of sorbent (1 mg) and a small volume of solvent (about 200 μL) were consumed. Derivatization of the extracted EDCs was conducted prior to GC-MS analysis and proved to be effective, giving low detection limits and acceptable repeatability. The surface modification approach has been demonstrated to be an effective way to improve the extraction capability of MIL-101 for analytes in aqueous samples. As shown in Figure 3-6, the modified MIL-101 exhibited better performance than the unmodified material.

CHAPTER 4. CARBONIZED POLYDOPAMINE AS COATING FOR SOLID-PHASE MICROEXTRACTION OF ORGANOCHLORINE PESTICIDES

4.1 Introduction

SPME has gained a lot of attention owing to its solventless nature, ease of operation and convenient hyphenation with analytical instrumentation, particularly GC. Most attention for SPME has been drawn to the coating of fibers with the aim to achieve better extraction performance, due to the fact that SPME is based on the equilibrium partition of target analytes between the sample matrix and the coating phase, and limited options of the commercially available SPME fibers [245]. In order to expand the choice of SPME fibers and avoid the disadvantages such like fragility and short lifespan of those commercial SPME fibers, various polymeric and inorganic composite materials have been fabricated as sorbent phases for SPME [122, 169, 246].

Carbon based materials have attracted considerable interest in analytical sciences, given their potential applications in electroanalysis, sensors and biosensors, adsorption and separation, which result from their unique features, such as high surface area, high mechanical strength as well as electro and thermal conductivity [247]. Diverse types of carbon materials which include mainly activated carbon, graphite, carbon nanotube, fullerene, graphene and other carbon configurations

have been applied in SPME. Comparatively, there have not been as many reports on carbon materials for SPME as for some other extraction techniques, which may be due to the challenging requirements for fabrication of proper SPME fibers involving these materials.

Polycrystalline graphites, i.e. pencil lead and low temperature glassy carbon rod have been directly used as SPME fibers [248]. Subsequently, different modification processes were employed to activate pencil leads, and it was demonstrated that heating under water vapor could improve the adsorption ability of these fibers [249]. For those carbonaceous materials without macroscopic architecture, the sol-gel technique is an easy and effective means to construct fibers, which has been widely adopted in the exploitation of immobilizing glassy carbon film [250], hydroxyfullerene [251], carbon nanotube [252], carbon aerogel and wormhole-like porous carbon [253], graphene [90] on supporting wires to make SPME fibers. In-situ chemical bonding has also been explored for coating carbon sorbent onto properly functionalized SPME substrates in order to establish stronger interaction of the coatings and the substrate, thereby enhancing the stability and lifetime of the carbon coatings. For instance, carbon nanotubes [254] and graphene [91] were successfully bonded to a gold wire pre-modified with a self-assembly monolayer which incorporated amine groups on its surface and fused silica fiber, respectively. The primary issue for the essential chemical bonding process is the selection of a proper substrate with functional groups on the surface and coating component. Recently, there has been some work that demonstrated fast coating procedures on untreated stainless steel fiber through a simple flame synthesis process [255], or the

acceleration of the polymerization via heating of the substrate fiber [256]. Although these two procedures exhibited good time efficiency in preparation, careful control of the ethanol flame and the heating of the fiber was very important. Thus, it might be not easy to ensure that the coating processes were controllable in terms of repeatability. Inspired by the advances of materials science, carbon monolith fiber [257], substrateless graphene fiber [200] and pencil lead derived graphene fiber [258], which could be readily applied for SPME, have been prepared through suitable synthetic routes. These coating free laboratory-tailored SPME fibers avoid the disadvantage of the extracting phase being stripped off too easily as observed in conventional fibers.

Carbon sources have a significant influence on the preparation process and the physical and chemical properties of the resultant carbon sorbents [259]. In addition to the aforementioned carbonaceous sorbents, PDA has emerged as a new carbon precursor in recent years. PDA is the self-polymerization product of dopamine which is a biomolecule with catechol and amine functional groups. This reaction can take place under alkaline conditions and the resultant PDA is rich in catechol groups, resulting in strong adhesion to bulk substrates or nanostructures [260]. Such properties not only allow PDA to serve as functional layer for many applications [261-263], but also enable it to be a promising carbon source for the preparation of carbon-coating materials. So far, carbonized PDA (C-PDA) has been exploited for the preparation of hollow carbon sphere and Au-carbon nanocomposite [264], lithium ion battery electrode materials [265], and magnetic adsorbent [266]. These studies demonstrated that PDA could form a hollow carbon layer on various

inorganic nanoparticles or substrates with good carbon yield and the C-PDA exhibited a multilayered structure with doped heteroatoms.

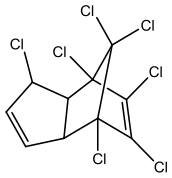
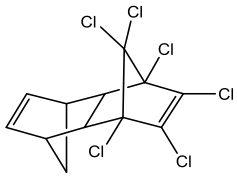
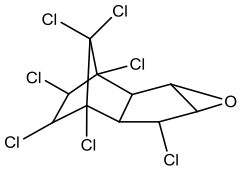
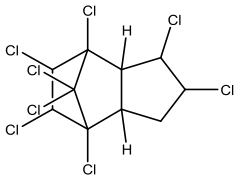
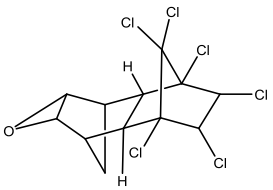
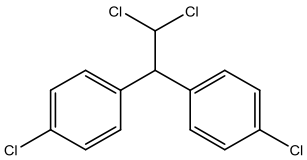
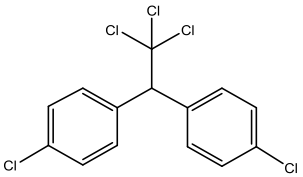
As PDA is utilized for SPME application, it has mostly been used as a binding agent to immobilize sorbents [115, 267, 268]. To the best of our knowledge, no study has been carried out to evaluate the application of C-PDA itself as an SPME coating phase. Considering the excellent coating ability and controllable coating thickness of PDA, C-PDA may be an alternative SPME coating phase as it possesses the attractive merits of carbon materials while only requiring facile fiber fabrication procedures. Thus, in the present work, we exploited C-PDA as a SPME coating material and investigated the thus fabricated SPME fiber for the extraction of trace OCPs from environmental water samples.

4.2 Experimental

4.2.1 Chemicals and materials

Dopamine hydrochloride and hydrofluoric acid solution (40%) were purchased from Sigma Aldrich (St. Louis, MO, USA). Tris(hydroxymethyl) aminomethane (Tris) was purchased from J.T. Baker (Phillipsburg, NJ, USA). Sodium chloride (NaCl) was bought from GCE Laboratory Chemicals (Singapore). Humic acid was supplied by Sigma-Aldrich (Milwaukee, WI, USA). Methanol of chromatographic grade was bought from Merck (Singapore). The standard solutions of the OCPs (heptachlor, aldrin, heptachlor epoxide (isomer A), α-chlordane, dieldrin, p,p'-DDD and p,p'-DDT) with a concentration of 1 mg/mL in methanol were obtained from

Table 4- 1 Physicochemical properties and characteristic ions of OCPs for their quantitative and quantitative analysis

Analyte	Structure	Mw	LogK_{ow}*	Characteristic ion (m/z)
Heptachlor		373.32	6.1	272, 274
Aldrin		364.92	6.5	263, 265
Heptachlor epoxide (isomer A)		389.32	4.98	353, 355
α-Chlordane		409.78	6.1	373, 375
Dieldrin		380.91	5.4	263, 265
p,p'-DDD		320.04	6.02	235, 237
p,p'-DDT		354.49	6.91	235, 237

* log K_{ow} data are obtained from Syracuse Research Corporation's PHYSPROP database.

SPEX CertiPrep (Stanmore, UK). A mixture of these OCPs was prepared by appropriation dilution of the stock standard solutions with methanol. Working standard solutions were prepared daily by spiking the standard solution into ultrapure water to the desired concentrations.

A commercial SPME manual holder and the fiber coated with 85 μm of Carboxen/PDMS (CAR/PDMS) (Supelco, Bellefonte, PA, USA) were used for comparison. A 1 μL plunger-in-needle microsyringe with a 26-gauge needle, 70 mm length was obtained from SGE (Ringwood, Victoria, Australia). A replacement needle of 23-gauge, 50 mm length and 0.63 mm internal diameter (SGE) was used for setting up the homemade SPME device [90]. A MR3001K (Heidolph, Kelheim, Germany) magnetic stirrer was used to control the stirring rate during extraction. SEM micrographs were recorded on a Philips XL-30 SEM system (SEMTech Solutions, North Billerica, MA, USA), and a JSM-6701F SEM system (JEOL, Tokyo, Japan).

4.2.2 GC-MS analysis

A Shimadzu QP2010 GC-MS system was employed for the analysis of the analytes. The GC capillary column (DB5-MS, 30 m length × 0.25 mm i.d. × 0.25 μm film thickness) from Agilent Technologies (Palo Alto, CA, USA) was used for the chromatographic separation. The GC-MS conditions were as follows: injector temperature, 300 ^{o}C; transfer line temperature, 280 ^{o}C; ion source temperature, 200 ^{o}C; initial oven temperature, 80 ^{o}C (held for 1 min), then increased to 240 ^{o}C at 20 ^{o}C/min (held for 5 min), and finally increased to 300 ^{o}C at 20 ^{o}C/min (held for 5

min). Splitless injection was used throughout. High purity helium (>99.999%) was used as the carrier gas with a column flow rate of 1 mL/min. The MS was operated in the electron impact ionization mode. Data acquisition was conducted in the SIM mode.

4.2.3 Preparation of C-PDA coated SPME fiber

The stainless steel wire of the plunger-in-needle microsyringe was cleaned by ultrasonication in ethanol and ultrapure water for 10 min respectively and then dried in air. It was immersed in hydrofluoric acid solution under ambient temperature (ca. 24 ^{o}C) to a depth of about 1.5 cm for etching for 15 min. After this, the wire was washed with ultrapure water immediately for 1 min.

For coating of the wire with PDA, the biomineralization approach utilized here was according to a previous report [260]. The treated end of the wire was immersed in 1.5 mL 10 mM tris buffer which was pre-adjusted to pH 8.5 with 1 M HCl, and 3 mg dopamine hydrochloride (2 mg/mL) was then added into the solution. The polymerization of dopamine was conducted for 24 h at room temperature under continuous magnetic stirring. The PDA coated wire was rinsed with ultrapure water in order to remove excess monomer and PDA precipitates that were physically adhered to the wire, followed by drying with N_2. A multiple coating process was used to ensure a certain thickness of PDA coating. Therefore, the deposition coating procedure was repeated for five cycles. The stainless steel wire with PDA coating was dried in air. Carbonization of the coating was carried out in a Carbolite (STF 16/180) tube furnace under an argon atmosphere. The heating was started from

ambient temperature to 700 ^{o}C at a rate of 5 ^{o}C/min. The furnace was maintained at 700 ^{o}C for 3 h and subsequently cooled down to ambient temperature slowly. The obtained fiber with C-PDA coating was installed in the microsyringe which was assembled with the replaceable needle mentioned above, so as to afford the homemade SPME device. Before extraction, the new fiber was washed by ultrapure water and further conditioned in GC injection port at 300 ^{o}C for 1 h.

4.2.4 Sample preparation

Drain water samples were collected near a local residential area. The samples were stored in clean glass bottles and kept at 4 ^{o}C in the dark. They were filtered through GFP filters (Kiriyama Glass, Tokyo, Japan) (0.8 μm) to remove suspending particles before use.

4.2.5 Analytical procedures

For extraction of the OCPs from aqueous solution, an aliquot of 7 mL of a working standard solution spiked at different concentrations ranging from 0.01 to 50 ng/mL of each individual OCP, or a drain water sample solution was placed in a 10 mL glass vial. The prepared C-PDA coated fiber was pushed out of the protective needle and immersed in the solution acting for DI-SPME. Extraction was allowed to take place for 20 min at ambient temperature (ca. 24 ^{o}C) with magnetic stirring at 700 rpm. After that, the SPME fiber was removed from the solution and withdrawn into needle for protection. For thermal desorption of the analytes, the needle was introduced to the GC injection port and the fiber exposed for 15 min,

and at 300 °C. One blank run of the fiber after every extraction was performed before the next extraction in order to minimize or eliminate carryover effects.

4.3 Results and discussion

4.3.1 Fabrication of C-PDA coating based SPME fiber

Stainless steel wire has been considered a good supporting substrate in commercial SPME fibers [269]. Chemically bonded coatings can be achieved through pre-modification, such as the introduction of a functional layer on and oxidization of the surface of the substrate wire. Recently, research on the formation and properties of PDA has led to an easy and universal surface modification approach [260]. Accordingly, we used this convenient approach for the fabrication of a new carbon material coated stainless steel wire, as strong bonds can be formed between the catechol polymer and metal oxides. To increase the amount of the coating, two measures were taken in the study. First, the smooth stainless steel wire was etched by hydrofluoric acid so as to provide a roughened surface with a higher surface area. Second, the coating procedure was repeated five times to ensure sufficient covering of the wire. Subsequently, the PDA coating was carbonized, resulting in a carbon coated wire, denoted as C-PDA coated fiber hereafter. The C-PDA coating potentially provided more active sites to increase the extraction capacity compared to the bare hydrofluoric acid etched stainless steel fiber. Figure 4-1 describes the general preparation process of the C-PDA fiber. Although this fabrication took a longer time than the flame synthesis method [255], it ensured a higher repeatability of the carbonization process in the sense that the chemical adhesion of PDA on

stainless steel wire was more robust than physical deposition. Moreover, numerous functional groups (e.g., -OH, -NH_2) of PDA would allow diverse chemical modifications, and more routes could be introduced in the future to prepare SPME coatings with particular properties.

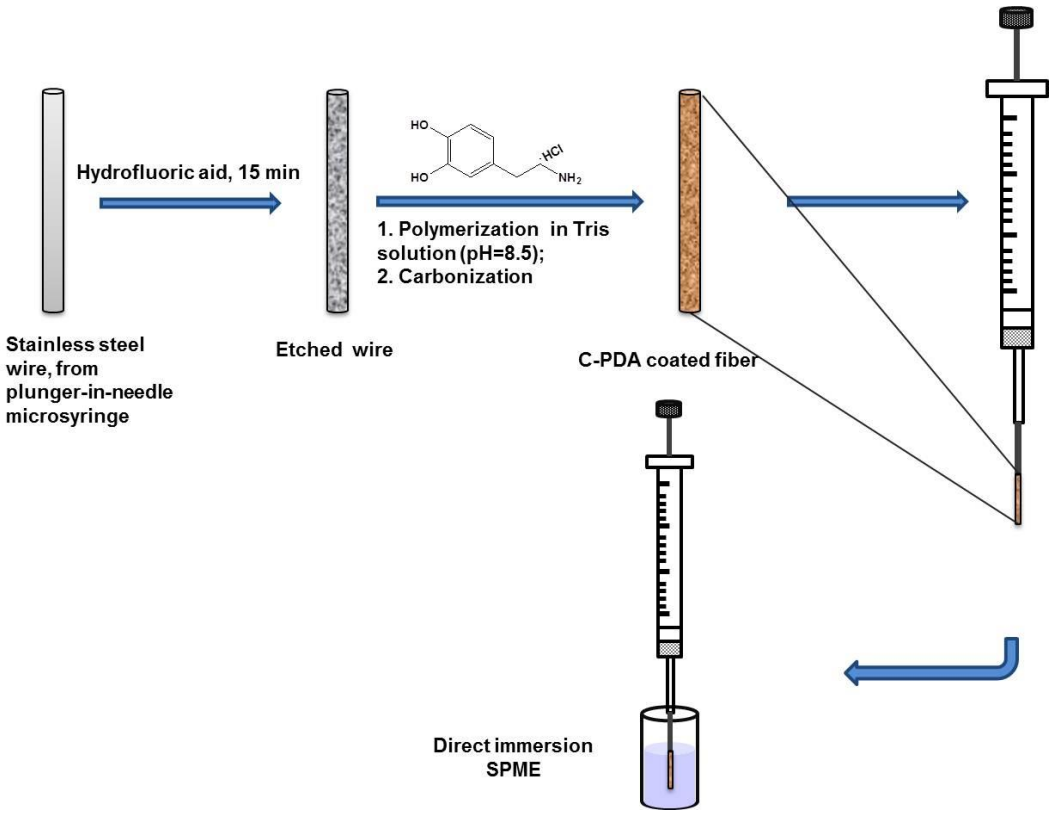


Figure 4- 1 Schematic of the preparation of C-PDA coated stainless steel fiber for SPME.

To study the change of the surface structure before and after treatment, SEM was used to examine the morphologies of the original, etched and coated wires (Figure 4-2). As shown in Figure 4-2 (B), hydrofluoric acid etching generated a rough and porous tree bark-like surface. After the polymerization of dopamine occurred in the alkaline solution, a thick and porous polymer coating covered the surface of the acid etched steel fiber (Figure 4-2 (C, D)). The carbonization treatment was then

applied and it led to the formation of a dense layer (Figure 4-2 (E, F, G)). The thickness of the C-PDA coating was estimated to be about 2 µm, according to the analyses of the SEM images. The C-PDA coating generated on the surface of the stainless steel wire in this study could have a graphite-like nanostructure consisting of stacked carbon layers as demonstrated previously [270].

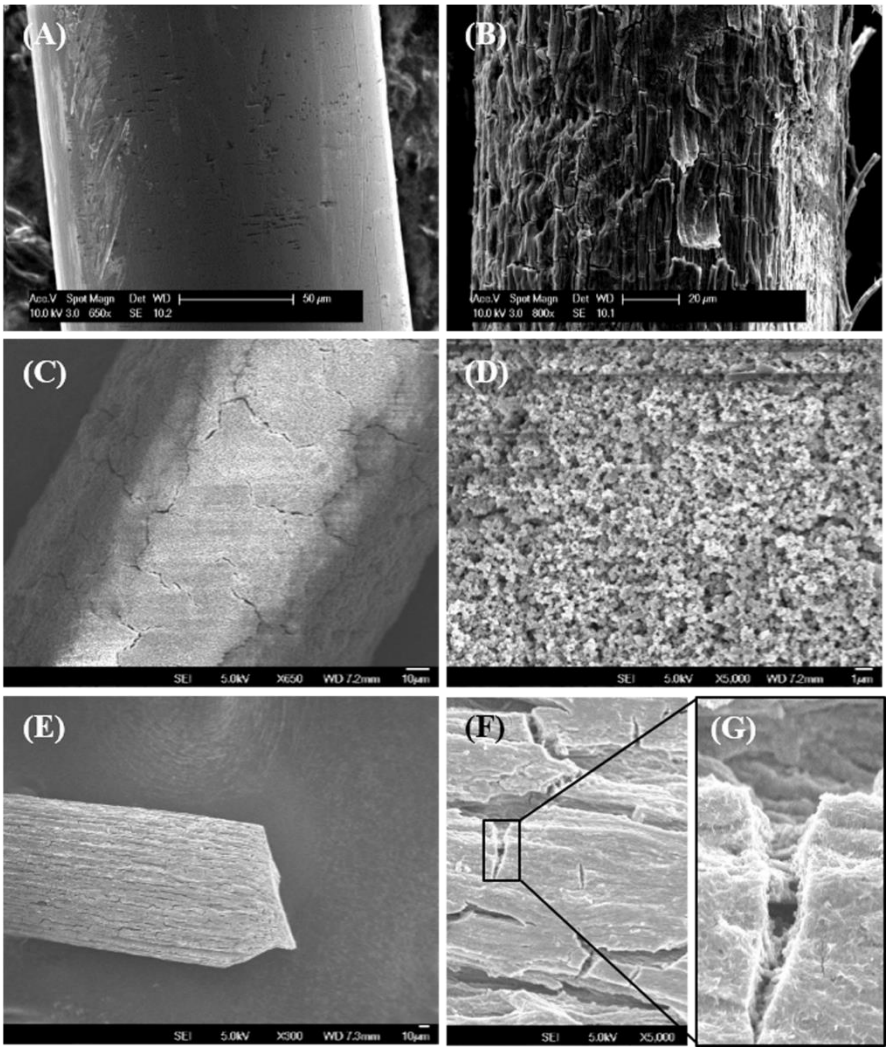


Figure 4- 2 SEM images of the morphologies of the stainless steel wire (A) before, (B) after acid etching and with (C, D) PDA and (E, F, G) C-PDA coating. The magnifications for (A-G) are 650x, 800x, 650x, 5000x, 300x, 5000x and 20000x, respectively. (G) is the enlarged image of the corresponding boxed area in (F).

4.3.2 Optimization of SPME conditions

The prepared SPME fiber was applied to the extraction of OCPs as model analytes in aqueous solution. To evaluate extraction performance, experimental conditions were investigated, including extraction time, agitation rate, ionic strength of samples and humic acid concentration.

4.3.2.1 Extraction time

For SPME, the extraction amount is closely associated with the contact time of extracting phase and sample matrix. The influence of extraction time for the C-PDA coated wire was studied in order to investigate the adsorption properties. In Figure 4-3, it can be seen that extension of the extraction time would result in noteworthy increases in the extraction amounts of all the analytes. It also indicates that the partitioning equilibrium was not fully reached within 60 min in the experiment. As is known, the diffusion rate of the analytes from the aqueous matrix to the extracting phase is the determining factor in adsorptive extraction. Therefore it is understandable that a longer time might be needed for C-PDA than for graphene as the sorbent phase [165, 200]. C-PDA has a stacking layered nanostructure which causes the diffusion rate of the analytes towards C-PDA to be slower than towards graphene. Therefore it is understandable that a longer time might be needed for C-PDA than for graphene as the sorbent phase [165, 200]. In principle, low molecular weight analytes would have shorter extraction equilibrium time. Nevertheless, as the extraction time was prolonged, the extraction amount for p,p′-DDD increased quickly, followed by p,p′-DDT, α-chlordane and the other

analytes. This observation suggests that p,p′-DDD and p,p′-DDT have higher affinities to the C-PDA coating, probably because the compound with a more planar aromatic structure can approach the carbon surface more effectively and thus has stronger interactions with the carbon sorbent [271]. To achieve a reconciliation of extraction efficiency and the time taken, 40 min was chosen as the most favorable extraction time.

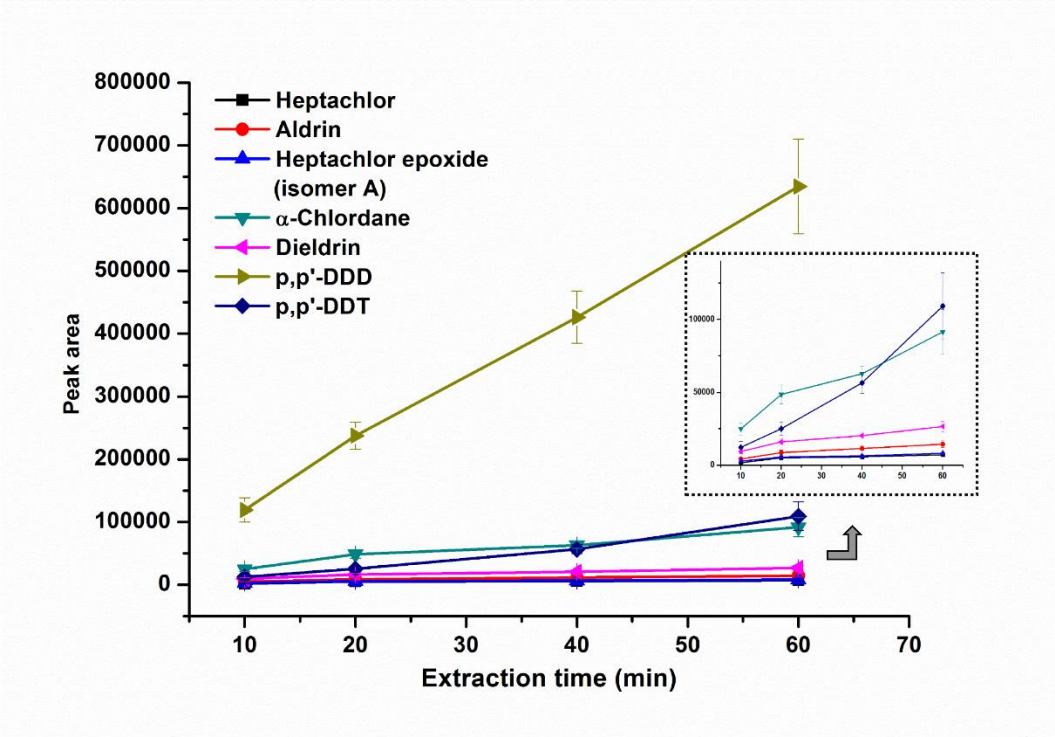


Figure 4- 3 Effect of extraction time on extraction of OCPs. Conditions: analyte concentrations, 0.01 µg/mL of each; agitation speed, 700 rpm; no adjustment of pH and ionic strength. The insert shows an enlarged view of the results for p,p′-DDT, α-chlordane, dieldrin, aldrin, heptachlor epoxide (isomer A) and heptachlor.

4.3.2.2 Agitation speed

Besides extraction time, extraction temperature and agitation rate also affect SPME efficiency. The experiments in the study were done under ambient temperature for practical considerations. Agitation would directly accelerate the mass transfer rate during extraction and increase the amount of analytes adsorbed by the coating phase. The extraction-agitation speed profiles in Figure 4-4 show significant improvement of the extraction performance for all the analytes when the stirring rate was increased from 0 to 1250 rpm. Although vigorous agitation may result in losses of the analytes to the atmosphere [272], such a result was not observed, as the OCPs under study have relatively low air-water partition coefficients (they are semi-volatile) and the extraction temperature was mild. Thus, 1250 rpm was selected as the most favorable agitation speed.

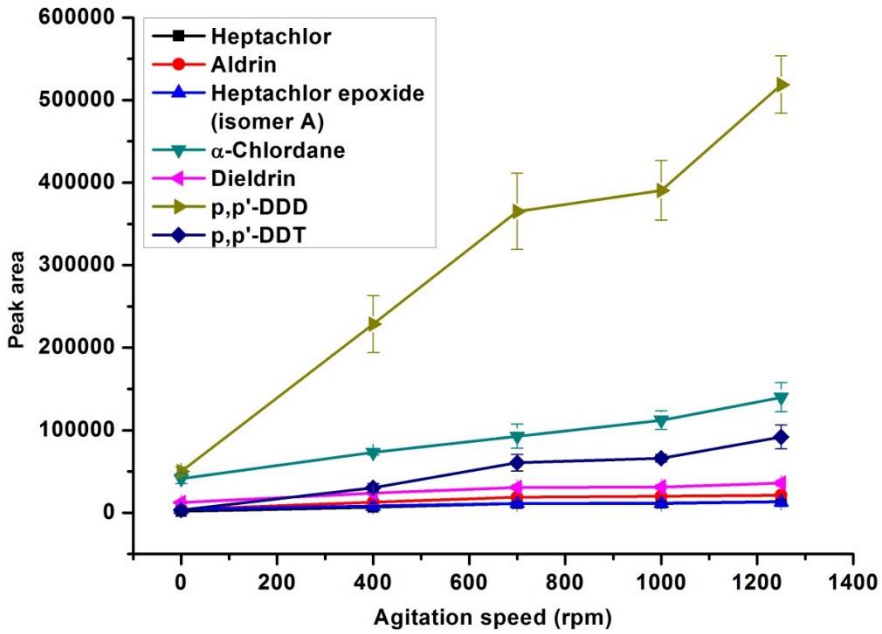


Figure 4- 4 Effect of agitation speed on the extraction of OCPs. Conditions: analyte concentrations, 0.01 μg/mL of each; extraction time, 40 min; no adjustment of pH and ionic strength.

4.3.2.3 Ionic strength

The salting-out effect is usually taken into account in order to improve the extraction performance. The influence of addition of NaCl on the extraction performance of the C-PDA wire was investigated by varying the concentrations of NaCl added separately (Figure 4-5). The results indicated that adding salt only slightly enhanced the amount of extracts of OCPs when the salt concentration was as low as 5% (w/v, %). Further increase in the concentration of NaCl (>10% (w/v, %)) did not improve the extraction, but led to decreased extraction amounts instead. The observation is not surprising, because the salting-out phenomenon has its negative influence as well. The addition of salt can make the sample matrix more viscous and denser, and lead to a slower kinetics of the extraction process [273]. Therefore, the addition of salt might affect each analyte differently, depending on their properties and extraction kinetics. In subsequent experiments, 5% (w/v, %) of NaCl was regarded as the most favorable salt concentration for extraction.

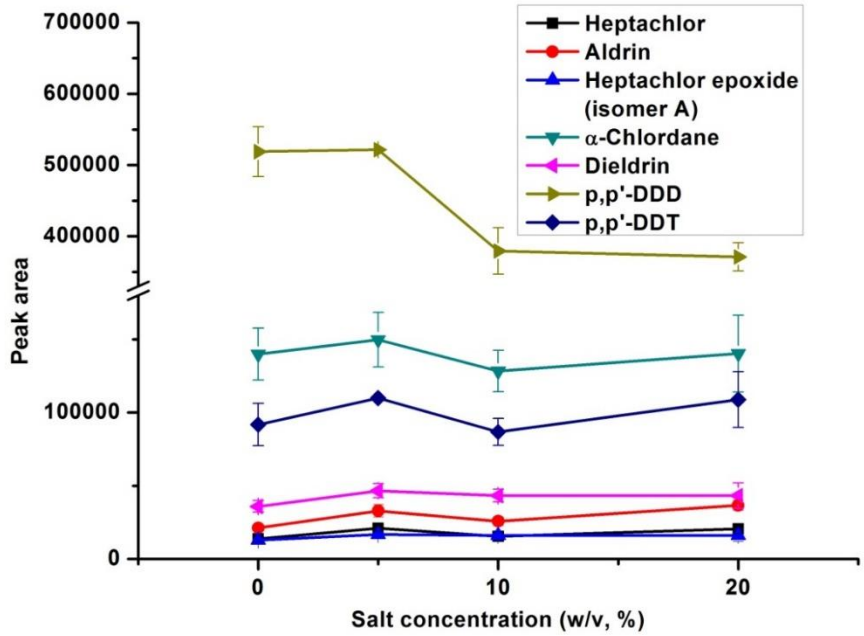


Figure 4- 5 Effect of concentration of NaCl added on the extraction of OCPs. Conditions: analyte concentrations, 0.01 µg/mL of each; extraction time, 40 min; agitation speed, 1250 rpm; no adjustment of pH.

4.3.3 Effect of humic acid

The humic acid in natural samples generally tends to inhibit extraction, including SPME because the dissolved organic matter with large molecular mass likely associates with the analytes or bind competitively to the adsorbent. It has been a significant concern to check for the interference arising from the presence of humic acid on the extraction performance [274]. Herein, to evaluate the extent of the humic acid effect in the proposed approach, extractions of OCPs from aqueous solutions with dissolved humic acid ranging from 0 to 50 mg/L were carried out. In most natural surface water, the concentration of humic matter is less than 10 mg/L [275]. The profiles in Figure 4-6 show that when humic acid concentration was at

20 mg/L, the extraction amounts of the analytes were maintained at more than 70% compared to the results obtained when no humic acid was added, except for p,p′-DDT (47%). For most of the analytes, a significant reduction in extraction amount was only observed when the humic acid concentration reached 50 mg/L. However, such a concentration exceeds the normal level in real water samples. These results showed that humic acid has limited negative effect on the present extraction method, suggesting the C-PDA coating phase has low adsorption potential in relation to humic acid. The reason may be ascribed to that the inner hierarchical nanostructure of C-PDA, as revealed previously [270], could effectively prevent relatively larger sized molecules from adsorbing to it.

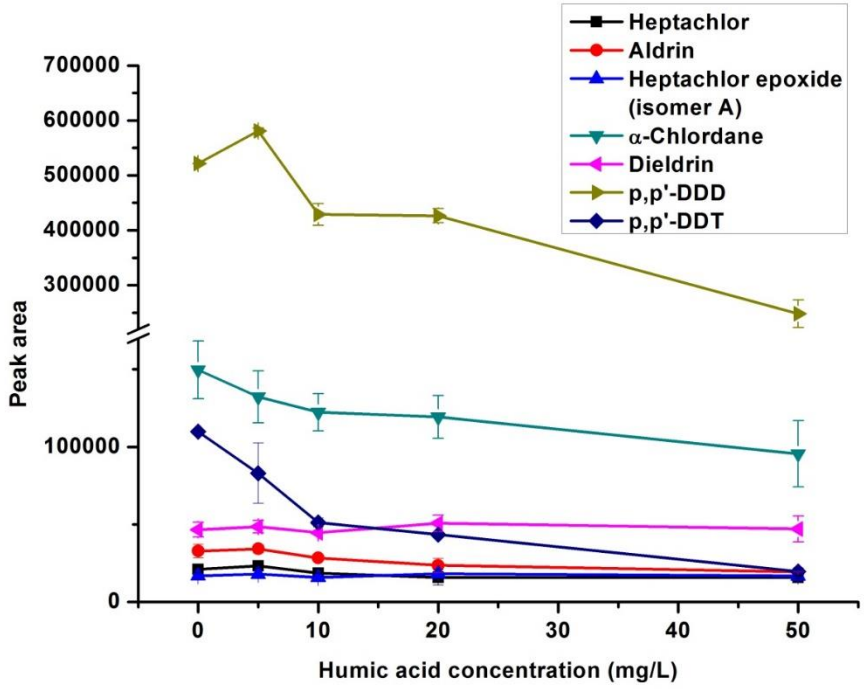


Figure 4- 6 Influence of humic acid on extraction of OCPs. Conditions: analyte concentrations, 0.01 μg/mL of each; extraction time, 40 min; agitation speed, 1250 rpm; salt concentration, 5% NaCl (w/v, %); no adjustment of pH.

4.3.4 Comparison of extraction performance amongst different SPME fibers

The extraction performance of the homemade C-PDA coated fiber was compared with that of a commercial SPME fiber with CAR/PDMS coating (85 μm thickness), and an uncoated hydrofluoric acid etched stainless steel wire. CAR/PDMS is a bipolar coating sorbent with porous carbon suspended in PDMS phase and is suitable for the extraction of most organic compounds. It is selected as a reference because of its similarity in the coating component to C-PDA. Figure 4-7 illustrates the effect of coating characteristics on the extraction concerning OCPs. The C-PDA coated fiber, as expected, exhibited prominent enhancement in extraction amount compared to the acid treated fiber, due to the extra adsorption capacity provided by the carbon coating anchored on the surface of the wire. In addition, it can be seen that the amounts of OCPs extracted by the C-PDA coated fiber are comparable to those by the CAR/PDMS fiber, although the latter worked marginally better for some analytes. It is conceivable that the reason could be due to the fact that the volume of coating phase of CAR/PDMS is higher than that of C-PDA. Consistent with the aforementioned observation, the C-PDA fiber showed a stronger adsorption affinity for p,p′-DDD and p,p′-DDT than the CAR/PDMS fiber. It was determined that a single C-PDA fiber remained stable after more than 150 extractions of OCPs (results not shown).

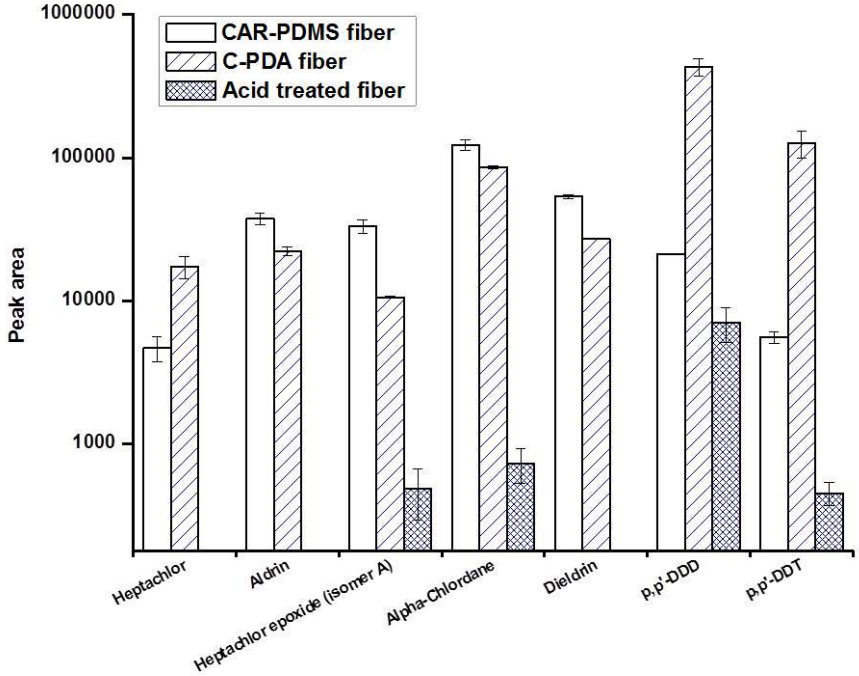


Figure 4- 7 Comparison of extraction of OCPs with three different fibers. Conditions: analyte concentrations, 5 ng/mL of each; extraction time, 40 min; agitation speed, 1250 rpm; salt concentration, 5% NaCl (w/v, %); no adjustment of pH.

4.3.5 Analytical performance of C-PDA coated fiber

Under the optimum extraction conditions, the analytical features of merit for the proposed SPME-GC-MS method using the C-PDA coated wire as extraction fiber for the determination of OCPs were determined and are summarized in Table 4-2. The LODs, calculated at a S/N ratio of 3, varied from 0.0014 to 0.015 ng/mL. Heptachlor, aldrin and α-chlordane exhibited linearity in the concentration range of between 0.05 and 10 ng/mL. For heptachlor epoxide and p,p′-DDD, the linear range was between 0.1 and 50 ng/mL. For dieldrin and p,p′-DDT, the linearity ranged from 0.05 to 50 ng/mL, and 0.01 to 10 ng/mL, respectively. The coefficients of

determination (r^2) of between 0.9971 and 0.9998 indicated that good linearity was achieved for all the analytes. The EF, defined as the ratio of the concentration for each analyte after extraction to the initial concentration spiked in the working solution, for the C-PDA fiber, was achieved to be from 102 to 757. The precision for one fiber was 1.3 to 8.0%, shown by the RSDs of triplicate extractions from working solutions containing with 5 ng/mL of each analyte. The method reproducibility was found to be 1.2 to 16.3% through the examination of three C-PDA coated fibers prepared in the same way for extraction of ultrapure water solutions spiked at 5 ng/L concentrations of each analyte. Compared with the LODs of some previous works focusing on SPME determination of OCPs [165, 200, 276, 277], the results (Table 4-2) suggested that the developed method could provide comparable sensitivity for most of the analytes.

Table 4- 2 Analytical figures of merit for the C-PDA coated fiber for SPME-GC-MS analysis of OCPs and comparison with LODs of other methods

Analyte	Linear range (ng/mL)	r^2	LOD (ng/mL)	Precision for one fiber (RSD%, n=3)	Reproducibility for fiber to fiber (RSD%, n=3)	EF	LODs of other methods (ng/mL)			
							Graphene fiber coupled with GC-ECD [200]	Graphene fiber coupled with GC-MS [165]	MOF-199/ GO fiber coupled with GC-ECD [276]	PDMS fiber coupled with GC-ITMS-MS [277]
Heptachlor	0.05-10	0.9998	0.015	4.7	13.1	130	-	0.0183	-	0.022
Aldrin	0.05-10	0.9997	0.0087	6.8	7.5	102	-	0.0083	0.0028	0.0045
Heptachlor epoxide (isomer A)	0.1-50	0.9996	0.011	1.3	13.6	238	-	-	0.0037	-
α-Chlordane	0.05-10	0.9971	0.0069	5.6	1.2	221	-	-	-	0.0016
Dieldrin	0.05-50	0.9997	0.0044	2.1	10.8	302	-	-	0.0043	0.0081
p,p'-DDD	0.1-50	0.9994	0.0071	8.0	16.3	757	0.00166	-	0.0023	-
p,p'-DDT	0.01-10	0.9990	0.0014	6.3	3.9	530	0.00435	0.00021	-	0.0263

4.3.6 Analysis of environmental water samples

The applicability of the optimized method in real sample analysis was assessed by using the C-PDA fiber to detect the OCPs in drain water samples collected from a local residential area. The results obtained are presented in Table 4-3.

Table 4- 3 Analytical results for determination of the OCPs in drain water samples

Analyte	Concentration detected (ng/mL)	Spiked concentration (ng/mL)	Relative recovery% (n=3)	RSD% (n=3)
Heptachlor	N.D.*	0.5	109	4.6
Aldrin	N.D.	0.5	107	9.4
Heptachlor epoxide (isomer A)	N.D.	0.5	73	2.2
α-Chlordane	N.D.	0.5	82	6.7
Dieldrin	N.D.	0.5	83	5.1
p,p'-DDD	N.D.	0.5	72	14.3
p,p'-DDT	N.D.	0.5	99	6.0

* Not detected.

There were no OCPs detected, suggesting either the absence of the seven OCP compounds studied in this work, or they were present at concentrations below the LODs as determined earlier. By spiking the drain water with standard solution at concentrations of 0.5 ng/mL of each OCP, relative recovery which indicated the effect of the sample matrix was in the range from 72% to 109%. The RSDs in the real water analysis were less than 14.3%. The accuracy and precision of the proposed method could be inferred from the above data to be acceptable and matrix

effect including those of humic acid had little effect when the method was applied to natural environmental water samples.

4.4 Conclusions

In the study, C-PDA was used for the first time as the coating phase of an SPME fiber with a stainless steel wire as the substrate. The C-PDA was generated on the surface of the substrate through the route of self-polymerization of dopamine and following carbonization of the PDA. The application of C-PDA as the sorbent in the extraction of seven OCP compounds from aqueous matrix was investigated. Compared with the original acid etched stainless steel wire, obvious enhancement of extraction capability was obtained due to surface modification by C-PDA coating. Comparable or better results were obtained compared to a commercial CAR/PDMS coated SPME fiber, in conjunction with GC-MS analysis. Under the optimum conditions, the developed C-PDA based SPME approach coupled with GC-MS gave satisfactory results in the determination of OCPs in real water samples. The ease of the preparation of the C-PDA fiber and the low detection limits achieved suggest that the developed method could be a promising SPME approach in the analysis of OCPs.

CHAPTER 5. COMPARATIVE STUDY OF POLYDOPAMINE AND ITS DERIVED CARBON DECORATED NANOPARTICLES IN MAGNETIC SOLID-PHASE EXTRACTION OF ESTROGENS

5.1 Introduction

Driven by the advances of synthetic strategies and nano-technology, magnetic composite materials have drawn considerable attention in multi-disciplinary fields, such as electronics, theranostic, biosensing and separation, and environmental treatment [278-281]. To achieve these applications, a number of magnetic composites have been fabricated, among which magnetic nanoparticles (MNPs) display better prospects due to their reproducibility and functionalization specificity. Analytical methodologies have been taking advantage of the promising features of MNPs to improve existing methods in the past decade [47, 282]. Given the fact that it can be retained under varying conditions, such as pH or surface charge, magnetism provides opportunities for tuning the functionality of MNPs to cater to various demands related to analytical practice. For sample preparation, well-designed MNPs have been exploited as sorbents in many extraction and enrichment procedures, for example, in-tube SPME [47], SPE [283, 284], combination of liquid-phase and solid-phase extraction [285] and high gradient magnetic separation [286].

Peripheral modification strategies for bare metal oxide MNPs can be realized by the introduction of inorganic (e.g., silica) or organic coatings (e.g., octadecylsilane, polymer and surfactant) to the surface of metal oxide nanoparticles [287]. Despite great progress in the application of silica coatings, research on polymer modification is relatively less successful, because of the challenges in grafting designed polymer on magnetic cores. MIPs are important modifiers for MNPs, as the resulting magnetic-organic hybrid materials combine the advantages of selective adsorption as well as the magnetic property in one sorbent [288]. There are limited examples of other synthetic polymers for magnetic separation assisted extraction. As a bioinspired oxidative self-polymerization product, PDA can grow on a variety of substrates forming a polymer film with reactive groups exposed for further functionalization. Therefore, it has attracted the interest of researchers [289]. PDA also has good environmental stability and biocompatibility. Recently, PDA has been shown to be a good decorating material to enhance the extraction capability, or as a support for immobilizing adsorptive reagents [290-292]. Given the potential of PDA as an adsorbent, PDA coated MNPs have been explored in developing facile analytical methods for the detection of microbial organism like Escherichia coli [293], and hazardous compounds, such as aflatoxins [294], PAHs [295] and heavy metal ions [296].

Carbon nanomaterials have played a significant role in diverse applications for the past few years, owing to their remarkable physiochemical properties, such as the chemical inertness and stability, large surface area and structure regularity [297-299]. Carbon nanomaterials with porous structures and magnetic components have

become an intensively studied topic in recent years. Conventional and commercially available carbon nanomaterials such like carbon nanotubes and graphene are widely investigated in the design and synthesis of novel and robust magnetic separation media [300-303]. As it can be generated by a fast and mild polymerization reaction, PDA has the potential to be a carbon source for the fabrication of carbon nanostructures. Besides, the strong adhesion of PDA to metal oxides would make it easy to introduce carbonaceous materials onto magnetic metal oxides. Materials obtained from this preparatory route were successfully utilized in the removal of Rhodamine B and 2,3,4-trichlorphenol from aqueous solution [266, 304], and enrichment of low-abundant peptides from biological samples [305].

Recently, Socas-Rodriguez et al. reported the application of core-shell Fe_3O_4@PDA MNPs for the extraction of estrogenic compounds [306]. In the present work, MNPs modified by PDA shell and its derivative porous carbon shell via a different route from that reported in [306], denoted as Fe_3O_4@PDA and Fe_3O_4@C, respectively, were explored as the sorbents in the magnetic solid-phase extraction (MSPE) of several steroid estrogen hormones, including E1, estradiol (E2), E3 and DES from aqueous samples, whose wide environmental presence has caused a lot of concern [307]. The abundant functional groups in PDA and the affinity of nanostructured carbon are anticipated to contribute to the suitability of adsorptive sites for these compounds. HPLC coupled with UV/Fluorescence detection (FD) was used as the analysis instrument. Orthogonal array design (OAD), which has been demonstrated to be a time-saving and cost-effective multivariate

optimization method in LPME [308] and CPE [309] among others, was applied to optimize the MSPE.

5.2 Experimental

5.2.1 Chemicals and materials

Ferric chloride ($FeCl_3$), sodium acetate, polyethylene glycol (Mw=10000), formic acid (> 98%) and dopamine chloride were obtained from Sigma-Aldrich (St. Louis, MO, USA). Anhydrous ethanol, methanol and acetonitrile (ACN) of HPLC grade were purchased from Fisher (Loughborough, UK), VWR (HiPerSolv CHROMANORM®; BDH Prolabo, Lutterworth, UK). Ethylene glycol and Tris were bought from J.T. Baker (Phillipsburg, NJ, USA). The estrogen standards, E1, E2, E3 and DES were obtained from Sigma-Aldrich. Other chemicals used were the same as those described previously.

5.2.2 HPLC-UV/Fluorescence analysis

HPLC analyses were performed by using a Prominence HPLC system (Shimadzu, Kyoto, Japan) equipped with a binary pump (LC-20AD), an autosampler (SIL-20A), a UV detector (SPD-20A) and a fluorescence detector (FD) (RF-10AXL), working with the LC solution software (version 1.22/MUL,E) (all from Shimadzu). The separations were performed at 40 °C on a Kinetex-C18 (Phenomenex, Torrance, CA, USA) column (100 × 4.60 mm, particle size 2.6 μm). The mobile phase consisted of 1 mM formic acid (solvent A) and acetonitrile containing 1 mM formic acid (solvent B) at a flow rate of 0.6 mL/min. The gradient program was conducted

as follows: 85:15 (v/v) A: B as the initial solvent ratio, gradually changed to 72:28 A: B in 1 min. Subsequently, the mobile phase composition was changed to 65:35 A: B in 5 min, and finally reached 100% of B in 17 min. The injection volume was 20 μL. E1 and DES were determined by UV detection at 230 nm. For E2 and E3, fluorescence detection was adopted with excitation (λ_{ex}) and emission (λ_{em}) wavelengths at 280 and 310 nm, respectively.

5.2.3 Preparation of Fe_3O_4, Fe_3O_4@PDA and Fe_3O_4@C

The Fe_3O_4 MNPs were synthesized by the solvothermal approach according to the literature [310]. Briefly, $FeCl_3$ (0.81 g) and ultrapure water (0.54 g) were dissolved in ethylene glycol (40 mL) under magnetic stirring. Then, sodium acetate (3.6 g) and polyethylene glycol (1.0 g) were added. The mixture was vigorously stirred for 30 min. The resultant solution was sealed in a teflon-lined stainless steel autoclave and heated in an oven at 200 ^oC for 12 h. After reaction, the product was allowed to cool down naturally. By magnetic separation, the products were washed several times with ultrapure water and ethanol, respectively, and finally dried at 60 ^oC under vacuum.

In a typical preparation of Fe_3O_4@PDA, the Fe_3O_4 (320 mg) was dispersed in 160 mL of 10 mM Tris-HCl solution (at pH 8.5) under ultrasonication for 10 min, followed by addition of 320 mg dopamine-hydrochloride. After continuous mechanical stirring at ambient temperature for 10 h, Fe_3O_4@PDA MNPs were collected by magnetic separation and washed with ultrapure water. Fe_3O_4@C was obtained by carbonizing the as-synthesized Fe_3O_4@PDA in a Carbolite tube

furnace in an Argon atmosphere. The Fe_3O_4@PDA was heated from ambient temperature to 600 ^oC at a heating rate of 5 ^oC/min, and then annealed at 600 ^oC for 1 h. After thermal treatment, the products were cooled down to room temperature at a rate of 5 ^oC/min.

5.2.4 Materials characterization

The morphologies and surface features of the three MNPs were surveyed by a JEOL (Tokyo, Japan) JSM-6701F field emission SEM system, and a TEM system (JEOL JEM 2010F) at the accelerating voltage of 200 kV. Powder XRD patterns and FT-IR spectra were collected on the same instruments as described in Chapter 2. Magnetization measurement was carried out with a Vibrating Sample Magnetometer (VSM7404, Lakeshore, OH, USA) at room temperature. Zeta potential was determined by electrophoretic light scattering using a Zetasizer system (Nano ZS90, Malvern, Worcestershire, UK).

5.2.5 Sample preparation

Separate stock solutions of individual analytes (1 mg/mL) were prepared by dissolving in methanol and stored at 4 ^oC in the darkness. They were diluted to the target concentrations for the experiment. Working solutions were prepared by spiking ultrapure water with the stock solutions. The tap water from our laboratory was analyzed using the proposed method.

5.2.6 MSPE procedures

Twenty milligrams of Fe_3O_4@PDA (or Fe_3O_4@C) was added to a working solution in a conical flask containing the analytes at known concentration. One minute ultrasonication was applied to make sure the sorbent MNPs were well dispersed in the solution. The latter was then shaken on a vortex mixer (Vortex-Genie 2, USA) for a prescribed time. The MNPs with entrapped analytes were isolated and separated from the sample solution by holding a permanent magnet against the flask; the sample solution was then decanted. Subsequently, the analytes were eluted with 1 mL of the selected solvent with the assistance of ultrasonication. The extract was evaporated to dryness under a gentle stream of nitrogen gas, followed by reconstitution in 50 μL of methanol. Twenty microliters of the supernatant were injected into HPLC for analysis. After desorption, the sorbent MNPs were washed twice with methanol to regenerate them for the next experiment.

5.2.7 Optimization strategy

Initially, a two level OAD matrix of OA16 (2^{15}) was chosen to acquire a general understanding of the influence of five main variables on extraction efficiency. These variables include: (1) desorption solvent (factor A); (2) extraction time (factor B); (3) desorption time (factor C); (4) pH of sample solution (factor D); (5) salt (NaCl) concentration of sample matrix (factor E). The assignment of the factors was conducted according to the literature [311] and shown in Table 5-1. The sum of EFs of four analytes was calculated and used as a response function for each trial, where EF is defined as the ratio of the final concentration of each analyte in the

solvent phase that would be injected into HPLC for analysis to the initial concentration of the analyte in the working solution (or sample solution). Through the results from this preliminary optimization step, the choices of desorption solvent and a more proper ionic strength were confirmed. The other factors need to be further investigated in order to finalize the optimal extraction conditions accurately.

Table 5- 1 Assignment of factors and level settings of the experiment runs in the OA_{16} (2^{15}) matrix

Level	Factors														
	A	B	AxB	C	AxC	BxC	DxE	D	AxD	BxD	CxE	CxD	BxE	AxE	E
1	Methanol	5		2				4							0
2	ACN	25		10				9							20

A= Type of desorption solvent; B= Extraction time (min); C= Desorption time (min); D= pH of sample matrix; E= concentration of NaCl added (w/v, %).

Thus, a four-level OAD matrix OA_{16} (4^5) was employed in the next step for this purpose. Based on the preliminary results (Tables 5-2 and 5-3), extraction time (factor A), desorption time (factor B) and pH of sample matrix (factor C) were set at four levels. The assignments of these factors for Fe_3O_4@PDA and Fe_3O_4@C were not the same; they are illustrated in Tables 5-4 and 5-5, respectively.

The obtained experimental data from OA_{16} (4^5) optimization (shown in Tables 5-6 and 5-8) were evaluated using the ANOVA statistical method. The corresponding ANOVA analyses for the two sorbents are presented in Tables 5-7 and 5-9, where

we could identify the best level of every studied factor and predict its percentage contribution (PC) to the total extraction efficiency.

5.3 Results and discussion

5.3.1 Characterization of Fe_3O_4@PDA and Fe_3O_4@C

The morphology of the two magnetic sorbents were first characterized by SEM. Figure 5-1 (a, b) show that the synthesized Fe_3O_4 are spherical and have a coarse surface. As shown in Figure 5-1 (c, d), Fe_3O_4@PDA is much smoother than that of Fe_3O_4. The images of Figure 5-1 (e, f) demonstrate that the calcination at 600 °C did not damage the integrity of the magnetic cores. Instead, the carbon coating was as smooth as the PDA coating. The structure features of Fe_3O_4@PDA and Fe_3O_4@C were further examined by TEM (Figure 5-2 (b, c, e)). Both of them exhibited a well-defined core-shell structure. However, the carbon coating of Fe_3O_4@C was thinner compared with the PDA coating, as a result of the shrinkage that occurred during thermal treatment [270]. According to the high-resolution TEM images (Figure 5-2 (d,f)), the components of two coatings are different. The graphite lattice fringe (d=0.34 nm) was observed for Fe_3O_4@C, suggesting that the PDA derived carbon coating was graphitized to some extent [266, 270], while the rest possibly remained amorphous. XRD patterns are presented in Figure 5-3. All the peaks from Fe_3O_4 were retained in Fe_3O_4@PDA and Fe_3O_4@C. These results indicate that the magnetic core was well preserved in the fabrication process as well as after several cycles of extraction.. Therefore, it can be inferred that the high stability would allow multiple reuse of the two sorbents.

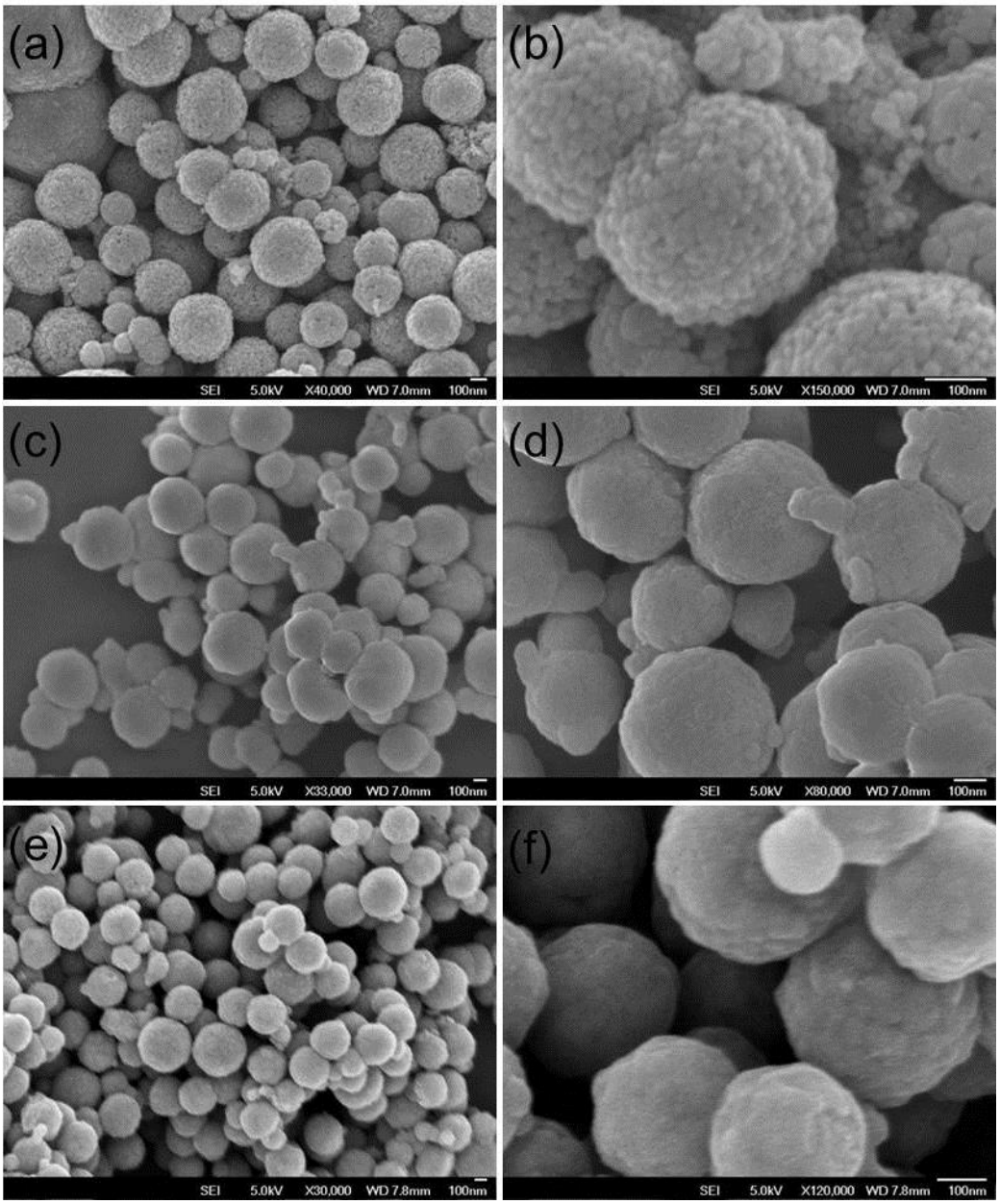


Figure 5- 1 SEM images of the prepared Fe_3O_4 (a,b), Fe_3O_4@PDA (c,d) and Fe_3O_4@C (e,f) MNPs at different magnifications.

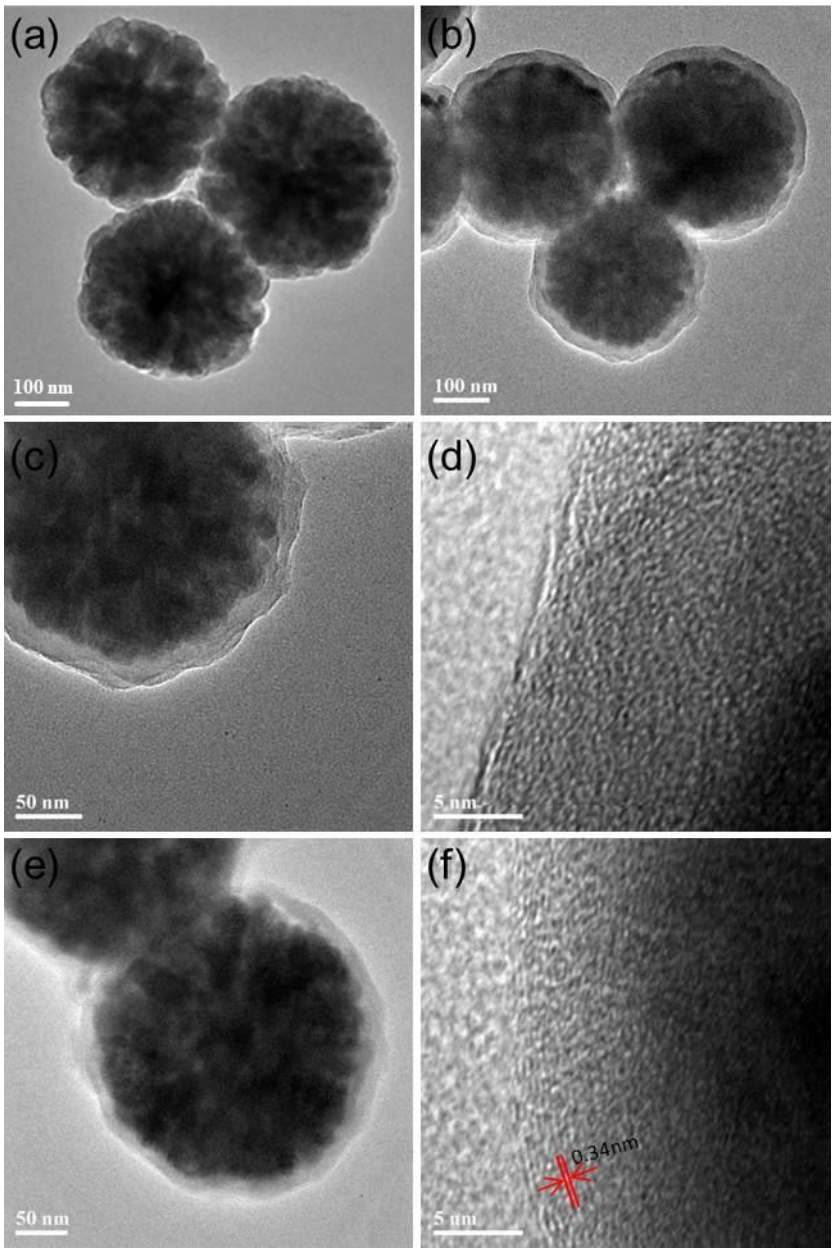


Figure 5- 2 TEM images of Fe_3O_4 (a), Fe_3O_4@PDA (b,c) and Fe_3O_4@C (e); High-resolution TEM images of the coating shell of Fe_3O_4@PDA (d) and Fe_3O_4@C (f).

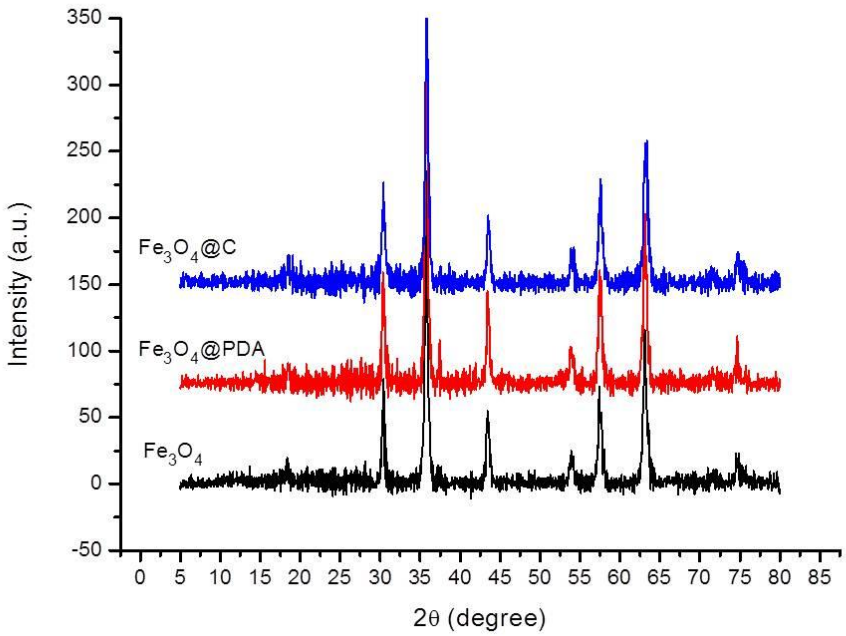


Figure 5- 3 XRD spectra of Fe_3O_4, Fe_3O_4@PDA and Fe_3O_4@C.

The FT-IR spectra are shown in Figure 5-4. For Fe_3O_4@PDA, there were some new absorbance bands between 1200 and 1800 cm^{-1} compared with Fe_3O_4. The peaks at 1289 and 1619 cm^{-1} belong to the characteristic absorption of the stretching of C-O bond and stretching vibration of the aromatic rings from PDA [296, 305]. The peaks 1400-1500 cm^{-1} could be attributed to the C-C stretching vibration. In addition, the relatively broad adsorption peaks at around 3200 and 3400 cm^{-1} were due to the vibration of O-H and N-H groups present on the surface of Fe_3O_4@PDA. After carbonization, the characteristic peaks of PDA disappeared, while the peaks left at 580 cm^{-1} was due to Fe-O bond, and 1610 cm^{-1} could be ascribed to the stretching of C=C bond from the carbon coating [312, 313].

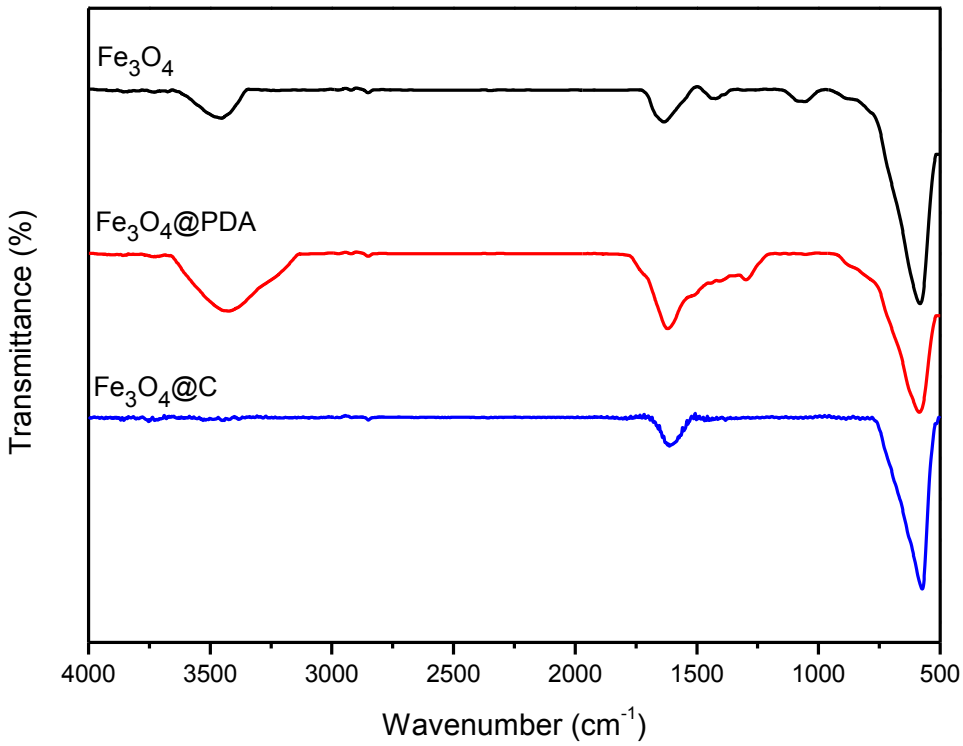


Figure 5- 4 FT-IR spectra of bare Fe_3O_4, Fe_3O_4@PDA and Fe_3O_4@C.

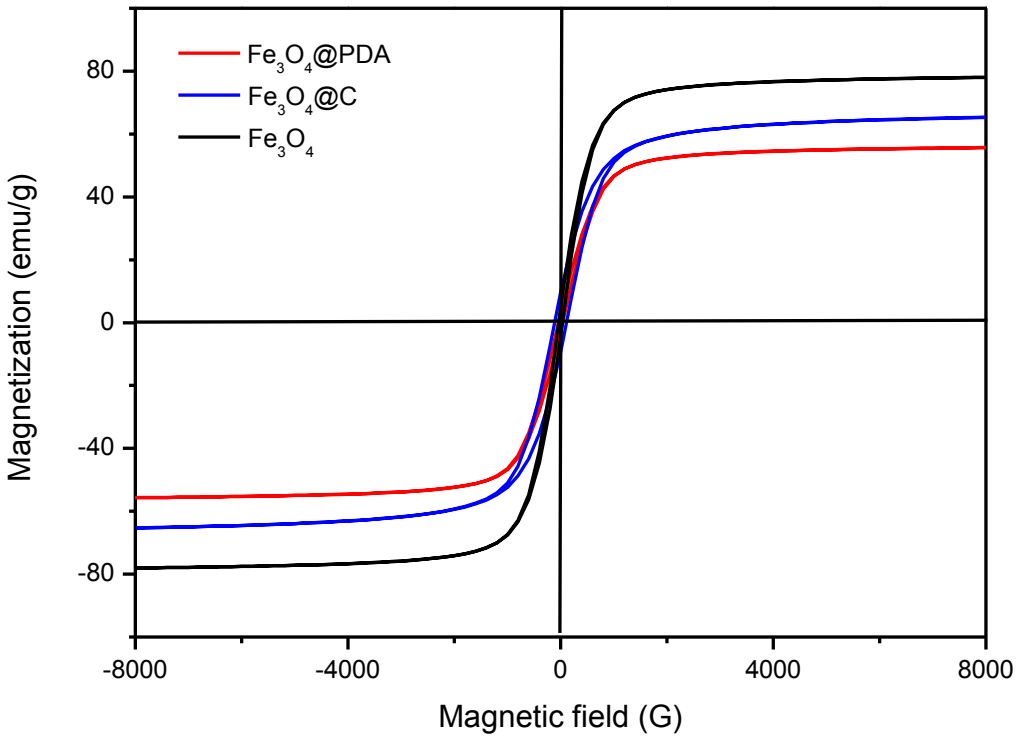


Figure 5- 5 Magnetization curves of Fe_3O_4, Fe_3O_4@PDA and Fe_3O_4@C.

To investigate the magnetism of the prepared magnetic particles, their hysteresis loops were measured at ambient temperature (Figure 5-5). The saturated magnetization values for Fe_3O_4, Fe_3O_4@PDA and Fe_3O_4@C were 78.0, 55.6 and 65.3 emu/g, respectively, indicating high magnetic response when placed in a magnetic field. This would afford fast and convenient separation of the sorbent from the sample solution after extraction.

5.3.2 Optimization of extraction conditions

5.3.2.1 Initial optimization using two-level OA_{16} (2^{15}) matrix

The responses for all the experimental trials in the two-level OAD matrix are shown in Tables 5-2 and 5-3. The sum of the four EFs was chosen to represent the extraction efficiency in each trail. The values of r_1 and r_2 were calculated by averaging the responses corresponding to the two different levels. Since the level setting in this step was low, direct observation analysis was used to make a rough estimate of the superior level for one experimental variable. The difference of mean responses d, between the maximum and minimum r values, was considered as an indicator of the superiority of an experimental factor.

The OA_{16} (2^{15}) optimization results for Fe_3O_4@PDA are shown in Table 5-2. It can be found that methanol and ACN gave almost equal eluting efficiency (compare the r_1 and r_2 in column 1), with the former being slightly better, suggesting both of the two solvents are quite compatible with Fe_3O_4@PDA. The addition of NaCl had negative effect on the extraction performance, because the r_2 obtained at a

concentration of 20% (w/v) NaCl decreased by 74 compared with r_1 when no NaCl was added. Generally, the salting-out effect by the decreased solubility of analytes could influence the extraction process. The hydrophilic PDA shell contains catechol and amino groups, which endow Fe_3O_4@PDA with good dispersibility and render it negatively charged in solution [314]. The presence of a high concentration of salt ions may shield the surface charge of Fe_3O_4@PDA [315], and impede the possible electrostatic and hydrogen bonding interactions between the PDA shell and the analytes. Therefore, the salting-out effect by adding NaCl at the adjusted level to sample solution did not improve the extraction efficiency for Fe_3O_4@PDA and no addition of salt was confirmed to be a better choice. The effect of pH of sample matrix was investigated at either acidic or basic condition. The big d value of 51 for the pH factor indicates that the pH might play an important role in the extraction performance. As illustrated in Table 5-2, higher EFs were achieved at pH 4. Considering that the molecular configurations of the estrogens whose pK_a values are in the range of 9.73-10.77 [316], and the PDA coating are susceptible to the pH environment, more investigation was necessary to obtain the optimal pH condition.

Extraction time and desorption time are also critical factors for sorbent phase based extraction. In general, the extraction time depends on the equilibrium of the participation of the analytes between the sample matrix and the sorbent phase. The higher affinity the sorbent possesses, the less time it would take to reach equilibrium. In Table 5-2, it is observed that relatively high EFs were obtained by Fe_3O_4@PDA at a shorter extraction (5 min) and desorption (2 min) time, indicating

fast extraction equilibrium. Although the differences between the two levels for extraction time and desorption (6 and 7, respectively) were not significant, the two-variable interaction between them (refer to the d value of column 6 in Table 5-2, which was larger compared with the others) was noticeable. Thus, further optimization for Fe_3O_4@PDA on the extraction time and desorption time was needed.

The OA_{16} (2^{15}) optimization results for Fe_3O_4@C are presented in Table 5-3. It showed that ACN was more efficient at eluting the estrogens. Carbonization treatment brought in loss of the polar functional groups of PDA and rendered the obtained carbon coating less polar. This may contribute to the higher elution efficiency of ACN which has a lower polarity. The addition of NaCl at 20% (w/v) yielded an extraction efficiency that was only about 60% of the efficiency when NaCl was at 0% (w/v) (compare r_1 with r_2 in column 15). This could be ascribed to the presence of a large amount of salt ions that increased the aqueous density and caused the Fe_3O_4@C particles to float on the surface of the sample solution, thus reducing the contact between the sorbent and the target analytes. The extraction performance of Fe_3O_4@C was also influenced by pH environment. The charge density of the carbon coating is pH dependent [317] and it may have a negative potential [305]. Therefore, the pH change would affect the extraction capacity of Fe_3O_4@C. The EF obtained at pH 4 was larger than that at pH 9.

Table 5- 2 OA_{16} (2^{15}) matrix with experimental results for Fe_3O_4@PDA

Trial	Column no.															Response (EF)				
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	E1	E2	E3	DES	Sum
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	160	167	95	103	525
2	1	1	1	1	1	1	1	2	2	2	2	2	2	2	2	128	149	119	18	414
3	1	1	1	2	2	2	2	1	1	1	1	2	2	2	2	200	174	150	89	613
4	1	1	1	2	2	2	2	2	2	2	2	1	1	1	1	165	169	121	106	561
5	1	2	2	1	1	2	2	1	1	2	2	1	1	2	2	199	178	150	82	609
6	1	2	2	1	1	2	2	2	2	1	1	2	2	1	1	179	186	140	136	641
7	1	2	2	2	2	1	1	1	1	2	2	2	2	1	1	146	156	91	103	496
8	1	2	2	2	2	1	1	2	2	1	1	1	1	2	2	126	144	114	33	417
9	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	186	168	130	73	557
10	2	1	2	1	2	1	2	2	1	2	1	2	1	2	1	162	178	120	109	569
11	2	1	2	2	1	2	1	1	2	1	2	2	1	2	1	168	172	103	128	571
12	2	1	2	2	1	2	1	2	1	2	1	1	2	1	2	140	148	117	74	479
13	2	2	1	1	2	2	1	1	2	2	1	1	2	2	1	172	175	115	135	597
14	2	2	1	1	2	2	1	2	1	1	2	2	1	1	2	109	121	95	55	380
15	2	2	1	2	1	1	2	1	2	2	1	2	1	1	2	154	155	124	68	501
16	2	2	1	2	1	1	2	2	1	1	2	1	2	2	1	177	184	133	108	602
r_1	535	536		537		510		559							570					
r_2	532	530		530		556		508							496					
d	3	6		7		46		51							74					

Table 5- 3 OA_{16} (2^{15}) matrix with experimental results for Fe_3O_4@C

Trial	Column no.															Response (EF)				
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	E1	E2	E3	DES	Sum
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	135	153	145	48	481
2	1	1	1	1	1	1	1	2	2	2	2	2	2	2	2	53	63	86	5	207
3	1	1	1	2	2	2	2	1	1	1	1	2	2	2	2	80	87	91	35	293
4	1	1	1	2	2	2	2	2	2	2	2	1	1	1	1	94	100	91	58	343
5	1	2	2	1	1	2	2	1	1	2	2	1	1	2	2	88	99	100	40	327
6	1	2	2	1	1	2	2	2	2	1	1	2	2	1	1	89	95	97	47	328
7	1	2	2	2	2	1	1	1	1	2	2	2	2	1	1	131	157	148	78	514
8	1	2	2	2	2	1	1	2	2	1	1	1	1	2	2	76	90	92	4	262
9	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	82	80	64	6	232
10	2	1	2	1	2	1	2	2	1	2	1	2	1	2	1	154	149	129	68	500
11	2	1	2	2	1	2	1	1	2	1	2	2	1	2	1	172	166	145	75	558
12	2	1	2	2	1	2	1	2	1	2	1	1	2	1	2	99	107	85	1	292
13	2	2	1	1	2	2	1	1	2	2	1	1	2	2	1	163	166	126	40	495
14	2	2	1	1	2	2	1	2	1	1	2	2	1	1	2	109	117	87	1	314
15	2	2	1	2	1	1	2	1	2	2	1	2	1	1	2	70	66	51	27	214
16	2	2	1	2	1	1	2	2	1	1	2	1	2	2	1	171	166	140	46	523
r_1	344	363		360				389							468					
r_2	391	372		375				346							267					
d	47	9		15				43							201					

In Table 5-3, it can be seen that for Fe_3O_4@C, the effect of extraction time and desorption time was more significant (bigger d value) than that for Fe_3O_4@PDA. Higher EFs were achieved for Fe_3O_4@C in a relatively longer extraction (25 min) and desorption duration (10 min). The possible reason could be that the main interactions between Fe_3O_4@C and the estrogens including π-π interaction and hydrophobic interaction are not as strong as those for the adsorption of Fe_3O_4@PDA. In the next optimization step for Fe_3O_4@C, the extraction and desorption time was based on 25 and 10 min, respectively.

On the basis of the discussions above, methanol and ACN could be selected as the optimal elution solvent for Fe_3O_4@PDA and Fe_3O_4@C, respectively. It could also be determined that for subsequent optimization there was no need to adjust the ionic strength by adding salt. The other three experimental conditions would be further studied in more detail to determine their optimal level values.

5.3.2.2 Optimization using four-level OA_{16} (4^5) matrix

The assignments of the three factors (extraction time, desorption time and pH) in OA16 (4^5) matrix are depicted in Tables 5-4 (for Fe_3O_4@PDA) and 5-5 (for Fe_3O_4@C). Dummy factors were included in the four-level design for estimation of errors in the experiment. The corresponding responses are summarized in Tables 5-6 and 5-8, respectively. According to the application of OAD in the literature [318], the experimental results were analyzed using ANOVA, with which the indices in Tables 5-7 and 5-9 were calculated.

Table 5- 4 Assignment of factors and level settings of the experiment runs in the OA_{16} (4^5) matrix for Fe_3O_4@PDA

Level	Factors				
	A	B	Dummy	Dummy	C
1	5	2			3
2	10	4			4
3	15	6			6
4	20	8			8

Table 5- 5 Assignment of factors and level settings of the experiment runs in the OA_{16} (4^5) matrix for Fe_3O_4@C

Level	Factors				
	A	B	Dummy	Dummy	C
1	10	4			3
2	15	6			4
3	20	10			6
4	25	14			8

As can be seen from columns 1 and 2 in Table 5-6, the highest sum of EFs was reached for Fe_3O_4@PDA, when the extraction time was 10 min (r_2 of column 1) and desorption time was 8 min (r_4 of column 2). This suggests that the extraction equilibrium was reached within 10 min. The stability of PDA at different pH values has been noted previously [260]. The pH range investigated was from 3 to 8 in this optimization step. The best extraction performance was obtained at pH 3. Fe_3O_4@PDA was demonstrated to be stable by the fact that adsorption capability was maintained even after 10 times of extraction. The TEM image of Fe_3O_4@PDA after extraction in sample solution of pH 3 is shown in Figure 5-6. There was no

significant change in the PDA coating compared to the pristine Fe_3O_4@PDA. PDA is a zwitterion with an isoelectric point around 4 [319], so the PDA shell would be negatively charged at pH > 4, due to the deprotonation of phenolic groups. According to the measurements of the zeta potentials at different pH values, the point of zero charge of the Fe_3O_4@PDA synthesized in the study is at ca. pH 2.9 (Figure 5-7). It can be inferred that when pH was 3, the negative charges of PDA were almost neutralized. Besides the dominant π-π interaction, other interactions such as hydrogen bonding and π-cation interaction might be established between the PDA shell and the analytes [320], benefitting from the abundant functional groups on PDA such as phenolic hydroxyl group, amino group, carbonyl group and the aromatic ring. From the ANOVA results in Table 5-7, the influences of extraction time, desorption time and pH of sample solution were significant at the 99% confidence level ($p<0.01$). The three factors had similar contributions (compare their PC values) to the total enrichment performance.

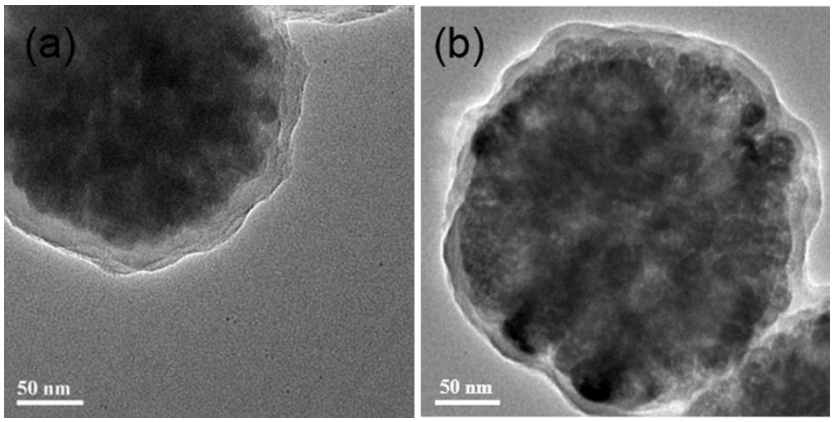


Figure 5- 6 Comparison of TEM images of (a) pristine Fe_3O_4@PDA particles and (b) Fe_3O_4@PDA after extraction in sample solution at pH 3 for more than five times.

Table 5- 6 OA_{16} (4^5) matrix with experimental results for Fe_3O_4@PDA

Trial	Column no.					Response (EF)				
	1	2	3	4	5	E1	E2	E3	DES	Sum
1	1	1	1	1	1	165	176	134	141	616
2	1	2	2	2	2	163	162	134	124	582
3	1	3	3	3	3	165	173	133	144	616
4	1	4	4	4	4	169	180	147	142	638
5	2	1	2	3	4	170	181	140	143	634
6	2	2	1	4	3	169	186	152	136	643
7	2	3	4	1	2	165	174	140	145	624
8	2	4	3	2	1	186	196	156	166	704
9	3	1	3	4	2	165	175	142	143	624
10	3	2	4	3	1	174	181	145	156	655
11	3	3	1	2	4	170	183	150	138	641
12	3	4	2	1	3	167	184	149	160	660
13	4	1	4	2	3	158	183	141	154	636
14	4	2	3	1	4	178	188	140	129	635
15	4	3	2	4	1	172	184	148	159	663
16	4	4	1	3	2	174	177	148	158	657
r_1	613	628	639	634	660					
r_2	651	629	635	641	622					
r_3	645	636	645	641	639					
r_4	648	665	639	642	637					
d	38	37	10	8	38					

Table 5- 7 An ANOVA analysis for experimental responses for Fe_3O_4@PDA in OA_{16} (4^5) matrix

Source	SS	d.f.	MS	F[a]	SS'	PC(%)
extraction time (A)	3747	3	1249	20.4**	3563	33.4
desorption time (B)	3620	3	1206.7	19.7**	3436	32.2
pH (C)	2932	3	977.3	15.9**	2748	25.8
Pooled errors†	368	6	61.3		920	8.6
Total	10667	15			10667	100

SS=sum of squares; d.f.=degrees of freedom; MS=mean squares; SS'=purified sum of squares; PC=percentage contribution.
†Resulted from pooling of dummy factors at column 3 and 4.
[a] Critical value $F_{(3,6)}$ is 23.7 (***p<0.001) and 9.78 (**p<0.01).

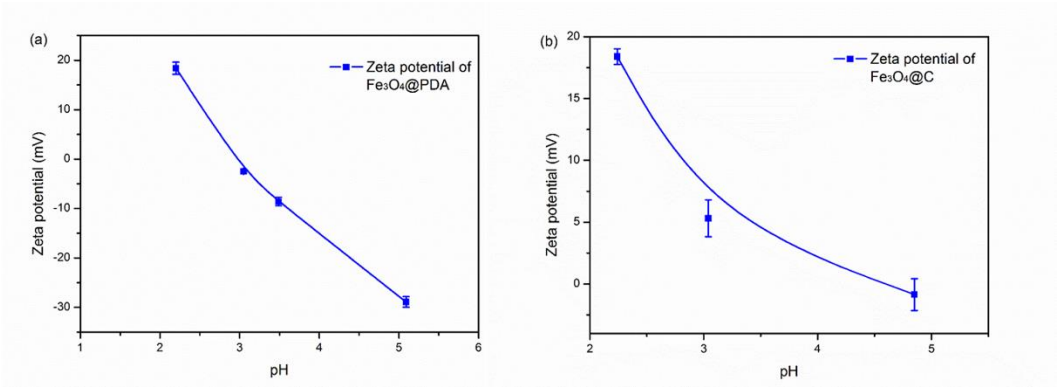


Figure 5- 7 Zeta potential measurements of (a) Fe_3O_4@PDA and (b) Fe_3O_4@C.

As for Fe_3O_4@C, the extraction duration of 20 min and desorption duration of 6 min gave the most satisfactory extraction results, as shown in Table 5-8 (r_3 of column 1 and r_2 of column 2). The relative longer extraction time and shorter desorption time suggest that the adsorption rate of the carbon coating was not as fast as that of the PDA with multifunctional groups. The optimal pH environment demonstrated to be at pH 4. Given that the carbon coating carries fewer negative

charges than the PDA coating [305], it should have a higher isoelectric point. The experiment data showed that the point of zero charge of Fe_3O_4@C is at ca. pH 4.5 (Figure 5-7). It is possible that the negative surface charge of the carbon coating was neutralized or minimized at around this acidic pH and more adsorption sites were therefore exposed with the removal of water cluster adsorbed [321], facilitating the π-π interaction between the carbon coating and the estrogens. Accordingly, the surface of Fe_3O_4@C would bear more positive charges at pH 3, thereby resulting in the formation of more water clusters on the surface. This probably decreased the active adsorption sites and hindered the access of the analytes to the carbon coating. As indicated in Table 5-9, the factor that contributed most to the extraction efficiency is the pH (41.5%). The extraction and desorption duration contributed almost equally (22.1% and 24.5%, respectively). The error contribution was 8.6% for Fe_3O_4@PDA, and 11.9% for Fe_3O_4@C in the four-level optimization. Nevertheless, these errors were not significantly high to impact adversely on the results.

5.3.3 Method evaluation

The analytical features of this method were evaluated under the optimized experimental conditions as discussed above. The linearity, repeatability, coefficient of determination (r^2), LODs, RSDs and absolute recovery (defined as the ratio of the extracted amount to the spiked amount and calculated as Recovery (%)=$C_{solv}V_{solv}/C_{sample}V_{sample} \times 100\%$, where the C_{solv}, V_{solv}, C_{spike}, V_{sample} are the concentration of the analytes in final organic phase after enrichment for HPLC

Table 5- 8 OA_{16} (4^5) matrix with experimental results for Fe_3O_4@C

Trial	Column no.					Response (EF)				
	1	2	3	4	5	E1	E2	E3	DES	Sum
1	1	1	1	1	1	181	176	129	86	572
2	1	2	2	2	2	189	175	147	89	600
3	1	3	3	3	3	171	171	143	85	570
4	1	4	4	4	4	179	168	141	73	561
5	2	1	2	3	4	164	174	139	75	552
6	2	2	1	4	3	170	170	144	87	571
7	2	3	4	1	2	187	177	145	83	592
8	2	4	3	2	1	174	170	139	82	565
9	3	1	3	4	2	174	179	150	88	591
10	3	2	4	3	1	183	183	137	102	605
11	3	3	1	2	4	186	178	143	78	585
12	3	4	2	1	3	173	174	142	83	572
13	4	1	4	2	3	171	169	140	75	555
14	4	2	3	1	4	176	177	145	78	576
15	4	3	2	4	1	172	174	129	91	566
16	4	4	1	3	2	176	174	146	88	584
r_1	576	568	578	578	577					
r_2	570	588	573	576	592					
r_3	588	578	575	578	567					
r_4	570	571	578	572	569					
d	18	20	5	6	25					

Table 5- 9 An ANOVA analysis for experimental responses for Fe_3O_4@C in OA_{16} (4^5) matrix

Source	SS	d.f.	MS	F[a]	SS'	PC (%)
extraction time (A)	864	3	288	10.3**	780	22.1
desorption time (B)	947	3	316.7	11.3**	863	24.5
pH (C)	1547	3	515.7	18.4**	1463	41.5
Pooled errors†	168	6	28		420	11.9
Total	3526	15			3526	100

SS=sum of squares; d.f.=degrees of freedom; MS=mean squares; SS'=purified sum of squares; PC =percentage contribution.
† Resulted from pooling of dummy factors at column 3 and 4.
[a] Critical value $F_{(3,6)}$ is 23.7 (***p<0.001) and 9.78 (**p<0.01).

analysis, the volume of organic phase after enrichment, the initial concentration of the analytes in sample solution and the volume of sample solution, respectively) are summarized in Tables 5-10 and 5-11. Good linearity of response was observed in the range of 0.01-5 ng/mL for E2 and E3, and 0.2-100 ng/mL for DES for both of the sorbents. For Fe_3O_4@PDA, the linear range of E1 was from 0.2 to 100 ng/mL, while for Fe_3O_4@C it was in the range of 0.5 to 100 ng/mL. All the r^2 values were $\geq$ 0.9995. LODs were calculated at a S/N ratio of 3 and they were found to be as low as from 0.0017 to 0.0062 ng/mL for E2 and E3, while the LODs of E1 and DES were between 0.072 and 0.15 ng/mL. The LODs obtained in this work were relatively low compared with the other methods [103, 237, 306, 316, 322-324] (Table 5-12), indicating satisfactory sensitivity of the proposed method. Furthermore, this method was environmental friendly as only about 1 mL of solvent was used for elution (another 2 mL of solvent would be consumed if regeneration was taken into account). Although a similar sorbent, i.e. Fe_3O_4@PDA was used for

extraction of estrogens recently [306], the sorbent (60 mg) and elution solvent (6 mL) consumed were more than those in the present study. The time efficiency for the extraction and desorption procedures in this work was higher than the SBSE [323] and comparable to that using a sol-gel polymer sorbent [324]methods, suggesting good adsorption properties of the PDA coating and PDA-derived carbon coating.

Table 5- 10 Analytical features of Fe_3O_4@PDA based method

Analyte	Linear range (ng/mL)	r^2	LOD (ng/mL)	RSD% (n=3)	Recovery% (n=3)	
					1 ng/mL	5 ng/mL
E1	0.2-100	0.9995	0.072	3.8	118	86.2
E2	0.01-5	0.9999	0.0022	2.7	89.1	84.3
E3	0.01-5	0.9999	0.0041	1.5	74.1	71.2
DES	0.2-100	0.9999	0.15	2.3	131	84.8

Table 5- 11 Analytical features of Fe_3O_4@C based method

Analyte	Linear range (ng/mL)	r^2	LOD (ng/mL)	RSD% (n=3)	Recovery% (n=3)	
					1 ng/mL	5 ng/mL
E1	0.5-100	0.9999	0.087	10.1	109	78.4
E2	0.01-5	0.9999	0.0017	6.4	80.6	84.7
E3	0.01-5	0.9997	0.0062	5.6	69.6	75.7
DES	0.2-100	0.9997	0.12	4.2	87.7	46.9

Table 5- 12 Comparison of the proposed method with other methods for the determination of estrogens

Method	Sorbent/ Extractant	Sample	Sorbent (mg)/ Extractant (mL)	LOD (ng/mL)				Ref.
				E1	E2	E3	DES	
m-µSPE-HPLC-MS	Fe_3O_4@PDA	Water	60	2.4	4.5	-	0.66	[306]
HF-LPME-HPLC-UV/FD	1-Octanol	Water	0.025	5.97	0.18	0.12	4.56	[316]
DLLME-HPLC-FD	Chlorobenzene-acetone	Water	2.2	-	0.002	-	-	[322]
CPE-HPLC-UV	Tergitol TMN-6	Urine	0.05	0.2	0.1	-	0.1	[237]
SPE-UHPLC-MS/MS	MIP	Water	100	0.0057	0.0043	0.0061	0.0085	[103]
SBSE-HPLC-UV	PDMS-MOF	Water	-	0.29	0.28	-	0.26	[323]
FPSE-HPLC-FD	Sol-gel poly-THF	Water	-	-	0.02	-	-	[324]
MSPE-HPLC-UV/FD	Fe_3O_4@PDA / Fe_3O_4@C	Water Water	20/ 20	0.072/ 0.087	0.0022/ 0.0017	0.0041/ 0.0062	0.15/ 0.12	This work

Table 5- 13 Results of analysis of the estrogens in real water samples with Fe_3O_4@PDA

Analyte	Tap water				Drain water				Bottled water			
	Unspiked		Spiked[a]		Unspiked		Spiked		Unspiked		Spiked[a]	
	Concentration detected (ng/mL)	RSD% (n=3)	RR[b] (%)	RSD% (n=3)	Concentration detected (ng/mL)	RSD% (n=3)	RR[b] (%)	RSD% (n=3)	Concentration detected (ng/mL)	RSD% (n=3)	RR[b]	RSD% (n=3)
E1	2.66	5.9	119	1.2	4.85	2.3	77.8	2.3	2.32	17	71.6	15
E2	-	-	89.5	11	-	-	47.9	8.4	-	-	73.4	12
E3	-	-	96.3	2.0	-	-	124	0.6	-	-	95.3	1.4
DES	-	-	112	1.8	-	-	78.6	14	-	-	86.8	3.8

[a] Spiked with 0.5 ng/mL of E1 and DES and 0.02 ng/mL of E2 and E3.

5.3.4 Analysis of tap water

Since the extraction performance of Fe_3O_4@PDA was better than that of Fe_3O_4@C, the former was applied to analysis of real water samples. Tap water samples from our laboratory, drain water from a residential area were extracted using the optimized MSPE method, followed by HPLC-UV/FD analysis (Table 5-13). E1 was surprisingly detected in the tap water (at a concentration of 2.66 ng/mL) and the drain water (4.85 ng/mL). Figures 5-8 and 5-9 show the chromatograms of the tap water and drain water extracts, respectively. Although the occurrence of such natural and synthetic estrogens in surface water have been reported elsewhere [325, 326], the concentration levels of E1 found in tap and drain water in the work seemed to be abnormally high. Moreover, E1 was previously detected in an urban catchment in Singapore in the concentration range of 0.001 to 0.304 ng/mL [327], much lower than in the present samples. It is believed the results observed in the present work might not be reliable, and the peak appearing at the same retention time as E1 could be due to an artefact. Given the surprising result of the tap water analysis, a commercial bottled mineral water sample was analyzed. It was also found to contain E1 (Figure 5-10). This further strengthened our fear that the observations were probably artefacts. In this light, the use of a more selective detector such as a mass spectrometer (MS) would perhaps provide better accuracy and sensitivity for determination of the estrogens, as indicated by the study [306] in which a similar sorbent Fe_3O_4@PDA was utilized for concentration of estrogens including E1 from water samples followed by liquid chromatography-tandem MS (LC-MS/MS) analysis, and no interferences were found. Nevertheless, the present

study revealed the potential of PDA coated magnetic materials for sample preparation and demonstrated an efficient extraction procedure. In any case, the target analytes were not found in blank samples, and after spiking at low concentrations, their peaks were observed and identified in the chromatograms (Figures 5-8, 5-9 and 5-10). The relative recovery of each analyte is presented in Table 5-13. These results demonstrate that the proposed method could be applied to the analysis of tap water samples with good extraction efficiency, particularly if coupled to LC-MS.

5.4 Conclusions

Magnetic nanoparticles with decoration of PDA and its derived carbon coating, Fe_3O_4@PDA and Fe_3O_4@C, were employed as sorbents for the MSPE of estrogens in aqueous samples and determination by HPLC-UV/FD analysis. OAD was first adopted to optimize the MSPE approach, which enabled a comparison of the performance of the two magnetic sorbents in terms of extraction conditions and EFs. The extraction with Fe_3O_4@PDA was shown to be faster and higher enrichment was obtained than with Fe_3O_4@C. This could be attributed to the multiple functional groups present in the polymer coating that benefit the effective interactions between the sorbent and the estrogens. The proposed method was simple in operation and consumed a relatively small amount of solvent. For each extraction 20 mg of sorbent was required; the material could be regenerated, and reused for at least 10 times. The LODs achieved in this work were 0.0017 to 0.0062 ng/mL for E2 and E3, and 0.072 to 0.15 ng/mL for E1 and DES. This method

provided high sensitivity and recoveries for the analysis of tap water. For samples of high complexity, such as environmental or waste water, in which the magnetic sorbents considered here are expected to be useful as well, their protection would be needed, as in membrane-protected μ-SPE [328]. Additionally, use of a MS detector would be desirable.

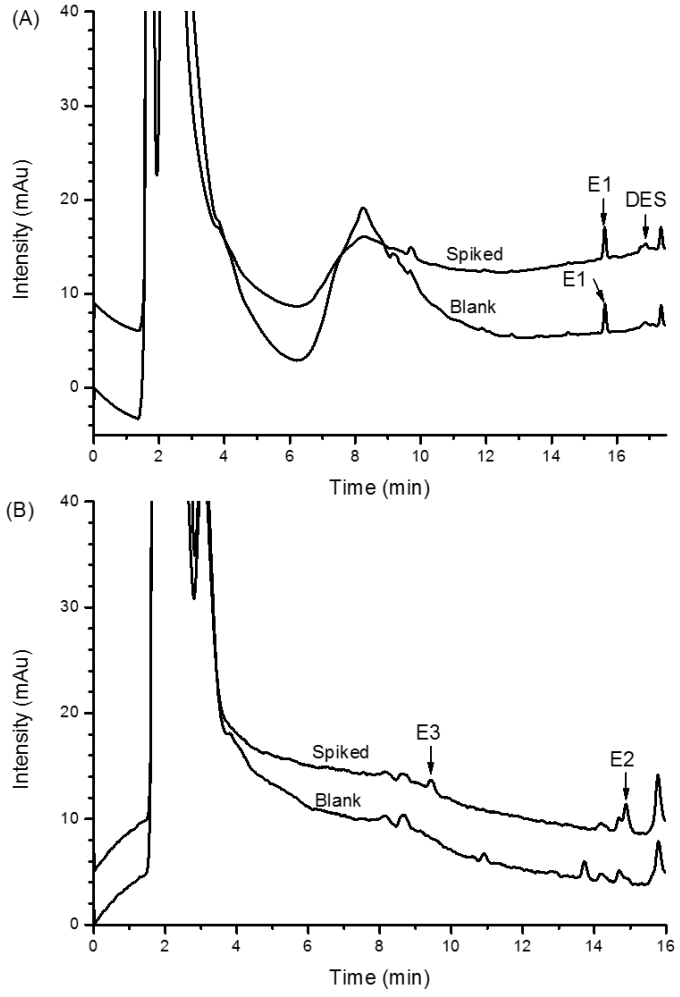


Figure 5- 8 HPLC-UV and -FD chromatograms of tap water samples extracted by the optimized MSPE using Fe_3O_4@PDA. The chromatogram (A) was obtained by UV detection at λ=230 nm and the chromatogram (B) by FD at λ_{ex}=280 nm, λ_{em}=310 nm. The sample was spiked with 0.5 ng/mL of E1 and DES and 0.02 ng/mL of E2 and E3.

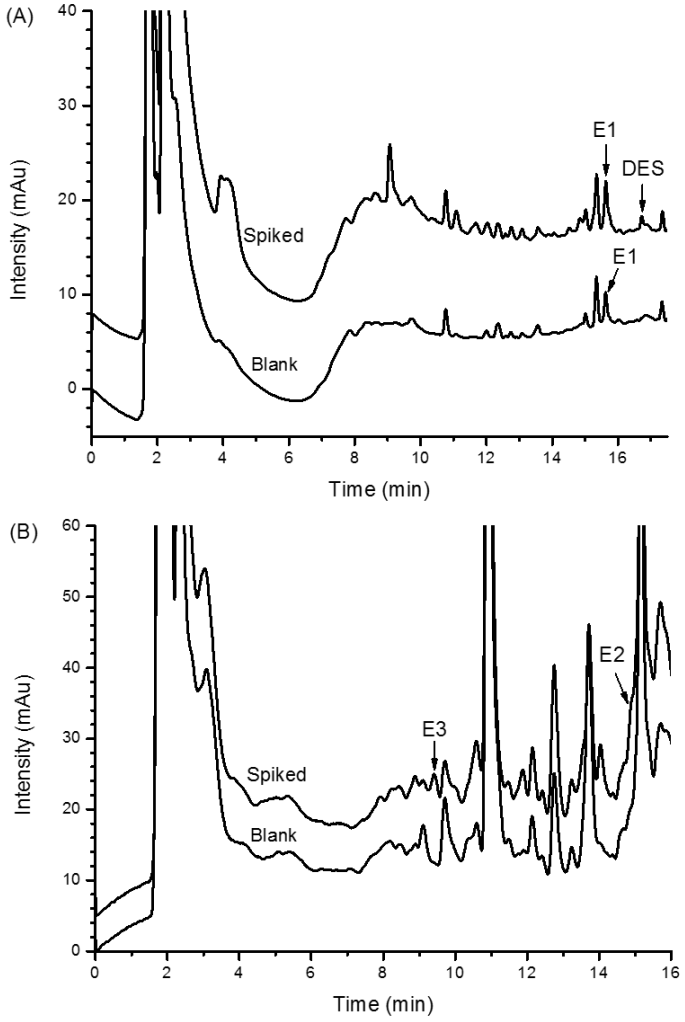


Figure 5- 9 HPLC-UV and -FD chromatograms of drain water samples extracted by the optimized MSPE using Fe_3O_4@PDA. The chromatogram (A) was obtained by UV detection at λ=230 nm and the chromatogram (B) by FD at λ_{ex}=280 nm, λ_{em}=310 nm. The sample was spiked with 0.5 ng/mL of E1 and DES and 0.02 ng/mL of E2 and E3.

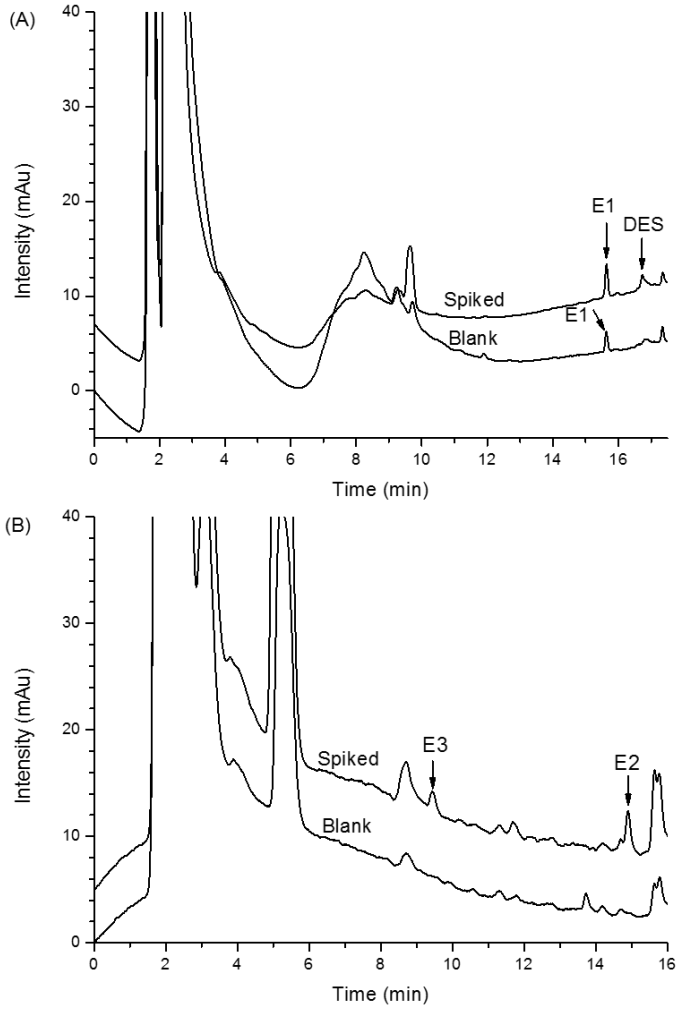


Figure 5- 10 HPLC-UV and -FD chromatograms of bottled water samples extracted by the optimized MSPE using Fe_3O_4@PDA. The chromatogram (A) was obtained by UV detection at λ=230 nm and the chromatogram (B) by FD at λ_{ex}=280 nm, λ_{em}=310 nm. The sample was spiked with 0.5 ng/mL of E1 and DES and 0.02 ng/mL of E2 and E3.

CHAPTER 6. CONCLUSIONS AND FUTURE WORK

With the advances achieved in materials science, the exploration of novel functional materials for the aim of developing environmental friendly sorbent based miniaturized extraction methods has been carried out in this study. Several materials suitable for microextraction, as well as extraction approaches were proposed and evaluated in the analysis of organic contaminants in environment aqueous samples. Micro-solid-phase extraction (μ-SPE) using MIL-101 and dispersive micro-solid-phase extraction (dSPE) using surfactant modified MIL-101 as sorbents were developed and evaluated. The potential applications of polydopamine (PDA) in extraction techniques of solid-phase microextraction (SPME) and magnetic solid-phase extraction (MSPE) were also investigated. The conclusions drawn from aforementioned studies can be summarized as follows.

MIL-101 was synthesized and utilized for the determination of organochlorine pesticides (OCPs) in water samples in membrane protected μ-SPE. Its stability in water and various solvents allowed MIL-101 to be readily used in the sample preparation of aqueous samples. The large pore size and high surface area endow the material with the capacity to extract OCPs from water samples. MIL-101 showed superior capability in the extraction efficiency compared to C8 and C18 silica sorbents, probably due to its porous structure and the presence of diverse adsorption sites on the surface. Combined with GC-MS detection, satisfactorily low limits of detection (LODs) of 0.0025 to 0.016 ng/mL for the five OCP compounds

were achieved. Each extraction device containing 4 mg of MIL-101 was demonstrated to be effective for more than twenty times of use. This study extended the application of MIL-101 from adsorption of small volatile organic compounds to relatively larger pesticide molecules present in relatively complex water samples. Conceivably, the same material may be used for the extraction of other relatively nonvolatile analytes from aqueous samples.

Considering that MIL-101 is naturally hydrophobic, this property probably impedes its dispersibility in solution and thus full contact with the analytes of higher solubility in water. Triton X-114 was made use of to modify MIL-101 crystals by forming hydrophilic protective layers on the surface of MIL-101 crystals. MIL-101 acting as the interior core of the hybrid sorbent provided a high extraction capability for these compounds through hydrophobic interaction. On the other hand, the hydrophilic external layer of Triton X-114 molecules increased the contact probability of the target analytes and the sorbent. Moreover, the separation and collection of the entrapped analytes were facilitated by the cloud point phase separation from Triton X-114. Therefore, the extraction process occurred synergistically with the combination of dSPE and cloud point extraction. The developed method was environmentally friendly in that only a small amount of sorbent (1 mg) and a small volume of solvent (about 200 μL) were consumed. Derivatization of the extracted EDCs was conducted prior to GC-MS analysis and yielded low LODs with acceptable repeatability. Therefore, the proposed surface modification approach has been demonstrated to be an effective way to improve the extraction capability of MIL-101 for analytes in aqueous samples.

In order to fabricate a robust and cost effective SPME device, PDA was considered owing to its unique merit of universal surface modification. Carbonized PDA (C-PDA) was generated on the surface of the substrate through the route of self-polymerization of dopamine followed by carbonization of the PDA. The resulting C-PDA showed the characteristic of graphite to a certain extent, while the rest component were mainly amorphous carbon. The application of C-PDA as the adsorbent in the extraction of OCPs from aqueous matrix was investigated. Compared to the original acid etched stainless steel wire, obvious enhancement of extraction capability was obtained due to surface modification by the C-PDA coating. The home-tailored fiber could provide comparable or better results compared to a commercial CAR/PDMS coated SPME fiber. The developed C-PDA based SPME approach coupled with GC-MS analysis proved to be effective in the determination of OCPs in real water samples.

The potential of PDA in the detection of estrogens in aqueous samples was investigated by adopting PDA and its derived C-PDA decorated Fe_3O_4 nanoparticles as the sorbents for MSPE. Orthogonal array design was used to facilitate the optimization of the proposed sample preparation approach. The highest EFs of the two sorbents were achieved under different experimental conditions, implying different interactions that dominated in the extraction process. The extraction with Fe_3O_4@PDA was shown to be faster, and higher enrichment results were obtained than Fe_3O_4@C. This could be attributed to the multiple functional groups present in the polymer coating that might favor contact and therefore interaction with the polar estrogens. Fe_3O_4@PDA was shown to be

slightly superior to Fe_3O_4@C in the enrichment of estrogens, suggesting stronger interactions being established between the PDA coating and the target compounds. The LODs obtained for Fe_3O_4@C were only slightly higher. By high-performance liquid chromatography coupled with ultraviolet and fluorescence detection, LODs of 0.072 to 0.15 ng/mL for E1 and DES, and 0.0017 to 0.0062 ng/mL for E2 and E3, were obtained.

According to the experimental results obtained and the observations therein, there are some aspects that may need further study to improve the extraction performance of these approaches as well as to broaden of their application range. They include:

(1) The surfactant molecules assisted MIL-101 in the extraction of analytes with a certain polarity and water solubility. The formation of the micelle layer is critical in regulating the dispersibility and adsorptive sites of the MIL-101. Besides Triton X-114, there are several kinds of surfactants with varied molecular chain lengths, polarities and charges. They would have different effects in the proposed approach. It may be interesting to find the most suitable modifier for MIL-101 as well as for other metal-organic frameworks.

(2) The introduction of C-PDA on stainless steel wire as a coating phase was demonstrated to enhance the extraction of some analytes. The results only proved the feasibility of the concept of this method. It is unknown how much more the C-PDA could be immobilized on the wire and if that would affect the extraction performance. One issue of interest is the repeatability afforded by the material.

(3) The proposed methods in the studies were not applied in automated extraction mode. It is worth attempting to implement some of these procedures for automated operations. For example, the extraction procedures of the magnetic sorbents could be conducted on a commercial autosampler.

(4) Some of these sorbents could be applied to known extraction approaches, such as in-tube SPME, for example, to further expand the applicability of this procedure.

REFERENCES

[1] L.M. Schell, M. Denham, Annu. Rev. Anthropol. 32 (2003) 111.

[2] R.L. Prueitt, N.L. Heather, Z. Ke , N.S. Sonja, J.V. Ferdinand, E.J. Goodman, Crit. Rev. Toxicol. 44 (2014) 791.

[3] M.J. Nieuwenhuijsen, X. Basagaña, P. Dadvand, D. Martinez,M. Cirach, R. Beelen, B. Jacquemin, Environ. Int. 70 (2014) 9.

[4] K.A. Furby, A. Apprill, J.M. Cervino, J.E. Ossolinski, K.A. Hughen, Mar. Environ. Res. 98 (2014) 29.

[5] Y. Zhang, P. Wang, L. Wang, G. Sun, J. Zhao, H. Zhang, N. Du, Sci. Total Environ. 506-507 (2015) 118.

[6] L. Hao, J. Li, A. Kappler, M. Obst, Appl. Environ. Microbiol. 79 (2013) 6524.

[7] M. Farré, R. Brix, D. Barceló, Trends Anal. Chem. 24 (2005) 532.

[8] A. Spietelun, Ł. Marcinkowskia, M. de la Guardiab, J. Namiesnika, J. Chromatogr. A 1321 (2013) 1.

[9] H.-G. Ni, H. Zeng, E.Y. Zeng, Trends Anal. Chem. 30 (2011) 1549.

[10] L. Ramos, J.J. Ramos, U.A.T. Brinkman, Anal. Bioanal. Chem. 381 (2005) 119.

[11] M. Michulec, W. Wardencki a, M. Partyka, J. Namieśnik, Crit. Rev. Anal. Chem. 35 (2005) 117.

[12] H. Prosen, Molecules 19 (2014) 6776.

[13] P.T. Anastas, Crit. Rev. Anal. Chem. 29 (1999) 167.

[14] H. Liu, P.K. Dasgupta, Anal. Chem. 68 (1996) 1817.

[15] M.A. Jeannot, F.F. Cantwell, Anal. Chem. 68 (1996) 2236.

[16] M.A. Jeannot, F.F. Cantwell, Anal. Chem. 69 (1997) 235.

[17] A.L. Theis, A.J. Waldack, S.M. Hansen, M.A. Jeannot, Anal. Chem. 73 (2001) 5651.

[18] Y. He, H.K. Lee, Anal. Chem. 69 (1997) 4634.

[19] W. Liu, H.K. Lee, Anal. Chem. 72 (2000) 4462.

[20] G. Ouyang, W. Zhao, J. Pawliszyn, J. Chromatogr. A 1138 (2007) 47.

[21] Y. Lu, Q. Lin, G. Luo, Y. Dai, Anal. Chim. Acta 566 (2006) 259.

[22] M.R. Khalili Zanjani, , Y. Yamini, S. Shariati, J. Åke Jönsson, Anal. Chim. Acta 585 (2007) 286.

[23] S. Pedersen-Bjergaard, K.E. Rasmussen, Anal. Chem. 71 (1999) 2650.

[24] X. Jiang, H.K. Lee, Anal. Chem. 76 (2004) 5591.

[25] S. Pedersen-Bjergaard, K.E. Rasmussen, J. Chromatogr. A 1109 (2006) 183.

[26] M. Rezaee, Y. Assadi, M.-R. Milani Hosseini, E. Aghaee, F. Ahmadi, S. Berijani, J. Chromatogr. A 1116 (2006) 1.

[27] J. Regueiro, M. Llompart, C. Garcia-Jares, J.C. Garcia-Monteagudo, R. Cela, J. Chromatogr. A 1190 (2008) 27.

[28] C. Jia, X. Zhu, J. Wang, E. Zhao, M. He, L. Chen, P. Yu, J. Chromatogr. A 117 (2010) 5868.

[29] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145.

[30] H. Bagheri, A. Mir, E. Babanezhad, Anal. Chim. Acta 532 (2005) 89.

[31] J. Chen, J.B. Pawliszyn, Anal. Chem. 67 (1995) 2530.

[32] Z. Zhang , J. Pawliszyn, Anal. Chem. 65 (1993) 1843.

[33] A. Llop, F. Borrull, E. Pocurull, J. Sep. Sci. 33 (2010) 3692.

[34] M.E. Torres Padron, Z.S. Ferrera, J.J. Santana Rodriguez, Biomed. Chromatogr. 23 (2009) 1175.

[35] J. Beranek, A. Kubatova, J. Chromatogr. A 1209 (2008) 44.

[36] W. Liu, L. Zhang, S. Chen, H. Duan, X. Chen, Z. Wei, G. Chen, Anal. Chim. Acta 631 (2009) 47.

[37] F. Du, M.N. Alam, J. Pawliszyn, Anal. Chim. Acta 845 (2014) 45.

[38] L.M. Ravelo-Pérez, J. Hernández-Borges, T.M. Borges-Miquel, Food Chem. 111 (2008) 764.

[39] M.W. Heaven, D. Nash, Food Control 27 (2012) 214.

[40] R. Eisert, J. Pawliszyn, Anal. Chem. 69 (1997) 3140.

[41] Y. Hu, C. Song, G. Li, J. Chromatogr. A 1263 (2012) 21.

[42] K. Jinno, M. Kawazoe, Y. Saito, T. Takeichi, M. Hayashida, Electrophoresis 22 (2001) 3785.

[43] W.M. Mullett, K. Levsen, D. Lubda, J. Pawliszyn, J. Chromatogr. A 963 (2002) 325.

[44] W.M. Mullett,P. Martin, J. Pawliszyn, Anal. Chem. 73 (2001) 2383.

[45] W. Xu, S. Su, P. Jiang, H. Wang, X. Dong, M. Zhang, J. Chromatogr. A 1217 (2010) 7198.

[46] Z. Lin, Y. Lin, X. Sun, H. Yang, L. Zhang, G. Chen, J. Chromatogr. A 1284 (2013) 8.

[47] Y. Moliner-Martinez, H. Prima-Garcia, A. Ribera, E. Coronado, Anal. Chem. 84 (2012) 7233.

[48] M. Abdel-Rehim, J. Chromatogr. B 801 (2004) 317.

[49] M. Abdel-Rehim, Z. Altun, L. Blomberg, J. Mass. Spectrom. 39 (2004) 1488.

[50] M.P. Martinez-Moral, M.T. Tena, J. Chromatogr. A 1364 (2014) 28.

[51] M.M. Moein, D. Jabbar, A. Colmsjö, M. Abdel-Rehim, J. Chromatogr. A 1366 (2014) 15.

[52] G. Grueiro Noche, M.E. Fernández Laespada, J.L. Pérez Pavón, B. Moreno Cordero, S. Muniategui Lorenzo, Anal. Bioanal. Chem. 405 (2013) 6739.

[53] J. Wu, W.M. Mullett, J. Pawliszyn, Anal. Chem. 74 (2002) 4855.

[54] X. Chai, Y. He, D. Ying, J. Jia, T. Sun, J. Chromatogr. A 1165 (2007) 26.

[55] E. Baltussen, P. Sandra, F. David, C. Cramers, J. Microcolumn. Sep. 11 (1999) 734.

[56] C. Lacroix, N. Le Cuff, J. Receveur, D. Moraga, M. Auffret, J. Guyomarch, J. Chromatogr. A 1349 (2014) 1.

[57] Z. Xu, Z. Yang, Z. Liu, J. Chromatogr. A 1358 (2014) 52.

[58] W. Zhang, Z. Zhang, J. Zhang, J. Meng, T. Bao, Z. Chen, J. Chromatogr. A 1351 (2014) 12.

[59] P.R. Loconto, J. Chromatogr. Sci. 47 (2009) 656.

[60] C. Yu, B. Hu, J. Sep. Sci. 33 (2010) 2176.

[61] M. Anastassiades, S.J. Lehotay, D. Stajnbaher, F.J. Schenck, J. AOAC Int. 86 (2003) 412.

[62] M.C. Bruzzoniti, L. Checchini, R.M. De Carlo, S. Orlandini, L. Rivoira, M. Del Bubba, Anal. Bioanal. Chem. 406 (2014) 4089.

[63] N. Li, Z. Wang, L. Zhang, L. Nian, L. Lei, X. Yang, H. Zhang, A. Yu, Talanta 128 (2014) 345.

[64] A.V. Herrera-Herrera, J. Hernández-Borges, M.M. Afonso, J.A. Palenzuela, M.A. Rodríguez-Delgado, Talanta 116 (2013) 695.

[65] C. Basheer, A.A. Alnedhary, B.S. Madhava Rao, S. Valliyaveettil, H.K. Lee, Anal. Chem. 78 (2006) 2853.

[66] C. Basheer, A.A. Alnedhary, B.S. Madhava Rao, H.K. Lee, J. Chromatogr. A 1216 (2009) 211.

[67] H. Bagheri, A. Aghakhani, M. Akbari, Z. Ayazi, Anal. Bioanal. Chem. 400 (2011) 3607.

[68] F. Augusto, E. Carasek, R.G.C. Silva, S.R. Rivellino, A.D. Batista, E. Martendal, J. Chromatogr. A 1217 (2010) 2533.

[69] L. Xie, R. Jiang, F. Zhu, H. Liu, G. Ouyang, Anal. Bioanal. Chem. 406 (2014) 377.

[70] Q. Liu, Q. Zhou, G. Jiang, Trends Anal. Chem. 58 (2014) 10.

[71] B.-T. Zhang, X. Zhang, H.-F. Li, J.-M. Lin, Anal. Chim. Acta 784 (2013) 1.

[72] J. Tian, J. Xu, F. Zhu, T. Lu, C. Su, G. Ouyang, J. Chromatogr. A 1300 (2013) 2.

[73] K.S. Novoselov, A. K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, Science 306 (2004) 666.

[74] J. Chang, G. Zhou, E.R. Christensen, R. Heideman, J. Chen, Anal. Bioanal. Chem. 406 (2014) 3957.

[75] T. Kuila, S. Bose, P. Khanra, A.K. Mishr, N.H. Kim, J.H. Lee, Biosens. Bioelectron. 26 (2011) 4637.

[76] M.A. Rafiee, J. Rafiee, Z. Wang, H. Song, Z.-Z. Yu, N. Koratkar, ACS Nano 3 (2009) 3884.

[77] M.A. Rafiee, J. Rafiee, I. Srivastava, Z. Wang, H. Song, Z.-Z. Yu, N. Koratkar, Small 6 (2010) 179.

[78] Q. Liu, J. Shi, L. Zeng, T. Wang, Y. Cai, G. Jiang, J. Chromatogr. A 1218 (2011) 197.

[79] O.C. Compton, S.T. Nguyen, Small 6 (2010) 711.

[80] X. Dong, J. Cheng, J. Li, Y. Wang, Anal. Chem. 82 (2010) 6203.

[81] Y. Liu, J. Liu, P. Yin, M. Gao, C. Deng, X. Zhang, J. Mass. Spectrom. 46 (2011) 804.

[82] Y. Liu, J. Liu, C. Deng, X. Zhang, Rapid Commun. Mass. Spectrom. 25 (2011) 3223.

[83] B. Gulbakan, E. Yasun, M. Ibrahim Shukoor, Z. Zhu, M. You, X. Tan, H. Sanchez, D.H. Powell, H. Dai, W. Tan, J. Am. Chem. Soc. 132 (2010) 17408.

[84] Y.-B. Luo, J.-S. Cheng, Q. Ma, Y.-Q. Feng, J.-H. Li, Anal. Methods 3 (2011) 92.

[85] Y.B. Luo, Z.-G. Shi, Q. Gao, Y.-Q. Feng, J. Chromatogr. A 1218 (2011) 1353.

[86] Q. Wu, C. Feng, Y. Gao, X. Ma, Q. Wu, Z. Wang, J. Chromatogr. A 1218 (2011) 7936.

[87] C. Tan, Y. Wang, Z. Deng, N. Xu, X. Song, H. Liu, M. Rong, X. Chen, Microchim. Acta 181 (2013) 821.

[88] W. Zhang, J. Zhang, T. Bao, W. Zhou, J. Meng, Z. Chen, Anal. Chem. 85 (2013) 6846.

[89] J. Chen, J. Zou, J. Zeng, X. Song, J. Ji, Y. Wang, J. Ha, X. Chen, Anal. Chim. Acta 678 (2010) 44.

[90] H. Zhang, H.K. Lee, J. Chromatogr. A 1218 (2011) 4509.

[91] S. Zhang, Z. Du, G. Li, Anal. Chem. 83 (2011) 7531.

[92] J. Zou, X. Song, J. Ji, W. Xu, J. Chen, Y. Jiang, Y. Wang, X. Chen, J. Sep. Sci. 34 (2011) 2765.

[93] M.H. Banitaba, S.S. Hosseiny Davarani, S. Kazemi Movahed, J. Chromatogr. A 1325 (2014) 23.

[94] C. Zhang, Z. Zhang, G. Li, J. Chromatogr. A 1346 (2014) 8.

[95] M.H. Banitaba, S.S. Davarani, H. Ahmar, S.K. Movahed, J. Sep. Sci. 37 (2014) 1162.

[96] Y. Ge, A.P. Turner, Chem. Eur. J. 15 (2009) 8100.

[97] P.S. Sharma, M. Dabrowski, F. D'Souza, W. Kutner, Trends Anal. Chem. 51 (2013) 146.

[98] G.-H. Yao, R.-P. Liang, C.-F. Huang, Y. Wang, J.-D. Qiu, Anal. Chem. 85 (2013) 11944.

[99] W.J. Cheong, S.H. Yang, F. Ali, J. Sep. Sci. 36 (2013) 609.

[100] A. Martín-Esteban, Trends Anal. Chem. 45 (2013) 169.

[101] H. Zeng, Y. Wang, X. Liu, J. Kong, C. Nie, Talanta 93 (2012) 172.

[102] X. Shi, J. Liu, A. Sun, D. Li, J. Chen, J. Chromatogr. A 1227 (2012) 60.

[103] P. Lucci, O. Nunez, M.T. Galceran, J. Chromatogr. A 1218 (2011) 4828.

[104] M.J. Lerma-García, M. Zougagh, A. Ríos, Microchim. Acta 180 (2013) 363.

[105] Q. Han, X. Wang, Z. Yang, W. Zhu, X. Zhou, H. Jiang, Talanta 123 (2014) 101.

[106] W. Rao, R. Cai, Y. Yin, F. Long, Z. Zhang, Talanta 128 (2014) 170.

[107] J. Pan, B. Wang, J. Dai, X. Dai, H. Hang, H. Ou, Y. Yan, J. Mater. Chem. 22 (2012) 3360.

[108] Y. Hu, Y. Wang, X. Chen, Y. Hu, G. Li, Talanta 80 (2010) 2099.

[109] X. Hu, G. Dai, J. Huang, T. Ye, H. Fan, T. Youwen, Y. Yu, Y. Liang, J. Chromatogr. A 1217 (2010) 5875.

[110] X. Hu, Q. Cai, Y. Fan, T. Ye, Y. Cao, C. Guo, J. Chromatogr. A 1219 (2012) 39.

[111] J. He, R. Lv, H. Zhan, H. Wang, J. Cheng, K. Lu, F. Wang, Anal. Chim. Acta 674 (2010) 53.

[112] D.-L. Deng, J.-Y. Zhang, C. Chen, X.-L. Hou, Y.-Y.Su, L. Wu, J. Chromatogr. A 1219 (2012) 195.

[113] X. Liu, N. Sun, Q. Zhu, M. Wu, Y. Ye, H. Chen, J. Chromatogr. A 1304 (2013) 10.

[114] J. Li, H. Chen, H. Chen, Y. Ye, J. Sep. Sci. 35 (2012) 137.

[115] Z. Lin, J. Wang, X. Tan, L. Sun, R. Yu, H. Yang, G. Chen, J. Chromatogr. A 1319 (2013) 141.
[116] X. Zhu, J. Cai, J. Yang, Q. Su, Y. Gao, J. Chromatogr. A 1131 (2006) 37.
[117] X. Zhu, Q. Zhu, J. Appl. Polym. Sci. 109 (2008) 2665.
[118] Z. Xu, Y. Hu, Y. Hu, G. Li, J. Chromatogr. A 1217 (2010) 3612.
[119] Y. Hu, J. Li, Y. Hu, G. Li, Talanta 82 (2010) 464.
[120] Y. Hu, J. Li, G. Li, J. Sep. Sci. 34 (2011) 1190.
[121] J. Dupont, Acc. Chem. Res. 44 (2011) 1223.
[122] T.D. Ho, A.J. Canestraro, J.L. Anderson, Anal. Chim. Acta 695 (2011) 18.
[123] J.-F. Liu, N. Li, G.-B. Jiang, J.-M. Liu, J. Å. Jönsson, M.-J Wen, J. Chromatogr. A 1066 (2005) 27.
[124] Y.-N. Hsieh, P.-C. Huang, I.W. Sun, T.-J. Whang, C.-Y. Hsu, H.-H. Huang, C.-H. Kuei, Anal. Chim. Acta 557 (2006) 321.
[125] R. Amini, A. Rouhollahi, M. Adibi, A. Mehdinia, J. Chromatogr. A 1218 (2011) 130.
[126] M. Liu, X. Zhou, Y. Chen, H. Liu, X. Feng, G. Qiu, F. Liu, Anal. Chim. Acta 683 (2010) 96.
[127] D. Mecerreyes, Prog. Polym. Sci. 36 (2011) 1629.
[128] F. Zhao, Y. Meng, J.L. Anderson, J. Chromatogr. A 1208 (2008) 1.
[129] Y. Meng , V. Pino, J.L. Anderson, Anal. Chem. 81 (2009) 7107.
[130] Y. Meng, J.L. Anderson, J. Chromatogr. A 1217 (2010) 6143.
[131] J. Lopez-Darias, V. Pino, J.L. Anderson, G.M. Graham, A.M. Afonso, J. Chromatogr. A 1217 (2010) 1236.
[132] J. Lopez-Darias, J.L. Anderson, V. Pino, A.M. Afonso, Anal. Bioanal. Chem. 401 (2011) 2965.
[133] J. Feng, M. Sun, L. Xu, J. Li, X. Liu, S. Jiang, J. Chromatogr. A 1218 (2011) 7758.
[134] A.M. Shearrow, G.A. Harris, L. Fang, P.K. Sekhar, L.T. Nguyen, E.B. Turner, S. Bhansali, A. Malik, J. Chromatogr. A 1216 (2009) 5449.
[135] A.M. Shearrow, S. Bhansali, A. Malik, J. Chromatogr. A 1216 (2009) 6349.

[136] T.-T. Wang, Y.-H. Chen, J.-F. Ma, M.-J. Hu, Y. Li, J.-H. Fang, H.-Q. Gao, Anal. Bioanal. Chem. 406 (2014) 4955.

[137] J.D. Rocca, D. Liu, W. Lin, Acc. Chem. Res. 18 (2011) 957.

[138] A. Corma, H. García, F.X. LIabrés I Xamena, Chem. Rev. 110 (2010) 4606.

[139] T. Rodenas, I. Luz, G. Prieto, B. Seoane, H. Miro, A. Corma, F. Kapteijn, F.X. LIabrés i Xamena, J. Gascon, Nat. Mater. 14 (2015) 48.

[140] Y. Ma, H. Su, X. Kuang, X. Li, T. Zhang, B. Tang, Anal. Chem. 86 (2014) 11459.

[141] X.-Y. Cui, Z.-Y. Gu., D.-Q Jiang, Y. Li, H.-F. Wang, X.-P. Yan, Anal. Chem. 81 (2009) 9771.

[142] Z.-Y. Gu, G. Wang, X.-P. Yan, Anal. Chem. 82 (2010) 1365.

[143] N. Chang, Z.-Y. Gu. H.-F. Wang, X.-P. Yan, Anal. Chem. 83 (2011) 7094.

[144] D. Ge, H.K. Lee, J. Chromatogr. A 1218 (2011) 8490.

[145] Y. Hu, C. Song, J. Liao, Z. Huang, G. Li, J. Chromatogr. A 1294 (2013) 17.

[146] G. Zhang, X. Zang, Z. Li, C. Wang, Z. Wang, Talanta 129 (2014) 600.

[147] C. Hu, M. He, B. Chen, C. Zhong, B. Hu, J. Chromatog. A 1356 (2014) 45.

[148] A. Borrell, A. Aguilar, Chemosphere 66 (2007) 347.

[149] J. De Boer, Q.T. Dao, S.P.J. van Leeuwen, M.J.J. Kotterman, J.H.M. Schobben, Environ. Polllut. 158 (2010) 1228.

[150] J. He, R. Balasubramanian, S. Karthikeyan, U.M. Joshi, Chemosphere 75 (2009) 640.

[151] M. Kosikowska, M. Biziuk, Trends Anal. Chem. 29 (2010) 1064.

[152] A.M. Carro, S. Fernández, I. Racamonde, D. García-Rodríguez, P. González, R.A. Lorenzo, J. Chromatogr. A 1253 (2012) 134.

[153] N.S. Quinete, E.D. de Oliveira, D.R. Fernandes, A.D. Avelar, R.E. Santelli, Environ. Pollut. 159 (2011) 3604.

[154] R. Westbom, A. Hussen, N. Megersa, N. Retta, L. Mathiasson, R. Björklund, Chemosphere **72** (2008) 1181.

[155] G. Zheng, A. Selvam, J.W.C. Wong, Environ. Sci. Technol. 46 (2012) 12062.

[156] T. Lin, L. Hu, X. Shi, Y. Li, Z. Guo, G. Zhang, Mar. Pollut. Bull. 64 (2012) 1549.

[157] D.-Q. Wang, Y.-X. Yu, X.-Y. Zhang, S.-H. Zhang, Y.-P. Pang, X.-L. Zhang, Z.-Q. Yu, M.-H. Wu, J.-M. Fu, Ecotoxicol. Environ. Saf. 82 (2012) 63.

[158] J.G. Schnitzler, J.P. Thomé, M. Lepage, K. Das, Sci. Total Environ. 409 (2011) 3680.

[159] J. Li, D. Liu, T. Wu, W. Zhao, Z. Zhou, P. Wang, Food Chem. 151 (2014) 47.

[160] Y. Zhang, H.K. Lee, J. Chromatogr. A 1252 (2012) 67.

[161] V.C. Fernandes, V. Subramanian, N. Mateus, V.F. Domingues, C. Delerue-Matos, Microchim. Acta 178 (2012) 195.

[162] Y. Li, P.-S. Chen, S.-D. Huang, J. Chromatogr. A 1300 (2013) 51.

[163] Z. Shen, Z. He, P. Wang, Z. Zhou, M. Sun, J. Li, D. Liu, Anal. Chim. Acta 793 (2013) 37.

[164] W. Zhao, J. Li, T. Wu, P. Wang, Z. Zhou, J. Sep. Sci. 37 (2014) 2599.

[165] Y. Ke, F. Zhu, F. Zeng, T. Luan, C. Su, G. Ouyang, J. Chromatogr. A 1300 (2013) 187.

[166] A. Guart, I. Calabuig, S. Lacorte, A. Borrell, Environ. Sci. Pollut. Res. Int. 21 (2014) 2846.

[167] Z. He, P. Wang, D. Liu, Z. Zhou, Talanta 127 (2014) 1.

[168] L. Vidal, M.L. Riekkola, A. Canals, Anal. Chim. Acta 715 (2012) 19.

[169] H. Bagheri, Z. Ayazi, M. Naderi, Anal. Chim. Acta 767 (2013) 1.

[170] C. Basheer, H.G. Chong, T.M. Hii, H. K. Lee, Anal. Chem. 79 (2007) 6845.

[171] L. Xu, H.K. Lee, J. Chromatogr. A 1192 (2008) 203.

[172] Z. Wang, X. Zhao, X. Xu, L. Wu, R. Su, Y. Zhao, C. Jiang, H. Zhang, Q. Ma, C. Lu, D. Dong, Anal. Chim. Acta 760 (2013) 60.

[173] C. Qiu, M. Cai, J. Chromatogr. A 1217 (2010) 1191.

[174] T. Zhou, X. Xiao, G. Li, Anal. Chem. 84 (2012) 420.

[175] Q. Han, Z. Wang, J. Xia, L. Xia, S. Chen, X. Zhang, M. Ding, J. Sep. Sci. 36 (2013) 3586.

[176] M.-S. Kim, T.W. Kang, H. Pyo, J. Yoon, K. Choi, J. Hong, J. Chromatogr. A 1208 (2008) 25.

[177] N.A. Khan, S.H. Jhung, Angew. Chem. Int. Ed. 51 (2012)1198.

[178] J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T.Hupp, Chem. Soc. Rev. 38 (2009) 1450.

[179] C.-Y.Huang, , M. Song, Z.-Y. Gu, H.-F. Wang, X.-P. Yan, Environ. Sci. Technol. 45 (2011) 4490.

[180] Y.-Y. Zhou, X.-P. Yan, K.-N. Kim, S.-W. Wang, M.-G. Liu, J, Chromatogr. A 1116 (2006) 172.

[181] Z.-Y. Gu, Y.-J. Chen, J.-Q. Jiang, X,-P. Yan, Chem. Commun. 47 (2011) 4787.

[182] S.-H. Huo, X.-P. Yan, Analyst 137 (2012) 3445.

[183] X.-Q. Yang, C.-X. Yang, X.-P. Yan, J. Chromatogr. A 1304 (2013) 28.

[184] X.-Y. Cui, Z.-Y. Gu, D.-Q. Jiang, Y. Li, H.-F. Wang, X.-P. Yan, Anal. Chem. 81 (2009) 9771.

[185] L.-Q. Yu, X.-P. Yan, Chem. Commun. 49 (2013) 2142.

[186] Y.-Y. Wu, C.-X. Yang, X.-P. Yan, J. Chromatogr. A 1334 (2014) 1.

[187] Z. Zhang, Y. Huang, W. Ding, G. Li, Anal. Chem. 86 (2014) 3533.

[188] Y.-Y. Zhou, X.-P. Yan, K.-N. Kim, S.-W. Wang, M.G. Liu, J. Chromatogr. A 1116 (2006) 1.

[189] C.-X. Yang, X.-P. Yan, J. Mater. Chem. 22 (2012) 17833.

[190] Y.-F. Huang, Y.-Q. Wang, Y. Li, J.-M. Zhang, RSC Adv. 4 (2014) 47921.

[191] Y. Zhai, N. Li, X. Yang, H. Zhang Anal. Methods 6 (2014) 9435.

[192] H. Zang, J.-P. Yuan, X.-F. Chen, C.-A. Liu, C.-G. Cheng, R.-S. Zhao, Anal. Methods 5 (2013) 4875.

[193] J. Guo, Y. Chen, Y. Jing, C. Wang, Z. Ma, Chem. J. Chinese U. 33 (2012) 668.

[194] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, Science, 309 (2005) 2040.

[195] J. Yang, Q. Zhao, J. Li, J. Dong, Micropor. Mesopor. Mater. 130 (2010)174.

[196] S. Brunauer, P.H. Emmett, E. Teller, J. Am. Chem. Soc. 60 (1938) 309.

[197] E.P. Barrett, L.G. Joyner, P.P. Halenda, J. Am. Chem. Soc. 73 (1951) 373.
[198] R. Rodil, P. Popp, J. Chromatogr. A 1124 (2006) 82.
[199] B.-H. Hwang, M.-R. Lee, J. Chromatogr. A 898 (2000) 245.
[200] Y.B. Luo, B.-F. Yuan, Q.-W. Yu, Y.-Q. Feng, J. Chromatogr. A 1268 (2012) 9.
[201] S.-P. Huang, S.-D. Huang, J. Chromatogr. A 1176 (2007) 19.
[202] S.H. Jhung, J.-H. Lee, C. Serre, G. Férey, J.-S. Chang, Adv. Mater. 19 (2007) 121.
[203] Y.-Y. Fu, C.-X. Yang, X.-P. Yan, Langmuir 28 (2012) 6794.
[204] O. Hamdaoui, E. Naffrechoux, L. Tifouti, C. Pétrier, Ultrason. Sonochem. 10 (2003) 109.
[205] M. Breitbach, D. Bathen, Ultrason. Sonochem. 8 (2001) 277.
[206] P.P. Bolaños, A.G. Frenich, J.L.M. Vidal, J. Chromatogr. A 1167 (2007) 9.
[207] R. Sawicki, L. Mercier, Environ. Sci. Technol. 40 (2006) 1978.
[208] P. Grossi, I.R.B. Olivares, D.R. de Freltas, F.M. Lancas, J. Sep. Sci. 31 (2008) 3630.
[209] Z. Du, M. Liu, G. Li, J. Sep. Sci. 36 (2013) 3387.
[210] X. Gao, M. Pan, G. Fang, W. Jing, S. He, S. Wang, Analy. Methods 5 (2013) 6128.
[211] Q. Zhou, Y. Huang, J. Xiao, G. Xie, Anal. Bioanal. Chem. 400 (2011) 205.
[212] J. Sculley, D. Yuan, H.-C. Zhou, Energy Environ. Sci. 4 (2011) 2721.
[213] Y. Liu, W. Xuan, Y. Cui, Adv. Mater. 22 (2010) 4112.
[214] A.C. McKinlay, R.E. Morris, P. Horcajada, G. Férey, P. Couvreur, C. Serre, Angew. Chem. Int. Ed. 49 (2010) 6260.
[215] A. Morozan, F. Jaouen, Energy Environ. Sci. 5 (2012) 9269.
[216] S. Yang, C. Chen, Z. Yan, Q. Cai, S. Yao, J. Sep. Sci. 36 (2013) 1283.
[217] Y.-H. Shih, C.-H. Chien, B. Singco, C.-L. Hsu, C.-H. Lin, H.-Y. Huang, Chem. Commun. 49 (2013) 4929.
[218] A.S. Münch, J. Seidel, A. Obst, E. Weber, F.O.R.L. Mertens, Chem. Eur. J. 17 (2011) 10958.
[219] W. Ma, Q. Jiang, P. Yu, L. Yang, L. Mao, Anal. Chem. 85 (2013) 7550.

[220] W. Zhan, Q. Kuang, J. Zhou, X. Kong, Z. Xie, L. Zheng, J. Am. Chem. Soc. 135 (2013) 1926.

[221] Y. Hu, Z. Huang, J. Liao, G. Li, Anal. Chem. 85 (2013) 6885.

[222] Y.-Y. Fu, X.-C. Yang, X.-P. Yan, Chem. Commun. 49 (2013) 7162.

[223] D. Ge, H.K. Lee, J. Chromatogr. A 1263 (2012) 1.

[224] J.D. Rocca, D. Liu, W. Lin, Acc. Chem. Res. 44 (2011) 957.

[225] W.J. Rieter, K.M.L. Taylor, W. Lin, J. Am. Chem. Soc. 129 (2007) 9852.

[226] X. Zhang, H. Niu, Y. Pan, Y. Shi, Y. Cai, Anal. Chem. 82 (2010) 2363.

[227] S. Liu, L. Zhai, C. Li, Y. Li, X. Guo, Y. Zhao, C. Wu, ACS Appl. Mater. Interfaces 6 (2014) 5404.

[228] E.K. Paleologos, D.L. Giokas, M.I. Karayannis, Trends Anal. Chem. 24 (2005) 426.

[229] Y. Bai, D. Lin, F. Wu, Z. Wang, B. Xing, Chemosphere 79 (2010) 362.

[230] H.-S. Chang, B. Lee, S.-J. Choi, J. Hazard. Mater. 172 (2009) 1.

[231] S.D. Richardson, Anal. Chem. 84 (2012) 747.

[232] G. Lu, S. Li, Z. Guo, O.K. Farha, B.G. Hauser, X. Qi, Y. Wang, X. Wang, S. Han, X. Liu, J.S. DuChene, H. Zhang, Q. Zhang, X. Chen, J. Ma, S.C. Loo, W.D. Wei, Y. Yang, J.T. Hupp, F. Huo, Nat. Chem. 4 (2012) 310.

[233] L. Wang, Y.-Q. Cai, B. He, C.-G. Yuan, D.-Z Shen, J. Shao, G.-B. Jiang, Talanta 70 (2006) 47.

[234] Y. Takagai, W.L. Hinze, Anal. Chem. 81 (2009) 7113.

[235] J.M. Jimenez-Soto, S. Cárdenas, M. Valcárcel, J. Chromatogr. A 1245 (2012) 17.

[236] J.B. Quintana, J. Carpinteiro, I. Rodríguez, R.A. Lorenzo, A.M. Carro, R. Cela, J. Chromatogr. A 1024 (2004) 177.

[237] Y. Zou, H. Jin, H. Tang, D. Zou, M. Liu, Y. Yang, Anal. Biochem. 421 (2012) 378.

[238] B. Chen, Y. Huang, M. He, B. Hu, J. Chromatogr. A 1305 (2013) 17.

[239] F.J. López-Jiménez, M. Rosales-Marcano, S. Rubio, J. Chromatogr. A 1303 (2013) 1.

[240] Y. Guan, C. Jiang, C. Hu, L. Jia, Talanta 83 (2010) 337.

[241] Y. Wang, S. Jin, Q. Wang, G. Lu,n J. Jiang, D. Zhu, J. Chromatogr. A 1291 (2013) 27.

[242] M. Caban, M. Czerwicka, P. Łukaszewicz, N. Migowska, P. Stepnowski, M. Kwiatkowski, J. Kumirska, J. Chromatogr. A 1301 (2013) 215.

[243] W. Yan, L. Zhao, Q. Feng, Y. Wei, J.-M. Lin, Chromatographia 69 (2009) 621.

[244] R. Sadowski, R. Gadzala-Kopciuch, J. Sep. Sci. 36 (2013) 2299.

[245] A.Kumar, Gaurav, A.K. Malik, D.K. Tewary, B. Singh, Anal. Chim. Acta 610 (2008) 1.

[246] A. Kloskowski, M. Pilarczyk, A. Przyjazny, J. Namieśnik, Crit. Rev. Anal. Chem. 39 (2009) 43.

[247] A. Walcarius, Trends Anal. Chem. 38 (2012) 79.

[248] R. Aranda, P. Kruus, R.C. Burk, J. Chromatogr. A 888 (2000) 35.

[249] D. Djozan, Y. Assadi, Chromatographia 60 (2004) 313.

[250] M. Giardina, S.V. Oiesik, Anal. Chem. 75 (2003) 1604.

[251] J. Yu, L. Dong, C. Wu, L. Wu, J. Xing, J. Chromatogr. A 978 (2002) 37.

[252] W. Zhang, Y. Sun, C. Wu, J. Xing, J. Li, Anal. Chem. 81 (2009) 2912.

[253] F. Zhu, j. Guo, F. Zeng, R. Fu, D. Wu, T. Luan, Y. Tong, J. Chromatogr. A 1217 (2010) 7848.

[254] H. Bagheri, Z. Ayazi, H. Sistani, Microchim. Acta 174 (2011) 295.

[255] M. Sun, J. Feng, H. Qiu, L. Fan, L. Li, C. Luo, J. Chromatogr. A 1300 (2013) 173.

[256] Y. Wang, X. Wang, Z. Guo, Y. Chen, Talanta 119 (2014) 517.

[257] Z.-G. Shi, F. Chen, J. Xing, Y.-Q. Feng, J. Chromatogr. A 1216 (2009) 5333.

[258] Q. Liu, M. Cheng, Y. Long, M. Yu, T. Wang, G. Jiang, J. Chromatogr. A 1325 (2014) 1.

[259] S. Li, Y. Liang, D. Wu, R. Fu, Carbon 48(2010) 839.

[260] H. Lee, S.M. Dellatore, W.M. Miller, P.B. Messersmith, Science 318 (2007) 426.

[261] M.E. Lynge, R. van der Westen, A. Postma, B. Städler, Nanoscale 3 (2011) 4916.

[262] C.-M. Liu, R.-P. Liang, X.-N. Wang, J.-W. Wang, J.-D. Qiu, J. Chromatogr. A 1294 (2013) 145.

[263] P.G. Ingole, W. Choi, K.H. Kim, C.H. Park, W.K. Choi, H.K. Lee, Chem. Eng. J. 243 (2014) 137.

[264] R. Liu, S.M. Mahurin, C. Li, R.R. Unocic, J.C. Idrobo, H. Gao, S.J. Pennycook, S. Dai, Angew. Chem. Int. Ed. 50 (2011) 6799.

[265] J. Kong, W.A. Yee, L. Yang, Y. Wei, S.L. Phua, H.G. Ong, J.M. Ang, X. Li, X. Lu, Chem. Commun. 48 (2012) 10316.

[266] R. Liu, Y. Guo, G. Odusote, F. Qu, R.D. Priestley, ACS Appl. Mater. Interfaces 5 (2013) 9167.

[267] J. Feng, M. Sun, L. Xu, J. Li, X. Liu, S. Jiang, J. Sep. Sci. 34 (2011) 2482.

[268] W. Zhang, Z. Chen, J. Chromatogr. A 1278 (2013) 29.

[269] J. Feng, H. Qiu, X. Liu, S. Jiang, Trends Anal. Chem. 46 (2013) 44.

[270] X. Yu, H. Fan, Y. Liu, Z. Shi, Z. Jin, Langmuir 30 (2014) 5497.

[271] R. M. BURGESS, S.A. Ryba, M.G. Cantwell, J.L. Gundersen, R. Tien, Environ. Toxicol. Chem. 25 (2006) 2028.

[272] H.-L. Xu, Y. Li., D.-Q. Jiang, X.-P. Yan, Anal. Chem. 81 (2009) 4971.

[273] M. Polo, G. Gómez-Noya, J.B. Quintana, M. Llompart, C. García-Jares, R. Cela, Anal. Chem. 76 (2004) 1054.

[274] O. Bercaru, F. UIberth, H. Emons, C. Vandecasteele, Anal. Bioanal. Chem. 384 (2006) 1207.

[275] R.E. Cantwell, R. Hofmann, M.R. Templeton, J. Appl. Microbiol. 105 (2008) 25.

[276] S. Zhang, Z. Du, G. Li, Talanta 115 (2013) 32.

[277] A. Derouiche, M.R. Driss, J.-P. Morizur, M.-H. Taphanel, J. Chromatogr. A 138 (2007) 231.

[278] H. Dong, a. Meininger, H. Jiang, K.-S. Moon, C.P. Wong, J. Electron. Mater. 36 (2007) 593.

[279] J.E. Lee, N. Lee, T. Kim, J. Kim, T. Hyeon, Acc. Chem. Res. 44 (2011) 893.

[280] S. Wang, Y. Tan, D. Zhao, G. Liu, Biosens. Bioelectron. 23 (2008) 1781.

[281] R. Jiang, J. Yao, H. Zhu, Y. Fu, Y. Guan, L. Xiao, G. Zeng, Desalin. Water Treat. 52 (2014) 238.

[282] H. Shiigi, T. Kinoshita, N. Shibutani, T. Nishino, T. Nagaoka, Anal. Chem. 86 (2014) 4977.

[283] Y. Zhang, M. Yu, C. Zhang, W. Ma, Y. Zhang, C. Wang, H. Lu, Anal. Chem. 86 (2014) 7920.

[284] J. Ko, H.B. Lim, Anal. Chem. 86 (2014) 4140.

[285] Z.-G. Shi, H.K. Lee, Anal. Chem. 82 (2010) 1540.

[286] L. Bromberg, S. Raduyk, T.A. Hatton, Anal. Chem. 81 (2009) 5637.

[287] L. Chen, T. Wang, J. Tong, Trends Anal. Chem. 30 (2011) 1095.

[288] J. Xie, L. Chen, C. Li, X. Xu, J. Chromatogr. B 788 (2003) 233.

[289] Y. Liu, K. Ai, L. Lu, Chem. Rev. 114 (2014) 5057.

[290] T.A. Morris, A.W. Peterson, M.J. Tarlov, Anal. Chem. 81 (2009) 5413.

[291] M. Zhang, X. Zhang, X. He, L. Chen, Y. Zhang, Nanoscale 4 (2012) 3141.

[292] Y. Yan, Z. Zheng, C. Deng, Y. Li, X. Zhang, P. Yang, Anal. Chem. 85 (2013) 8483.

[293] Z. Iqbal, E.P.C. Lai, T.J. Avis, Microchim. Acta. 176 (2011) 193.

[294] C. McCullum, P. Tchounwou, L.-S. Ding, X. Liao, Y.-M. Liu, J. Agric. Food Chem. 62 (2014) 4261.

[295] Y. Wang, S. Wang, H. Niu, Y. Ma, T. Zeng, Y. Cai, Z. Meng, J. Chromatogr. A 1283 (2013) 20.

[296] Q. Song, M. Li, L. Huang, Q. Wu, Y. Zhou, Y. Wang, Anal. Chim. Acta 787 (2013) 64.

[297] M. Zhu, G. Diao, Nanoscale 3 (2011) 2748.

[298] D. Jariwala, V.K. Sangwan, L.J. Lauhon, T.J. Marks, M.C. Hersam, Chem. Soc. Rev. 42 (2013) 2824.

[299] D.-M. Sun, C. Liu, W.-C. Ren, H.-M. Cheng, Small 9 (2013) 1188.

[300] J.-L. Gong, B. Wang, G.-M. Zeng, C.-P. Yang, C.-G. Niu, Q.-Y. Niu, W.-J. Zhou, Y. Liang, J. Hazard. Mater. 164 (2009) 1517.

[301] C.L. Chen, X.K. Wang, M. Nagatsu, Environ. Sci. Technol. 43 (2009) 2362.

[302] C. Wang, C. Feng, Y. Gao, X. Ma, Q. Wu, Z. Wang, Chem. Eng. J. 173 (2011) 92.

[303] Q. Ye, L. Liu, Z. Chen, L. Hong, J. Chromatogr. A 1329 (2014) 24.

[304] S. Wang, H. Niu, T. Zeng, X. Ma, Y. Cai, X. Zhao, Cryst. Eng. Commun. 16 (2014) 5598.

[305] G. Cheng, M.-D. Zhou, S.-Y. Zheng, ACS Appl. Mater. Interfaces 6 (2014) 12719.

[306] S. Rodriguez-Mozaz, M.J.L. de Alda, D. Barcelo, Anal. Chem. 76 (2004) 6998.

[307] S. Rodriguez-Mozaz, M.J. Lopez de Alda, D. Barcelo, Anal. Chem. 76 (2004) 6998.

[308] J. Wu, H.K. Lee, J. Chromatogr. A 1092 (2005) 182.

[309] S.M. Majedi, H.K. Lee, B.C. Kelly, Anal. Chem. 84 (2012) 6546.

[310] H. Deng, X. Li, Q. Peng, X. Wang, J. Chen, Y. Li, Angew. Chem. Int. Ed. 44 (2005) 2782.

[311] W.G. Lan, M.K. Wong, N. Chen, Y.M. Sin, Analyst 119 (1994) 1659.

[312] H. Bae, T. Ahmad, I. Rhee, Y. Chang, S.-U. Jin, S. Hong, Nanoscale Res. Lett. 7 (2012) 44.

[313] S. Zhang, H. Niu, Z. Hu, Y. Cai, Y. Shi, J. Chromatogr. A 1217 (2010) 4757.

[314] B. Yu, J. Liu, S. Liu, F. Zhou, Chem. Commun. 46 (2010) 5900.

[315] X. Zhang, J. Liu, S. Liu, F. Zhou, Appl. Surf. Sci. 314 (2014) 166.

[316] B. Socas-Rodríguez, M. Asensio-Ramos, J. Hernández-Borges, M.A. Rodríguez-Delgado, J. Chromatogr. A 1313 (2013) 175.

[317] C. Moreno-Castilla, J. Rivera-Utrilla, M.V. López-Ramón, F. Carrasco-Marín, Carbon 33 (1995) 845.

[318] W.G. Lan, M.K. Wong, N. Chen, Y.M. Sin, Analyst 119 (1994) 1669.

[319] Q. Liu, B. Yu, W. Ye, F. Zhou, Macromol. Biosci. 11 (2011) 1227.

[320] A.I. Schäfer, I. Akanyeti, and A.J.C. Semião, Adv. Colloid Interface Sci. 164 (2011) 100.

[321] M. Franz, H.A. Arafat, N.G. Pinto, Carbon 38 (2000) 1807.

[322] D.L.D. Lima, C.P. Silva, M. Otero, V.I. Esteves, Talanta 115 (2013) 980.

[323] C. Hu, M. He, B. Chen, C. Zhong, B. Hu, J. Chromatogr. A 1310 (2013) 21.

[324] R. Kumar, Gaurav, Heena, A.K. Malik, A. Kabir, K. G. Furton, J. Chromatogr. A 1359 (2014) 16.

[325] A. Wenzel, J. Müller, T. Ternes, Study on endocrine disrupters in drinking water. Final report ENV.D.1/ETU/2000/0083, European Comission: Brussels, 2003.

[326] P.M. Bradley, C.A. Journey, J. Am. Water Resour. Assoc. 50 (2014) 388.

[327] Y. Xu, F. Luo, A. Pal, K.Y.-H. Gin, M. Reinhard, Chemosphere 83 (2011) 963.

[328] C. Basheer, H.G. Chong, T.M. Hii, H.K. Lee, Anal. Chem. 79 (2007) 6845.