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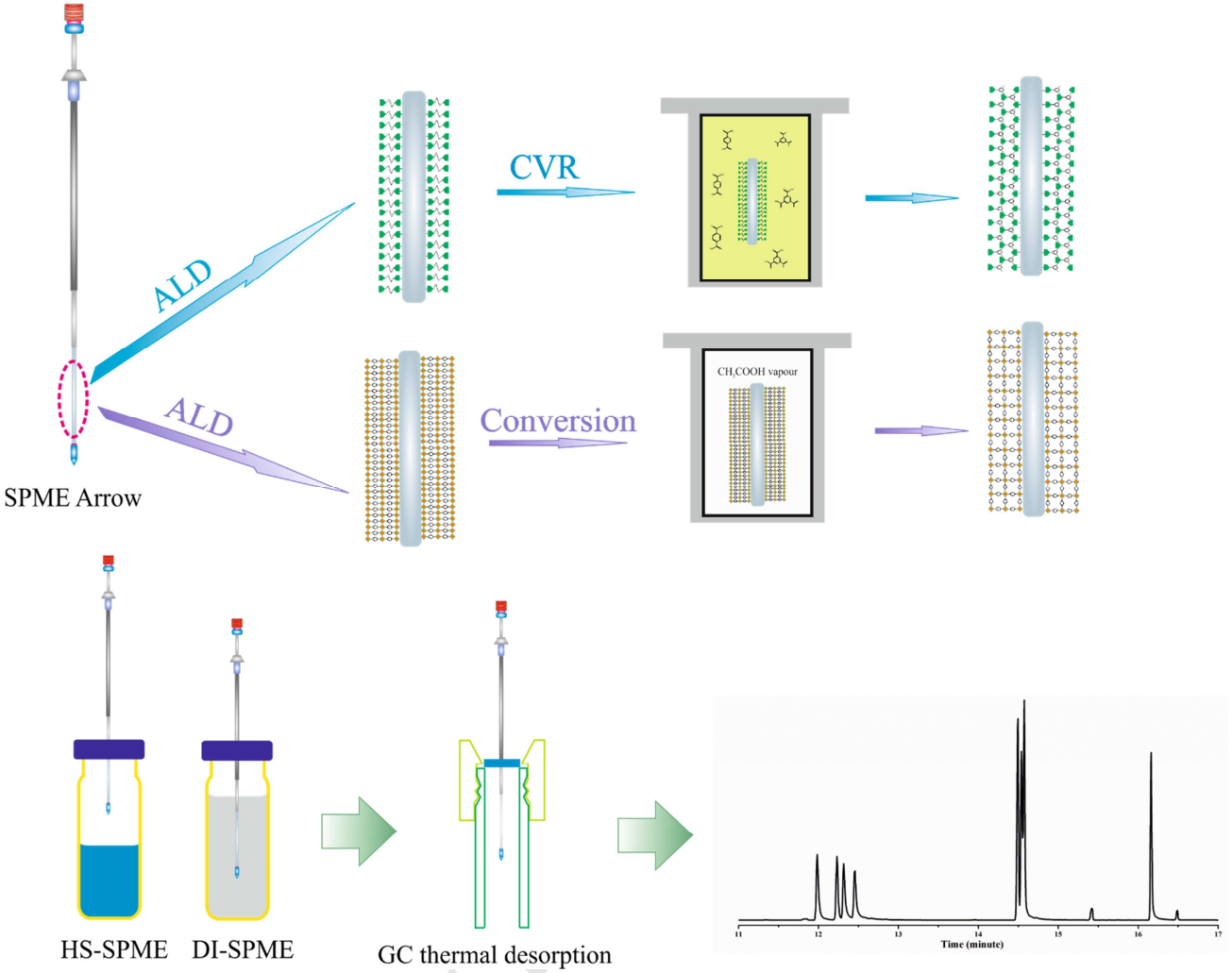

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Integrated atomic layer deposition and chemical vapor reaction for the preparation of metal organic framework coatings for solid-phase microextraction Arrow

Hangzhen Lan, Leo D. Salmi, Tuukka Rönkkö, Jevgeni Parshintsev, Matti Jussila, Kari Hartonen, Marianna Kemell, Marja-Liisa Riekkola*

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Abstract

New chemical vapor reaction (CVR) and atomic layer deposition (ALD)-conversion methods were utilized for preparation of metal organic frameworks (MOFs) coatings of solid phase microextraction (SPME) Arrow for the first time. With simple, easy and convenient one-step reaction or conversion, four MOF coatings were made by suspend ALD iron oxide (Fe_2O_3) film or aluminum oxide (Al_2O_3) film above terephthalic acid (H_2BDC) or trimesic acid (H_3BTC) vapor. UIO-66 coating was made by zirconium (Zr)-BDC film in acetic acid vapor. As the first documented instance of all-gas phase synthesis of SPME Arrow coatings, preparation parameters including CVR/conversion time and temperature, acetic acid volume, and metal oxide film/metal-ligand films thickness were investigated. The optimal coatings exhibited crystalline structures, excellent uniformity, satisfactory thickness (2-7.5 μm), and high robustness (>80 times usage). To study the practical usefulness of the coatings for the extraction, several analytes with different chemical properties were tested. The Fe-BDC coating was found to be the most selective and sensitive for the determination of benzene ring contained compounds due to its highly hydrophobic surface and unsaturated metal site. UIO-66 coating was best for small polar, aromatic, and long chain polar compounds owing to its high porosity. The usefulness of new coatings were evaluated for gas chromatography-mass spectrometer (GC-MS) determination of several analytes, present in wastewater samples at three levels of concentration, and satisfactory results were achieved.

Keywords: Atomic layer deposition; Chemical vapor reaction; Metal organic frameworks; Solid phase microextraction Arrow; Gas chromatography-mass spectrometry

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1. Introduction

As a miniaturized sampling technique, solid phase microextraction (SPME) has attracted a lot of interest due to its time-efficient, cost-effective, simple, and reliable properties. Recently introduced solid phase microextraction (SPME) Arrow has overcome its widely mentioned drawbacks, such as low sensitivity and fragility, by introducing stainless steel rod as the substrate and increasing adsorbent volume [1-8].

As well known, the sorbent plays an important role in the performance of SPME technique. This has led to the development of various commercial and tailor-made coatings. Various materials and their composite coatings are commercially available [9], and carbon nanotubes (CNTs), graphene, ionic liquids, molecularly imprinted polymers (MIPs), and metal organic frameworks (MOFs) [10-14] coatings have been reported in the literature. The coating method itself plays also an important role in the developments of different SPME systems. Especially coatings containing crystalline powder or particle sorbent having the requirements of the uniformity and reproducibility, which can affect the extraction performance and intra SPME fiber/Arrow repeatability, have attracted special interest. Moreover, the useful coating method should allow the automation, accurate control, high through-put, sustainability, and solvent-free procedure. Up to now, SPME coating preparation protocols are based mainly on dipping, sol-gel, electrochemical deposition, electrospinning, in-situ crystallization at high temperature, slow diffusion and seeded growth methods [15]. Unfortunately the difficulties related to the preparation of the coatings have still prevented their wider exploitation.

Atomic layer deposition (ALD), an advanced variation of chemical vapor deposition (CVD), is a thin film deposition method based on alternate pulses of gaseous precursors separated by inert gas purging

[16]. The precursors react only on the surface, which leads to a self-limiting growth mechanism. ALD enables accurate control over film thickness, superior conformality even on complicated 3D structures, and large-area uniformity. Molecular layer deposition (MLD) is a closely related method to ALD. In MLD, layers of whole molecules are deposited during one self-limiting reaction step. ALD and MLD have been utilized in MOF thin film deposition either directly or by using post-deposition treatments [17-21]. Metal-organic ligand film deposited directly by ALD and converted into a MOFs film have been reported by Leo et al in 2013 [19], requiring an additional solvent conversion step. Recently, Lausund et al. reported that when ALD deposited Zr-BDC film was converted into UIO-66 in acetic acid vapor, UIO-66 film with good uniformity and porosity could be obtained [18].

Chemical vapor reaction method is a way to convert thin metal oxide film into MOFs layer with a simple vapor-solid reaction procedure [21]. Previously zinc oxide (ZnO) film was firstly deposited using diethylzinc and oxygen plasma as precursors. Then ZnO film was converted to a crystalline ZIF-8 structure by suspending the ZnO coated substrate above 2-methylimidazole in a closed reactor vessel at 100 ^{o}C for 30 minutes so that metal oxide could react with vaporized organic ligand. Not only the adjustable thickness, but many other materials, such as ZIF-61, ZIF-67, and ZIF-72 MOFs and CCDC EHETER and CCDC NIFMIY coordination polymers could be prepared by just changing the organic ligand or/and metal oxide layer. This method was also very flexible for MOFs layer deposition on a high-aspect-ratio features substrate, PDMS pillar being as example. These studies with several merits inspired us to test the suitability of integrated atomic layer deposition and chemical vapor reaction for the preparation of metal organic framework coatings for SPME Arrow system.

The feasibility of MOFs coatings, such as Fe-BDC, Fe-BTC, Al-BDC, Al-BTC, and UIO-66, for SPME Arrow by ALD-chemical vapor reaction and ALD-conversion methods for the extraction of a wide range of target compounds with different characteristics was clarified. To our best knowledge,

this is the first paper to present ALD-chemical vapor reacted or ALD-converted SPME coating. Satisfactory results were obtained in terms of coating extraction capacity, selectivity, limits of detection, and quantification in comparison with several commercial coatings. In addition, the applicability of coatings for influent and effluent wastewater samples was carried out.

2. Experimental

2.1. Reagents and materials

Standard solution for phenolic compounds (20 mg mL^{-1} in dichloromethane) was purchased from AccuStandard, Inc. (New Haven, CT); caryoplyllene oxide was from Acros Organics (Geel, Belgium); decane (>99%), 1-naphthylamine (≥99.0%), 1,2,4-trichlorobenzene (≥99%), terephthalic acid (H_2BDC) (≥99%), and naphthalene (99%) were from Fluka (The Netherlands); hexachlorobutadiene (96%) and acetic acid (100%) were from Merck (Darmstadt, Germany); 2-bromopropane (99%), atrazine, hexachlorobenzene (99%), pentyl acetate (99%), alpha-pinene (98%), trimesic acid (H_3BTC) (95%), nonanal (95%), and trimethylamine hydrochloride (TMA·HCl) (98%) were from Sigma-Aldrich (St. Louis, USA); aniline was from Aldrich-Chemie (Steinheim, West-Germany); 2-propanol (HPLC grade), methanol (HPLC fluorescence grade), and sodium chloride (NaCl) were from Fisher Scientific (Loughborough, Leics, UK); pyridine (100%), chloroform (HPLC grade), and potassium hydroxide (KOH) were from VWR Chemicals (Pennsylvania, USA).

Ultrapure water was prepared by a water purification system (Millipore DirectQ-UV, Billerica, MA, USA) and used for stock, standard, and sample solution preparation. All of the stock solutions were 1000 μg mL^{-1} in methanol except hexachlorobenzene (100 μg mL^{-1} in chloroform) and hexachlorobutadiene (100 μg mL^{-1} in 2-propanol) because of their low solubility in methanol.

Carboxen/WR Arrow (sorbent film thickness 120 μm and the sorbent length 20 mm), and PAL RTC auto-sampler were kindly provided by CTC Analytics AG (Zwingen, Switzerland). Uncoated solid phase microextraction Arrows (for coating length of 20 mm) were from BGB Analytik AG (Zurich, Switzerland). PDMS, PDMS/DVB, and PA SPME fibers were from Supelco (Bellefonte, PA, USA).

2.2. Preparation of coatings

2.2.1. Preparation of iron- and aluminum- based MOFs coating

Al_2O_3 films were deposited at 250 °C using trimethylaluminum (Chemtura, Axion PA 1300) and H_2O as the precursors. Pulse and purge times for both precursors were kept in one second. Fe_2O_3 films were deposited at 400 °C using $FeCl_3$ (Aldrich, ≥99.99%) and H_2O as the precursors. Pulse time for both precursors was one second and purge time two seconds. TMA and H_2O were led into the reactor from external sources at room temperature and $FeCl_3$ was evaporated inside the reactor at 145 °C. After ALD deposition of iron oxide (Fe_2O_3) or aluminum oxide (Al_2O_3) films on silicon substrate or blank Arrow, another conversion step was needed to convert them into MOFs coating. For silicon substrate, it was cut into 40 mm×5 mm blade (blade SPME) in order to fit its size with conversion reactor and self-made thermal desorption unit (TDU). 0.5 g H_2BDC or H_3BTC was added into a steel reactor, then Fe_2O_3 or Al_2O_3 coated blade or Arrow was transferred inside the reactor. After conversion of 40 hours conversion at 350 ^oC for Fe/Al-BDC and 330 ^oC for Fe/Al-BTC, Fe-BDC, Fe-BTC, Al-BDC or Al-BTC coatings were obtained. The blades and Arrows were then pre-conditioned in TDU under N_2 flow at 250 ^oC and in GC inlet at 250 ^oC under N_2 flow for 60 minutes, respectively.

2.2.2. Preparation of UIO-66 coating

Zr-BDC films were deposited at 250 °C using $ZrCl_4$ (Aldrich, ≥99.9%) and H_2BDC (Fluka, ≥99%) as the precursors, evaporated inside the reactor at 185 °C and 190 °C. Pulse time was one second and

purge time two seconds. Three seconds long acetic acid pulse (Fisher Chemical, 99.8%) from an external source was used for modulation between the cycles. For the conversion of Zr-BDC film into UIO-66 coating, the conditions were similar to those reported in literature with small modifications[18]. At first, a 500 mL Teflon vessel and Zr-BDC coated blade (also in 40 mm×5 mm size) or Arrow were pre-heated together in an oven for 10 min. Then, 4 mL acetic acid in a 20 mL glass vial was immediately transferred into the Teflon vessel and sealed for 23 hours. After conversion, blade or Arrow was moved out of the vessel quickly. The converted UIO-66 coating was cooled down to ambient temperature. Then, the blades were pre-conditioned, in order to remove any residuals left from ALD or conversion periods, in TDU at 250 ^{o}C under nitrogen flow and the Arrows in GC inlet at 250 ^{o}C under helium flow for 60 minutes, respectively.

2.3. Instruments and GC-MS analysis

All film depositions were done in a hot-wall, flow-type F-120 ALD reactor (ASM Microchemistry Ltd., Helsinki, Finland). The carrier and purging gas was nitrogen (Aga, 99.999 %), and the pressure inside the reactor ~0.7 kPa.

Two different GC-MS systems were utilized in this study. An Agilent 6890 N gas chromatograph coupled with an Agilent 5973C mass selective detector was used for the GC-MS analysis of comparison samples of blade SPME. An Agilent 6890 N gas chromatograph coupled with an Agilent 5975C mass selective detector (Agilent Technologies, Palo Alto, USA) was used for optimization of SPME Arrow parameters, method validation, and analysis of natural samples. An HP-5 (Agilent Technologies, Palo Alto California, USA) capillary column (30 m length, 0.25 mm id, with 0.25 μm film) was utilized for the chromatographic separation in both systems. GC-MS conditions and TDU system are described in detail in the Supplementary Material (Page 2 and Table S1).

X-ray diffraction (XRD) patterns were measured by a PANalytical X'Pert Pro MPD diffractometer. The surface morphology of the Fe-BDC and UIO-66 SPME Arrows were studied by scanning electron microscopy (SEM) (Hitachi, model S-4800, Japan). Thermogravimetric analyses (TGA) were performed with a Mettler Toledo Stare system at a heating rate of 10 ^{o}C min^{-1} from 30 to 600 ^{o}C under nitrogen flow.

2.4. Blade SPME procedures

MOFs (Fe-BDC, Fe-BTC, Al-BDC, Al-BTC, and UIO-66) coated blade SPME was firstly tested with compounds having different chemical properties, such as hydrophobicity (Table S2). The extraction and desorption conditions were showed in Table S3. Due to low volatility, 1,2,4-trichlorobenzene, hexachlorobutadiene, hexachlorobenzene, and atrazine were extracted in immersion extraction, and 15 mL of each was used to fully immerse the sorbent.

2.5. SPME Arrow procedures

Fe-BDC and UIO-66 coated SPME Arrows by utilizing CTC RTC autosampler were employed for the optimization of sampling parameters, method validation, and wastewater analysis with chlorinated phenols, hexachlorobutadiene and hexachlorobenzene, respectively.

For Fe-BDC-coated SPME Arrow, 5 mL of diluted standard solution of chlorinated phenols (pH=1, adjusted by sulfuric acid (96%, JT Baker, Deventer, Holland)) and solid NaCl placed in a 20 mL headspace vial equipped with a PTFE/silicone septum screw-cap (Phenomenex, Torrance, California, USA). Fe-BDC-coated SPME Arrow was exposed to headspace inside the vial for extraction after 10 min incubation at 40 ^{o}C.

For UIO-66 coated SPME Arrow, 15 mL diluted hexachlorobutadiene and hexachlorobenzene mixed standard solution was added into a 20 mL extraction vial and then incubated at 40 ^{o}C for 10 min.

Extraction time and agitation speed were optimized because of their large effect on extraction efficiency of the UIO-66 coating. In GC-MS analysis, compounds were desorbed at 280 ^{o}C for 3 minutes.

2.6. Optimization of experimental design.

The most significant parameters that have influence on MS response of target compounds were confirmed after the preliminary tests of selected parameters. Plackett-Burman design was used to determine the final parameters that affect the extraction of the analytes by using SPME Arrow system and their effect were evaluated using response surface methodology (RSM). For Fe-BDC Arrow, there were three variables, namely, extraction time (x_3, 20-60 minutes), NaCl (x_2, 0-2 g), and extraction temperature (x_1, 40-80 ^{o}C), were evaluated. For UIO-66 Arrow, there were two variables, agitation speed (x_1, 150-750 rpm) and extraction time (x_2, 20-60 minutes), that were evaluated.

Minitab 18 statistical software (Minitab, State College, USA) was used for the experimental design and data analysis.

2.7. Wastewater analysis.

Both influent and effluent wastewater samples were from Viikinmäki municipal wastewater treatment plant (WWTP), Helsinki, Finland. Samples were filtered through cotton wool to remove large particles followed by 1 μm pore size Acrodisc syringe filter (Gelman Laboratory, MI) and 0.45 μm pore size Durapore membrane filter (Millipore, Ireland) and then stored in a refrigerator at 4 ^{o}C before analysis. For recovery experiments of Fe-BDC Arrow, 5 mL sample was spiked with 5, 25, and 100 μL of 10 μg mL^{-1} chlorinated phenols standard solution, and resulted in 10, 50, and 200 ng mL^{-1} solutions. For UIO-66 Arrow, 15 mL sample was spiked with 15, 75, and 150 μL 10 μg mL^{-1} hexachlorotutadiene

and hexachlorobenzene standard solution, and resulted in 10, 50, and 100 ng mL^{-1} hexachlorotutadiene and hexachlorobenzene in spiked samples.

3. Results and discussion

The performance of all the coatings (Fe-BDC, Fe-BTC, Al-BDC, Al-BTC, and UIO-66) on blade SPME were first tested with a wide range of compounds (section 3.2). Superior Fe-BDC and UIO-66 coatings were then utilized for SPME Arrow. Extraction and desorption steps were optimized, and the validated method was applied to wastewater samples (sections 3.3-3.5).

3.1. Chemical conversion and ALD-converted coatings

H_2BDC or H_3BTC were selected for MOF coating precursors due to their hydrophobicity and water stability as environmental samples frequently contain water. MIL-53 (Fe), MIL-100 (Fe), MIL-53 (Al), and MIL-100 (Al), including iron or aluminum as metal precursor and H_2BDC or H_3BTC as organic ligand are hydrophobic and nonreactive with water [22]. We first deposited the metal oxide (iron oxide or aluminum oxide) film which act as oxide precursor film via ALD. The thickness of iron oxide or aluminum oxide film was ~200 nm. The conversion temperature of H_2BDC was as high as 350 ^oC and that of H_3BTC 330 ^oC owing to their high boiling points. To guarantee the possibility to reuse the organic ligand bed the ligands were kept at temperatures below their boiling points. Thicker coating was obtained after increase of the conversion time from 20 hours to 40 hours, resulting in higher extraction capacities. So 40 hours was selected for Fe-BDC, Fe-BTC, Al-BDC, and Al-BTC MOFs film conversion time. The resulted MOFs films demonstrated crystalline structure (Figure S1), even though their x-ray diffraction (XRD) patterns did not match well with that of MIL-101 (Fe), MIL-100

(Fe), MIL-101 (Al), and MIL-100 (Al) [23-26]. Furthermore, the preparation conditions of optimal Fe- and Al- based MOFs films were employed for SPME Arrow coating. According to SEM images of Fe-BDC coating, the average thickness of the coating was around 2 μm (Figure 1), meaning that its thickness had increased roughly 10 times after solid-vapor reaction (ALD). Due to the small extraction capacities of Fe-BTC, Al-BDC, and Al-BTC, their SEM images are not presented here.

Zr-BDC, an organic-inorganic hybrid material, and subsequently obtained crystalline UIO-66 film resulted in good porosity [18]. Here we studied the possibility to deposit Zr-BDC film on rod SPME Arrow and convert it into a UIO-66 coating. For this procedure we optimized first conversion parameters (pre-heating, acetic acid volume, conversion time, and conversion temperature) for Zr-BDC coating (~200 nm thickness) on silicon wafer. Pre-heating was a crucial step because Zr-BDC could be easily decomposed when it was simultaneously heated in Teflon vessel together with acetic acid due to condensed acetic acid droplets on film surface. By preheating the film at conversion temperature for 10-20 minutes, the condensation of acetic acid droplets could be eliminated resulting in a uniformly converted film. 10 minutes pre-heating time was selected for further experiments because longer pre-heating time had no effect on final UIO-66 film. Too small acetic acid volume (<4 mL) and too short conversion time (<21 hours) led to incomplete conversion of Zr-BDC film to UIO-66 film. With lower temperature (<200 ^{o}C), weaker XRD signal intensity was achieved. 4 mL acetic acid and 23 hours of conversion at 200 ^{o}C were the optimal Zr-BDC conversion conditions. In addition, XRD pattern matched well with UIO-66 (Figure S1) [18]. Then the effect of Zr-BDC thickness on the extraction capacity of resulting UIO-66 was clarified, and higher film thickness (0.9 μm) assured the highest density UIO-66 film (7.5 μm thickness) (Figure 1). Thicker coatings were not tested due to the limitation of ALD procedure.

3.2. Comparison of coatings

Blade SPME coupled with TDU unit was utilized due to its convenient preparation and operation. Commercially available SPME fibers and Arrows (PDMS, PDMS/DVB, and PA SPME fibers and Carboxen WR SPME Arrow) were selected for extraction efficiency comparison. Sorbent volumes for all the coatings are listed in Table S4.

The comparison of the results for different coatings are shown in Figures 2 and S2. Only PA SPME fiber was used for the extraction comparison of phenols because of its excellent performance [27]. Fe- and Al-based MOFs and UIO-66 coatings gave different extraction efficiencies with phenols due to the π-π interactions between the benzene rings. Fe-BDC and Fe-BTC coated blade SPME provided much better extraction efficiencies than PA SPME fiber and Al-BDC/BTC coated blade SPME probably owing to their higher hydrophobicity which prevents water from occupying the extraction sites of the adsorbent surface [28, 29]. Due to high affinity of PA coating towards water, its extraction efficiency was decreased in high humidity conditions. Fe-based adsorbent with stronger hydrophobic interactions demonstrated higher extraction efficiencies toward chlorinated phenols, compared to those of phenol and methylphenols. This trend agrees well with previously reported results [30, 31]. In addition, Fe-based MOFs, opposite to Al-based MOFs, have open metal sites (Fe^{3+}) that accelerate the extraction of phenolic compounds [32]. The synthesized MOF coatings exhibited good extraction efficiencies also to some other aromatic compounds such as naphthalene, 1,2,4-trichlorobenzene, and hexachlorobenzene, the values being comparable to those obtained with commercial coatings. UIO-66 adsorbent extracted high amounts of small compounds, such as acetic acid, pyridine, and trimethylamine. Molecular mass affected significantly the adsorption performance of UIO-66, seen from extraction efficiency that was decreased with the increased molecular mass for pyridine, aniline and 1-naphthylamine. Furthermore, polarity of the analytes played an important role as proved by efficient extraction of some polar compounds with long chain hydrocarbons, such as pentyl acetate, nonanal and hexachlorobutadiene,

compared to nonpolar decane. In addition, MOF adsorbents did not extract neither nonpolar nor nonaromatic alpha pinene, nor nonaromatic caryophyllene oxide with larger molecular mass. PDMS/DVB and CarboxenWR adsorbents provided good extraction efficiencies for atrazine and 2-bromopropane.

In summary, Fe-based MOF coatings gave best extraction efficiencies for compounds that contained a benzene ring. Their efficiencies further increased as the hydrophobicity of target compounds increased. UIO-66 coating proved to be suitable for the extraction of small polar compounds, aromatic compounds and long chain polar compounds. For chlorinated phenols, acetic acid, pyridine, trimethylamine, nonanal, hexachlorobenzene and naphthalene, the MOF coatings gave better or comparable performance with commercial SPME coatings.

Because chlorinated phenols, hexachlorobutadiene, and hexachloribenzene need to be monitored in water in EU and Fe-BDC and UIO-66 coatings provided the best extraction for these compounds, these chemicals and coatings were exploited in further studies. In addition, results of TGA analysis for Fe-BDC (up to 270 ^{o}C) and UIO-66 coatings (up to 480 ^{o}C) showed their suitability for thermal-desorption processes.

3.3. Clarification of the final extraction and desorption conditions for SPME Arrows

The goal was first to find the most important preliminary extraction and desorption parameters for the successful extraction of different chemical compounds by Fe-BDC and UIO-66 coated SPME Arrow systems before the final optimization by utilizing response statistical design.

3.3.1. Selection of preliminary extraction and desorption parameters

The addition of NaCl, agitation, longer extraction time and low pH increased the extraction efficiency of Fe-BDC coated SPME Arrow. Only one minute desorption time was needed to release all

the analytes completely. Increased extraction temperature had a positive effect on extraction of tetrachlorophenols and pentachlorophenol, and a negative effect on that of di- and trichlorophenols. Based on these results, NaCl amount, extraction time and temperature were the most significant variables.

With UIO-66 Arrow, longer extraction time, additional agitation and incubation increased the extraction of hexachlorobutadiene and hexachlorobenzene. Extra added NaCl and higher extraction temperatures decreased their extraction, and only some less soluble analytes could be transferred to the headspace. In addition, higher temperatures caused faster kinetics from UIO-66 coating. Three minutes desorption was long enough to desorb all the analytes. So extraction time and agitation speed were selected as the main parameters for the extraction of hexachlorobutadiene and hexachlorobenzene.

3.3.2. Optimization using response statistical models

A central composite design (CCD) allows the optimization of the most significant variables with decreased number of runs, needed [33-35]. For Fe-BDC Arrow, the experimental design comprised of 20 tests (8 tests of the full factorial design with three factors, 6 tests of the star points, and 6 tests in the center, Table S5). For UIO-66 Arrow, only 13 tests (4 tests of the full factorial design with three factors, 5 tests of the star points, and 4 tests in the center, Table S6) were needed.

Response surface plots (RSPs) demonstrate the effect of extraction time, extraction temperature, and NaCl addition on the extraction of chlorinated phenols (response variables) by Fe-BDC SPME Arrow (Figures 3 and S3). Results demonstrated that most of response areas of target compounds increased with the increasing NaCl amount. Enhanced extraction time above 20 ^{o}C improved the response area although for some compounds areas decreased at 80 ^{o}C. To guarantee that coatings were applicable for

longtime use, optimal extraction conditions for Fe-BDC Arrow were 30 minutes extraction at 40 ^{o}C with 2 g NaCl.

For UIO-66 coated SPME Arrow, the longer the extraction time ,less amounts of hexachlorobutadiene (>40 minutes) and increased amounts of hexachlorobenzene were obtained (Figure S4). Higher agitation speed accelerated extraction of both hexachlorobutadiene and hexachlorobenzene, 40 minutes and fastest agitation speed 750 rpm were selected for the optimal conditions.

3.4. Method validation

The analytical performances of Fe-BDC SPME Arrow-GC-MS and UIO-66 SPME Arrow-GC-MS methods for the analysis of chlorinated phenols, hexachlorobutadiene and hexachlorobenzene were investigated with the PAL autosampler sampling and GC-MS analysis in SIM mode, and the linear ranges, the coefficient of determination (R^2), the limits of quantifications (LOQs), and precision are shown in Table S7.

The LOQs, calculated as the ten times standard deviation divide the slop of the calibration curve at the lowest concentration, were from 0.07 to 0.46 ng mL^{-1} for all the target compounds, being lower than the maximum allowable concentration (MAC) in surface water by European Union and in drinking water by US Environmental Protection Agency [36, 37]. The linear range for tri-, tetra-, and pentachlorophenols were 0.5-500 ng mL^{-1}, and for 2,6-dichlorophenol was 1-500 ng mL^{-1}. The linear ranges for hexachlorobutadiene and hexachlorobenzene were 0.1-250 ng mL^{-1}. The calibration curves of Fe-BDC SPME Arrow for chlorinated phenols and UIO-66 SPME Arrow for hexachlorobutadiene and hexachlorobenzene were conducted with seven data points with triplicate measurements. The

correlation coefficients (R^2) were within the range of 0.9835-0.9995. The RSDs of all the compounds in the linear range were 0.3-26.4%. In summary, the Fe-BDC SPME Arrow-GC-MS and UIO-66 SPME Arrow-GC-MS methods exhibited wide linear ranges, low LOQs, and good repeatability. In addition, our experimental results also demonstrated that both Fe-BDC and UIO-66 coated SPME Arrow can be reused over 80 times without significant losses in the extraction performance.

3.5. Wastewater analysis

Fe-BDC and UIO-66 SPME Arrows were applied to the determination of chlorinated phenols, hexachlorobutadiene and hexachlorobenzene in influent and effluent wastewater samples to confirm their applicability to natural samples. Since no residual target compounds were detected, recovery experiments were conducted in spiked wastewater samples (Table 1). The recoveries (n=3) of chlorinated phenols by Fe-BDC coated SPME Arrow were ranging from 67.7 to114.2% (RSDs=1.3-16.4%) in effluent wastewater samples and from 60.4 to 93.5% (RSDs=2.1-23.1%) in influent wastewater samples. Those of hexachlorobutadiene and hexachlorobenzene by UIO-66 coated SPME Arrow were in the range of 69.2-92.9% with 2.8-11.8% RSDs in influent wastewater samples and in the range of 78.8-91.8% with 7.2-11.8% RSDs in effluent wastewater samples. As could be expected lower recoveries and higher RSDs values, were obtained for influent wastewater samples due to the more complex sample matrix.

4. Conclusions

In this study, the MOF coatings for SPME Arrow by chemical vapor reaction method and ALD-conversion method were successfully prepared. These methods enable the automation and high through-put of the reproducible preparation of the coatings without the use of organic solvents due to

the atomic level control of the coating growth by the ALD deposition and gas phase reaction/conversion. The coatings prepared were first characterized by XRD, SEM, and TGA, and the results confirmed their good crystalline structure, satisfactory uniformity and thickness, and good thermal stability which proved their applicability to SPME sampling, followed by GC thermal desorption. Their suitability for the analytes with different chemical properties was also tested. Fe-BDC and UIO-66 coatings gave much better or comparable extraction efficiencies and selectivities for most of the tested polar compounds, but weaker extraction efficiencies towards nonpolar compounds compared to commercial PDMS, PDMS/DVB, PA, and CarboxenWR coatings. These new SPME Arrow coatings were exploited with success for the sampling of influent and effluent wastewater samples. The new coating preparation methods developed here can be also utilized for the fabrication of other coating materials.

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Figure legends

Figure 1. SEM images of Fe-BDC (A and C) and UIO-66 (B and D) coated SPME Arrows.

Figure 2. Comparison of home-made Fe-BDC, Fe-BTC, Al-BDC, Al-BTC, and UIO-66 SPME blade coatings with commercial PA coating for chlorinated phenols in terms of GC-MS peak areas.

Figure 3. Represent response surface models of chlorinated phenols using Fe-BDC SPME Arrow. (a) 2,6-dichlorophenol, (b) 2,3,5-trichlorophenol, (c) 2,3,4-trichlorophenol, (d) 2,3,6-trichlorophenol, (e) 2,4,6-trichlorophenol, (f) 2,3,4,6-tetrachlorophenol, (g) 2,3,4,5-tetrachlorophenol, and (h) Pentachlorophenol.

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Table 1. Analytical results of Fe-BDC SPME Arrow and UIO-66 SPME Arrow for the extraction and GC-MS analysis of spiked wastewater samples.

	Effluent Wastewater						Influent Wastewater					
	10 ng mL^{-1}		50 ng mL^{-1}		200 ng mL^{-1}		10 ng mL^{-1}		50 ng mL^{-1}		200 ng mL^{-1}	
Fe-BDC SPME arrow	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
2,6-dichlorophenol	76.9	4.2	114.2	13.9	82.7	14.3	68.7	11.0	89.2	8.6	69.9	23.1
2,3,5-trichlorophenol	91.7	5.7	90.2	6.6	89.4	4.3	90.2	2.5	74.7	11.9	78.4	7.1
2,3,4-trichlorophenol	93.6	4.7	95.4	6.9	104.9	2.3	88.2	5.1	84.9	9.9	94.3	5.7
2,3,6-trichlorophenol	99.9	4.7	93.7	5.2	94.5	5.7	94.1	2.7	91.6	3.5	82.2	7.9
2,4,6-trichlorophenol	67.7	5.0	114.1	5.0	104.3	4.5	60.5	5.5	93.5	5.0	92.2	6.6
2,3,4,6-tetrachlorophenol	71.9	4.3	74.2	4.3	86.1	10.3	60.4	2.3	70.5	2.5	86.8	4.7
2,3,4,5-tetrachlorophenol	81.7	8.1	99.8	15.5	84.5	16.4	70.5	15.1	84.5	6.7	73.6	10.1
Pentachlorophenol	80.4	1.3	91.7	5.8	83.6	4.9	78.2	2.1	78.5	2.1	72.0	4.8
	10 ng mL^{-1}		50 ng mL^{-1}		100 ng mL^{-1}		10 ng mL^{-1}		50 ng mL^{-1}		100 ng mL^{-1}	
UIO-66 SPME arrow	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Hexachlorobutadiene	69.2	2.8	88.0	10.1	92.9	10.1	88.0	10.1	86.5	10.7	84.3	11.4
Hexachlorobenzene	89.7	8.9	91.8	11.8	91.2	9.3	91.8	11.8	78.8	7.5	79.5	7.2

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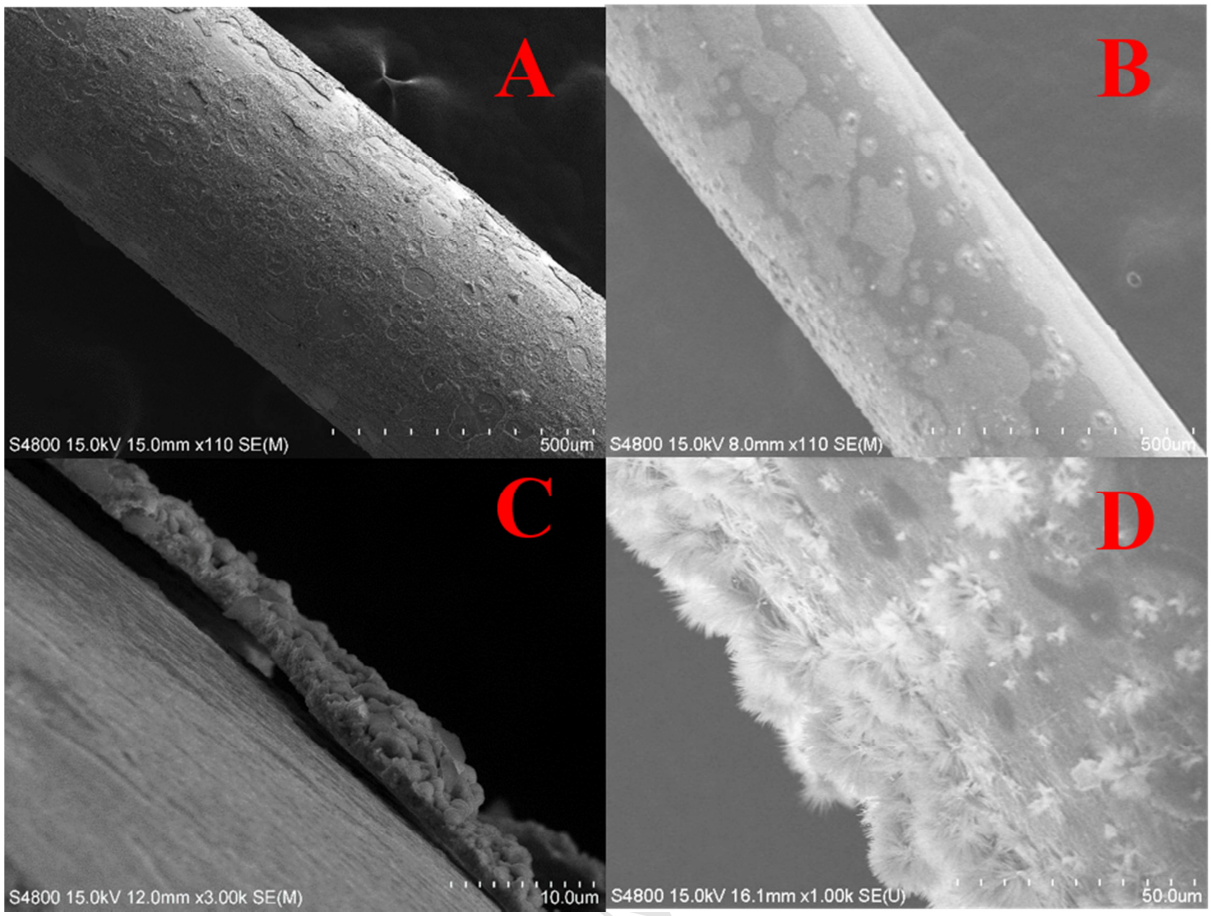

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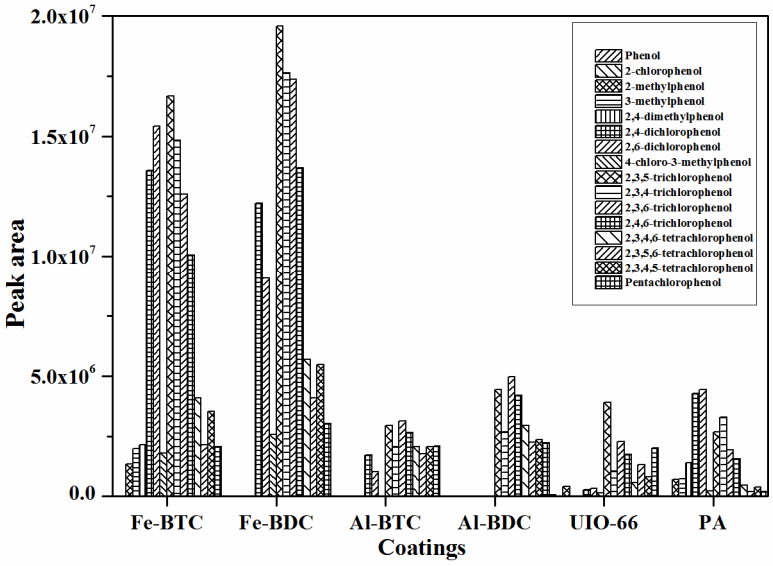

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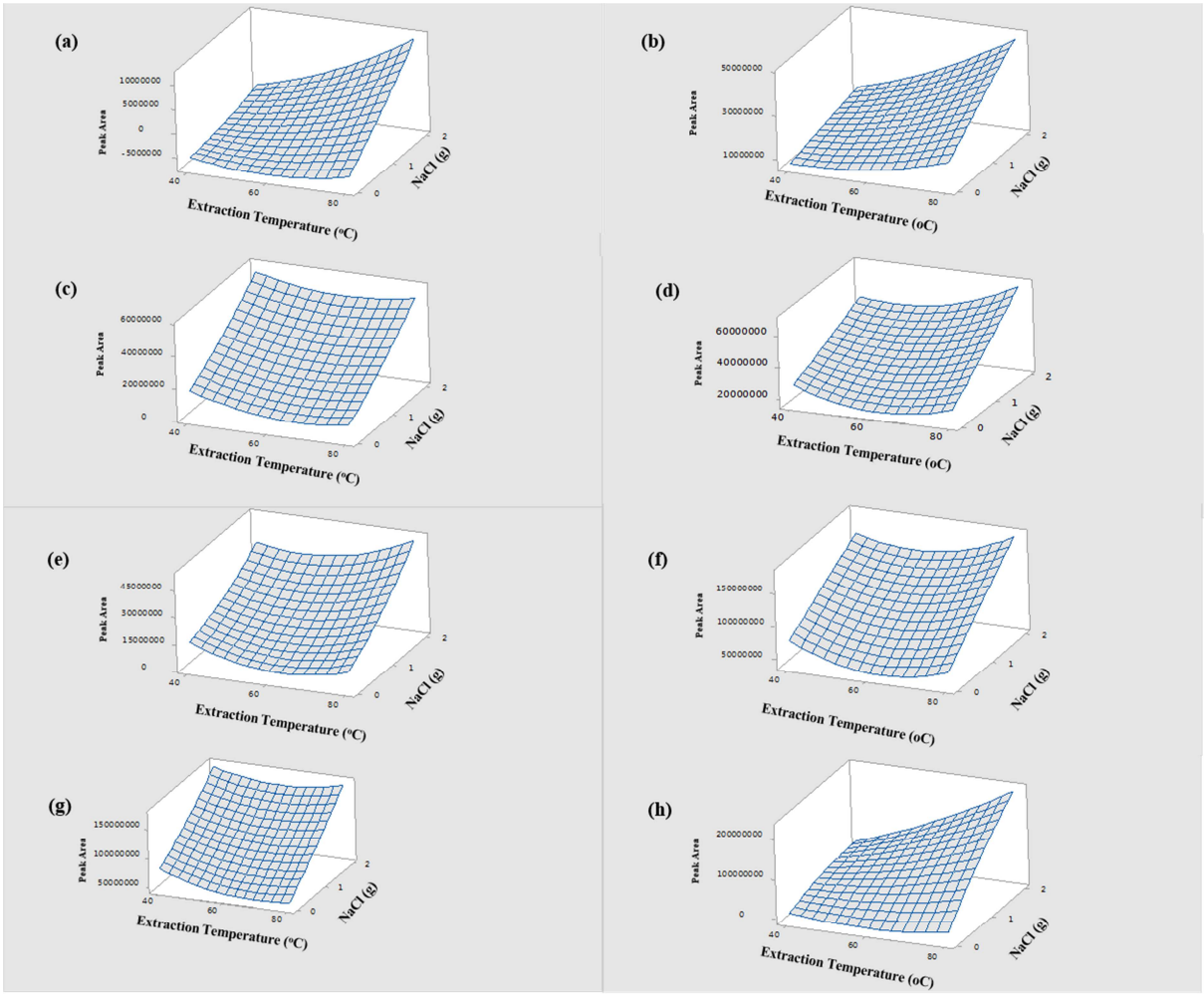

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Highlights

- New procedure was developed for the preparation of solid phase microextraction Arrow coatings
- Coating process included integrated chemical vapor reaction and atomic layer deposition-conversion methods
- Four different metal organic frameworks coatings were successfully prepared
- For the first documented all-gas phase synthesis of SPME Arrow coatings the effect of different parameters on preparation were tested
- Usefulness of new coatings was evaluated for determination of several analytes, in wastewater samples

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