รายงานวิจัยฉบับสมบูรณ์

วัสดุชนิดใหม่สำหรับการสกัดระดับจุลภาคโดยอาศัยตัวดูดซับของสารมลพิษอินทรีย์ทางสิ่งแวดล้อม

โดย รองศาสตราจารย์ ดร. รจนา บุระคำ

มิถุนายน 2562

สัญญาเลขที่ RSA5980034

รายงานวิจัยฉบับสมบูรณ์

วัสดุชนิดใหม่สำหรับการสกัดระดับจุลภาคโดยอาศัยตัวดูดซับของสารมลพิษอินทรีย์ทางสิ่งแวดล้อม

รองศาสตราจารย์ ดร. รจนา บุระคำ มหาวิทยาลัยขอนแก่น

สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัยและมหาวิทยาลัยขอนแก่น

Executive summary

ทุนพัฒนานักวิจัย สกว. (RSA5980034)

1. ชื่อโครงการวิจัย (ภาษาไทย) วัสดุชนิดใหม่สำหรับการสกัดระดับจุลภาคโดยอาศัยตัวดูดซับของสารมลพิษอินทรีย์ทางสิ่งแวดล้อม

(ภาษาอังกฤษ) New materials for sorbent-based microextraction of organic environmental pollutants

2. หัวหน้าโครงการ

รองศาสตราจารย์ ดร. รจนา บุระคำ
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3. สาขาวิชาที่ทำการวิจัย เคมีวิเคราะห์ เน้นการพัฒนาเครื่องมือและระบบการวิเคราะห์แบบใหม่

4. งบประมาณทั้งโครงการ 1,500,000 บาท (หนึ่งล้านห้าแสนบาทถ้วน)

5. ระยะเวลาดำเนินงาน 3 ปี (16 มิถุนายน 2559 – 15 มิถุนายน 2562)

6. ความสำคัญและที่มาของปัญหา

It has been known that sample preparation is an essential part of analytical process. As the front end of the analytical protocol, the sample preparation is a critical part of the workflow to eliminate undesirable matrices and unwanted compounds. Sample preparation steps typically account for most analysis time, and, in some circumstances, it has a significant impact on the quality of analytical results. Therefore, improvement of sample preparation in terms of speed, reliability and sensitivity is of great interest.

Nowadays, modern analytical chemistry trend towards the simplification and miniaturization of sample preparation and reduction of toxic solvent used. Efforts have been made to minimize classical extraction methods resulted in improved extraction techniques, called microextraction, that use much smaller amounts of organic solvent. Generally, sample preparation approaches can be divided into two categories according to the different extraction phases concerned, including solvent-based microextraction and sorbent-based microextraction. However, some polar analytes such as degradation products of organic pollutants are often partly soluble in aqueous samples and cannot be extracted with good recoveries whatever the organic solvent selected in solvent-based microextraction. This pointed out the need for alternative methods to solvent-based microextraction.

Microextraction using solid sorbent is popular and practical method due to its high accuracy, high enrichment factor, low consumption of organic solvent, short extraction time, and ease of automation. However, the choice of sorbent is the main key point because it controls the analytical performance, such as selectivity, affinity, and the capacity of the method. In the past few years, many researches contributed to the area of sample preparation have been with respect to the discovery and the application of novel materials as sorbents for analyte extraction. The impact of material chemistry in chemical analysis cannot be overemphasized. Further investigation of new materials with promising structural and chemical reactive properties are increasingly interested for sample preparation technology.

The research interest focuses on discovering of the new sorbent materials for application in sorbent-based microextraction of organic environmental pollutants prior to their determination using chromatographic techniques. In addition, diverse designs of micro-solid phase extraction procedures/devices, both off-line and on-line configurations, will be developed. The analytes of environmental concern including multi-class pesticides and phenol compounds will be studied using liquid chromatography and gas chromatography, respectively.

7. วัตถุประสงค์ของโครงการ

7.1 To explore new sorbents for microextraction of some organic pollutants

7.2 To develop sorbent-based microextraction procedures/devices for preconcentration of organic pollutants prior to chromatographic analysis

7.3 To evaluate the feasibility of the developed methodologies for application in environmental samples

8. ผลงานที่ได้จากโครงการ

8.1 ได้วัสดุชนิดใหม่สำหรับการประยุกต์ใช้ในการพัฒนาวิธีสกัดสารมลพิษอินทรีย์ 5 ระบบ ดังนี้

8.1.1 วัสดุ polyaniline-modified zeolite NaY สำหรับการสกัดสารกำจัดศัตรูพืชหลายกลุ่มด้วยวิธีการสกัดแบบ dispersive solid phase extraction

8.1.2 วัสดุโลหะโครงข่ายอินทรีย์ชนิด NH_2-MIL-53(Al) สำหรับการสกัดสารมลพิษฟีนอลด้วยวิธีการสกัดแบบ vortex-assisted dispersive micro-solid phase extraction

8.1.3 วัสดุโลหะโครงข่ายอินทรีย์ชนิด NH_2-MIL-53(Al) สำหรับการสกัดสารมลพิษคลอโรฟีนอลด้วยวิธีการสกัดแบบ sorbent-injection vortex-assisted dispersive micro-solid phase extraction

8.1.4 วัสดุโลหะโครงข่ายอินทรีย์ชนิด NH_2-MIL-101(Fe) สำหรับการสกัดสารมลพิษฟีนอลด้วยวิธีการสกัดแบบ dispersive solid phase extraction

8.1.5 วัสดุที่มีสมบัติแม่เหล็กชนิด polyaniline coated zerovalent iron-silica สำหรับการสกัดสารมลพิษฟีนอลด้วยวิธีการสกัดแบบ magnetic solid phase extraction

8.2 ผลงานตีพิมพ์ในวารสารวิชาการระดับนานาชาติ จำนวน 3 เรื่อง และอยู่ในระหว่างการแก้ไขตามคำแนะนำของผู้ทรงคุณวุฒิ (Revision) จำนวน 2 เรื่อง ดังนี้

8.2.1 P. Arnnok, N. Patdhanagul, R. Burakham, Dispersive solid-phase extraction using polyaniline-modified zeolite NaY as a new sorbent for multiresidue analysis of pesticides in food and environmental samples, Talanta, 164 (2017) 651–661.

8.2.2 T. Boontongto, K. Siriwong, R. Burakham. Amine-functionalized metal-organic framework as a new sorbent for vortex-assisted dispersive micro-solid phase extraction of phenol residues in water samples prior to HPLC analysis: Experimental and computational studies. Chromatographia, 81 (2018) 735–747.

8.2.3 S. Soonrat, T. Boontongto, K. Siriwong, R. Burakham. Exploiting a combined computational/experimental sorbent-injection vortex-assisted dispersive micro-solid phase extraction for chromatographic determination of priority phenolic pollutants in water samples. J. Iran. Chem. Soc., 15 (2018) 685–695.

8.2.4 J. Gamonchuang, K. Grudpan, R. Burakham. Magnetic solid phase extraction of phenolic pollutants in water samples using a facile synthesized polyaniline coated zerovalent iron-silica as an efficient sorbent. RSC Advances, Revision in progress.

8.2.5 T. Boontongto, R. Burakham. Evaluation of metal-organic framework NH2-MIL-101(Fe) as an efficient sorbent for dispersive solid phase extraction of phenolic pollutants in environmental water samples. Heliyon, Revision in progress.

8.3 ผลงานนำเสนอในที่ประชุมวิชาการระดับนานาชาติ จำนวน 12 เรื่อง ดังนี้

8.3.1 T. Boontongto, R. Burakham, Metal-organic framework NH_2-MIL-53(Al): A new sorbent for dispersive micro-solid phase extraction of phenol residues using HPLC, Oral presentation (by T. Boontongto), The 13th Asian Conference on Analytical Sciences (ASIANALYSIS XIII), 8–11 December 2016, The Empress International Convention Center, Chiang Mai, Thailand.

8.3.2 S. Soonrat, R. Burakham, Sample preparation and high performance liquid chromatographic analysis of phenolic pollutants, Poster presentation, The 13th Asian Conference on Analytical Sciences (ASIANALYSIS XIII), 8–11 December 2016, The Empress International Convention Center, Chiang Mai, Thailand.

8.3.3 R. Burakham, Application of ultrasonic radiation and vortex agitation in surfactant-based microextraction techniques, Invited lecture, The 13th Asian Conference on Analytical Sciences (ASIANALYSIS XIII), 8–11 December 2016, The Empress International Convention Center, Chiang Mai, Thailand.

8.3.4 T. Boontongto, R. Burakham, Determination of phenol residues in agricultural surface water by dispersive solid-phase extraction coupled with HPLC, Poster Presentation, 254th ACS National Meeting & Expo, 20–24 August 2017, Washington DC, USA.

8.3.5 J. Kamonchuang, R. Burakham, Polyaniline covering zerovalent iron-silica magnetic particle for magnetic solid phase extraction of trace phenolic compounds, Poster Presentation, Pure and Applied Chemistry International Conference 2018 (PACCON2018), 7–9 February 2018, The 60th Anniversary of His Majesty the King's Accession to the Throne International Convention Center, Hat Yai, Songkhla, Thailand.

8.3.6 S. Soonrat, R. Burakham, Determination of priority phenolic pollutants by vortex-assisted dispersive micro-solid phase extraction via sorbent injection and HPLC, Poster Presentation, Pure and Applied Chemistry International Conference 2018 (PACCON2018), 7–9 February 2018, The 60th Anniversary of His Majesty the King's Accession to the Throne International Convention Center, Hat Yai, Songkhla, Thailand.

8.3.7 J. Gamonchuang, R. Burakham, Magnetic solid phase extraction of trace phenolic pollutants using polyaniline modified zerovalent iron-silica magnetic particle as sorbent, Poster Presentation, 47th International Symposium on High Performance Liquid Phase Separations and Related Techniques (HPLC 2018), 29 July – 2 August 2018, Washington DC, USA.

8.3.8 R. Burakham, Sorbent materials for preconcentration of toxic residues using solid-phase extraction and liquid chromatography: Offline and online approaches, Invited Speaker, 14th International Conference on Flow Analysis (Flow Analysis 2018), 2–7 December 2018, Arnoma Grand Bangkok Hotel, Bangkok, Thailand.

8.3.9 R. Burakham, Green perspective in sample preparation methods for chromatographic analysis, Invited speaker, International Symposia on Research towards Green Innovation 2018, 8–9 December 2018, The Empress International Convention Center, Chiang Mai, Thailand.

8.3.10 T. Boontongto, R. Burakham, Metal organic frameworks as dispersive micro-solid-phase extraction sorbent for the determination of phenols in surface waters, Poster Presentation, International Symposia on Research towards Green Innovation 2018, 8–9 December 2018, The Empress International Convention Center, Chiang Mai, Thailand.

8.3.11 J. Gamonchuang, R. Burakham, Fabrication of polyaniline coated zerovalent iron silica magnetic sorbent for determination of trace phenols in environmental water resources, Poster Presentation, International Symposia on Research towards Green Innovation 2018, 8–9 December 2018, The Empress International Convention Center, Chiang Mai, Thailand.

8.3.12 R. Burakham, P. Arnnok, P. Salesaeng, T. Boontongto, J. Gamonchuang, S. Soonrat, K. Siriwong, N. Patdhanagul. Sorbent-based microextraction systems for monitoring of toxic residues, Invited Speaker, The 6th NRCT-IFS-PERCH-CIC Workshops: ASEAN Research and Innovation Initiatives, 19–24 February 2019, Chiang Mai Grandview Hotel & Convention Center, Chiang Mai, Thailand.

8.6 นักศึกษาระดับบัณฑิตศึกษาที่สำเร็จการศึกษา จำนวน 1 คน ดังนี้

8.6.1 นางสาวศิริพรรณ สูญราช (2018) ปริญญาโท

บทคัดย่อ

ชื่อโครงการวิจัย วัสดุชนิดใหม่สำหรับการสกัดระดับจุลภาคโดยอาศัยตัวดูดซับของ
สารมลพิษอินทรีย์ทางสิ่งแวดล้อม

หัวหน้าโครงการ รองศาสตราจารย์ ดร. รจนา บุระคำ

โครงการวิจัยนี้มุ่งเน้นการพัฒนาวัสดุชนิดใหม่เพื่อการประยุกต์ใช้ในการสกัดระดับจุลภาคที่อาศัยตัวดูดซับสำหรับสารมลพิษอินทรีย์ก่อนการวิเคราะห์ด้วยเทคนิคโครมาโทกราฟี โดยได้ศึกษาวัสดุชนิดใหม่ 2 กลุ่ม ได้แก่ กลุ่มโลหะโครงข่ายอินทรีย์ และ วัสดุที่ปรับปรุงด้วยพอลิอะนิลีน ได้ออกแบบวิธีการสกัดระดับจุลภาคที่อาศัยเฟสของแข็งที่หลากหลายร่วมกับเทคนิคโครมาโทกราฟีของเหลวสมรรถนะสูง สารเป้าหมายที่วิเคราะห์ ได้แก่ สารมลพิษกลุ่มฟีนอล และสารกำจัดศัตรูพืชหลายกลุ่ม

ได้สังเคราะห์โลหะโครงข่ายอินทรีย์ที่มีการเติมหมู่ฟังก์ชันอะมิโน และมีอะลูมิเนียมและเหล็กเป็นองค์ประกอบ และนำไปประยุกต์สำหรับการพัฒนาระบบการเตรียมตัวอย่างสำหรับสารมลพิษกลุ่มฟีนอล 3 ระบบ ได้แก่ (1) การสกัดระดับจุลภาคด้วยเฟสของแข็งแบบแพร่กระจายและใช้วอร์เท็กซ์ช่วย โดยใช้ NH_2-MIL-53(Al) (2) การสกัดระดับจุลภาคด้วยเฟสของแข็งแบบแพร่กระจายที่มีการฉีดตัวดูดซับและใช้วอร์เท็กซ์ช่วย โดยใช้ NH_2-MIL-53(Al) และ (3) การสกัดระดับจุลภาคด้วยเฟสของแข็งแบบแพร่กระจาย โดยใช้ NH_2-MIL-101(Fe) และได้สังเคราะห์วัสดุที่ปรับปรุงด้วยพอลิอะนิลีน 2 ชนิด ได้แก่ ซีโอไลต์ที่ปรับปรุงด้วยพอลิอะนิลีน และวัสดุแม่เหล็กที่ปรับปรุงด้วยซิลิกาและพอลิอะนิลีน สำหรับการประยุกต์ใช้ในการเตรียมตัวอย่างของสารกำจัดศัตรูพืชหลายกลุ่มและสารมลพิษฟีนอล ตามลำดับ

จากผลการวิจัยที่ได้จะเห็นว่า วัสดุดูดซับที่นำเสนอมีความสามารถในการเพิ่มความเข้มข้นของสารเป้าหมายที่สนใจ วิธีการสกัดระดับจุลภาคโดยอาศัยตัวดูดซับที่พัฒนาขึ้นให้สมรรถนะทางการวิเคราะห์ที่ดีและสามารถนำไปประยุกต์ใช้ในการวิเคราะห์สารเป้าหมายในตัวอย่างจริงได้ โดยโครงการวิจัยนี้แสดงให้เห็นถึงการประยุกต์ใช้ความรู้ด้านเทคโนโลยีการเตรียมตัวอย่างสำหรับส่งเสริมการผลิตอาหารปลอดภัยและการเฝ้าระวังด้านสิ่งแวดล้อม

ABSTRACT

Title: New materials for sorbent-based microextraction of organic environmental pollutants

Principal investigator: Assoc. Prof. Dr. Rodjana Burakham

This research project focused on discovering of the new sorbent materials for application in sorbent-based microextraction of organic environmental pollutants prior to their determination using chromatographic techniques. Two groups of new sorbents were synthesized and applied in sample preparation procedures, including metal-organic frameworks (MOFs)-based and polyaniline-based materials. Diverse designs of micro-solid phase extraction procedures coupling with high performance liquid chromatography have been developed. The analytes of environmental concern including phenol compounds and multi-class pesticides were studied.

Amino-functionalized MOFs based on aluminum and iron were synthesized and applied as efficient sorbents in sample preparation of various phenolic pollutants. There are 3 developed sample preparation systems based on using MOF-based sorbents, including (1) vortex-assisted dispersive micro-solid phase extraction using NH_2-MIL-53(Al), (2) sorbent-injection vortex-assisted dispersive micro-solid phase extraction using NH_2-MIL-53(Al), and (3) dispersive solid phase extraction using NH_2-MIL-101(Fe). Polyaniline-based materials, including polyaniline-modified zeolite NaY and polyaniline coated zerovalent iron-silica, were synthesized and applied in sample preparation of multi-class pesticides and phenolic pollutants, respectively.

It has been proved that all proposed sorbent materials are promising for enrichment of the target analytes. All developed sorbent-based microextraction methodologies provided good analytical performance and could be successfully applied for determination of the target compounds in real sample matrices. This project showed good application of the knowledge in sample preparation technology for serving food safety and environmental monitoring.

รายงานวิจัยทุนพัฒนานักวิจัย สกว. (RSA5980034)

1. ชื่อโครงการวิจัย (ภาษาไทย) วัสดุชนิดใหม่สำหรับการสกัดระดับจุลภาคโดยอาศัยตัวดูดซับของสารมลพิษอินทรีย์ทางสิ่งแวดล้อม

(ภาษาอังกฤษ) New materials for sorbent-based microextraction of organic environmental pollutants

2. หัวหน้าโครงการ

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3. ความสำคัญและที่มาของปัญหา

It has been known that sample preparation is an essential part of analytical process. As the front end of the analytical protocol, the sample preparation is a critical part of the workflow to eliminate undesirable matrices and unwanted compounds. Sample preparation steps typically account for most analysis time, and, in some circumstances, it has a significant impact on the quality of analytical results. Therefore, improvement of sample preparation in terms of speed, reliability and sensitivity is of great interest.

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The research interest focuses on discovering of the new sorbent materials for application in sorbent-based microextraction of organic environmental pollutants prior to their determination using chromatographic techniques. Diverse designs of micro-solid phase extraction procedures have been developed. The analytes of environmental concern including phenol compounds and multi-class pesticides were studied using high performance liquid chromatography.

4. สรุปย่อเนื้อหางานวิจัย

4.1 Sorbent materials based on metal-organic frameworks (MOFs)

4.1.1 Amine-functionalized metal-organic framework as a new sorbent for vortex-assisted dispersive micro-solid phase extraction of phenol residues in water samples

Metal-organic frameworks (MOFs) are a new class of hybrid inorganic-organic microporous crystalline materials, which possess unique properties such as high surface area, tunable pore size, and good thermal stability. These unique characteristics make MOFs interesting targets for sample pretreatment. In this work, MIL-53 material based on aluminum and containing amine functional groups (NH_2-MIL-53(Al)) was synthesized and applied as an efficient sorbent for development of vortex-assisted dispersive micro-solid phase extraction (VA-D-μ-SPE) for eight United States Environmental Protection Agency's priority phenols from aqueous samples prior to analysis by high performance liquid chromatography with photodiode-array detection (HPLC-PDA).

The amine-functionalized MOF sorbent was synthesized by means of a solvothermal treatment. Aluminum chloride hexahydrate and 2-aminoterephthalic acid were mixed with *N,N*-dimethylformamide in a Teflon-lined autoclave and then heated at 403 K in an oven under static condition for 72 h. After cooling to the room temperature, the resulting yellow powder was filtered under vacuum and washed with acetone. To remove organic species trapped within the pores, the samples were activated in boiling methanol overnight and stored at 373 K.

The determination of phenol pollutants was carried out by VA-D-μ-SPE using amine-functionalized MOF as sorbent followed by HPLC-PDA. For this purpose, an aliquot of 10.00 mL aqueous phenol standard or sample solution was added to a centrifuge tube containing 30 mg of sorbent. The mixture was then placed in a vortex mixer for 10 s to accelerate the sorption of the target analytes onto the sorbent. Subsequently, the solid sorbent was isolated from the solution by centrifugation for 1 min. After that, the supernatant was discarded. Then, 1500 μL of acetonitrile-acetic acid mixture (9.5:0.5, v/v) was added in the centrifuge tube. The analytes were desorbed by vortex mixing for 10 s. The mixture was centrifuged for 1 min. The desorption solvent which contained analytes of interest was filtered through 0.45 μm membrane and evaporated to dryness by rotary evaporator. The residue was reconstituted in 50 μL of acetonitrile before HPLC analysis.

The HPLC system consisted of an in-line degasser, a 600E quaternary pump, and a Waters 2996 photodiode array (PDA) detector. The system was equipped with a Rheodyne injector with a 10-μL loop, and a Phenomenex Luna C18 (4.6 mm × 150 mm, 5 μm) analytical column. The separation was performed using acetonitrile (solvent A) and 0.1% acetic acid in water (solvent B) as mobile phase. The gradient program was as follows: 0–3 min, 40% solvent A; 4–8 min, 50% solvent A; 9–12 min, 70% solvent A; 13–17 min, 100% solvent A. A re-equilibration period of 2 min with 40% solvent A was carried out between individual runs. The detections were performed at 271 nm for phenol; at 317 nm for 4-nitrophenol; at 258 nm for 2,4-dinitrophenol; at 276 nm for 2-nitrophenol; 281 nm for 4-chloro-3-methylphenol; at 286 nm for 2,4-dichlorophenol; at 266 nm for 2-methyl-4,6-dinitrophenol; and at 288 nm for 2,4,6-trichlorophenol. Separation of eight phenols was achieved within 14 min with the following order of elution: phenol (t_R=4.0 min), 4-nitrophenol (t_R=4.9 min), 2,4-dinitrophenol (t_R=7.0 min), 2-nitrophenol (t_R=8.1 min), 4-chloro-3-methylphenol (t_R=9.5 min), 2,4-dichlorophenol (t_R=10.6 min), 2-methyl-4,6-dinitrophenol (t_R=11.3 min), and 2,4,6-trichlorophenol (t_R=13.8 min).

For preconcentration of phenol compounds, the optimum VA-D-μ-SPE condition using NH_2-MIL-53(Al) as sorbent was applied before analysis by HPLC. This method exhibited a good linearity in the range of 0.0015–10.000 μg mL^{-1} with the R^2 greater than 0.9929. The low LODs and LOQs were obtained in the range of 0.0004–0.0133 μg mL^{-1} and 0.0013–0.0519 μg mL^{-1}, respectively. Precisions in terms of intra- and inter-day experiments were investigated by replicate analyses of standard mixture of the analytes (0.05 μg mL^{-1} each) in a day (n = 5) and several days (n = 5 × 3), respectively. The intra-day RSDs of retention time and peak area were below 2.24% and 9.05%, respectively. For inter-day experiments, the RSD values were below 2.03% and 9.56% for retention time and peak area, respectively. The enrichment factors (EFs) for all analytes, which were obtained by comparing the concentrations before and after the VA-D-μ-SPE process, were in the range from 45 to 205.

To evaluate the applicability of the developed VA-D-μ-SPE-HPLC for determination of phenol compounds in real sample matrices, eleven water samples, including lake water, treated waste waters, river water, seawater, tap water and three drinking waters were analyzed. No analyte residue was detected in the studied samples. In order to evaluate the accuracy, a recovery study was performed by spiking the samples with the analytes at the concentration levels of 0.10 μg mL^{-1} and 0.15 μg mL^{-1} before analysis by the proposed method. The recoveries were all in the acceptable range of 72.3–111.4 % (on average) with RSDs less than 10.4%. Based on the results above, the proposed method gave good analytical performance for the analysis of target phenols in the studied water samples.

The adsorption ability of MOFs depends directly on the interaction between the analytes and MOFs. In order to investigate such interaction and to understand the adsorption at a molecular level, a molecular docking has been performed. The binding free energies were calculated and the orientation of the analytes in the binding site of NH_2-MIL-53(Al) was investigated. From the results, by substituting one nitro group the interaction was increased about 1.2 times compared to that of phenol. The increase of more than 1.3 times was obtained when substituting with two nitro groups, especially, when methyl group was included. This is due to not only the hydroxyl group but also the substituted nitro groups can form hydrogen bonding with MOFs, leading to the larger binding ability. Similarly, chloro substitutions provided the higher energy than -6 kcal/mol (about 1.3 times) due to the dipole-dipole interaction between the chloro groups and polar hydrogen atoms of NH_2-MIL-53(Al) taking place. In addition, the binding modes showed that the orientations of 4-chloro-3-methylphenol, 2,4-dinitrophenol and 2-methyl-4,6-dinitrophenol molecular planes were parallel to the benzyl group of MOFs yielding the π-π interaction and thus enhancing the interaction. The parallel orientations were not observed for other compounds. In summary, the calculated binding free energies are in good agreement with the adsorption ability observed experimentally.

4.1.2 Amine-functionalized metal-organic framework as sorbent for sorbent-injection vortex-assisted dispersive micro-solid phase extraction of phenolic pollutants in water samples

An amine-functionalized metal-organic framework based on aluminium (NH_2-MIL-53(Al)) was synthesized and employed as a sorbent for extraction of phenolic pollutants. A new designed sorbent-injection vortex-assisted dispersive micro-solid phase extraction (SI-VA-D-μ-SPE) was proposed in which the sorbent suspension was simply injected into the sample solution.

The HPLC system consisted of an in-line degasser, a 600E quaternary pump, and a Waters 2996 photodiode array (PDA) detector. The system was equipped with a Rheodyne injector with a 10-μL sample loop, and an Inertsil® ODS-3 (4.6 mm × 150 mm, 5 μm) analytical column. The separation was performed using methanol (solvent A) and water (solvent B) as mobile phase. The gradient program was as follows: 50% solvent A (0–4 min); increased to 70% solvent A (4–5 min); held for 2 min (5–7 min); ramped to 100% solvent A (7–8 min); held for 5 min (8–13 min; before returning to 50% solvent A (13–14 min). A re-equilibration period of 1 min with 50% solvent A was carried out between individual runs. The detection was performed at 275 nm.

The determination of phenolic pollutants was carried out by a sorbent-injection vortex-assisted dispersive micro-solid phase extraction (SI-VA-D-μ-SPE) using NH_2-MIL-53(Al) as sorbent followed by HPLC-PDA. For this purpose, the suspension of NH_2-MIL-53(Al) was prepared by mixing of 0.64 g sorbent in 16 mL water, and stirred using the magnetic stirrer. An aliquot of 10.00 mL aqueous phenolic pollutants or sample solution was placed in a centrifuge tube, then the sorbent suspension (1.50 mL) was injected rapidly. The mixture was then placed in a vortex mixer for 1 min to accelerate the sorption of the target analytes onto the sorbent. Subsequently, the solid sorbent was isolated from the solution by centrifugation for 2 min. After that, the supernatant was discarded. Then, 500 μL of acetone was added in the centrifuge tube to desorb the analytes from the sorbent. After that, the mixture was filtered using a 0.45 μm nylon membrane syringe filter before being injected to HPLC system. Herein the experimental parameters affected the extraction efficiency for the target analytes were optimized, including volume of sorbent suspension, vortex agitation time, eluent type and its volume, and sample volume. Good linearity was obtained in the concentration range of 0.1–10.0 mg L^{-1} with the correlation coefficients in the range of 0.9970–0.9981. The LODs and LOQs were in the ranges of 0.030–0.055 mg L^{-1} and 0.090–0.150 mg L^{-1}, respectively. The results of the intra- and inter-day experiments showed good precision of peak area with the relative standard deviation (RSD) values of better than 5.82% and 7.85%, respectively. The developed method has been successfully applied to determine phenolic residues in water samples. The satisfactory recoveries were obtained in the range of 83.0–122.4% with the RSDs of less than 12.9%.

In addition, molecular docking was performed to predict the adsorption ability of NH_2-MIL-53(Al) sorbent towards the target analytes. The binding free energies ($\Delta G_{binding}$) obtained from molecular docking showed that phenol yields lower negative value of $\Delta G_{binding}$ compared to its derivatives. This indicates that the interaction between phenol and MOF is rather small which is in good agreement with the adsorption ability observed experimentally. By substituting chloro and/or methyl groups, the interactions were increased about 20% (for 2-chlorophenol) and 30% (for two group substituted compounds). The NH_2-MIL-53(Al) composes of functional groups that can form various interactions with the analytes. The docked structures reveal that all compounds form hydrogen bonds between oxygen atom of carboxyl group and hydrogen atom of hydroxyl group in MOF. Due to the hydrophobic interaction resulted from methyl group(s), and the dipole-dipole interaction between the chloro group(s) and polar hydrogen atoms of NH_2-MIL-53(Al), the increase of interaction for phenol derivatives was therefore obtained. The orientations of phenol, 2-chlorophenol and 4-chloro-3-methylphenol molecular planes were parallel to the benzyl group of MOF providing the π-π interaction. Although the parallel orientation was not observed for 2,4-dimethylphenol and 2,4-dichlorophenol, their large negative values of $\Delta G_{binding}$ seem to be mainly contributed from the hydrophobic and dipole-dipole interactions. The computational results were in good agreement with data obtained experimentally.

4.1.3 An NH_2-MIL-101(Fe) as an efficient sorbent for dispersive solid phase extraction of phenolic pollutants in environmental water samples

This work proposes an application of amine-functionalized metal-organic framework (NH_2-MIL-101(Fe)) as sorbent for dispersive solid phase extraction (DSPE) of ten priority phenolic pollutants. The HPLC system consisted of an in-line degasser, a 600E quaternary pump, and a Waters 2996 photodiode array (PDA) detector. The system was equipped with a Rheodyne injector with a 10-μL injection loop, and a Phenomenex Luna C18 (4.6 mm × 150 mm, 5 μm) analytical column. The separation was performed using acetonitrile (solvent A) and 0.1% acetic acid in water (solvent B) as mobile phase. The gradient program was as follows: 0–3 min, 40% solvent A; 3–4 min, ramped to 50% solvent A; 4–8 min, 50% solvent A; 8–9 min, ramped to 70% solvent A; 9–12 min, 70% solvent A; 12–13 min, ramped to 100% solvent A; 13–17 min, 100% solvent A; 17–18 min, decreased to 40% solvent A. A re-equilibration period of 2 min with 40% solvent A was carried out between individual runs. The detections were performed at 271 nm for phenol; 317 nm for 4-nitrophenol; 258 nm for 2,4-dinitrophenol; 276 nm for 2-nitrophenol and 2-chlorophenol; 280 nm for 4-chloro-3-methylphenol and 24-dimethylphenol; 266 nm for 2-methyl-4,6-dinitrophenol; 286 nm for 2,4-dichlorophenol; and 288 nm for 2,4,6-trichlorophenol.

The sorbent was simply synthesized under facile condition by solvothermal treatment. Briefly, a solution of 2-aminoterephthalic acid in DMF was mixed with a solution of ferric chloride anhydrous in DMF. The mixture was stirred for 10 min before thermal treatment in a stainless-steel autoclave at 110 ^{o}C for 24 h. The product was filtered under vacuum, then washed with DMF and dried at room temperature.

The determination of phenolic pollutants was carried out by DSPE using amine-functionalized MOF (NH_2-MIL-101(Fe)) as sorbent followed by HPLC with photodiode array detector. For this purpose, an aliquot of 10.00 mL aqueous phenol standard or sample solution was added to a centrifuge tube containing 50 mg of sorbent. The mixture was then placed in a vortex mixer for 10 s to accelerate the sorption of the target analytes onto the sorbent. Subsequently, the solid sorbent was isolated from the solution by centrifugation at 5000 rpm for 1 min. After that, the supernatant was discarded. Then, 2.0 mL of 0.5% acetic acid/acetonitrile mixture was added in the centrifuge tube. The analytes were desorbed by vortex mixing for 10 s. The mixture was centrifuged at 5000 rpm for 1 min. The desorption solvent which contained analytes of interest was filtered through 0.45 μm membrane and evaporated to dryness by rotary evaporator. The residue was reconstituted in 50 μL of acetonitrile before further injecting to HPLC for analysis.

The entire DSPE process was optimized by studying the effect of experimental parameters affecting the extraction recovery of the target analytes. The final extract was analyzed using high performance liquid chromatography with photodiode array detector. Under the optimum condition, the proposed procedure can be applied for wide linear calibration ranges between 1.25–5000 μg L^{-1} with the correlation coefficients of greater than 0.9900. The limits of detection (LODs) and limits of quantitation (LOQs) were in the ranges of 0.4–9.5 μg L^{-1} and 1.25–30 μg L^{-1}, respectively. The precision evaluated in terms of the relative standard deviations (RSDs) were below 1.3% and 13.9% for retention time and peak area, respectively. High enrichment factors up to 99 were reached. The developed method has been successfully applied to determine phenol residues in environmental water samples. The satisfactory recoveries in the range of 68.4–114.4% were obtained. The results demonstrate that the NH_2-MIL-101(Fe) material is promising sorbent in the DSPE of phenolic pollutants.

4.2 Sorbent materials based on polyaniline

4.2.1 Polyaniline-modified zeolite NaY as a new sorbent for dispersive solid-phase extraction of pesticide multiresidue in food and environmental samples

In this part, an effective sorbent along with a practical extraction procedure was focused. The novel PANI-modified zeolite NaY was proposed for the dispersive solid-phase extraction (DSPE) of pesticide residues. The applicability of polyaniline (PANI)-modified zeolite NaY as sorbent for multi-class pesticides extraction was investigated. In order to declare the applicability of the sorbent for diverse residues in environmental samples and foods especially agricultural products, several groups of commonly used pesticides including organophosphate, sulfonylurea, pyrethroid and neonicotinoid were chosen as the model analytes in addition to carbamate insecticides. The developed multi-residue analysis method includes DSPE and the high-performance liquid chromatography coupled with photodiode array (PDA) detection.

Chromatographic separation was performed using a Waters HPLC system consisting of an in-line degasser, a Waters 600 multisolvent delivery system, a Rheodyne injector with a 20 μL injection loop, and a Waters 2996 photodiode array detector. Empower software was used for controlling the system and data acquisition.

A Symmetry Shield RP18 (4.6 × 150 mm, 5 μm) analytical column maintained at ambient temperature was used. The separation of twenty pesticides was carried out using a gradient elution of acetonitrile and water at a flow rate of 1.0 mL min^{-1}. The gradient program was started with 20% acetonitrile (0–8 min), ramped to 68% acetonitrile (8–28 min), changed to 45% acetonitrile (28–35 min), ramped to 80% acetonitrile (35–42 min), held for 8 min (42–50 min), before returning to 20% acetonitrile (50–52 min) and holding for 8 min (52–60 min). Detection of each analyte was performed at its maximum absorption wavelength.

For preparation of zeolite NaY, briefly, seed gel which consisted of 10.67 Na_2O:Al_2O_3:10 SiO_2:180 H_2O (mole ratio) was slowly added to feedstock gel which consisted of 4.30 Na_2O:Al_2O_3:10 SiO_2:180 H_2O (mole ratio). The mixture was stirred vigorously before aging at room temperature for 24 h. After that the gel was refluxed at 100 °C for 2 h and the obtained zeolite was dried at 110 °C for 3 h. The synthesized zeolite NaY was then modified with polyaniline via oxidative polymerization of aniline. 1 g of the zeolite was suspended in 10 mL of methanol and sonicated in an ultrasonic bath for 20 min. Subsequently 12 mL of 1 mol L^{-1} HCl and 50 mL of 0.2 mol L^{-1} aniline were added. pH of the suspension was adjusted using 3 mol L^{-1} HCl/3 mol L^{-1} NaOH. The suspension was stirred at 0–2 °C whilst 50 mL of 0.2 mol L^{-1} ammonium peroxydisulfate was added dropwise. After the suspension was continuously stirred and kept cool for 12 h, supernatant was decanted and the obtained sorbent was washed twice with 50% methanol. The modified sorbent was dried at 110 °C for 3 h.

The synthesized material was characterized by several analytical techniques. The PANI-coated zeolite NaY was successfully created via oxidative polymerization of aniline onto the surface of the zeolite. The sorbent was applied for dispersive solid phase extraction (DSPE) of commonly used pesticides belonging to five different chemical groups, involving carbamate, organophosphate, sulfonylurea, pyrethroid and neonicotinoid. The target pesticides were extracted and preconcentrated by DSPE using PANI-coated zeolite NaY sorbent before analysis by HPLC-PDA. Before that pH of the sample solution was adjusted to 8 using 3 mol L^{-1} NaOH. The DSPE procedure started by adding 150 mg of the sorbent to 125 mL of pH adjusted sample. A suspension was then mechanically shaken at 100 rpm for 4 min to allow sorption of the pesticides onto the sorbent. After that the suspension was transferred to the 3-mL polypropylene syringe column which was served as the SPE eluting column. A piece of filter paper which fit tightly inside the column was inserted into the outlet of the syringe and the cotton wool was placed on the paper in order to entrap the sorbent in the column while allowing liquid to flow through. Salts, sugars and polar interferences were disposed of by washing the SPE column with 10 mL of water. Subsequently target pesticides adsorbed on the solid sorbent were eluted by passing an appropriate eluent through the column. The eluate composed alkaline solution was neutralized by 3 mol L^{-1} HCl. The final extract was filtered through a 0.45 μm nylon membrane filter before HPLC analysis.

The coupling of DSPE and HPLC-PDA resulted in an efficient method for multiresidue analysis of pesticides. The sorbent had a sorption capacity of 833 mg kg^{-1} sorbent and preconcentration factor of 42 in the mixture of twenty pesticides. The proposed method gave LODs and LOQs in the ranges of 0.001–1.00 mg L^{-1} and 0.005–2.50 mg L^{-1}, respectively. The method was applied for determination of pesticide residues in environmental and food samples including drinking water, pond waters, soils, honey, cabbages, cucumbers, tomatoes and strawberries which were collected in Khon Kaen Province, Thailand. Recoveries of the target pesticides were in the range of 64–128% with RSDs less than 12% using matrix matched calibration for all sample matrices. Eight pesticides were found in fruit and vegetable samples at concentrations of 0.003–0.033 mg kg^{-1} whereas a few compounds contaminated in contaminated pond waters have concentrations of 0.046–0.092 mg L^{-1}. The interesting occurrence of high concentration up to 1.26 mg kg^{-1} was found in the soil samples.

4.2.2 Polyaniline coated zerovalent iron-silica as an efficient sorbent for magnetic solid phase extraction of phenolic pollutants in water samples

The magnetic sorbent based on polyaniline coated zerovalent iron-silica ($Fe@SiO_2@PANI$) was simply synthesized using a facile manner under low energy consumption. The zerovalent iron nanoparticles were prepared via reduction of ferrous sulfate using sodium borohydride. In brief, ferrous sulfate was dissolved in water. Then, sodium borohydride solution was added with vigorous stirring for 15 min. After that, the black solid was separated by magnet, washed several times with water and ethanol, and dried in vacuum. The $Fe@SiO_2$ particles were synthesized via sol-gel method using TEOS as precursor, and then polyaniline coated $Fe@SiO_2$ particle was prepared through oxidative polymerization of aniline in the presence of ammonium peroxydisulfate. Firstly, the zerovalent iron nanoparticles were dispersed in ethanol, then water and ammonium hydroxide solution were subsequently added with sonication for 30 minutes. Next, TEOS was gradually dropped and the mixture was shaken for 24 hours at ambient temperature. The product was separated by external magnet, washed with ethanol until the pH became 6–7. After that, as-prepared $Fe@SiO_2$ particle was dispersed in water, then HCl and CTAB were slowly added with sonication for 1 hour. Subsequently, the mixture was added slowly with aniline and shaken for 1 hour in an ice bath. Finally, ammonium peroxydisulfate solution was gradually dropped and the mixture was shaken for 5 hours in ice bath. The dark green of polyaniline coated $Fe@SiO_2$ was collected by magnet, washed several times with water and methanol, and dried. The product was defined as Fe@SiO_2@PANI. The spherical-like shape with particle size of 235±11 nm was obtained. The as-prepared material was characterized and applied as sorbent for development of magnetic solid phase extraction (MSPE) of phenolic pollutants prior to their determination by HPLC-PDA.

Eight phenolic compounds were selected as target analytes, including phenol, 4-nitrophenol, 2-chlorophenol, 2,4-dinitrophenol, 2,4-dimethylphenol, 4-chloro-3-methylphenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol. The HPLC system consisted of an in-line degasser, a 600E quaternary pump, and a Waters 2996 photodiode array (PDA) detector. The system was equipped with a Rheodyne injector with a 10-μL loop, and an ACE 5 C18 (4.6 mm×250 mm, 5 μm) analytical column. The separation was performed using acetonitrile (solvent A) and 0.1% acetic acid in water (solvent B) as mobile phase at a flow rate of 1.0 mL min-1. The gradient program was as follows: 0–3 min, 45% solvent A; 3–4 min, ramped to 55% solvent A; 4–8 min, held at 55% solvent A; 8–9 min, ramped to 65% solvent A; 9–12 min, held at 65% solvent A; 12–13 min, ramped to 75% solvent A; and 13–16 min, held at 75% solvent A. After that solvent A was decreased to 45% before the next run. The detection was performed at 280 nm.

The MSPE process was performed as follows. First, 70 mg Fe@SiO_2@PANI sorbent was added to 25 mL aqueous sample solution in an extraction vial. The mixture was vortexed for 2 min. Then, the magnetic sorbent enriched with target analytes were collected by external magnet before decanting supernatant solution. Subsequently, desorption of analytes was carried out using 0.5 mL acetonitrile as desorption solvent and vortexed for 0.5 min. The magnet was applied for 30 sec to settle down sorbents and the solution was filtered through a 0.45 μm nylon membrane before further injecting into the HPLC system for analysis. The main parameters influencing MSPE method, such as sorbent amount, adsorption time, sample volume, type of desorption solvent and its volume, and desorption time, were optimized. Under the selected condition, wide linear calibration curves were achieved in the concentration range of 0.020–10.000 μg mL^{-1} with the coefficients of determination above 0.9926. The limits of detection (LODs) and the limits of quantitation (LOQs) were in the ranges of 0.001–0.050 μg mL^{-1} and 0.020–0.120 μg mL^{-1}, respectively. The precision in term of RSDs were below than 11%. The determination of phenolic residues in environmental water samples showed the recoveries in the range of 70.7–118.5%. The synthesized Fe@SiO_2@PANI magnetic sorbent exhibits good adsorption affinity which can be further applied for determination of trace phenolic compounds in other sample matrices.

Output ที่ได้จากโครงการ

1. ผลงานตีพิมพ์ในวารสารวิชาการระดับนานาชาติ จำนวน 3 เรื่อง และอยู่ในระหว่างการแก้ไขตามคำแนะนำของผู้ทรงคุณวุฒิ (Revision) จำนวน 2 เรื่อง ดังนี้

1.1 P. Arnnok, N. Patdhanagul, R. Burakham, Dispersive solid-phase extraction using polyaniline-modified zeolite NaY as a new sorbent for multiresidue analysis of pesticides in food and environmental samples, Talanta, 164 (2017) 651–661.

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1.5 T. Boontongto, R. Burakham. Evaluation of metal-organic framework NH2-MIL-101(Fe) as an efficient sorbent for dispersive solid phase extraction of phenolic pollutants in environmental water samples. Heliyon, Revision in progress.

2. ผลงานนำเสนอในที่ประชุมวิชาการระดับนานาชาติ จำนวน 12 เรื่อง ดังนี้

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2.3 R. Burakham, Application of ultrasonic radiation and vortex agitation in surfactant-based microextraction techniques, Invited lecture, The 13th Asian Conference on Analytical Sciences (ASIANALYSIS XIII), 8–11 December 2016, The Empress International Convention Center, Chiang Mai, Thailand.

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2.8 R. Burakham, Sorbent materials for preconcentration of toxic residues using solid-phase extraction and liquid chromatography: Offline and online approaches, Invited Speaker, 14th International Conference on Flow Analysis (Flow Analysis 2018), 2–7 December 2018, Arnoma Grand Bangkok Hotel, Bangkok, Thailand.

2.9 R. Burakham, Green perspective in sample preparation methods for chromatographic analysis, Invited speaker, International Symposia on Research towards Green Innovation 2018, 8–9 December 2018, The Empress International Convention Center, Chiang Mai, Thailand.

2.10 T. Boontongto, R. Burakham, Metal organic frameworks as dispersive micro-solid-phase extraction sorbent for the determination of phenols in surface waters, Poster Presentation, International Symposia on Research towards Green Innovation 2018, 8–9 December 2018, The Empress International Convention Center, Chiang Mai, Thailand.

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3.นักศึกษาระดับบัณฑิตศึกษาที่สำเร็จการศึกษา จำนวน 1 คน ดังนี้

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Dispersive solid-phase extraction using polyaniline-modified zeolite NaY as a new sorbent for multiresidue analysis of pesticides in food and environmental samples

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Multiresidue analysis

ABSTRACT

The applicability of polyaniline (PANI)-modified zeolite NaY as a sorbent for multi-class pesticides extraction was investigated. The sorbent had a sorption capacity of 833 mg kg^{-1} sorbent and preconcentration factor of 42 in the mixture of twenty pesticides. The PANI-coated zeolite NaY was successfully created via oxidative polymerization of aniline onto the surface of the zeolite. The sorbent was applied for dispersive solid phase extraction (DSPE) of commonly used pesticides belonging to five different chemical groups, involving carbamate, organophosphate, sulfonylurea, pyrethroid and neonicotinoid. The coupling of DSPE and HPLC-PDA resulted in an efficient method for multiresidue analysis of pesticides. The proposed method gave LODs and LOQs in the ranges of 0.001–1.00 mg L^{-1} and 0.005–2.50 mg L^{-1}, respectively. The method was applied for determination of pesticide residues in environmental and food samples including drinking water, pond waters, soils, honey, cabbages, cucumbers, tomatoes and strawberries which were collected in Khon Kaen Province, Thailand. Recoveries of the target pesticides were in the range of 64–128% with RSDs less than 12% using matrix matched calibration for all sample matrices. Eight pesticides were found in fruit and vegetable samples at concentrations of 0.003–0.033 mg kg^{-1} whereas a few compounds in contaminated pond waters have concentrations of 0.046–0.092 mg L^{-1}. The occurrence of high concentration of up to 1.26 mg kg^{-1} in the soil samples is noteworthy.

1. Introduction

Global awareness of the environmental and human health impacts due to the increased use of pesticides brings with it the need to analyse these substances [1–3]. Although numerous methods have been reported for the determination of pesticide residues [4–9], development of new methods particularly for sample preparation is still important because pesticide residues are present in various complex matrices, at part per billion level and lower [2,3,6]. Hence, effective sample preparation steps are extremely important for isolation of trace amounts of the target substances from complex matrices, clean-up and preconcentration before analysis. For these purposes, solid phase extraction (SPE) has been frequently used [10–15] owing to its compatibility with a variety of sample matrices. Even though numerous sorbents are commercially available [15–19], creation of a new efficient sorbent has been challenging not only for extraction but also for the separation technique. Our works are also intended to develop new materials for extraction of chemical residues as well as to propose a sample preparation procedure. In previous works, the laboratory-synthesized zeolite NaY was selected as the supporting material to develop solid sorbent for carbamate pesticides extraction [20–22]. Zeolite adsorption is a useful application for removal of various substances [23–25] though its use in extraction techniques is rarely reported [26–28], thus we are interested in widening the applicability of this material. The zeolite that was modified with surfactant, presented good efficacy for carbamate insecticides extraction, unfortunately the modified sorbent was not quite as stable as it needed to be in re-modified form before re-using [21]. Hence we are still seeking a new stable modifier and attempting to create an efficient sorbent which has more stability. Conductive polymers have attracted our interest as they have taken part in the development of solid sorbent for extraction of organic compounds. The use of conductive polymers as sorbent is not

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only because of their stability but also their multiple properties which can involve an extraction mechanism such as hydrophobicity, acid-base character, π-π interaction, polar functional groups, ion exchange property, hydrogen bonding and electro-activity [29–33]. Amongst conductive polymers, polyaniline (PANI) has been frequently used to modify the surface of different materials such as silica [34–36], fiber [13], polymers [37,38], magnetic particles [14,39,40] and noble metals [41,42] for several applications including biosensors, electrodes, gas separation membranes, and others [38,39,43–47]. The modification was generally conducted by dispersing support materials in the polymerization media and then the materials were trapped in the polymer [13,36,39]. Additionally, the use of PANI as a sorbent for the extraction technique has frequently shown up in the recent years [13,14,30,34,36,39,40,48–50].

Therefore, an effective sorbent along with a practical extraction procedure is the focus of the current work. The novel PANI-modified zeolite NaY was proposed for the dispersive solid-phase extraction (DSPE) of pesticide residues. In order to declare the applicability of the sorbent for diverse residues in environmental samples and foods especially agricultural products, several groups of commonly used pesticides including organophosphate, sulfonylurea, pyrethroid and neonicotinoid were chosen as the model analytes in addition to carbamate insecticides. The developed multi-residue analysis method includes DSPE and high performance liquid chromatography coupled with photodiode array (PDA) detection. Determination of pesticide residues in environmental samples and agricultural products was conducted to ensure the applicability of the method and to evaluate the current occurrence of these toxic substances.

2. Experimental

2.1. Chemicals and materials

All standard pesticides are analytical standard grade. Standard pesticides along with their properties are listed in Table S1 (Supplementary material). A stock solution (1000 mg L^{-1}) of each pesticide was prepared in methanol, then a 50 mg L^{-1} intermediary standard mixture and working solutions were achieved by diluting the stock solutions with ultrapure water (Millipore, Massachusetts, USA). Chromatography grade methanol and acetonitrile were supplied from Merck KGaA (Darmstadt, Germany). The other reagents were at least analytical reagent grade. Ultrapure water was used throughout the experiment.

2.2. Preparation of PANI-modified zeolite NaY sorbent

Zeolite NaY was prepared according to the procedure proposed by Patdhanagul et al. [51]. Briefly, seed gel which consisted of 10.67 $Na_2O:Al_2O_3:10\ SiO_2:180H_2O$ (mole ratio) was slowly added to feedstock gel which consisted of 4.30 $Na_2O:Al_2O_3:10\ SiO_2:180H_2O$ (mole ratio). The mixture was stirred vigorously before aging at room temperature for 24 h. After that the gel was refluxed at 100 °C for 2 h and the obtained zeolite was dried at 110 °C for 3 h. The synthesized zeolite NaY was then modified with polyaniline via oxidative polymerization of anilline. 1 g of the zeolite was suspended in 10 mL of methanol and sonicated in an ultrasonic bath for 20 min. Subsequently 12 mL of 1 mol L^{-1} HCl and 50 mL of 0.2 mol L^{-1} aniline were added. pH of the suspension was adjusted using 3 mol L^{-1} HCl/ 3 mol L^{-1} NaOH. The suspension was stirred at 0–2 °C whilst 50 mL of 0.2 mol L^{-1} ammonium peroxydisulfate was added dropwise. After the suspension was continuously stirred and kept cool for 12 h, supernatant was decanted and the obtained sorbent was washed twice with 50% methanol. The modified sorbent was dried at 110 °C for 3 h.

2.3. Sample collection and preparation

2.3.1. Fruit and vegetable

All samples were collected from Khon Kaen Province in the north-eastern region of Thailand. Fruit and vegetable samples including strawberries, tomatoes, cucumbers and cabbages were purchased from local markets. The samples were washed twice with tap water, air dried and collectively weighed. Juices were made by pressing whole fruits and vegetables through a juicer. Tomato, cucumber and cabbage juices were directly filtered through a 0.45 µm nylon membrane (Whatman International Ltd., UK) while strawberry juice (250 mL) was mixed with ultrapure water up to 1000 mL before filtration. All juices were kept at 4 °C before extraction.

2.3.2. Honey

A honey sample was obtained from a supermarket. 10 mL of the sample was diluted to 1000 mL with ultrapure water. The diluted honey was filtered through a 0.45 µm nylon membrane and kept at 4 °C until analysis.

2.3.3. Soil

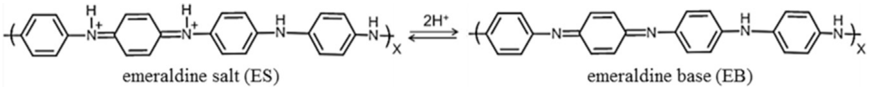
Two soil samples were collected from cultivated areas; one sample was collected from a vegetable farm where pesticides were used and the other was collected from the home vegetable garden without pesticides treatment yet located in the same area as the farm. Samples were taken from the surface (0–10 cm depth). Soils were air-dried, ground and sifted through a 2-mm sieve. After that, samples were extracted using the method proposed by Meghesan-Breja and Morar [9] with some modification. In detail, the accurately weighed 20*g* soil sample was mixed with 20 mL of water, then 20 mL of acidified acetonitrile (1% acetic acid) was added. The samples were mechanically shaken at 200 rpm for 10 min before adding 24 g of anhydrous sodium sulfate and 6 g of anhydrous sodium acetate, after which the mixture was shaken by hand for a few minutes. The supernatant was subsequently transferred to a 50 mL polypropylene centrifuge tube. A 10 mL aliquot of the upper layer was taken and mixed with water up to 125 mL before applying to DSPE.

2.3.4. Water

Local bottled water was also purchased from the supermarket. The sample was filtered through a 0.45 µm nylon membrane and kept at 4 °C.

2.4. DSPE procedure

The target pesticides were extracted and preconcentrated by DSPE using PANI-coated zeolite NaY sorbent and the pH of the sample solution was adjusted to 8 using 3 mol L^{-1} NaOH before analysis by HPLC-PDA. The DSPE procedure was commenced by adding 150 mg of the sorbent to 125 mL of pH adjusted sample. A suspension was then mechanically shaken at 100 rpm for 4 min to allow sorption of the pesticides onto the sorbent. After that the suspension was transferred to the 3-mL polypropylene syringe column which was served as the SPE eluting column. A piece of filter paper which fitted tightly inside the column was inserted into the outlet of the syringe and the cotton wool was placed on the paper in order to entrap the sorbent in the column while allowing liquid to flow through. Salts, sugars and polar interferences were disposed of by washing the SPE column with 10 mL of water. Subsequently target pesticides adsorbed on the solid sorbent were eluted by passing an appropriate eluent through the column. The eluate composed alkaline solution was neutralized by 3 mol L^{-1} HCl. The final extract was filtered through a 0.45 µm nylon membrane filter before HPLC analysis.



Scheme 1. Transformation of PANI (emeraldine form).

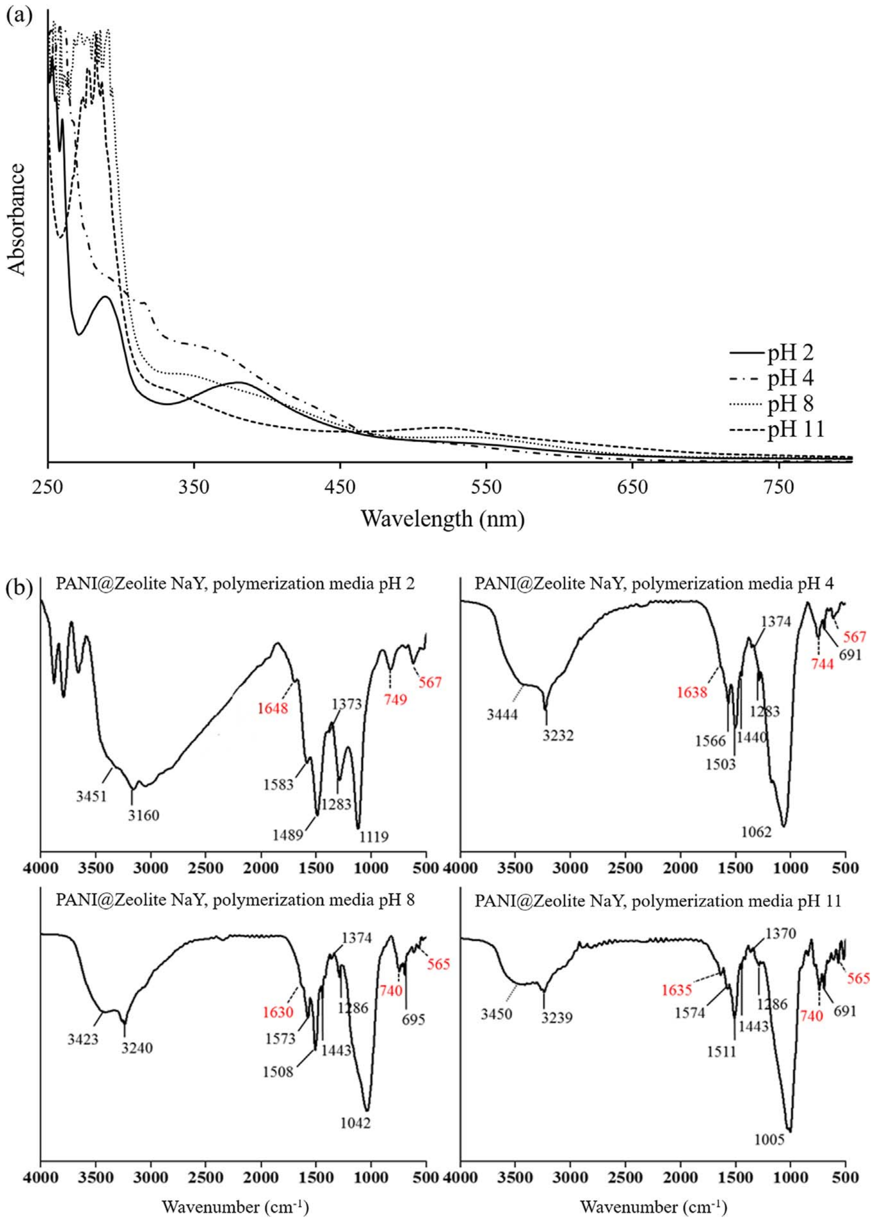


Fig. 1. (a) UV–visible spectra of aniline polymerization in media of different pHs and (b) FTIR spectra of PANI-modified zeolite obtained from polymerization in various pHs.

2.5. Instrumentation

The synthesized zeolite NaY and the PANI-modified zeolite NaY sorbent were characterized using a Spectrum One FT-IR spectrometer (PerkinElmer, Massachusetts, USA). Additionally, aniline monomers in the starting solution was characterized by an Agilent 8453 UV–visible spectroscopy system (Agilent Technologies, CA, USA) to observe the form of PANI. A morphology, as well as an element analysis, was conducted using scanning electron microscopy (SEM) (Hitachi S3000N scanning electron microscope, Hitachi, Tokyo, Japan) together with an elemental analysis by energy-dispersive X-ray spectroscopy (EDS) (Horiba EMAX energy dispersive X-ray analyzer, HORIBA Scientific, London, UK).

Chromatographic separation was performed using a Waters HPLC system (Waters, Massachusetts, USA) consisting of an in-line degasser, a Waters 600 multisolvent delivery system, a Rheodyne injector with a 20 µL injection loop, and a Waters 2996 photodiode array detector. Empower software was used for controlling the system and data acquisition. A Symmetry Shield RP18 (4.6×150 mm, 5 µm) analytical column (Waters, Massachusetts, USA) maintained at ambient temperature was used.

The separation of twenty pesticides was carried out using a gradient elution of acetonitrile and water at a flow rate of 1.0 mL min^{-1}. The gradient program was started with 20% acetonitrile (0–8 min), ramped to 68% acetonitrile (8–28 min), changed to 45% acetonitrile (28–35 min), ramped to 80% acetonitrile (35–42 min), held for 8 min (42–50 min), before returning to 20% acetonitrile (50–52 min) and holding for 8 min (52–60 min). The detection wavelengths of the pesticides are

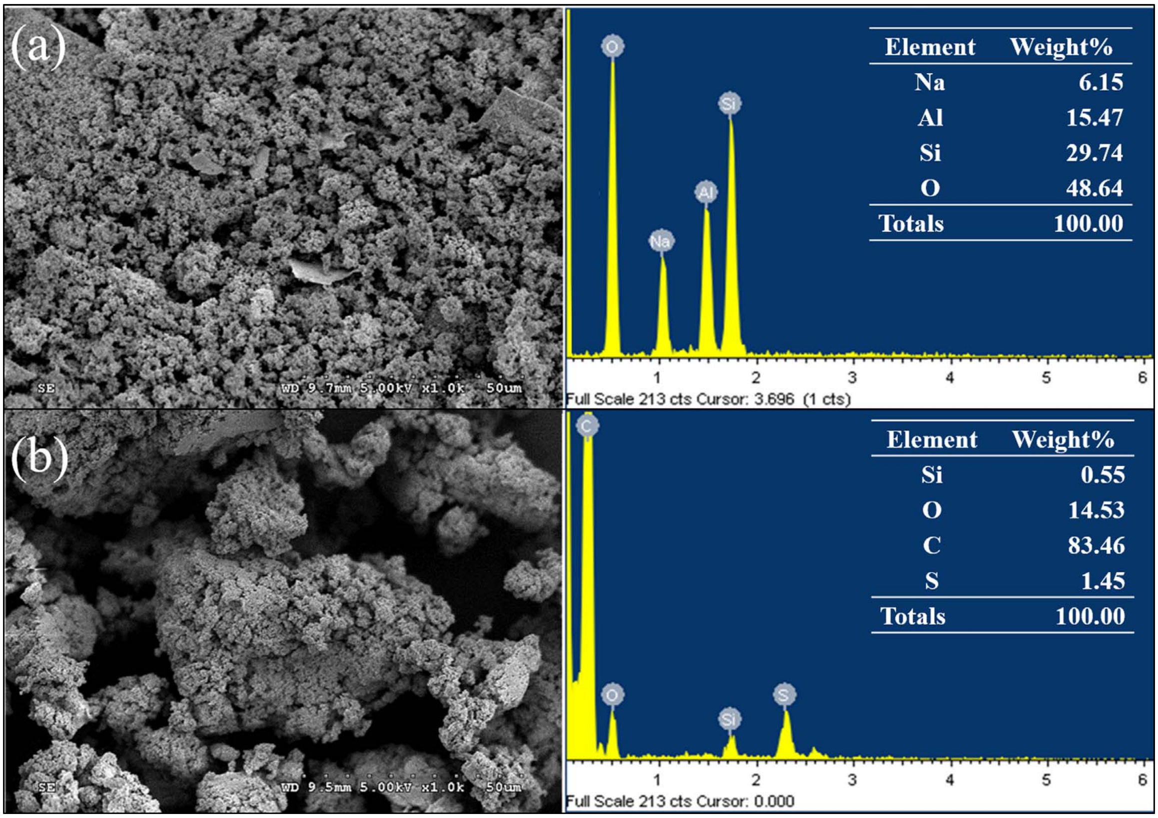


Fig. 2. SEM and EDS images of (a) zeolite NaY and (b) PANI-modified zeolite NaY.

summarized in Table S1 (Supplementary material).

3. Results and discussion

3.1. Characterization of PANI-modified zeolite NaY and its sorption capability for pesticides

Generally, PANI form can be varied depending on acidity. Thus we synthesized PANI onto the surface of the zeolite under various pH conditions and evaluated the efficacy for pesticide sorption of the various PANI-modified products. The oxidative polymerization of 0.2 mol L^{-1} aniline was carried out using the stoichiometric amount of a strong oxidant, 0.25 mol L^{-1} ammonium persulfate that provided the complete monomer to polymer conversion. The pH of the starting solution was observed at 2, 4, 8 and 11. However, the oxidative polymerization of aniline is a dynamic process as acidity of the mixture always increases during the reaction. The pH of the starting and ending solutions along with sorption ability of the obtained polymers are demonstrated in Table S2 (Supplementary material). The adsorption capability of the PANI-modified sorbents was improved for several pesticides including tribenuron-methyl, methomyl, thiamethoxam, imidacloprid, acetamiprid, isoprocarb and bensulfuron-methyl. The improvement of adsorption was distinguished for more hydrophilic pesticides (log K_{ow} < 2.4). It was not surprising that chlorsulfuron, the compound presented as the first peak of the chromatogram (Fig. S1, Supplementary material) did not adsorb all sorbents under the studied conditions. Amongst the tested sorbents, the PANI-modified zeolite NaY obtained from the strong acid condition (pH 2–pH 1) exhibited a great adsorption for most pesticides. Therefore, this sorbent was selected for the development of DSPE. In addition, the adsorption of pesticides by unmodified zeolite NaY, pure PANI and PANI-modified zeolite NaY was comparatively investigated (see Fig. S2, Supplementary material). It revealed that the modification of zeolite NaY with inexpensive aniline monomers can enhance the performance of sorbent for pesticide sorption particularly for more hydrophilic pesticides.

The oxidative polymerization of aniline by ammonium persulfate produces an emeraldine form which is the most stable form of PANI [52]. This form can change in different pHs caused by protonation (emeraldine salt form, ES) or deprotonation (emeraldine base form, EB) [53], as illustrated in Scheme 1.

The synthesized zeolite and all modified materials were characterized using FTIR; and UV–visible spectroscopy was used to indicate the aniline form in the solution. As the UV–visible spectra of the solution of polymerization in different pHs shown in Fig. 1(a), the oxidation of aniline in a strong acid solution (initial pH of 2) demonstrated the characteristic absorption bands at 383 and around 550 nm which corresponded to the green color for the ES form. The first band shifted to 366 nm and the second peak was still present at around 550 nm whilst the oxidation was started under a mildly acidic condition (initial pH of 4). The brown color was observed and any sharp adsorption band did not appear in all alkaline solutions (initial pH of pH 8 and 11). FTIR spectra of the PANI-modified zeolite NaY sorbents obtained by the oxidation reaction in various acidities are shown in Fig. 1(b). All modified sorbents exhibited the characteristic IR absorption bands of the support material, zeolite NaY (the red labels in Fig. 1(b)), consisted of the shoulders at 1630–1648 cm^{-1} represented Al–O–Al asymmetric stretching, Si–O–Si or Al–O–Al bending presented around 565 cm^{-1} and symmetric stretching of internal tetrahedra of the zeolite was observed around 740 cm^{-1}. PANI-coated zeolite NaY showed response of N–H stretching at 3200 cm^{-1}. The spectra demonstrated the characteristic peaks of the bone structure of PANI, for the peak of quinonoid ring stretching at 1566–1583 cm^{-1} along with benzenoid ring stretching at 1489–1511 cm^{-1}. The shoulders at 1440–1444 cm^{-1} assigned to the presence of ortho-coupled aniline were observed in the spectra of the products obtained from mildly acidic and alkaline conditions but it disappeared in the product of strong acid oxidation. This finding is consistent with the previous report [54] that the shoulder was not observed in PANI polymerized under acidic condition. The small peaks at 1370–1374 cm^{-1} were typically attributed to N–H stretching and C–N stretching in the neighborhood of a quinonoid ring and they are also the standard peak of PANI [54]. The oxidation of aniline under strongly acidic media presented the sharp peak of C–N vibration of secondary aromatic amine at 1283 cm^{-1} [55] whereas this signal decreased in the products of mildly acidic and alkaline media.

The morphology of unmodified and the selected PANI-modified zeolite NaY were studied by SEM, and the elemental analysis was conducted by EDS as well. The SEM images and EDS patterns of the sorbents are illustrated in Fig. 2. The results revealed that sodium ions and aluminum atoms were not detected on the surface of PANI-modified zeolite NaY sorbent. It indicated that ion exchange between sodium ions on the zeolite surface and anilinium ions occurred during polymerization, consequently the zeolite surface was almost completely covered with PANI.

3.2. Quantification of multi-class pesticides by HPLC-PDA

Under the HPLC condition described above, separation of twenty multi-class pesticides was achieved within 52 min as depicted in Fig. S1 (Supplementary material), with the following order of elution: chlorosulfuron, tribensulfuron-methyl, methomyl, thiametoxam, imidacloprid, acetameprid, aldicarb, carbofuran, carbaryl, isoprocarb, primisulfuron-methyl, bensulfuron-methyl, azinphos-methyl, parathion-methyl, diazinon, tetramethrin-1, tetramethrin-2, chlorpyrifos, fenpropathrin, fenvalerate, permethrin-1 and permethrin-2. Linearity was observed in the concentration range of 0.05–50.0 mg L^{-1} together with the coefficients of determination (r^2) of greater than 0.9951. The limits of detection (LODs) and limits of quantification (LOQs) were considered as the concentrations giving a signal-to-noise ratio of 3 and 10, respectively. The LODs and LOQs of the instrument method ranged from 0.05 to 1.00 mg L^{-1} and 0.20–7.00 mg L^{-1}, respectively. Precision of the method was expressed as the relative standard deviations (RSDs) of the retention time and peak area of the analytes. The intra-day RSDs (n=6) were less than 1.4% and 11.6% while the inter-day RSDs (n=6×3) were lower than 1.4% and 12.9% for the retention time and peak area, respectively.

3.3. Optimization of the DSPE procedure

3.3.1. Effect of sample pH

Polymerization of PANI on the zeolite NaY surface was conducted under highly acidic conditions (pH 2–1) and the emeraldine form of PANI was obtained as explained in Section 3.1. Since the surface of the modified sorbent can be protonated or deprotonated in different acidities (Scheme 1), the effect of sample pH on the retention of multi-class pesticides on PANI-modified zeolite NaY was evaluated. The pH was observed in the range of 2.2–8.0 according to the usable pH range of the LC column. The results (Fig. 3(a)) demonstrated that the EB form in the basic sample provided better adsorption of most pesticides than the ES form in the acidic sample and it improved adsorption of some pesticides such as thiametoxam, aldicarb, isoprocarb and diazinon. The improvement was possibly due to more hydrophobic interaction between pesticide molecules and sorbent surfaces in the basic form. As for the structure presented in Scheme 1, the EB form presented more hydrophobicity than the ES form. For these reasons, the basic condition at pH 8 was chosen to sustain the EB form. Additionally, the linear relationship between the percentage adsorption and log K_{ow} of pesticides is illustrated in Fig. 4. The adsorption of non-polar to slightly polar pesticides, having pK_a ≥1.1, established a linear relation between the percentage adsorption and log K_{ow} (%Adsorption=13.65 log K_{ow}+19.659, r^2=0.7637). It should be pointed out that the adsorption of these compounds onto the sorbent surfaces was mainly due to hydrophobic interaction. Likewise, non-polar pesticides, having large log K_{ow} (log K_{ow} ≥4.7) including tetramethrin, chropyrifos, fenpropathrin, fenvalerate and permethrin, were greatly adsorbed on the modified sorbent at all studied pHs with a percentage adsorption of higher than 70.

3.3.2. Effect of sorbent amount

Different amounts of the modified sorbent: 100, 150 and 200 mg, were studied to evaluate the effect of the sorbent quantity on the extraction efficacy of multi-class pesticides. The results are shown in Fig. 3(b). The percentage adsorption of most pesticides increased with increasing the amount of the sorbent from 100 to 150 mg, then the adsorption of pesticides did not improve by increasing the amount of the sorbent up to 200 mg; therefore, the sorbent amount of 150 mg was found as the optimum value. Generally, commercial sorbents have been used for plant cleanup and environmental matrices. For instance, 200 mg C_{18} was used for the treatment of 10 g soil before the analysis of seventy pesticides [9]; 10 g Florisil was reported for the nineteen pesticides analysis in 20 g vegetables [6]; 400 mg graphitized carbon ENYI-Carb was also proposed to treat 5 g fruit and vegetable matrices for the determination of twenty-five pesticides [15]. Recently, silica modified with PANI film was proposed for the treatment of plant materials; 200 mg of the modified silica was used for cleanup 0.1–0.02 g matrix for determination of triterpenic acids [34]. In the present work, juices were made from whole fruits and vegetables then the juices were directly extracted and the cleanup by the proposed sorbent, accordingly the case of a high matrix to sorbent ratio was achieved. Only 150 mg of the sorbent was used for 135–330 g plant matrix and 10 g soil.

3.3.3. Effect of sorption time

Mechanical shaking was selected to accelerate sorption of the target pesticides onto the sorbent surface. After adding the sample solution to the sorbent, the suspension was shaken at 100 rpm using a VS-202D Orbital Shaker (Vision Scientific Co, Ltd., Daejeon-Si, Korea). Shaking time was investigated in the range of 1–10 min. Adsorption of multi-class pesticides onto PANI-modified zeolite NaY was the dynamic interaction as shown in Fig. 3(c). The percentage adsorption increased at the beginning and reached a steady state in 3 or 4 min for all studied compounds (3 min for fenpropathrin, methomyl and tribensulfuron-methyl); after that, adsorption amounts of some pesticides decreased slightly because of self-elution. Hence the sorption time of 4 min was selected for the DSPE process.

3.3.4. Effect of sample volume and sorption capacity

A mixed solution containing 1 mg L^{-1} of each pesticide was used to study the effect of the sample volume. The volume of the pesticide solution was varied from 10 to 200 mL. As illustrated in Fig. 3(d), the peak area of most pesticides increased rapidly with increasing the sample volume from 10 to 125 mL; afterward, some of these decreased due to self-elution by the exceeded solution. Accordingly, the developed approach allowed 125 mL as the maximum sample volume. Furthermore, the sorption capacity which is defined as the amount of adsorbed pesticide per unit of sorbent was evaluated. The sorption capacity was calculated using the equation:

$$Sorption\quad capacity = \frac{C_0 x V_E}{m}$$

where C_0 is the studied concentration, V_E is the maximum volume of the solution passed through the sorbent without self-elution, m is mass of the sorbent. As a result, the sorption capacity of the sorbent was 833 mg kg^{-1} sorbent for each pesticide in the mixture of twenty pesticides.

3.3.5. Desorption of pesticides

Various eluents including methanol, acetonitrile, mixture of acetonitrile/water, mixture of acetonitrile/acetic acid solution and mixture of acetonitrile/sodium hydroxide solution were tested for elution of

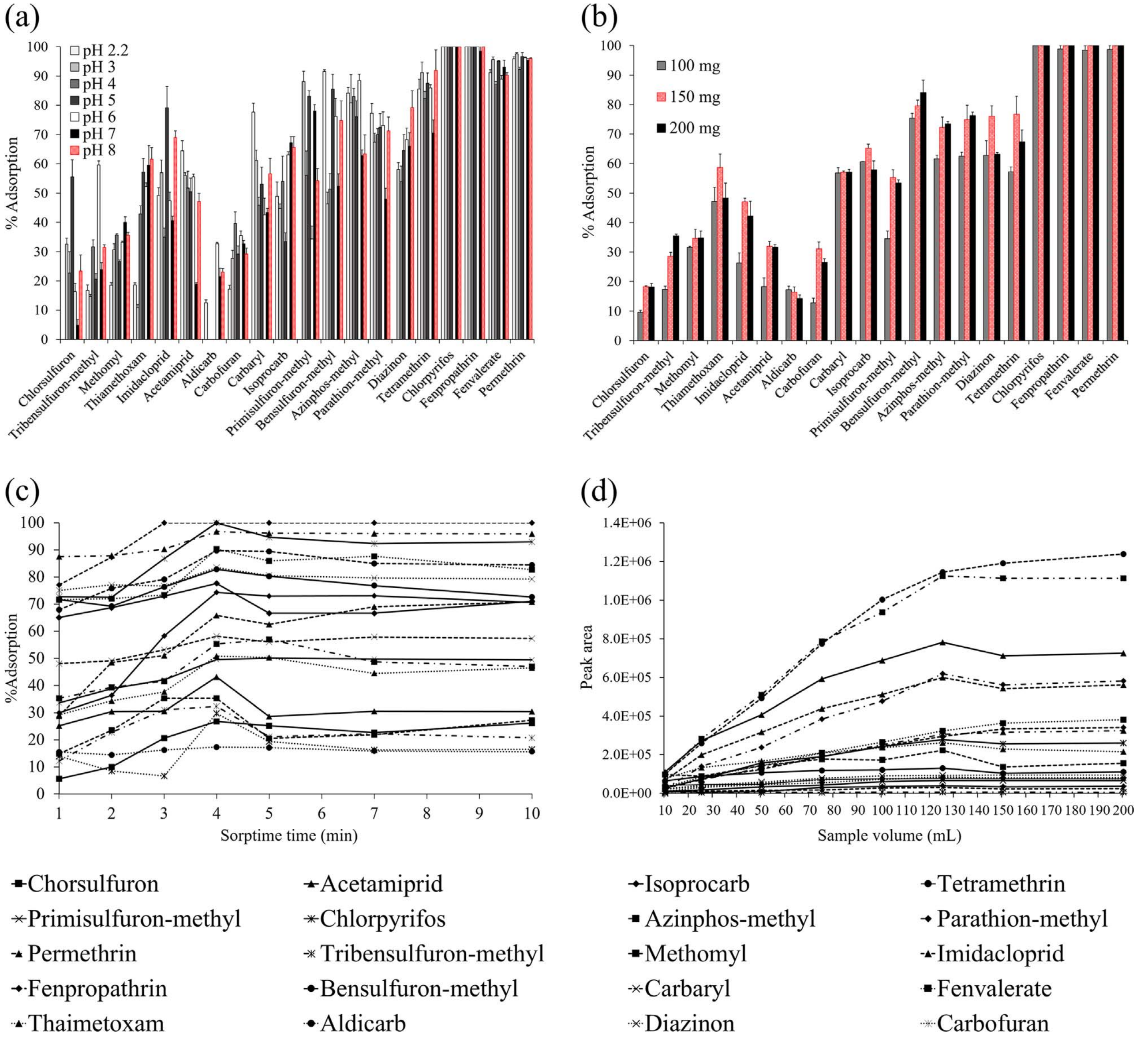


Fig. 3. Effect of (a) sample pH, (b) sorbent amount, (c) sorption time and (d) sample volume on adsorption of pesticides onto PANI-modified zeolite NaY, - The enlargement of each inset is provided in Supplementary material.

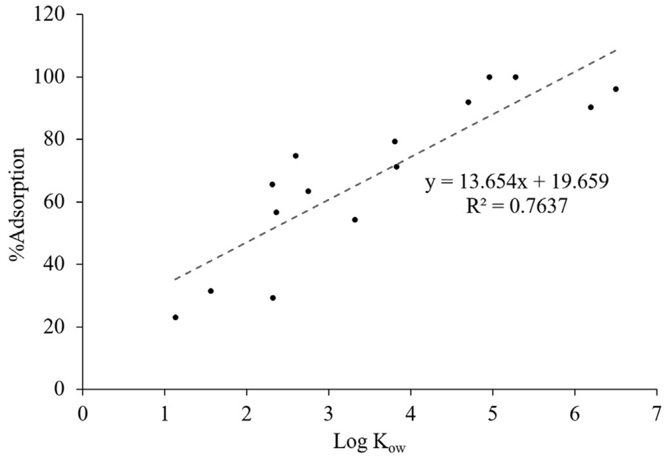


Fig. 4. Relation between adsorption of pesticides on PANI-modified zeolite NaY and log K_{ow}.

pesticides from the PANI-modified sorbent. The obtained results are demonstrated in Fig. 5(a). The mixture of acetonitrile and sodium hydroxide allowed better extraction than that of other eluents. A base-organic mixture might be needed to stabilize EB form of PANI, thus the effect of the sodium hydroxide content was further investigated. The comparative study was conducted using 0.02 mol L^{-1} sodium hydroxide in acetonitrile/water (80/20) and 0.01 mol L^{-1} sodium hydroxide in acetonitrile/water (90/10). It was found that decreasing of sodium hydroxide solution in the eluent enhanced desorption of several compounds (the bars with * in Fig. 5(a)), in particular compounds that have low sensitivity, such as chlorsulfuron, isoprocarb and diazinon. Enhancement of the eluting power was caused by more organic content in the eluent whereas basic component incorporated by stabilizing form of PANI on sorbent surfaces. Therefore, the mixture of 0.01 mol L^{-1} sodium hydroxide in 90% acetonitrile was chosen as the proper eluent.

Also, the effect of the eluent volume was considered in the range of 0.5–5.0 mL (Fig. 5(b)). The results indicated that increasing the eluent volume up to 3.0 mL led to an increase in desorption of the pesticides; although the desorption of chorsulfuron, isoprocarb and diazinon were

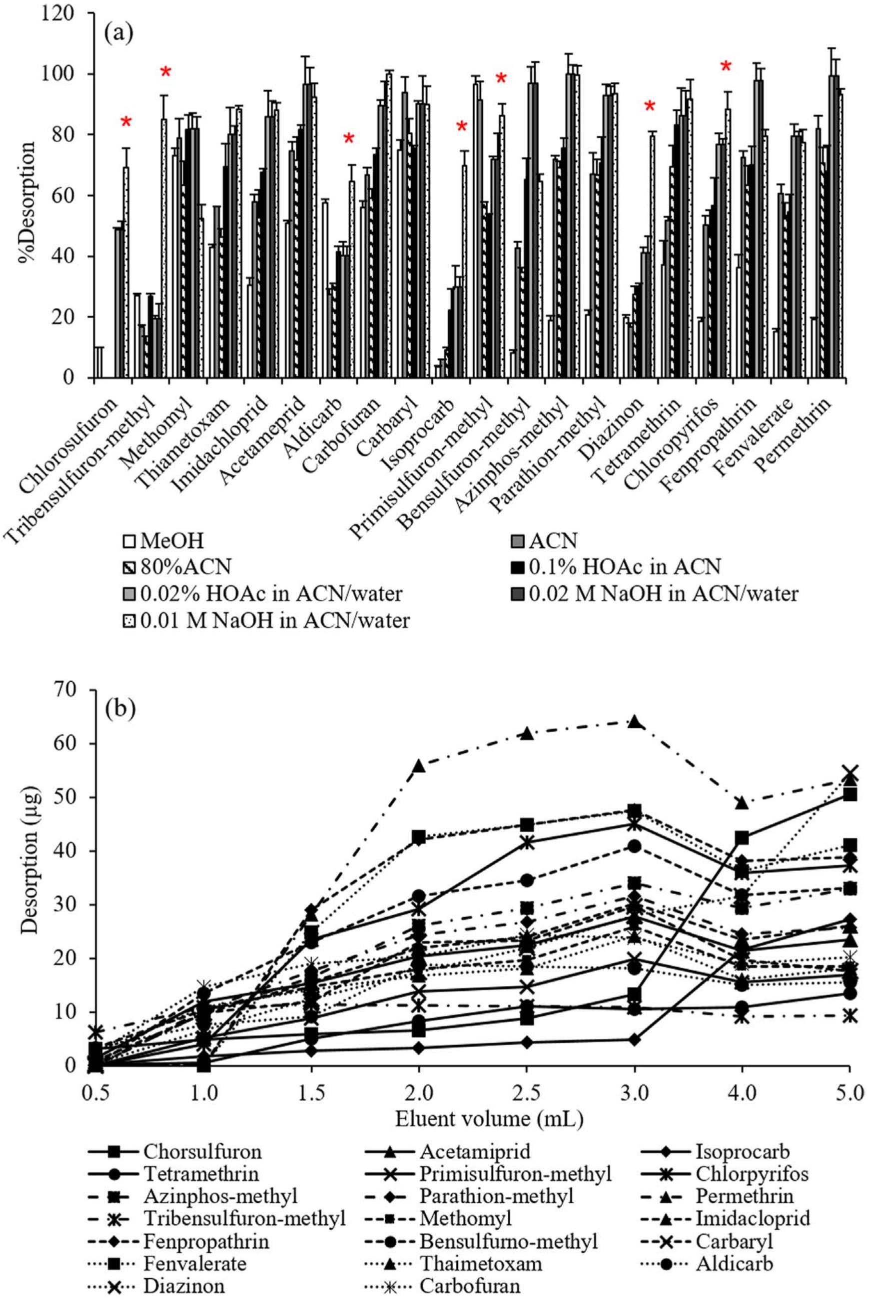


Fig. 5. Effect of (a) type of eluent, *-The stars showed pesticides which percentage desorptions were improved by decreasing of sodium hydroxide in the eluent. (b) volume of eluent on desorption of pesticides from PANI-modified zeolite NaY.

different. High desorption of these compounds was observed when the eluent volume was greater than 3.0 mL while desorption of most compounds was considerably decreased. Therefore, the eluent volume of 3.0 mL was chosen as the best compromise for desorption of most target analytes.

3.4. Analytical performance

The analytical performance of the developed DSPE procedure using PANI-modified zeolite NaY sorbent was evaluated for the cleanup and preconcentration of multi-class pesticides. Analytical figures of merit of the method are summarized in Table S3 (Supplementary material). The preconcentration factor (PCF) of pesticides which is defined as the concentration ratio of the analyte in the initial solution and in the final extract ready for its determination, was also evaluated. Under the optimized conditions, a sample volume of 125 mL was applied to DSPE and the pesticides were concentrated in the final solution of 3 mL; hence, the PCF of 42 was considered for this procedure.

LODs of the twenty pesticides were in the range of 0.001–1.00 mg L^{-1} and LOQs ranged from 0.005 to 2.50 mg L^{-1}. Moreover, the precision at LOD of each pesticide was demonstrated by RSD of the peak area. The experiments were conducted by analyzing six replicates (intra-day precision) on six different days (inter-day precision). RSDs of less than 4.3% and 12.7% were obtained for intra-day and inter-day precision, respectively.

The linearity of the method was tested by preparing the calibration graphs for all studied pesticides in ultrapure water. The observed linear range that depended on the sensitivity of each compound, ranged from 0 to 25 mg L^{-1} and r^2 of greater than 0.9943 were achieved. In addition, the effect of the sample matrices were observed by matrix-matched calibration curves. Matrix-matched standard solutions were prepared by adding the pesticide standards mixture to the blank

Table 1
Analytical results of water and soil samples.

Pesticide	Drinking water					Pond water 1			Pond water 2			Soil 1			Soil 2		
	Found (mg L^{-1})	%R_1[a]	%R_2[b]	*C_{18},%R_1*[c]	*C_{18},%R_2*[d]	Found (mg L^{-1})	%R_1[a]	%R_2[b]	Found (mg L^{-1})	%R_1[a]	%R_2[b]	Found (mg kg^{-1})	%R_1[a]	%R_2[b]	Found (mg kg^{-1})	%R_1[a]	%R_2[b]
Chlorsulfuron	–	82(3)	90(3)	*77(2)*	*75(3)*	–	104(8)	94(6)	–	107(5)	100(7)	–	77(9)	99(7)	–	94(7)	99(9)
Tribensulfuron-methyl	–	90(4)	103(1)	*79(4)*	*80(4)*	–	89(4)	96(4)	–	100(4)	103(3)	–	117(8)	100(6)	–	118(8)	96(9)
Methomyl	–	88(5)	96(2)	*81(4)*	*88(5)*	–	114(4)	87(1)	0.092	70(5)	88(8)	1.261	78(8)	85(9)	–	109(8)	95(4)
Thiamethoxam	–	75(6)	91(3)	*83(2)*	*82(1)*	–	109(5)	88(4)	–	84(2)	97(1)	–	76(5)	78(8)	–	77(6)	78(8)
Imidacloprid	–	76(6)	82(4)	*69(6)*	*76(3)*	–	76(1)	81(1)	–	84(10)	85(8)	–	103(7)	92(12)	–	103(10)	102(11)
Acetamiprid	–	72(2)	83(1)	*87(2)*	*95(3)*	–	96(5)	103(3)	–	106(10)	109(3)	–	113(8)	97(9)	–	86(5)	77(8)
Aldicarb	–	104(10)	106(5)	*79(1)*	*82(1)*	–	103(9)	90(1)	–	101(8)	104(2)	–	76(3)	85(4)	–	104(7)	94(10)
Carbofuran	–	85(7)	93(6)	*74(7)*	*96(5)*	–	76(5)	81(3)	–	84(4)	84(2)	–	108(5)	94(3)	–	95(3)	109(10)
Carbaryl	–	91(2)	96(4)	*80(1)*	*94(6)*	–	80(4)	92(1)	–	71(1)	90(1)	–	86(5)	98(3)	–	95(4)	95(2)
Isoprocarb	–	84(3)	91(2)	*77(2)*	*85(3)*	–	84(5)	86(3)	–	84(3)	83(1)	–	91(10)	93(7)	–	80(5)	93(7)
Primisulfuron-methyl	–	111(10)	112(6)	*93(9)*	*95(7)*	–	84(2)	85(1)	–	80(2)	115(2)	–	86(7)	85(7)	0.178	98(4)	95(6)
Bensulfuron-methyl	–	103(1)	94(3)	*80(6)*	*108(6)*	–	103(3)	104(3)	–	112(9)	91(2)	–	121(9)	92(2)	–	103(8)	92(6)
Azinphos-methyl	–	102(1)	92(4)	*93(1)*	*107(9)*	–	105(7)	102(5)	–	87(6)	96(2)	–	114(9)	94(6)	–	84(8)	94(6)
Parathion-methyl	–	79(2)	95(7)	*100(7)*	*106(5)*	0.046	73(8)	81(6)	0.090	86(4)	84(3)	0.087	83(7)	93(4)	0.145	84(8)	76(3)
Diazinon	–	79(9)	83(1)	*99(3)*	*98(4)*	–	92(2)	105(4)	–	77(7)	87(6)	–	90(9)	91(7)	–	102(7)	95(3)
Tetramethrin	–	85(4)	85(3)	*78(2)*	*87(1)*	–	71(6)	109(5)	–	95(2)	86(6)	–	73(3)	87(2)	–	106(9)	97(4)
Chlorpyrifos	–	88(3)	87(9)	*89(7)*	*94(3)*	–	73(1)	85(1)	–	84(40	94(10)	–	75(7)	94(4)	–	82(2)	92(5)
Fenpropathrin	–	76(3)	81(3)	*90(8)*	*85(3)*	–	112(10)	106(7)	–	84(2)	95(5)	0.209	80(5)	84(5)	0.268	89(4)	96(3)
Fenvalerate	–	84(6)	101(4)	*70(2)*	*80(4)*	–	86(2)	85(3)	–	74(3)	73(3)	0.105	74(6)	83(6)	–	87(5)	86(10)
Permethrin	–	85(3)	83(2)	*97(2)*	*102(8)*	–	71(9)	77(3)	–	82(4)	85(4)	0.223	72(4)	78(3)	–	94(8)	85(7)

The standard deviations (SD) are shown in parentheses.

[a] %R of spiked concentrations#1: 2.5 mg L^{-1} (mg kg^{-1}) chlorosulfuron; 1.0 mg L^{-1} (mg kg^{-1}) tribensulfuron-methyl and isoprocarb; 0.5 mg L^{-1} (mg kg^{-1}) aldicarb, carbofuran, carbaryl, diazinon, tetramethrin and chlorpyrifos; 0.05 mg L^{-1} (mg kg^{-1}) methomyl, thiametoxam, imidacloprid, acetameprid, primisulfuron-methyl, bensulfuron-methyl, parathion-methyl, fenpropathrin, fenvalerate, and permethrin; 0.005 mg L^{-1} (mg kg^{-1}) azinphos-methyl.

[b] %R of spiked concentrations#2: 4.0 mg L^{-1} (mg kg^{-1}) chlorosulfuron; 2.0 mg L^{-1} (mg kg^{-1}) tribensulfuron-methyl and isoprocarb; 1.0 mg L^{-1} (mg kg^{-1}) aldicarb, carbofuran, carbaryl, diazinon, tetramethrin and chlorpyrifos; 0.1 mg L^{-1} (mg kg^{-1}) methomyl, thiametoxam, imidacloprid, acetameprid, primisulfuron-methyl, bensulfuron-methyl, parathion-methyl, fenpropathrin, fenvalerate, and permethrin; 0.01 mg L^{-1} (mg kg^{-1}) azinphos-methyl.

[c] %R of spiked concentrations#1 using C_{18} sorbent.

[d] %R of spiked concentrations#2 using C_{18} sorbent.

Table 2
Analytical results of honey, vegetable and fruit samples.

Pesticide	Honey			Cabbage			Cucumber			Tomato			Strawberry		
	Found ($mg\ L^{-1}$)	$\%R_1$[a]	$\%R_2$[b]	Found ($mg\ kg^{-1}$)	$\%R_1$[a]	$\%R_2$[b]	Found ($mg\ kg^{-1}$)	$\%R_1$[a]	$\%R_2$[b]	Found ($mg\ kg^{-1}$)	$\%R_1$[a]	$\%R_2$[b]	Found ($mg\ kg^{-1}$)	$\%R_1$[a]	$\%R_2$[b]
Chlorsulfuron	–	102(6)	82(3)	–	84(8)	83(3)	–	94(7)	92(6)	–	95(8)	93(9)	–	101(11)	96(6)
Tribensulfuron-methyl	–	95(4)	93(4)	–	81(8)	93(7)	–	102(6)	99(7)	–	95(3)	95(7)	–	86(9)	103(9)
Methomyl	–	78(2)	95(4)	–	64(6)	88(9)	0.033	71(3)	83(3)	–	117(11)	100(9)	–	73(7)	86(7)
Thiamethoxam	–	75(2)	95(2)	–	77(6)	97(8)	–	65(8)	88(5)	–	87(10)	98(8)	0.031	75(10)	81(9)
Imidacloprid	–	78(5)	97(3)	–	80(8)	73(5)	–	69(5)	73(7)	–	72(6)	88(4)	–	70(4)	89(8)
Acetamiprid	–	75(4)	109(4)	–	123(10)	118(8)	–	116(10)	96(10)	–	68(3)	83(5)	–	94(5)	95(5)
Aldicarb	–	83(5)	89(2)	0.025	94(6)	97(8)	–	76(7)	75(7)	0.016	120(9)	103(7)	–	107(6)	107(10)
Carbofuran	–	95(6)	116(2)	–	106(9)	96(8)	–	94(7)	119(10)	–	98(6)	113(8)	0.012	104(9)	107(7)
Carbaryl	–	81(2)	125(4)	0.012	99(5)	91(7)	–	72(2)	76(6)	–	70(6)	74(3)	–	84(9)	97(10)
Isoprocarb	–	95(5)	103(4)	–	122(9)	97(8)	–	77(6)	94(9)	–	67(6)	76(5)	–	102(7)	99(6)
Primisulfuron-methyl	–	92(7)	99(6)	0.013	128(12)	81(4)	0.012	103(8)	104(6)	0.007	94(4)	90(4)	–	112(10)	108(11)
Bensulfuron-methyl	–	69(9)	88(3)	–	116(10)	95(5)	–	120(11)	94(6)	–	97(6)	94(8)	–	113(7)	97(9)
Azinphos-methyl	–	94(5)	121(7)	–	100(6)	102(5)	–	93(6)	87(6)	–	93(6)	115(8)	–	80(7)	102(12)
Parathion-methyl	–	72(5)	90(2)	0.003	83(3)	104(5)	0.014	81(7)	104(7)	–	81(8)	109(9)	–	82(9)	99(10)
Diazinon	–	70(3)	71(4)	–	88(4)	105(9)	–	78(9)	116(10)	–	105(8)	95(9)	–	102(8)	93(9)
Tetramethrin	–	96(3)	95(6)	–	74(7)	102(8)	–	91(6)	82(8)	–	95(6)	98(5)	–	90(9)	83(8)
Chlorpyrifos	–	68(4)	70(4)	–	81(4)	102(8)	–	70(4)	73(6)	–	74(5)	92(7)	–	102(11)	98(6)
Fenpropathrin	–	71(5)	93(3)	–	69(6)	87(6)	–	75(8)	89(7)	–	118(8)	96(6)	–	79(7)	85(4)
Fenvalerate	–	83(4)	127(8)	0.005	113(10)	84(6)	0.005	84(6)	105(9)	–	103(3)	111(5)	–	81(9)	96(7)
Permethrin	–	94(6)	123(10)	–	76(2)	105(6)	–	74(4)	124(9)	–	74(8)	77(9)	–	87(5)	106(8)

The standard deviations (SD) are shown in parentheses.

[a] %R of spiked concentrations#1: 2.5 $mg\ kg^{-1}$ chlorosulfuron; $mg\ kg^{-1}$ tribensulfuron-methyl and isoprocarb; 0.5 $mg\ kg^{-1}$ aldicarb, carbofuran, carbaryl, diazinon, tetramethrin and chlorpyrifos; 0.05 $mg\ kg^{-1}$ methomyl, thiametoxam, imidacloprid, acetameprid, primisulfuron-methyl, bensulfuron-methyl, parathion-methyl, fenpropathrin, fenvalerate, and permethrin; 0.005 $mg\ kg^{-1}$ azinphos-methyl.

[b] %R of spiked concentrations#2: 4.0 $mg\ kg^{-1}$ chlorosulfuron; 2.0 $mg\ kg^{-1}$ tribensulfuron-methyl and isoprocarb; 1.0 $mg\ kg^{-1}$ aldicarb, carbofuran, carbaryl, diazinon, tetramethrin and chlorpyrifos; 0.1 $mg\ kg^{-1}$ methomyl, thiametoxam, imidacloprid, acetameprid, primisulfuron-methyl, bensulfuron-methyl, parathion-methyl, fenpropathrin, fenvalerate, and permethrin; 0.01 $mg\ kg^{-1}$ azinphos-methyl.

sample extracts. The matrix effect was estimated by the slope ratio of the matrix-matched calibration curve and ultrapure water calibration curve. The matrix effect of soil, honey, drinking water as representative of water matrix, cabbage as representative of vegetable matrix and strawberry as representative of fruit matrix are shown in Table S3 (Supplementary material). The matrix effect was not present in the water sample for the calculated values in the range of 0.71–1.26, whereas matrix effects were observed in other samples as the slope ratios were found between 0.17 and 8.17. For this reason, matrix-matched calibration curves were used for quantifying of the target pesticides in soil, honey, vegetable and fruit samples.

The accuracy of the method, expressed in terms of percentage recovery (%R) was investigated in all sample matrices (see Table 1 and Table 2) using the calibration curves described above. Recoveries of twenty pesticides were evaluated at two spiked levels which related to their sensitivities. The recovery of chlorosulfuron was observed at 2.5 and 4.0 $mg\ L^{-1}$. Tribensulfuron-methyl and isoprocarb were spiked at 1.0 and 2.0 $mg\ L^{-1}$. Six pesticides including aldicarb, carbofuran, carbaryl, diazinon, tetramethrin and chlorpyrifos were studied at 0.5 and 1.0 $mg\ L^{-1}$. Pesticides that were spiked at 0.05 and 0.1 $mg\ L^{-1}$ included methomyl, thiametoxam, imidacloprid, acetameprid, primisulfuron-methyl, bensulfuron-methyl, parathion-methyl, fenpropathrin, fenvalerate, and permethrin. The accuracy of azinphos-methyl was evaluated at 0.005 and 0.01 $mg\ L^{-1}$. As for the results, the pesticides of interest exhibited recoveries between 64% and 128% along with RSDs of less than 12% in all matrices. Even though the acceptable recoveries were achieved for most target analytes according to the AOAC official method of analysis (2016) [56] especially for low spiked levels, recoveries of higher than 120% were found for some pesticides in soil, honey and cabbage. It was noticed that some complex matrices still influenced the extraction of pesticides. Therefore, we suggest that more sample treatment and cleanup steps might be required for the complex matrices. In this way, not only cleaner samples but also an increase of PCF would be obtained. This work clearly demonstrated the successful application of PANI-modified zeolite NaY as an effective sorbent for the extraction of pesticides in various sample matrices with an acceptable extraction efficiency and a good preconcentration capability.

Furthermore, the capability of the proposed sorbent for the determination of multi-class pesticides was compared with the commercial C_{18} sorbent (Lichroprep® RP-18, Merck KGaA, Germany). The recoveries of twenty pesticides were also evaluated in drinking water using C_{18} sorbent. The obtained result revealed that the low cost monomer-modified zeolite NaY had a comparable ability to that of the commercial one for extraction of multi-class pesticides. The applicability of zeolite NaY in analytical chemistry was remarked as well.

3.5. Application to real sample

The proposed method was applied for the determination of multi-class pesticides in drinking water, pond waters, soils, honey, cabbages, cucumbers, tomatoes and strawberries. The results are presented in Table 1 and Table 2. No pesticides were detected in drinking water and honey while some pesticides were detected in pond water, soil, fruit and vegetable samples. Parathion-methyl was found in both pond waters at concentrations of 0.046 and 0.090 $mg\ L^{-1}$ for pond waters 1 and 2, respectively. Methomyl which is one of the most highly toxic pesticides in Thailand [57,58] was detected at a concentration of 0.092 $mg\ L^{-1}$ in pond water 1 and occurred at a high level (1.261 $mg\ kg^{-1}$) in a soil sample that was collected from a cultivated area where the pesticides were used. In addition to methomyl, four more pesticides, namely parathion-methyl, fenpropathrin, fenvalerate and permethrin were detected in the range of 0.087–0.223 $mg\ kg^{-1}$ in this soil sample. Interestingly, contamination of primisulfuron-methyl, parathion-methyl and fenpropathrin, ranging from 0.0145 to 0.268 mg kg^{-1}, was observed in the soil sample that was collected from the area without previous pesticide treatment. Environmental water is the major route of transferring pesticides, thus the chemicals spread out over the area. This is the reason that pesticides were found near the area where the pesticide are used. Concerning contamination in fruits and vegetables, eight pesticides were detected in fruit and vegetable samples in the range of 0.003–0.033 mg kg^{-1}. Among these pesticides, aldicarb and primisulfuron-methyl were detected in tomatoes at a concentration of less than maximum residue limits (MRLs) established by the European commission (EU No. 396/2005) [59] as well as thiamethoxam in strawberries, methomyl in cucumbers and parathiol-methyl in cabbages. Fenvalerate was also found at a concentration of less than the MRLs [54] in cucumbers and cabbages. Contamination at higher levels than the MRLs [54] involved carbofuran in strawberries, parathion-methyl in cucumbers, two carbamate insecticides in cabbages and primisulfuron-methyl in both cucumbers and cabbages. The results point out that in addition to the concern of pesticide residues and their effects, pesticide use should be carefully regulated.

4. Conclusion

PANI-modified zeolite NaY was proposed as a new sorbent for multi-residue analysis of pesticides. PANI was successfully coated on the zeolite NaY surface via oxidative polymerization of aniline, subsequently the PANI-modified zeolite NaY was applied as sorbent for extraction of multi-class pesticides in waters, soils, honey, fruits and vegetables. Although PANI-modified zeolite NaY was an applicable sorbent for the pre-cleanup and pre-concentration of pesticides, the matrix effect is still observed in real samples due to a variety of complex matrices. Thus, matrix-matched calibration was applied to overcome various sample matrices. The developed multi-residue analysis method, consisting of the sample preparation procedure using the new sorbent and quantification by HPLC-PDA, demonstrated an effective applicability for pesticide determination in food and environmental samples with various matrices.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.talanta.2016.11.003.

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Amine-Functionalized Metal–Organic Framework as a New Sorbent for Vortex-Assisted Dispersive Micro-Solid Phase Extraction of Phenol Residues in Water Samples Prior to HPLC Analysis: Experimental and Computational Studies

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Abstract

Metal–organic frameworks (MOFs) are a new class of hybrid inorganic–organic microporous crystalline materials, which possess unique properties such as high surface area, tunable pore size, and good thermal stability. These unique characteristics make MOFs interesting targets for sample pretreatment. In this work, MIL-53 material based on aluminum and containing amine functional groups (NH_2-MIL-53(Al)) was synthesized and applied as an efficient sorbent for development of vortex-assisted dispersive micro-solid phase extraction for eight United States Environmental Protection Agency's priority phenols from aqueous samples prior to analysis by high-performance liquid chromatography with photodiode-array detection. A simple extraction process was designed. The parameters affecting the extraction efficiency, such as amount of sorbent, extraction time, type of desorption solvent and its volume were investigated. The good linearity in the concentration range of 0.0015–10.0000 μg mL^{-1} with the coefficients of determination of greater than 0.9929, low limits of detection (0.0004–0.0133 μg mL^{-1}) and relative standard deviations of lower than 10% were obtained. The proposed method has been successfully applied to the determination of phenol compounds in different water sample matrices including treated water, waste water, river water, sea water, lake water, drinking water and tap water. In addition, computational simulation was performed to predict the adsorption ability of NH_2-MIL-53(Al) towards the studied phenolic compounds. The computational results were in agreement with the experimental studies and it has been proved that NH_2-MIL-53(Al) is promising for enrichment of phenolic pollutants.

Keywords Metal–organic frameworks · Vortex-assisted dispersive micro-solid phase extraction · Phenols · HPLC · Molecular docking

Introduction

Industrial processes and human activities generate various kinds of pollutant in the environment that can cause serious damage to ecosystems and human health. Phenol and its derivatives are one of the most toxic water pollutants, which come out from various industries such as the production of paper, detergents, polymers, pharmaceuticals, adhesives, explosives, phenolic resins, and petrochemical products. Owing to their high toxicities even at low concentrations and prevalent presence in environment, the United States Environmental Protection Agency (US EPA) and the European Union (EU) have classified them as priority pollutants in aquatic environment [1, 2]. Consequently, sensitive and reliable analytical methods for monitoring these compound residues are usually required.

To date, diverse separation techniques have been widely used for determination of phenol compounds [3–12]. High-performance liquid chromatography (HPLC) and gas chromatography (GC) with different detection modes

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are the most intensively used for phenols determination. The polar features and low volatility of phenol compounds have favored the use of HPLC, because it avoids the need of derivatization processes. However, direct determination of phenols in environmental samples is usually difficult because of their low concentrations (sub µg L^{-1}). Hence, suitable sample preparation methods are still required for isolation of trace amounts of the target substances from complex matrices, clean-up and preconcentration prior to instrumental analysis. For these purposes, several sample preparation procedures, based on both liquid–liquid extraction (LLE) [4, 6, 7, 12] and solid-phase extraction (SPE) [2, 3, 5, 8–11], have been used incorporating with instrumental techniques for determination of phenol residues. Among these sample pretreatment approaches, SPE has become a widely used technique due to its simplicity and flexibility of the approach.

Dispersive solid-phase extraction (DSPE), which was firstly introduced by Anastassiades et al. [13], has been proposed as a valuable alternative SPE technology. The method exhibits some advantages over conventional SPE such as without sophisticated equipment, less solvent waste, short time requirement, increase surface area between the analytes and sorbent and avoiding channeling or blocking of cartridges or disks, as occurs in traditional SPE. Generally, DSPE is based on four main steps: dispersion of the sorbent in a sample solution containing target analytes, extraction by sorption, separation of the sorbent with retained analytes from the solution, and solvent elution of the analytes [2]. Recently, the analytical chemists have turned to DSPE-based miniaturized technique, micro-DSPE, which is acquiring a lot of attention nowadays from an environment-friendly point of view, due to the impressive decrease in the amounts of sorbents required (by definition: lower than 500 mg of sorbent) [14]. Hence, dispersive micro-solid phase extraction (D-µ-SPE), a miniaturized mode of DSPE based on using milligram amounts of solid sorbent has been introduced [14, 15].

Solid sorbent are important for the SPE-based technique because it contains the active sites to allow the interaction between sorbent and analytes. Generally, the main requirements for properties of solid sorbent include the fast and quantitative adsorption and desorption, a high capacity and high dispersibility in liquid samples. Many different kinds of materials are potential candidates for extraction and preconcentration of various analytes, such as layered double hydroxides (LDHs) [2], molecularly imprinted polymers (MIPs) [3, 5], polymeric sorbent [8], and zeolite NaY [15]. However, most sorbents are intended for specific substances. Therefore, it is conductive to find a kind of high selective and effective adsorbent for the D-µ-SPE of the analytes of interest.

Metal–organic frameworks (MOFs) are a new class of hybrid inorganic–organic microporous crystalline materials constructed from metal ions and organic linkers through coordination bonds and have been popular materials since the beginning of this century [16]. They have received increasing interests due to their unique structures and fascinating chemical properties, including large surface areas, large internal pore volumes, tunable pore sizes, tailorable molecular structures, and catalysis activity. These properties make MOFs promising in diverse applications, such as gas storage [17, 18], separation [19–21], catalysis [21, 22], chemical sensing [23], adsorption [24, 25] and sequestration of toxic metals from water [26, 27]. A large number of reports have shown that the MOFs possess great potential in sorption-related fields. The applications of MOFs for D-µ-SPE procedure has also been reviewed [28].

In this work, amine-functionalized frameworks based on well-known MIL family topology, since these are thermally and chemically stable compared to other MOFs [21, 29], is expected to show promising potential for extraction of phenol compounds via hydrogen bonding and π–π interaction. Most of amine-functionalized MOFs studies focused on the CO_2 adsorption and separation properties [20, 21, 30]. Previously, NH_2-MIL-101(Al) has been reported for adsorption and separation of phenol and *p*-nitrophenol from aqueous solutions through hydrogen bonding [24]. Luo et al. reported the synthesis of NH_2-MIL-53(Al)-incorporated poly(styrene-divinylbenzene-methacrylic acid) monolith column and its application for in-tube solid-phase microextraction of estrogens in human urine [31]. The prepared monolith column showed well properties after more than 100 extraction cycles. However, fabrication of such a monolith column is rather complicated.

Here, we report the synthesis and application of amine-functionalized MOF sorbent for extraction and preconcentration of phenol residues in different water sample matrices for the first time. Development and optimization of a simple and effective vortex-assisted dispersive micro-solid phase extraction (VA-D-µ-SPE) procedure is also proposed. In addition, molecular modeling was used to predict the adsorption ability of the synthesized sorbent towards phenolic compounds. The free binding energies were calculated and the molecular interactions were demonstrated using molecular docking. This work presented the combined study of computational modeling and experimental application in sample preparation technology.

Experimental

Chemicals and Reagents

Eight analytical phenol standards with a purity of ≥ 99% were used. 2,4-Dinitrophenol (2,4-DNP), 4-chloro-3-methylphenol (4-C-3-MP), 2-methyl-4,6-dinitrophenol (2-M-4,6-DNP), and 2,4,6-trichlorophenol (2,4,6-TCP) were supplied by Sigma-Aldrich (Germany). Phenol (Ph) was obtained from Sigma-Aldrich (USA). 4-Nitrophenol (4-NP) and 2,4-dichlorophenol (2,4-DCP) were purchased from Sigma-Aldrich (India). 2-Nitrophenol (2-NP) was supplied by Fluka (China). Stock standard solutions of phenols at concentration of 1000 µg mL^{-1} were prepared using methanol as the solvent and diluted to 100 µg mL^{-1} with water. Working solutions were prepared daily from 100 µg mL^{-1} of stock standard solutions by dilution with water. Deionized water (18.2 MΩ cm) used in all experiments was prepared by a RiOs Type I Simplicity 185 water purification system (Millipore, USA).

2-Aminoterephthalic acid ($HO_2C\text{-}C_6H_3NH_2\text{-}CO_2H$) (99%, Sigma-Aldrich, USA), aluminum chloride hexahydrate ($AlCl_3{\bullet}6H_2O$) (99%, Sigma-Aldrich, Germany) and *N,N*-dimethylformamide (≥ 99%, Merck, Germany) were used for synthesis of amine-functionalized MOF sorbent. Acetonitrile (isocratic grade, Merck, China), methanol (gradient grade, Merck, Germany), ethanol (AR grade, Merck, Germany), acetone (AR grade, Qrëc, New Zealand) and glacial acetic acid (AR grade, Carlo Erba, Italy) were used for HPLC separation and VA-D-µ-SPE procedure.

Apparatus and Chromatographic Conditions

The HPLC system (Waters, USA) consisted of an in-line degasser, a 600E quaternary pump, and a Waters 2996 photodiode array (PDA) detector. Empower software was employed to acquire and analyze chromatographic data. The system was equipped with a Rheodyne injector with a 10-µL loop, and a Phenomenex Luna C_{18} (4.6 mm × 150 mm, 5 µm) (Phenomenex, USA) analytical column. The separation was performed using acetonitrile (solvent A) and 0.1% acetic acid in water (solvent B) as mobile phase. The gradient program was as follows: 0–3 min, 40% solvent A; 4–8 min, 50% solvent A; 9–12 min, 70% solvent A; 13–17 min, 100% solvent A. A re-equilibration period of 2 min with 40% solvent A was carried out between individual runs. The detections were performed at 271 nm for Ph; at 317 nm for 4-NP; at 258 nm for 2,4-DNP; at 276 nm for 2-NP; 281 nm for 4-C-3-MP; at 286 nm for 2,4-DCP; at 266 nm for 2-M-4,6-DNP; and at 288 nm for 2,4,6-TCP.

The X-ray diffraction (XRD) patterns were recorded with an Empyrean X-ray diffractometer (XRD) (PANalytical, The Netherlands) using Cu K_α radiation (λ = 1.5418 Å) over the angular range from 5° to 50°. Fourier transform infrared (FTIR) spectra were recorded on a TENSOR27 infrared scanner (Bruker, Germany) with a resolution of 2 cm^{-1} and a spectral range of 4000–550 cm^{-1}. The weight loss curves (TG–DTG) were recorded using a simultaneous thermal analyzer (STA) model STA7200 (Hitachi, Japan) from 100 to 600 °C at a heating rate of 10 °C min^{-1} under nitrogen.

Other instruments were used in the procedure, including a vortex mixer model G560E (50 Hz) (Scientific Industries, USA), a rotavapor model R-200 (Buchi Labortechnik AG, Switzerland), a centrifuge model Z206A (Hermle Labortechnik, Germany) and an oven model UN110 (Memmert, Germany).

Synthesis of Sorbent

The amine-functionalized MOF sorbent was synthesized by means of a solvothermal treatment adapted from the published procedures [21]. Aluminum chloride hexahydrate (0.51 g) and 2-aminoterephthalic acid (0.56 g) were mixed with *N*,*N*-dimethylformamide (30 mL) in a Teflon-lined autoclave and then heated at 403 K in an oven under static condition for 72 h. After cooling to the room temperature, the resulting yellow powder was filtered under vacuum and washed with acetone. To remove organic species trapped within the pores, the samples were activated in boiling methanol overnight and stored at 373 K.

VA-D-µ-SPE Procedure

The determination of phenol pollutants was carried out by VA-D-µ-SPE using amine-functionalized MOF as sorbent followed by high-performance liquid chromatography with photodiode-array detection (HPLC-PDA). For this purpose, an aliquot of 10.00 mL aqueous phenol standard or sample solution was added to a 15-mL centrifuge tube containing 30 mg of sorbent. The mixture was then placed in a vortex mixer for 10 s to accelerate the sorption of the target analytes onto the sorbent. Subsequently, the solid sorbent was isolated from the solution by centrifugation at 5000 rpm for 1 min. After that, the supernatant was discarded. Then, 1500 µL of acetonitrile–acetic acid mixture (9.5:0.5, v/v) was added in the centrifuge tube. The analytes were desorbed by vortex mixing for 10 s. The mixture was centrifuged at 5000 rpm for 1 min. The desorption solvent which contained analytes of interest was filtered through a 0.45-µm membrane and evaporated to dryness by rotary evaporator. The residue was reconstituted in 50 µL of acetonitrile before HPLC analysis. The proposed D-µ-SPE-HPLC procedure is schematically depicted in Fig. 1.

Sample Collection

Two lake water samples were collected from different areas in Khon Kaen province, Northeastern Thailand (16°24′58.3″N 102°50′07.4″E and 16°26′55.6″N 102°51′03.0″E). Treated water sample (16°28′23.0″N 102°49′07.2″E) and two wastewater

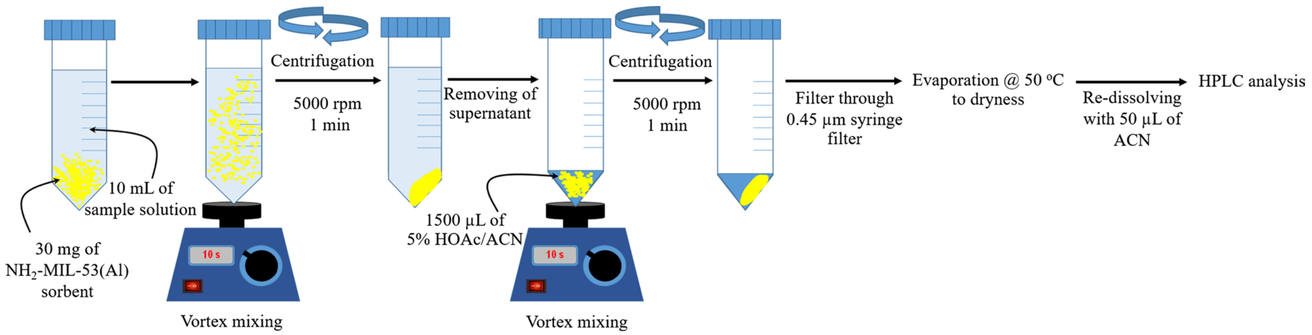

Fig. 1 Scheme of the proposed VA-D-µ-SPE procedure for determination of phenol pollutants

samples (16°27′38.3″N 102°48′26.0″E and 16°27′25.6″N 102°48′31.0″E) were collected in Khon Kaen University campus. River water sample was taken from Chi river (Maha Sarakham province, Northeastern Thailand, 16°13′55.0″N 103°15′58.6″E) and seawater sample was taken from Bangsaen beach (Chonburi province, Eastern Thailand, 13°20′32.4″N 100°55′31.0″E). Tap water sample was freshly collected from the laboratory (16°28′33.6″N 102°49′26.6″E) and drinking water samples were bottled water from three different companies sold in Khon Kaen (16°28′39.1″N 102°49′23.7″E). All samples were passed through a Whatman No. 42 filter paper before analysis by the proposed VA-D-µ-SPE-HPLC method.

Molecular Docking

The adsorption ability of MOFs depends directly on the interaction between the analytes and MOFs. In order to investigate such interaction and to understand the adsorption at a molecular level, a molecular docking, a computational technique used to predict the small-molecule conformations adopted within the binding sites of macromolecular targets as well as their interaction, has been performed. The studied amine-functionalized MOF (NH_2-MIL-53(Al)) crystal structure was taken from the Cambridge Crystallographic Data Centre (CCDC number: 901254) [32]. All phenolic compound structures were downloaded from PubChem (https://pubchem.ncbi.nlm.nih.gov) and the structures were re-optimized with quantum calculation B3LYP/6-31G(d) level using Gaussian 09 program [33]. All docking calculations were performed with a grid box size of $60 \times 60 \times 60$ Å^3, grid spacing of 0.375 Å, 2.5×10^6 energy evaluations, and 200 runs of the Lamarckian genetic algorithm searches using AutoDock 4.2 program [34]. The binding free energies were calculated and the orientation of the analytes in the binding site of NH_2-MIL-53(Al) was investigated.

Results and Discussion

Characterization of the Prepared Sorbent

The synthesized sorbent was characterized by XRD, TGA, and FTIR experiments (Fig. S1, Supplementary Information). The framework structure of as-synthesized sorbent was identified by XRD and the pattern is shown in Fig. S1A. As can be seen, the XRD pattern of the as-synthesized sorbent was in good accordance with the simulated MIL-53, indicating that the pure phase of NH_2-MIL-53(Al) was obtained. It has been reported that by starting from the similar synthesis mixture at the same temperature, different MIL structure can be obtained just by changing the synthesis time, 24 h for MIL-101 and 72 h for MIL-53 [22]. This also supports the formation of NH_2-MIL-53(Al) in the present work. In order to analyze the molecular structure and identify the functional groups of as-synthesized sorbent, the FTIR spectroscopy was used and the results are shown in Fig. S1B. A series of peaks appeared in the range of 1400–1700 cm^{-1} were assigned to carboxylic acid that coordinated with $A1^{3+}$ and the carbonyl groups of DMF molecule which adhered to channels of the sorbent. The absorption peaks around 1600 and 1500 cm^{-1} attributed to asymmetric stretchings of carbonyl, while two peaks at about 1440 and 1400 cm^{-1} were carbonyl symmetric stretchings. An observed absorption peak at 1670 cm^{-1} is assigned to stretching vibration of carbonyl group in molecules of free DMF, and the bands at 3500 and 3380 cm^{-1} are due to the stretching vibration of NH_2 group. Therefore, the results from XRD and FTIR analysis clearly confirm the formation of NH_2-MIL-53(Al) structure.

The thermal behavior of the synthesized NH_2-MIL-53(Al) was studied by TG measurement (Fig. S1C). TGA curve showed a two-step weight loss. First step showed a weight loss of 7% up to 120 °C corresponding to the release of methanol molecules trapped in the pores of the framework structure. The TGA data revealed that the MIL-53 was stable up to 420 °C. At this temperature it showed the starting of a second step weight loss related to the decomposition of organic ligand, aminoterephthalic acid [35].

Optimization of the VA-D-μ-SPE Conditions

The synthesized NH_2-MIL-53(Al) was applied as sorbent for development of VA-D-μ-SPE for eight target phenol compounds, including Ph, 4-NP, 2,4-DNP, 2-NP, 4-C-3-MP, 2,4-DCP, 2-M-4,6-DNP and 2,4,6-TCP. In order to obtain the best extraction efficiency, various extraction parameters, including the amount of sorbent, desorption solvent and its volume, vortex and centrifugation time for adsorption and desorption were optimized. The test solutions, containing analytes at 0.80 μg mL^{-1} for 4-C-3-MP, 2,4-DCP and 2,4,6-TCP and 0.50 μg mL^{-1} for the other five phenols, were used to perform the optimization experiments which were carried out in triplicate.

Effect of the Sorbent Amount

An appropriate sorbent amount is crucial for excellent extraction efficiency. The goal was to minimize it as much as possible, to ensure a real microextraction procedure. To study the influence of sorbent amount on adsorption efficiency, 10.00 mL of mixed standard solution of phenol compounds was added to different amounts of solid sorbent, then vortexed for 10 s. In the present work, the amount of NH_2-MIL-53(Al) in the range of 10–120 mg was tested. After centrifugation for 10 min, the supernatant was filtered through a 0.45-μm membrane and the remaining analytes were analyzed by HPLC–PDA. The adsorption percentage (%Adsorption) of each analyte was calculated by the following equation:

$$\%\text{Adsorption} = (C_A/C_0) \times 100,$$

where C_A is the concentration of analyte adsorbed on the sorbent and C_0 is the initial concentration of analyte.

The results in Fig. S2 (Supplementary Information) revealed that the adsorption increased with the increase of sorbent amounts from 10 to 30 mg and remained constant afterwards. No analytes except for Ph was detected after the adsorption experiment, indicating that the sorbent has good adsorption capability for the target analytes. Consequently, 30 mg of NH_2-MIL-53(Al) was sufficient for effective extraction of the target analytes and was selected for further experiments.

The possible adsorption mechanism of phenol molecules on NH_2-MIL-53(Al) is based on the π–π interaction between phenols and phenyl rings of aminoterephthalic acid ligand in the framework of NH_2-MIL-53(Al). In addition, all of the studied phenols can enter the pores of NH_2-MIL-53(Al) as their kinetic dynamic diameters (3.9–5.4 Å) [36] are smaller than the pores (7.3 Å × 7.7 Å) [37] of NH_2-MIL-53(Al). Moreover, the hydrogen bonding can be formed between the nitro group of the nitrophenol as proton acceptor and amino groups as proton donors in the framework [24]. In case of Ph, the adsorption was unable to reach 100% because it contains only one hydroxyl group for forming hydrogen bonding and other noncovalent weak interactions with NH_2-MIL-53(Al), leading to a less adsorption efficiency compared with other analytes [38].

Effect of the Adsorption Time

The adsorption time is one of the most important factors affecting the adsorption efficiency of analytes. To ensure that the analytes were adsorbed to a maximum extent, the vortex was selected for accelerating the adsorption of analytes onto the sorbent. The effect of vortex time was investigated in the range of 0–60 s using the sorbent amount of 30 mg and sample volume of 10.00 mL. As illustrated in Fig. S3 (Supplementary Information), the adsorption of 4-NP increased significantly in case of using vortex for 10 s when compared to the result obtained from the experiment without vortex process. The satisfactory results for all analytes could be obtained using vortex agitation for 10 s and further increase of vortex time did not contribute to any improvement of the %Adsorption. Therefore, the obtained results led to the selection of 10 s adsorption time using vortex agitation for further studies. At this point, the centrifugation after adsorption process was also optimized. Different centrifugation times were studied in the range of 1–13 min, but 1 min was found to be enough to settle down the sorbent and gave adequate extraction efficiency. Longer times did not improve any extraction efficiency (data not shown). Therefore, after adsorption process, the mixture was centrifuged for 1 min to separate the solid sorbent from the aqueous sample solution.

Effect of Desorption Solvent and Its Volume

The desorption solvent is also a critical variable for VA-D-μ-SPE technique. In this study, several solvents and solvent mixtures including methanol, acetonitrile, ethanol, methanol–acetic acid (9.5:0.5, v/v), acetonitrile–acetic acid (9.5:0.5, v/v) and ethanol–acetic acid (9.5:0.5, v/v) were evaluated as desorption solvent with vortex for 10 s for desorption of the analytes from the solid sorbent. The other experimental conditions were kept as follows: sample volume, 10.00 mL; sorbent amount, 30 mg; vortex time, 10 s; centrifugation after adsorption, 1 min at 5000 rpm; desorption solvent volume, 1000 µL; centrifugation after desorption, 10 min at 5000 rpm. The obtained results in Fig. S4 (Supplementary Information) show that high desorption efficiency was obtained using acetonitrile as desorption solvent. Moreover, the addition of acetic acid resulted in increasing of extraction recoveries for some analytes, i.e., Ph, 2,4-DNP, 2-NP and 2-M-4,6-DNP, due to its strongest dissolving ability to analytes. Thus, the mixture of acetonitrile–acetic acid (9.5:0.5) was chosen as desorption solvent for further studies.

The volume of the acetonitrile–acetic acid mixture was investigated in the range of 100–2000 µL. It should be noted that in this optimization process the solvent containing desorbed analytes was injected into the HPLC system without evaporation. As shown in Fig. S5 (Supplementary Information), the peak area of the analytes increased with increasing the volume of desorption solvent from 125–1500 µL and remained almost constant afterward. Therefore, 1500 µL of acetonitrile–acetic acid mixture was selected for desorption of the phenol compounds from NH_2-MIL-53(Al) sorbent.

Effect of Desorption Time

The desorption time is another important factor that affects the extraction recovery of analyte. In this work, vortex was chosen to enhance the desorption of analytes from sorbent. The vortex desorption times were varied in the range of 0–60 s. The highest desorption of analytes were obtained when the vortex desorption time was at 10 s. After 10 s, the desorption remained constant (see Fig. S6, Supplementary Information). Hence, the vortex desorption time of 10 s was selected as optimum condition. At this point, the centrifugation time was also optimized. Different times in the range of 1–10 min were studied; however, 1 min was adequate to separate sorbent from solution. Longer times did not improve the extraction of analytes (data not shown).

Considering the results obtained from adsorption experiments, it could be observed that the NH_2-MIL-53(Al) sorbent exhibited effectively quantitative adsorption for most phenol compounds (except for Ph). However, desorption of total amounts of adsorbed analytes from the sorbent could not be performed as expected. Only about 20% (for 2,4-DNP) to 65% (for 4-NP) were desorbed from the sorbent under the selected extraction condition. Anyway, the satisfactory sensitivity was achieved for determination of phenol compounds in real samples. In the present work, the sorbent was disposed after each determination for preventing the effect of carry over.

Analytical Features of Direct HPLC and the Proposed VA-D-µ-SPE-HPLC Procedure

Under the optimum HPLC condition as described in the experimental section, separation of eight phenols was achieved within 14 min, with the following order of elution: Ph (t_R = 4.0 min), 4-NP (t_R = 4.9 min), 2,4-DNP (t_R = 7.0 min), 2-NP (t_R = 8.1 min), 4-C-3-MP (t_R = 9.5 min), 2,4-DCP (t_R = 10.6 min), 2-M-4,6-DNP (t_R = 11.3 min), and 2,4,6-TCP (t_R = 13.8 min). Linearity was observed in the concentration range of 0.4000–50.000 µg mL^{-1} with the coefficients of determination (R^2) greater than 0.9936. The limits of detection (LODs) and limits of quantification (LOQs) were considered as the concentrations obtaining a signal-to-noise ratio of 3 and 10, respectively. The LODs and LOQs ranged from 0.12–0.46 and 0.39–1.54 µg mL^{-1}, respectively. The intra-day precision ($n = 5$) of the method, expressed as the relative standard deviations (RSDs) of the retention time and peak area of the phenols at 5 µg mL^{-1}, was less than 0.33 and 4.36%, respectively. The inter-day experiments ($n = 5 \times 3$) showed the RSDs of the retention time and peak area of less than 0.64 and 6.30%, respectively.

For preconcentration of phenol compounds, the optimum VA-D-µ-SPE condition using NH_2-MIL-53(Al) as sorbent was applied before analysis by HPLC. This method exhibited a good linearity in the range of 0.0015–10.000 µg mL^{-1} with the R^2 greater than 0.9929. The low LODs and LOQs were obtained in the range of 0.0004–0.0133 and 0.0013–0.0519 µg mL^{-1}, respectively. Precisions in terms of intra- and inter-day experiments were investigated by replicate analyses of standard mixture of the analytes (0.05 µg mL^{-1} each) in a day ($n = 5$) and several days ($n = 5 \times 3$), respectively. The intra-day RSDs of retention time and peak area were below 2.24 and 9.05%, respectively. For inter-day experiments, the RSD values were below 2.03 and 9.56% for retention time and peak area, respectively. The enrichment factors (EFs) for all analytes, which were obtained by comparing the concentrations before and after the VA-D-µ-SPE process, were in the range of 45 to 205. The analytical features of the proposed method are summarized in Table 1. Chromatograms of phenols obtained from the direct HPLC and the proposed VA-D-µ-SPE procedure are presented in Fig. 2.

Application to Real Samples

To evaluate the applicability of the developed VA-D-µ-SPE-HPLC for determination of phenol compounds in real sample matrices, 11 water samples, including lake water, treated waste waters, river water, seawater, tap water and three drinking waters were analyzed. No analyte

Table 1 Analytical features of direct HPLC and the proposed VA-D-µ-SPE-HPLC method for determination of phenol compounds

Analyte	Linear range (µg mL^{-1})	Linear equation	R^2	LOD (µg mL^{-1})	LOQ (µg mL^{-1})	EF	%RSD			
							Intra-day ($n = 5$)		Inter-day ($n = 5 \times 3$ days)	
							t_R	Peak area	t_R	Peak area
Ph	0.005–10.000	$y = 167129.6x + 45909.5$	0.9978	0.0020	0.0050	63	0.70	7.99	1.38	8.25
	(0.700–50.000)	($y = 10986.0x + 2333.9$)	(0.9965)	(0.1900)	(0.7000)		(0.19)	(2.20)	(0.48)	(5.27)
4-NP	0.0075–10.000	$y = 3665850.0x + 544072.3$	0.9929	0.0017	0.0073	96	2.24	3.96	2.03	5.69
	(0.400–50.000)	($y = 52236.1x - 268632.2$)	(0.9995)	(0.125)	(0.400)		(0.24)	(1.47)	(0.64)	(6.30)
2,4-DNP	0.015–10.000	$y = 4236130.0x + 397329.8$	0.9939	0.0035	0.0118	79	0.55	7.48	1.66	8.68
	(0.750–50.000)	($y = 21673.0x - 19491.0$)	(0.9936)	(0.2100)	(0.7100)		(0.33)	(3.15)	(0.54)	(3.41)
2-NP	0.030–10.000	$y = 2198340.0x - 111329.2$	0.9970	0.0080	0.0268	45	0.33	4.65	1.27	9.07
	(0.850–50.000)	($y = 29124.8x - 22211.5$)	(0.9978)	(0.2500)	(0.8500)		(0.20)	(1.33)	(0.50)	(3.00)
4-C-3-MP	0.050–10.000	$y = 949491.2x - 150985.1$	0.9958	0.0069	0.0397	88	0.24	5.49	0.89	6.30
	(1.250–50.000)	($y = 8471.4x - 7019.2$)	(0.9975)	(0.4000)	(1.2400)		(0.09)	(3.67)	(0.29)	(3.66)
2,4-DCP	0.055–10.000	$y = 735962.7x - 60262.3$	0.9982	0.0133	0.0519	61	0.14	9.05	0.92	9.56
	(1.500–50.000)	($y = 9776.5x - 13473.1$)	(0.9979)	(0.4000)	(1.5000)		(0.13)	(4.36)	(0.35)	(4.29)
2-M-4,6-DNP	0.0015–10.000	$y = 4534820.0 + 361950.0$	0.9972	0.0004	0.0013	205	0.08	1.66	1.15	7.64
	(0.400–50.000)	($y = 50881.1x - 12912.1$)	(0.9984)	(0.1200)	(0.3900)		(0.16)	(0.90)	(0.36)	(2.41)
2,4,6-TCP	0.020–10.000	$y = 678720.8x - 29884.7$	0.9977	0.0050	0.0171	109	0.08	2.81	0.43	9.47
	(1.550–50.000)	($y = 8295.6x - 3509.3$)	(0.9940)	(0.4600)	(1.5400)		(0.12)	(2.41)	(0.17)	(2.93)

The values in parentheses were obtained from direct HPLC

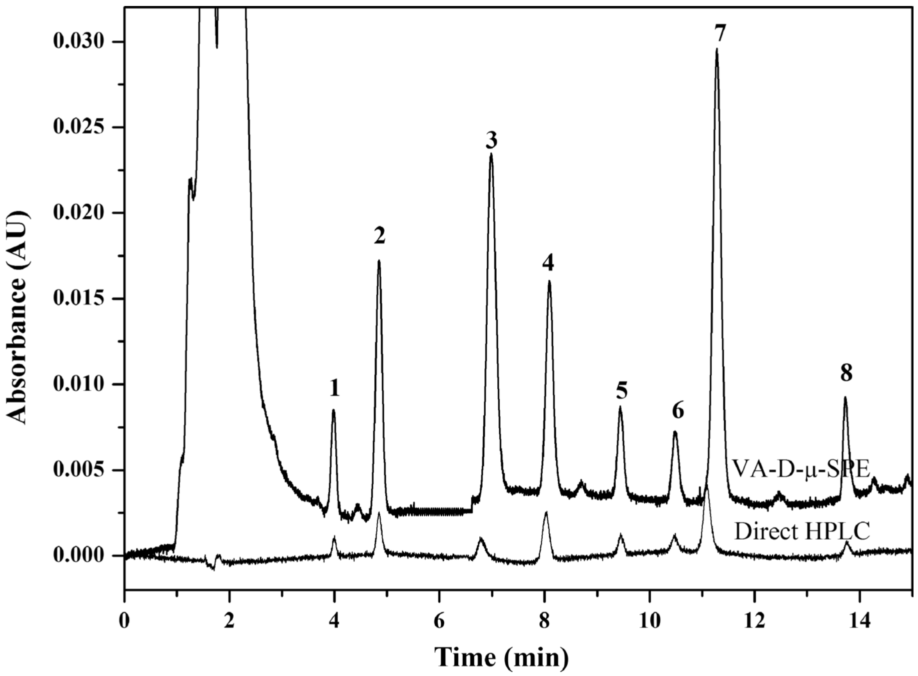

Fig. 2 Chromatograms of the phenols obtained by direct HPLC (1.0 µg mL^{-1}) and concentrated by VA-D-µ-SPE method (0.05 µg mL^{-1}). Detection at 280 nm. Peak assignment: 1, Ph; 2, 4-NP; 3, 2,4-DNP; 4, 2-NP; 5, 4-C-3-MP; 6, 2,4-DCP; 7, 2-M-4,5-DNP; 8, 2,4,6-TCP

residue was detected in the studied samples. In order to evaluate the accuracy, a recovery study was performed by spiking the samples with the analytes at the concentration levels of 0.10 and 0.15 µg mL^{-1} before analysis by the proposed method. As summarized in Table 2, the recoveries were all in the acceptable range of 72.3–111.4% (on average) with RSDs less than 10.4%. Fig. S7 (Supplementary Information) shows typical chromatograms of tap water sample with spiked phenols at various concentrations. Based on the results above, the proposed method gave good analytical performance for the analysis of target phenols in the studied water samples.

Comparison of the VA-D-µ-SPE to Other Methods

The developed VA-D-µ-SPE procedure using NH$_2$-MIL-53(Al) as sorbent for determination of phenol compounds was compared to different SPE techniques, as summarized in Table 3. The sensitivity in term of LODs is comparable to that obtained from the MSPE method using molecular imprinted polymer [5]. However, the wide linear range for determining a variety of phenol compounds was obtained using the proposed procedure. For comparison with other MOF sorbents, the amount of sorbent, extraction conditions, linearity and LODs were considered. As can be seen in Table 3, the proposed NH$_2$-MIL-53(Al) sorbent exhibits shorter extraction time and wider linearity range compared with those obtained from Fe$_3$O$_4$@SiO$_2$-MOF-177 [36], Zn/Co$_{7:1}$-MPC [39] and UiO-66-coated stainless steel fiber [40]. In addition, the developed method offers simple extraction process in short extraction time (less than 3 min) and low sample consumption, compared to those reported by other methods, in which can meet the requirements of the determination of a variety of phenolic compounds in various water matrices.

Molecular Docking

The binding free energies ($\Delta G_{\text{binding}}$) obtained from molecular docking are listed in Table 4. Note that, a larger negative value of $\Delta G_{\text{binding}}$ refers to higher analyte–MOFs interaction and adsorption ability. As a result, by substituting one nitro group the interaction was increased about 1.2 times compared to that of Ph. The increase of more than 1.3 times was obtained when substituting with two nitro groups, especially, when methyl group was included. This is due to not only the hydroxyl group, but also the substituted nitro groups can form hydrogen bonding with MOFs, leading to the larger binding ability (see Fig. 3b). Similarly, chloro substitutions provided the higher energy than − 6 kcal/mol (about 1.3 times) due

Table 2 Determination of phenol residues in water samples

Analyte	Added (μg mL^{-1})	Lake water I			Lake water II			Treated water			Waste water I		
		Found (μg mL^{-1})	%*R*	%RSD	Found (μg mL^{-1})	%*R*	%RSD	Found (μg mL^{-1})	%*R*	%RSD	Found (μg mL^{-1})	%*R*	%RSD
Ph	–	ND			ND			ND			ND		
	0.10	0.10	100.2	2.9	0.09	90.1	10.4	0.10	95.1	2.4	0.09	94.7	4.8
	0.15	0.14	92.7	3.5	0.13	88.3	5.5	0.13	85.7	10.4	0.14	94.9	0.8
4-NP	–	ND			ND			ND			ND		
	0.10	0.10	102.7	7.2	0.10	100.8	6.1	0.10	99.3	2.3	0.10	96.0	4.5
	0.15	0.14	90.3	4.2	0.12	81.2	1.4	0.14	94.5	3.6	0.14	92.4	6.7
2,4-DNP	–	ND			ND			ND			ND		
	0.10	0.09	93.7	0.3	0.10	99.2	1.8	0.10	97.7	2.0	0.09	91.4	1.7
	0.15	0.12	82.0	2.3	0.12	81.6	1.8	0.13	84.8	3.7	0.12	81.7	1.8
2-NP	–	ND			ND			ND			ND		
	0.10	0.08	82.8	6.4	0.08	82.2	5.2	0.08	82.9	6.2	0.08	80.0	4.0
	0.15	0.12	76.7	7.1	0.12	77.4	7.0	0.13	84.5	10.1	0.15	98.6	7.0
4-C-3-MP	–	ND			ND			ND			ND		
	0.10	0.10	102.0	4.8	0.10	101.0	1.2	0.10	101.4	1.4	0.10	101.9	7.5
	0.15	0.14	96.2	3.1	0.14	95.3	2.4	0.15	101.9	2.1	0.14	96.4	5.1
2,4-DCP	–	ND			ND			ND			ND		
	0.10	0.09	90.0	4.1	0.09	93.0	2.8	0.10	103.1	3.3	0.10	97.1	5.4
	0.15	0.12	80.8	4.5	0.12	81.0	2.9	0.14	92.7	3.1	0.14	93.8	5.8
2-M-4,6-DNP	–	ND			ND			ND			ND		
	0.10	0.09	91.7	1.2	0.09	89.6	4.4	0.09	93.4	7.3	0.09	88.1	1.4
	0.15	0.13	85.9	4.2	0.12	80.2	1.6	0.13	83.9	5.3	0.11	76.1	2.1
2,4,6-TCP	–	ND			ND			ND			ND		
	0.10	0.09	94.6	3.1	0.10	101.4	2.8	0.11	109.7	4.4	0.10	102.7	4.2
	0.15	0.12	81.4	2.9	0.13	87.8	1.2	0.14	93.0	3.7	0.13	88.3	2.1

Analyte	Added (μg mL^{-1})	Waste water II			River water			Seawater			Tap water		
		Found (μg mL^{-1})	%*R*	%RSD	Found (μg mL^{-1})	%*R*	%RSD	Found (μg mL^{-1})	%*R*	%RSD	Found (μg mL^{-1})	%*R*	%RSD
Ph	–	ND			ND			ND			ND		
	0.10	0.09	92.6	4.5	0.10	101.3	2.5	0.09	91.8	8.0	0.08	83.2	7.1
	0.15	0.14	90.2	1.3	0.16	105.5	2.8	0.12	81.9	6.1	0.15	100.4	0.8
4-NP	–	ND			ND			ND			ND		
	0.10	0.10	99.5	4.4	0.10	100.5	4.2	0.10	97.8	2.5	0.10	97.3	5.9
	0.15	0.14	96.4	5.5	0.15	100.4	9.0	0.15	100.2	3.4	0.14	93.8	5.4
2,4-DNP	–	ND			ND			ND			ND		
	0.10	0.10	98.1	0.8	0.10	97.5	2.0	0.10	97.1	2.0	0.10	103.6	5.3
	0.15	0.13	86.5	2.6	0.13	86.3	2.7	0.12	81.5	7.8	0.14	91.2	2.3
2-NP	–	ND			ND			ND			ND		
	0.10	0.08	83.1	8.9	0.11	110.5	8.1	0.11	107.6	7.1	0.09	93.3	8.6
	0.15	0.12	80.1	5.3	0.17	111.4	5.2	0.12	81.5	4.8	0.11	76.0	5.1
4-C-3-MP	–	ND			ND			ND			ND		
	0.10	0.10	99.8	6.1	0.10	104.0	0.6	0.10	98.1	5.2	0.10	100.7	3.2
	0.15	0.15	96.8	1.8	0.14	93.7	1.6	0.15	98.9	2.0	0.15	98.8	0.5
2,4-DCP	–	ND			ND			ND			ND		
	0.10	0.09	87.4	4.8	0.10	99.6	2.8	0.10	96.7	2.3	0.08	84.7	5.5
	0.15	0.14	91.0	3.1	0.15	97.0	9.1	0.14	92.5	0.3	0.14	92.8	6.1

Table 2 (continued)

Analyte	Added (μg mL^{-1})	Waste water II			River water			Seawater			Tap water		
		Found (μg mL^{-1})	*%R*	%RSD	Found (μg mL^{-1})	*%R*	%RSD	Found (μg mL^{-1})	*%R*	%RSD	Found (μg mL^{-1})	*%R*	%RSD
2-M-4,6-DNP	–	ND			ND			ND			ND		
	0.10	0.10	96.1	5.0	0.10	96.6	3.4	0.09	91.3	0.5	0.11	107.9	6.1
	0.15	0.13	89.4	9.5	0.12	82.4	2.4	0.11	73.1	3.9	0.14	93.2	1.9
2,4,6-TCP	–	ND			ND			ND			ND		
	0.10	0.10	99.1	4.0	0.10	99.3	0.9	0.10	99.2	9.8	0.10	100.6	4.0
	0.15	0.13	83.6	3.1	0.14	95.2	3.3	0.15	96.7	2.5	0.15	98.2	6.8

Analyte	Added (μg mL^{-1})	Drinking water I			Drinking water II			Drinking water III		
		Found (μg mL^{-1})	*%R*	%RSD	Found (μg mL^{-1})	*%R*	%RSD	Found (μg mL^{-1})	*%R*	%RSD
Ph	–	ND			ND			ND		
	0.10	0.09	88.6	5.1	0.10	101.1	3.6	0.08	83.7	6.9
	0.15	0.14	95.5	1.3	0.15	96.7	4.1	0.12	79.4	4.4
4-NP	–	ND			ND			ND		
	0.10	0.10	96.6	1.7	0.09	93.6	3.0	0.09	87.2	2.2
	0.15	0.15	98.0	1.4	0.14	95.7	1.6	0.13	84.2	4.7
2,4-DNP	–	ND			ND			ND		
	0.10	0.09	94.2	1.3	0.09	94.4	0.8	0.10	102.7	2.2
	0.15	0.12	77.7	6.6	0.11	74.6	10.1	0.12	81.7	3.7
2-NP	–	ND			ND			ND		
	0.10	0.09	86.6	7.6	0.10	96.0	1.7	0.08	79.6	8.1
	0.15	0.14	93.1	7.2	0.14	94.8	0.4	0.12	77.9	3.7
4-C-3-MP	–	ND			ND			ND		
	0.10	0.10	101.6	1.7	0.10	101.3	2.8	0.10	96.2	2.6
	0.15	0.14	92.3	2.5	0.15	99.0	1.8	0.12	82.6	4.1
2,4-DCP	–	ND			ND			ND		
	0.10	0.10	98.6	2.4	0.10	97.9	0.3	0.09	89.2	6.5
	0.15	0.14	93.7	1.0	0.15	97.8	2.6	0.12	78.2	5.9
2-M-4,6-DNP	–	ND			ND			ND		
	0.10	0.09	91.3	0.8	0.09	91.6	2.6	0.10	98.5	3.0
	0.15	0.11	75.7	1.8	0.11	72.3	7.1	0.13	85.4	4.9
2,4,6-TCP	–	ND			ND			ND		
	0.10	0.10	100.3	3.4	0.10	98.7	0.7	0.10	102.6	1.9
	0.15	0.14	95.8	1.7	0.15	97.9	5.4	0.13	87.3	3.2

ND not detected refers to values below detection limits

to the dipole–dipole interaction between the chloro groups and polar hydrogen atoms of NH_2-MIL-53(Al) taking place. In addition, the binding modes showed that the orientations of 4-C-3-MP, 2,4-DNP and 2-M-4,6-DNP molecular planes were parallel to the benzyl group of MOFs yielding the π–π interaction and thus enhancing the interaction. Parallel orientations were not observed for other compounds, as displayed in Fig. 3a (for other analytes, see also Fig. S8, Supporting Information). In summary, the calculated binding free energies are in good agreement with the adsorption ability observed experimentally.

Conclusions

In this work, the metal–organic framework, NH_2-MIL-53(Al) was successfully applied as sorbent for the VA-D-μ-SPE of eight phenols in different water

Table 3 Comparison of the developed VA-D-μ-SPE to other microextraction techniques for determination of phenol residues

Method [Ref.]	Analytes	Sample matrix	Linear range	LODs	EFs
MIMSPE-HPLC/UV [5] Sorbent: MIP with 2,4,6-TCP template Elution solvent: 2.0 mL acetonitrile containing 0.3% v/v acetic acid Extraction time: 50 min Sample: 60 mL	Ph; 4-CP; 2,4-DCP; 2,4,6-TCP; PCP	Tap water; river water; sewage water	0.005–2.0 mg L^{-1}	0.56–4.5 μg L^{-1}	NR
MIP-SPE-HPLC/UV [3] Sorbent: MIP with 2-NP template Elution solvent: 3.0 mL alkaline methanol Sample: 120 mL	2-NP; 3-NP; 4-NP; 2,4,6-TCP	Environmental water	1–300 ng mL^{-1}	0.10–0.22 ng mL^{-1}	NR
In syringe DSPE-HPLC/DAD [2] Sorbent: 6.0 mg LDO-HSs Sample: 100 mL Elution solvent: 200 μL TFA (10%)	Ph; 4-NP; 2-CP; 2,4-DNP; 2-NP; 2,4-DEP; 4-C-3-MP; 2,4-DCP; 2-M-4,6-DNP; 2,4,6-TCP; PCP	River water	0.05–40 μg L^{-1}	0.005–0.153 μg L^{-1}	36–459
MSPE-GC/MS [36] Sorbent: 20 mg Fe_3O_4@SiO_2 + 20 mg MOF-177 Sample: 20 mL Ultrasonication: 25 min Elution solvent: 2 mL acetonitrile under ultrasonication (30 s), blowing under N_2 to 0.5 mL	Ph; 2-MP; 4-MP; 2,4-DMP; 2,4-DCP; 3-M-4-CP	River water; lake water; waste water	1–200 μg L^{-1}	16.8–208.3 ng L^{-1}	NR
MSPE-HPLC/UV [40] Sorbent: 15 mg Zn/$Co_{7:1}$-MPC Sample: 100 mL Extraction time: 20 min shaking Elution solvent: 1% alkaline methanol (0.4 mL)	2-CP; 3-CP; 2,3-DCP; 3,4-DCP	Tap water; honey tea	0.5–100 ng mL^{-1}	0.1–0.2 ng mL^{-1}	NR
SPME-GC/MS [41] Sorbent: UiO-66-coated stainless steel fiber Sample: 10 mL; pH 4; 35% NaCl Extraction temperature: 50 °C (50 min); speed 600 rpm Desorption temperature: 280 °C (3 min)	Ph; 2,6-DMP; 2,4-DCP; 2,6-DCP; *o*-cresol; *p*-cresol	River water; lake water	1–1000 μg L^{-1}	0.11–1.23 μg L^{-1}	160–3769
VA-D-μ-SPE-HPLC/PDA [this study] Sorbent: 30 mg NH_2-MIL-53(Al) Sample: 10.00 mL Adsorption: vortex (10 s), centrifugation (1 min) Desorption solvent: 1500 μL acetonitrile:acetic acid Desorption: vortex (10 s), centrifugation (1 min)	Ph; 4-NP; 2,4-DNP; 2-NP; 4-C-3-MP; 2,4-DCP; 2-M-4,6-DNP; 2,4,6-TCP	Treated water; waste water; river water; sea water; lake water; drinking water; tap water	0.005–10.000 μg mL^{-1}	0.0004–0.0133 μg mL^{-1}	45–205

NR not reported

samples. The developed approach exhibits good analytical performance and offers the simple operation process with time-saving and small sorbent amount usage. Furthermore, the docking calculations were investigated in terms of binding free energy and orientation of the analytes in the binding site of NH_2-MIL-53(Al). The computational results were in good agreement with the experimental studies. The results proved that the NH_2-MIL-53(Al) sorbent possesses great potential in the preconcentration of phenolic pollutants in trace levels.

Table 4 The binding free energy ($\Delta G_{\text{binding}}$) of the analytes obtained from the molecular docking

Analytes	$\Delta G_{\text{binding}}$ (kcal/mol)
Ph	– 4.66
2-NP	– 5.38
4-NP	– 5.79
2,4-DNP	– 6.01
4-C-3-MP	– 6.17
2,4-DCP	– 6.15
2-M-4,6-DNP	– 6.50
2,4,6-TCP	– 6.44

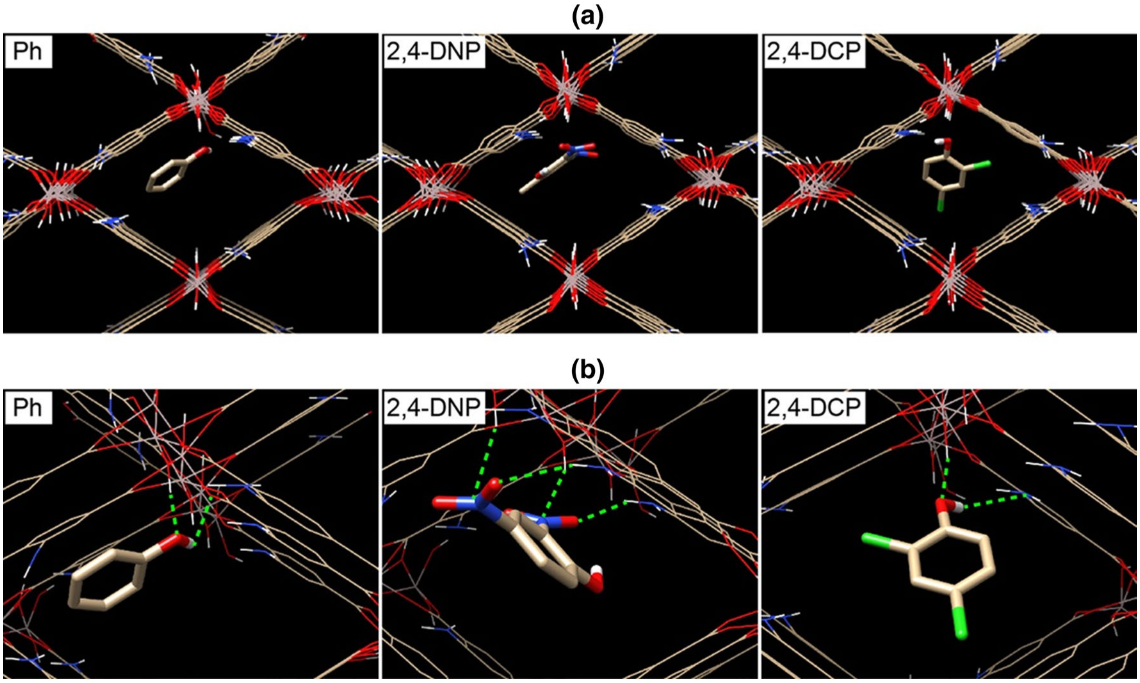

Fig. 3 Binding modes between MOFs and selected analytes exhibiting **a** orientation of the analytes in binding pocket and **b** hydrogen bonding (dashed line). The figures were generated by UCFS Chimera 1.11 program [39]

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Compliance with Ethical Standards

Conflict of interest All authors declare that they have no conflict of interest.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

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ORIGINAL PAPER

Exploiting a combined computational/experimental sorbent-injection vortex-assisted dispersive microsolid-phase extraction for chromatographic determination of priority phenolic pollutants in water samples

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Abstract

An amine-functionalized metal–organic framework based on aluminum (NH_2-MIL-53(Al)) was synthesized and employed as a sorbent for the extraction of phenolic pollutants. A new designed sorbent-injection vortex-assisted dispersive microsolid-phase extraction was proposed in which the sorbent suspension was simply injected into the sample solution. Herein the experimental parameters that affected the extraction efficiency for the target analytes were optimized, including volume of sorbent suspension, vortex agitation time, eluent type and its volume, and sample volume. Good linearity was obtained in the concentration range of 0.1–10.0 mg L^{-1} with the correlation coefficients in the range of 0.9970–0.9981. The LODs and LOQs were in the ranges of 0.030–0.055 and 0.090–0.150 mg L^{-1}, respectively. The results of the intra- and inter-day experiments showed good precision of peak area with the relative standard deviation (RSD) values of better than 5.82 and 7.85%, respectively. The developed method has been successfully applied to determine phenolic residues in water samples. The satisfactory recoveries were obtained in the range of 83.0–122.4% with the RSDs of less than 12.9%. In addition, molecular docking was performed to predict the adsorption ability of NH_2-MIL-53(Al) sorbent toward the target analytes. The computational results were in good agreement with data obtained experimentally.

Keywords Metal–organic frameworks · Sorbent injection · Dispersive solid-phase extraction · Phenol · HPLC · Molecular docking

Introduction

Phenol compounds are toxic and carcinogenic to human beings, animals, and wildlife. They are hazardous pollutants that are difficult to remove from groundwater and surface waters due to their stability and solubility in water. These compounds enter the environment during manufacturing and processing as well as result of pesticides degradation. Owing to their high toxicities even at low concentrations and prevalent presence in environment, the United States Environmental Protection Agency (US EPA) and the European Union (EU) have classified them as priority pollutants in aquatic environment. Phenol is one of the first compounds inscribed into the US EPA. Chlorophenols are the most widespread and the largest group of phenols. The presence of chlorophenols in the environment is mainly related to the use of organic compounds such as pesticides, whose biodegradation leads to the formation of phenol, 2-chlorophenol (2-CP), and 2,4-dichlorophenol (2,4-DCP). In addition, 2-CP and 2,4-DCP are used as herbicides. Methylphenols that commonly exist in the environment are also often in considerable concentrations [1]. Therefore, simple, sensitive, and reliable analytical methods are required. Generally, phenol compounds have been determined using different strategies. Liquid chromatography is one of the most widely used techniques since derivatization of analytes is avoided. However, direct determination of phenols in environmental samples is usually difficult because of their low concentrations (sub μg L^{-1}). Hence, suitable sample preparation and

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preconcentration methods are still required prior to instrumental analysis.

Several modern sample preparation procedures have been proposed incorporating with instrumental techniques for the determination of phenol residues. These include solvent-based microextraction techniques using in-syringe dispersive liquid–liquid microextraction [2], liquid-phase microextraction [3] and liquid-phase microextraction with back extraction (LPME/BE) [4]. Different sorbent-based microextractions have also been employed such as micro-solid-phase extraction using molecularly imprinted polymers [5, 6], in-syringe dispersive solid-phase extraction using dissolvable layered double oxide hollow spheres [7], and solid-phase extraction using $Fe_3O_4@SiO_2$-MOF-177 [8] and metal–organic framework MIL-101(Cr) [9]. The sorbent-based extraction technique named dispersive solid-phase extraction or DSPE, firstly introduced by Anastassiades et al. [10], is popular method due to some advantages over conventional SPE such as high surface area between analytes and the sorbent and avoiding channeling or blocking of cartridges or disks as occurs in traditional SPE, high enrichment factor, low consumption of organic solvent, and short extraction time. The principle of DSPE is based on four main steps, including (1) dispersion of the sorbent in a sample solution, (2) extraction of the analytes by selective sorption to the sorbent, (3) separation of the analyte-retained sorbent from the solution, and (4) eluting the analytes from the sorbent using an appropriate solvent. Since its introduction, the method has been widely applied as effective extraction procedure for various analytes in a variety of matrices. However, the solid sorbent must be accurately weighed for the extraction of each sample. Moreover, the DSPE has been nowadays turned to dispersive microsolid-phase extraction or D-μ-SPE in which a few milligram amounts (lower than 500 mg) of solid sorbent have been used. Therefore, to avoid laborious extraction steps especially in practical routine analyses containing numbers of sample to be analyzed, the extraction procedure should be simplified. Injection of the sorbent slurry into the sample solution is proposed in this work as an alternative.

In addition, the choice of sorbent is the main key point because it controls the analytical performance, such as selectivity, affinity, and the capacity of the method. Significant works have been achieved over the past few years in the creation and synthesis of new materials as sorbents for analyte extraction, including functionalized silica, multi-walled carbon nanotubes, graphene, and modified magnetic nanoparticles (NPs) [11]. Khezeli and Daneshfar [12] reported the application of monodisperse SiO_2@3-mercaptopropyltriethoxysilane@Au core–shell NPs for the extraction of phenol and dihydroxybenzene from water samples. The use of trace-chitosan-wrapped multi-walled carbon nanotube as a sorbent in D-μ-SPE was reported for the extraction of phenolic compounds in beverages [13]. Graphene oxide was applied as sorbent in D-μ-SPE together with UHPLC/MS for the determination of phenolic compounds in dietary supplements [14]. Saraji and Ghani [15] described the dissolvable Mg–Al-layered double hydroxide-coated Fe_2O_3 NPs for the extraction of phenolic acids in fruit juices. However, the impact of material chemistry in chemical analysis cannot be overemphasized. Further investigation of new materials with promising structural and chemical reactive properties is increasingly interested for sample preparation technology.

Metal–organic frameworks (MOFs) are a new class of hybrid materials formed by the self-assembly of metal ions of clusters and polydentate-bridging ligands. In comparison with conventional porous inorganic frameworks, such as zeolites or carbon-based materials, MOFs possess remarkably large surface area, high porosity, and thermal and chemical stability. MOFs are promising materials for adsorption-related applications because of the easy modification. The variety of elements used in MOFs, along with the large choice of organic linkers, provides a substantial number of possibilities for creating new MOFs for selective adsorption of some specific guest molecules having particular functional groups. MOFs have found various applications in respect of gas storage [16], separation [17, 18], catalysis [19], and drug delivery [20]. Recently, MOF-type materials have also been investigated widely for the adsorptive removal of various hazardous materials from the environment [21, 22]. However, investigation on analytical chemistry applications of MOFs is relatively lagging behind other topics.

Zhou et al. [23] reported the first application of MOFs for employing the sorbent material to trap eight polycyclic aromatic hydrocarbons (PAHs) from water. Wu et al. [24] fabricated novel MIL-88B films on etched stainless steel fibers for the SPME of polychlorinated biphenyls (PCBs) from water and soil samples. The MIL-88B-coated fiber was stable enough for 150 extraction cycles without a significant loss of extraction efficiency. MIL-101 and HKUST-1 were also proposed as solid sorbents for application in DSPE of benzophenones and parabens, respectively [25, 26]. Recently, Liv et al. [27] proposed a magnetic nanoporous carbon (NMC) synthesized using MOF template as adsorbent in magnetic solid-phase extraction (MSPE) for the enrichment of phenylurea herbicides. The use of magnetic adsorbent can make the phase separation process easier and faster without the need of additional centrifugation or filtration procedures and can avoid the time-consuming column passing operations encountered in SPE.

NH_2-MIL-53(Al), first reported by Arstad et al. [28], is formed by connecting together chains of $(AlO_4(OH)_2)$ corner-sharing octahedra with 2-amino-terephthalic acid. MIL-53 exhibits three-dimensional microporous framework structure with 1D diamond-shaped channels. Previously, almost of NH_2-MIL-53(Al) material studies focused on the CO_2 adsorption and separation properties [29–31]. In the present work, we exploit the application of NH_2-MIL-53(Al) as sorbent for the development of a modified vortex-assisted dispersive microsolid-phase extraction via sorbent injection for phenolic pollutants prior to HPLC determination. The extraction process was simplified as the sorbent slurry was precisely injected into the sample solution instead of weighing of small amount of sorbent for each determination as presented in conventional DSPE procedure. The applicability of the proposed procedure was demonstrated for the determination of phenolic pollutants in various water samples. In addition, the molecular modeling was used to predict the adsorption ability of NH_2-MIL-53(Al) toward the studied phenol compounds. The free binding energies were calculated, and the molecular interactions were demonstrated using molecular docking. This work presented the combined study of computational modeling and experimental application of the synthesized NH_2-MIL-53(Al) with newly designed extraction procedure.

Experimental

Reagents and chemicals

Five phenolic compound standards with a purity of ≥ 99% were used in this study. Phenol (P) was obtained from Sigma-Aldrich (USA). 2-Chlorophenol (2-CP) was purchased from Sigma-Aldrich (China). 2,4-Dichlorophenol (2,4-DCP) was obtained from Sigma-Aldrich (India). 4-Chloro-3-methylphenol (4-C-3-MP) and 2,4-dimethylphenol (2,4-DMP) were supplied by Sigma-Aldrich (Germany). Stock standard solution of each phenol at the concentration of 1000 mg L^{-1} was prepared in methanol. Working solutions were obtained by appropriate dilution with water. Deionized water (18.2 MΩ cm^{-1}) obtained from a RiOs Type I Simplicity 185 water purification system (Millipore, USA) was used throughout the experiments.

2-Aminoterephthalic acid ($HO_2C–C_6H_3NH_2–CO_2H$) (99%, Sigma-Aldrich, USA), aluminum chloride hexahydrate ($AlCl_3·6H_2O$) (99%, Sigma-Aldrich, Germany), and *N*,*N*-dimethylformamide (≥ 99%, Merck, Germany) were used for the synthesis of NH_2-MIL-53(Al). Acetonitrile (isocratic grade, Merck, China), methanol (gradient grade, Merck, Germany), ethanol (Merck, Germany), acetone (QRëc, New Zealand), and glacial acetic acid (Carlo Erba, Italy) of analytical reagent grade were used for HPLC separation and extraction procedure.

Apparatus

The HPLC system (Waters, USA) consisted of an in-line degasser, a 600E quaternary pump, and a Waters 2996 photodiode array (PDA) detector. Empower software was employed to acquire and analyze chromatographic data. The system was equipped with a Rheodyne injector with a 10-μL sample loop and an Inertsil® ODS-3 (4.6 mm × 150 mm, 5 μm) (GL Sciences, Japan) analytical column. The separation was performed using methanol (solvent A) and water (solvent B) as mobile phase. The gradient program was as follows: 50% solvent A (0–4 min); increased to 70% solvent A (4–5 min); held for 2 min (5–7 min); ramped to 100% solvent A (7–8 min); held for 5 min (8–13 min); and before returning to 50% solvent A (13–14 min). A re-equilibration period of 1 min with 50% solvent A was carried out between individual runs. The detection was performed at 275 nm.

Other instruments were used in the procedure, including a vortex mixer model G560E (50 Hz) (Scientific Industries, USA), a rotavapor model R-200 (Buchi Labortechnik AG, Switzerland), a centrifuge model Z206A (Hermle Labortechnik, Germany), and an oven model UN110 (Memmert, Germany).

Synthesis of NH_2-MIL-53(Al) sorbent

The NH_2-MIL-53(Al) was synthesized by solvothermal process using the conditions proposed by Serra-Crespo et al. [32]. In brief, aluminum chloride hexahydrate (0.51 g) and 2-aminoterephthalic acid (0.56 g) were mixed with *N*,*N*-dimethylformamide (30 mL) in a Teflon-lined autoclave and then heated for 72 h at 403 K in an oven under static condition. After cooling to the room temperature, the resulting yellow powder was filtered under vacuum and washed with acetone. The sorbent was activated in boiling methanol overnight to remove organic species trapped within the pores and then stored at 373 K.

Extraction procedure

The determination of phenolic pollutants was carried out by a sorbent-injection vortex-assisted dispersive microsolid-phase extraction (SI-VA-D-μ-SPE) using NH_2-MIL-53(Al) as sorbent followed by HPLC–PDA. For this purpose, the suspension of NH_2-MIL-53(Al) was prepared by the mixing of 0.64 g sorbent in 16 mL water and stirred using the magnetic stirrer. An aliquot of 10.00 mL aqueous phenolic pollutants or sample solution was placed in a 15-mL centrifuge tube; then, the sorbent suspension (1.50 mL) was injected rapidly. The mixture was then placed in a vortex mixer for 1 min to accelerate the sorption of the target analytes onto the sorbent. Subsequently, the solid sorbent was isolated from the solution by centrifugation at 4000 rpm

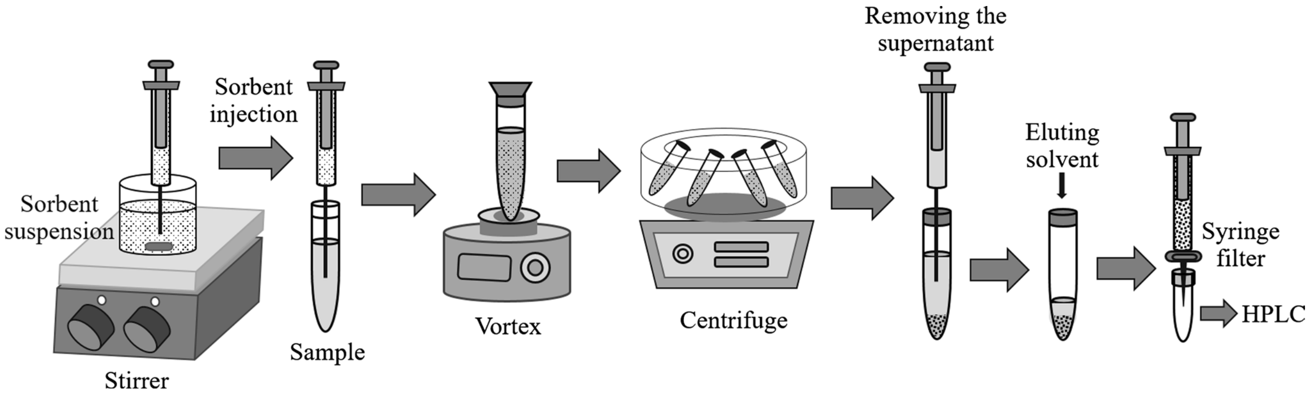

Fig. 1 Scheme of the proposed SI-VA-D-μ-SPE-HPLC method for phenolic pollutants using NH_2-MIL-53(Al) as sorbent

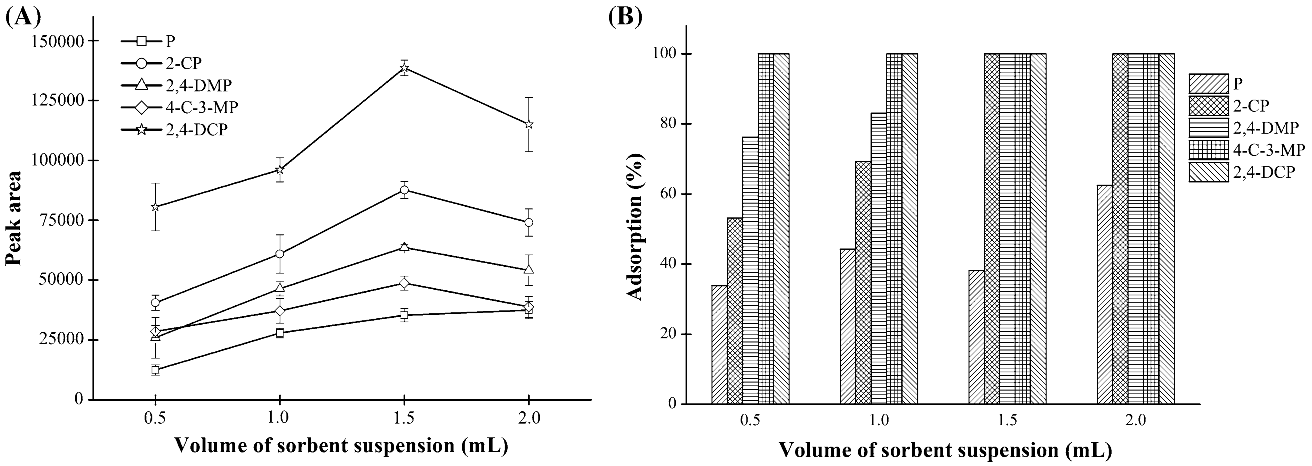

Fig. 2 **a** Effect of volume of sorbent suspension on SI-VA-D-μ-SPE of phenol pollutants and **b** adsorption capability of the NH_2-MIL-53(Al)

for 2 min. After that, the supernatant was discarded. Then, 500 μL of acetone was added in the centrifuge tube to desorb the analytes from the sorbent. After that, the mixture was filtered using a 0.45-μm nylon membrane syringe filter before being injected to HPLC system. The proposed SI-VA-D-μ-SPE-HPLC method for phenolic pollutants using NH_2-MIL-53(Al) as sorbent is schematically depicted in Fig. 1.

Molecular docking

A molecular docking simulation, a computational technique used to predict the predominant binding mode of a small molecule with a macromolecule of known three-dimensional structure, was performed. The crystal structure of NH_2-MIL-53(Al) was taken from the Cambridge Crystallographic Data Centre (CCDC) [33], whereas all phenolic compound structures were downloaded from PubChem (https://pubchem.ncbi.nlm.nih.gov). The structures of these compounds were re-optimized with quantum calculation B3LYP/6-31G(d) level using Gaussian 09 program [34]. All docking simulations were performed using AutoDock 4.2 program [35] with a cubic grid box of 60 Å in each direction, grid spacing of 0.375 Å, energy evaluation of 2.5×10^6, and 200 runs of the Lamarckian genetic algorithm searches. The binding mode and binding free energies between the analytes and MOF were evaluated.

Results and discussion

Chromatographic separation of phenolic pollutants

Optimization of the separation condition for the target analytes was carried out using trial and error approach. Under the HPLC condition described in section "Apparatus," separation of five phenolic pollutants was achieved within 15 min, with the following order of elution: P ($t_R = 4.7$ min),

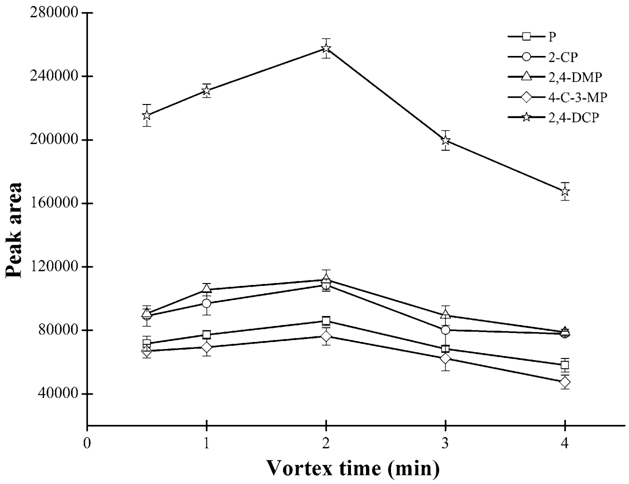

Fig. 3 Effect of vortex adsorption time

2-CP (t_R = 8.9 min), 2,4-DMP (t_R = 10.9 min), 4-C-3-MP (t_R = 12.0 min), and 2,4-DCP (t_R = 12.8 min). Linearity was observed in the concentration range of 2.0–40.0 mg L^{-1} with the coefficients of determination greater than 0.9987. The limits of detection (LODs) and limits of quantification (LOQs) were considered as the concentrations giving a signal-to-noise ratio of 3 and 10, respectively. The LODs and LOQs ranged from 0.35–0.70 to 1.04–1.81 mg L^{-1}, respectively. The precision of the method, expressed as the relative standard deviations (RSDs) of the retention time and peak area of the phenolic compounds (concentrations: 2.0 mg L^{-1} P, 3.0 mg L^{-1} 2-CP and 2,4-DMP, and 4.0 mg L^{-1} 4-C-3-MP and 2,4-DCP), were less than 0.46% and 2.67%, respectively.

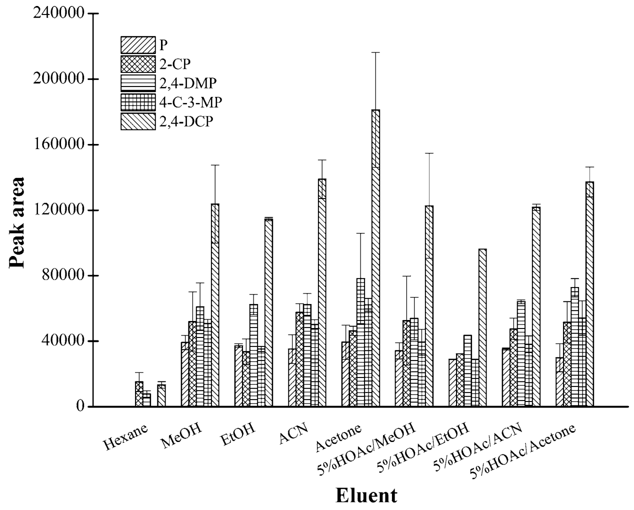

Fig. 4 Effect of eluent type

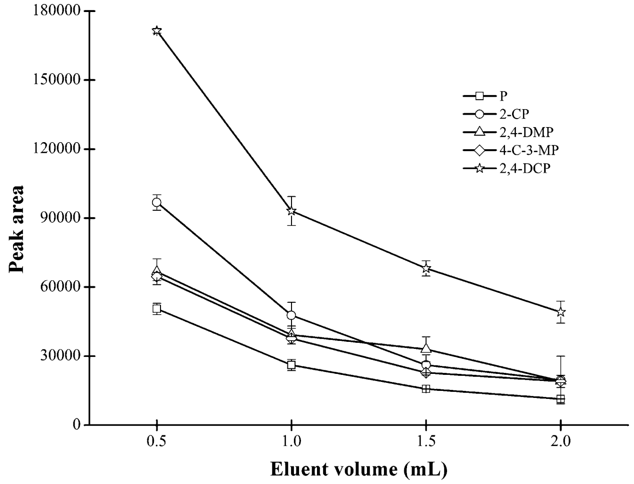

Fig. 5 Effect of eluent volume

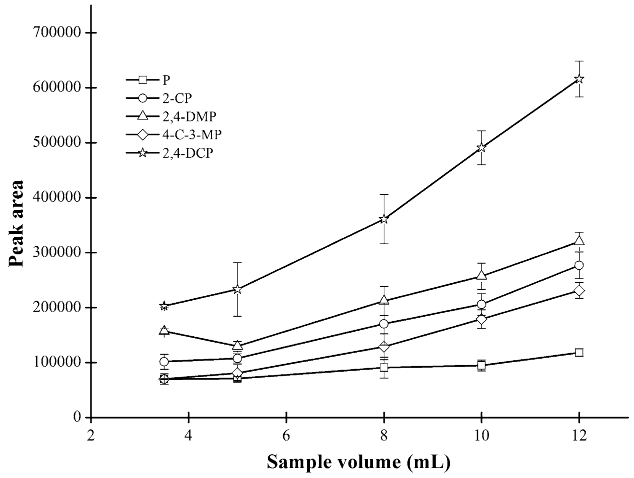

Fig. 6 Effect of sample volume

Optimization of the SI-VA-µ-SPE conditions

Effect of the volume of sorbent suspension

For sorbent-based extraction techniques, the sorbent amount usually plays an important role in extraction efficiency. In this work, the synthesized NH_2-MIL-53(Al) sorbent was prepared as slurry before injection into the sample solution. Therefore, the volume of sorbent slurry was optimized. The amount of sorbent can be calculated from the density of the sorbent stock suspension and the injection volume. In the process of optimization of the volume of sorbent suspension, aqueous standard solutions (5.00 mL) containing 1.0 mg L^{-1} P, 2-CP, 2,4-DMP, and 4-C-3-MP, and 3.0 mg L^{-1} 2,4-DCP were tested. Considering the results presented in Fig. 2a, the extraction efficiency in terms of peak area increased as increasing the volume of sorbent suspension from 0.5 to 1.5 mL and

Table 1 Analytical features of the proposed SI-VA-D-μ-SPE-HPLC procedure for phenol pollutants

Analyte	Linear range (mg L^{-1})	Linear equation	R^2	LOD (mg L^{-1})	LOQ (mg L^{-1})	EF	%RSD			
							Intra-day ($n = 5$)		Inter-day ($n = 5×3$)	
							t_R	Peak area	t_R	Peak area
P	0.5–10.0 (2.0–40.0)	$y = 41{,}416.99x + 9550.42$ ($y = 11{,}787.31x - 2864.87$)	0.9978 (0.9994)	0.054 (0.620)	0.360 (1.66)	5	0.35 (0.31)	4.97 (2.40)	0.29 (0.31	6.17 (2.57)
2-CP	0.5–10.0 (2.0–40.0)	$y = 141{,}933.07x + 4527.93$ ($y = 14{,}106.40x - 5115.44$)	0.9970 (0.9987)	0.055 (0.650)	0.150 (1.67)	10	0.34 (0.36)	5.82 (1.43)	0.24 (0.46)	6.20 (2.60)
2,4-DMP	0.1–5.0 (2.0–40.0)	$y = 168{,}791.95x + 3709.55$ ($y = 15{,}291.47x - 6161.98$)	0.9980 (0.9989)	0.040 (0.350)	0.090 (1.040)	11	0.08 (0.08)	4.72 (0.49)	0.11 (0.12)	7.85 (1.71)
4-C-3-MP	0.1–7.0 (2.5–40.0)	$y = 88{,}143.13x + 9387.84$ ($y = 8577.04x - 3323.71$)	0.9981 (0.9993)	0.030 (0.700)	0.096 (1.770)	14	0.07 (0.08)	1.16 (2.67)	0.08 (0.10)	5.26 (2.31)
2,4-DCP	0.5–7.0 (2.5–40.0)	$y = 78{,}102.38x + 6904.34$ ($y = 7955.00x - 3481.21$)	0.9972 (0.9993)	0.035 (0.660)	0.110 (1.810)	13	0.09 (0.08)	5.57 (1.86)	0.06 (0.20)	6.06 (2.15)

The values in parentheses were obtained from direct HPLC

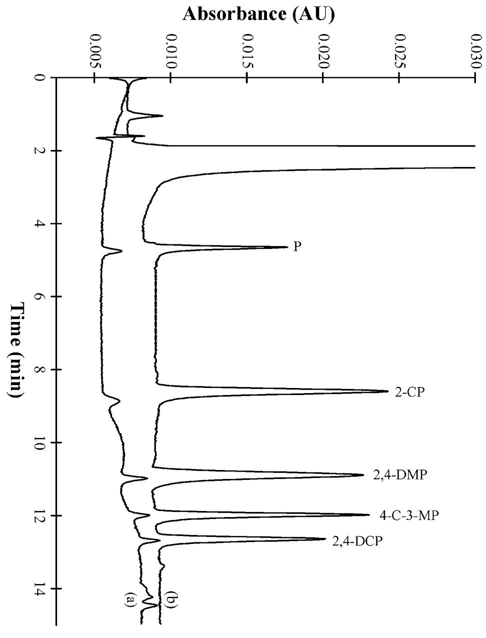

Fig. 7 Chromatograms of phenol standards obtained by *a* direct HPLC and *b* concentrated by SI-VA-D-μ-SPE method (concentrations: 1.0 mg L^{-1} each)

slightly decreased afterward. Using high amount of sorbent, it might be difficult to elute analytes efficiently by small volume of eluting solvent (0.5 mL in this work). Some analytes may be remained in the sorbent. Therefore, decrease in signals was observed. Taking into account the above results, the volume of sorbent suspension of 1.5 mL (corresponding to 60 mg sorbent) was selected for SI-VA-D-μ-SPE of phenolic pollutants in further optimization experiments.

In addition, the remaining analytes in the solutions were analyzed by HPLC. The adsorption percentage (%Adsorption) of each phenolic pollutant was calculated using equation: $\%\text{Adsorption} = (C_A/C_0) \times 100$, where C_A and C_0 are the concentrations of analyte adsorbed on the sorbent and the initial concentration of the analyte, respectively. As illustrated in Fig. 2b, no analyte except for phenol was detected in the supernatant after adsorption process using 1.5 mL volume of sorbent suspension, indicating that the NH_2-MIL-53(Al) sorbent has a good adsorption capability for the target analytes.

Effect of agitation time

In the present work, vortex was applied as external force during the extraction process to maintain the dispersion of the sorbent and enhance the adsorption of the analytes in the aqueous sample solution onto the sorbent via provision of the maximum contact area. The vortex times were studied in the range of 0.5–4.0 min, as the results shown in Fig. 3. It revealed that for all analytes except for 2,4-DCP, a slight increase in peak area was observed when the vortex time was increased from 0.5 to 1.0 min

Table 2 Determination of phenol pollutants in water samples

Analyte	Added (µg L^{-1})	Reservoir water-1			Reservoir water-2			Waste water			River water			Lotus field water		
		Found (µg L^{-1})	%*R*	%RSD	Found (µg L^{-1})	%*R*	%RSD	Found (µg L^{-1})	%*R*	%RSD	Found (µg L^{-1})	%*R*	%RSD	Found (µg L^{-1})	%*R*	%RSD
P	–	ND	–	–	ND	–	–	ND	–	–	ND	–	–	61.7 ± 2.9	–	–
	400	417.1 ± 12.1	104.3	2.9	402.2 ± 6.0	100.5	1.5	408.4 ± 10.7	102.1	3.6	481.3 ± 15.1	120.3	3.1	430.2 ± 20.6	92.1	5.6
	600	553.2 ± 19.5	92.2	3.5	605.1 ± 8.7	101.8	1.4	629.0 ± 19.5	104.8	2.6	671.4 ± 86.5	111.9	12.9	612.2 ± 31.4	91.8	5.7
2-CP	–	ND	–	–	ND	–	–	ND	–	–	ND	–	–	ND	–	–
	200	219.0 ± 20.4	109.5	9.3	210.8 ± 0.5	105.4	0.3	201.9 ± 5.3	100.9	2.7	194.2 ± 10.9	97.1	5.6	202.0 ± 0.9	100.9	0.5
	400	379.1 ± 3.6	94.8	1.0	391.2 ± 5.9	97.8	1.5	438.6 ± 16.8	106.7	3.9	420.0 ± 0.6	105.0	0.2	356.7 ± 21.0	89.1	5.9
2,4-DMP	–	ND	–	–	ND	–	–	ND	–	–	ND	–	–	ND	–	–
	100	109.6 ± 9.6	109.6	8.7	113.1 ± 6.8	113.1	6.0	97.5 ± 5.9	97.5	6.1	95.0 ± 20.9	95.0	2.2	119.2 ± 5.9	119.2	4.9
	200	196.0 ± 11.9	98.0	6.1	202.2 ± 6.1	101.1	3.0	205.9 ± 10.26	102.9	5.0	240.4 ± 0.3	120.2	0.2	212.7 ± 0.7	106.3	0.3
4-C-3-MP	–	ND	–	–	ND	–	–	ND	–	–	ND	–	–	ND	–	–
	100	99.6 ± 4.3	99.6	4.3	106.0 ± 6.9	105.9	6.5	86.4 ± 2.3	86.4	2.3	94.7 ± 0.2	94.7	0.2	122.4 ± 9.3	122.4	7.6
	200	203.6 ± 6.4	101.8	3.1	201.3 ± 2.4	100.7	1.2	212.6 ± 18.0	106.3	8.5	226.4 ± 10.0	113.2	4.5	217.8 ± 12.3	108.8	5.7
2,4-DCP	–	ND	–	–	ND	–	–	ND	–	–	ND	–	–	ND	–	–
	200	173.6 ± 14.8	86.8	8.5	192.0 ± 6.0	96.0	3.1	206.0 ± 26.4	103.0	12.8	192.0 ± 2.4	96.0	1.2	166.3 ± 11.0	83.1	6.6
	400	331.9 ± 13.7	83.0	4.1	452.3 ± 19.4	113.0	4.3	440.4 ± 7.9	110.1	1.8	410.4 ± 44.3	102.6	10.8	395.0 ± 17.6	98.7	4.5

ND not detected

and then almost flattened out before slightly decreased after 2 min. Only for 2-4-DCP that the maximum signal was obtained using vortex time of 2 min. Therefore, 1 min was adopted as the most favorable vortex agitation time.

Effect of eluent type

Generally, choice of desorption solvent is also crucial for the extraction efficiency of the target analytes in sorbent-based microextraction techniques. To study the desorption of five phenolic pollutants from the NH_2-MIL-53(Al), nine different solvent systems were investigated using the constant volume of 500 µL. The studied eluent includes hexane, methanol, ethanol, acetonitrile, acetone, 5% acetic acid in methanol, 5% acetic acid in ethanol, 5% acetic acid in acetonitrile, and 5% acetic acid in acetone. The results are demonstrated in Fig. 4. Desorption using acetone could achieve the highest extraction recoveries in terms of peak area for most target analytes.

Effect of eluent volume

Further investigation was carried out using acetone as desorption solvent, and its volume was varied in the range from 0.5 to 2.0 mL. The appropriate desorption solvent should meet the requirements of high solubility for the target analytes with low consumption volume. The minimum eluent volume of 0.5 mL was selected because it provides high extraction recovery for most analytes, as illustrated in Fig. 5. Using the eluent volume of less than 0.5 mL, collection of the eluate was problematic such that the precision of the extraction was also consequently affected.

Effect of sample volume

The influence of sample volume was evaluated in the range of 3.5–12.0 mL because of the limited capacity of extraction vessel. As can be seen in Fig. 6, the extraction efficiency increased significantly with increasing the sample volume due to increasing analyte enrichment. Considering the extraction recoveries and enrichment factors, the volume of 12.0 mL was selected as the most favorable sample volume.

Analytical performance

To assess the analytical performance of the developed method, the linearity, precision, LODs, LOQs, and enrichment factors (EFs) were investigated under the most favorable experimental conditions. The results are summarized in Table 1. Linear regression analyses were carried out using the peak areas obtained by the proposed method against the corresponding concentrations. The linear range of the method was 0.1–10.0 mg L^{-1} with the correlation coefficients in the range of 0.9970–0.9981. The LODs and LOQs, defined as the lowest concentrations with the signal-to-noise ratios of 3 and 10, respectively, were in the ranges of 0.030–0.055 and 0.090–0.150 mg L^{-1}, respectively. The results of the intra- and inter-day experiments (concentrations: 5.0 mg L^{-1} P, 1.0 mg L^{-1} 2-CP and 2,4-DMP, and 2.0 mg L^{-1} 4-C-3-MP and 2,4-DCP) showed good precision (of peak area) with the RSD values of less than 5.82 and 7.85%, respectively.

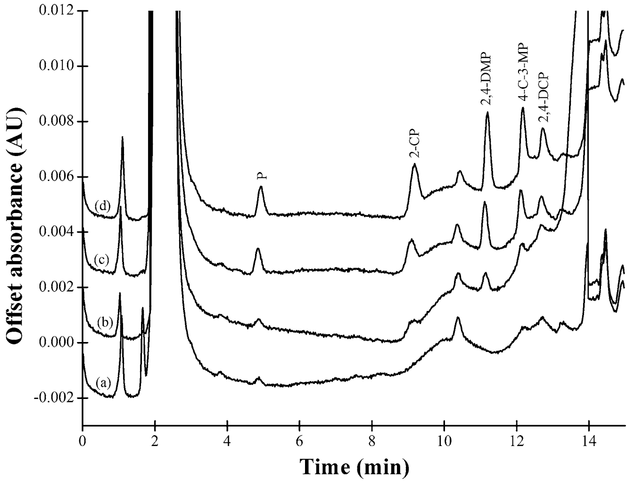

Fig. 8 Typical chromatograms of blank and spiked lotus field water sample: *a* sample blank, *b* spiked with 0.1 mg L^{-1} P, 2-CP, 2,4-DMP, 4-C-3-MP, and 0.05 mg L^{-1} 2,4-DCP, *c* spiked with 0.4 mg L^{-1} P, and 0.2 mg L^{-1} 2-CP, 2,4-DMP, 4-C-3-MP 2,4-DCP, *d* spiked with 0.6 mg L^{-1} P and 0.4 mg L^{-1} 2-CP, 2,4-DMP, 4-C-3-MP 2,4-DCP

Table 3 The binding free energies ($\Delta G_{\text{binding}}$) of the analytes obtained from molecular docking

Analytes	$\Delta G_{\text{binding}}$ (kcal mol^{-1})
P	− 4.66
2-CP	− 5.65
2,4-DMP	− 6.00
4-C-3-MP	− 6.17
2,4-DCP	− 6.15

The practical demonstration of the enrichment attained by the proposed method is presented in Fig. 7. The EFs were calculated comparing the concentrations of the analytes obtained with and without applying the proposed SI-VA-D-µ-SPE-HPLC procedure, and the resulted EF values were satisfactory as summarized in Table 1.

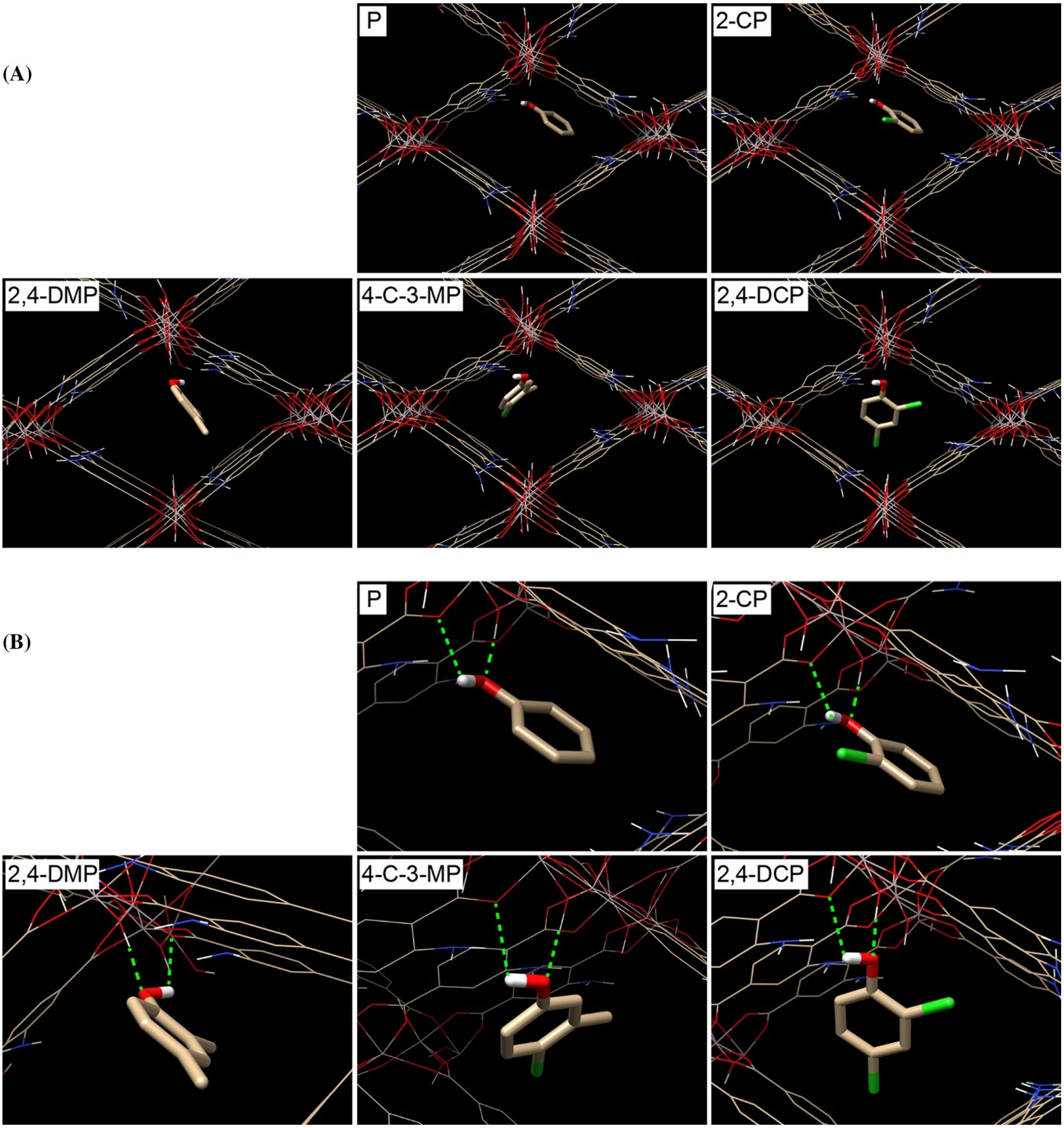

Fig. 9 Binding modes between MOF and the analytes exhibiting **a** orientation of the analytes in binding pocket and **b** hydrogen bonding (dashed line). The figures were generated by UCSF Chimera 1.11 program [36]

Application to real samples

To further investigate the applicability of the developed procedure, five real water samples were determined, including two natural water samples collected from different reservoirs in northeastern Thailand, river water, lotus field water, and waste water collected from beverage production plant. All samples were filtered before applying the proposed SI-VA-D-μ-SPE-HPLC procedure. The results are presented in Table 2. Contamination of phenol was observed in water sample collected from lotus field at the concentration of 61.7 μg L^{-1}. The results indicated that this method could be used to determine some polluted water samples.

The recovery experiments were also carried out to evaluate the accuracy of the method in all sample matrices. Two different concentrations of the target analytes were spiked into the real samples. Determinations were performed in triplicate. The results are also shown in Table 2. The range of mean recoveries was 83.0–122.4%, and the RSD values were less than 12.9%. Figure 8 shows the chromatogram recorded for lotus field water sample. On the basis of the above results and the figures of merit, the proposed SI-VA-D-μ-SPE-HPLC method is feasible for preconcentration and quantification of phenol pollutants in water matrices.

Molecular modeling

The binding free energies ($\Delta G_{\text{binding}}$) obtained from molecular docking are summarized in Table 3. It can be seen that phenol yields lower negative value of $\Delta G_{\text{binding}}$ compared to its derivatives. This indicates that the interaction between phenol and MOF is rather small which is in good agreement with the adsorption ability observed experimentally. By substituting chloro and/or methyl groups, the interactions were increased about 20% (for 2-CP) and 30% (for two group substituted compounds). The NH_2-MIL-53(Al) composes of functional groups that can form various interactions with the analytes. The docked structures reveal that all compounds form hydrogen bonds between oxygen atom of carboxyl group and hydrogen atom of hydroxyl group in MOF (see Fig. 9). Due to the hydrophobic interaction resulted from methyl group(s), and the dipole–dipole interaction between the chloro group(s) and polar hydrogen atoms of NH_2-MIL-53(Al), the increase in interaction for phenol derivatives was therefore obtained. As illustrated in Fig. 9, the orientations of P, 2-CP and 4-C-3-MP molecular planes were parallel to the benzyl group of MOF providing the π–π interaction. Although the parallel orientation was not observed for 2,4-DMP and 2,4-DCP, their large negative values of $\Delta G_{\text{binding}}$ seem to be mainly contributed from the hydrophobic and dipole–dipole interactions.

Conclusion

In this study, NH_2-MIL-53(Al) was proposed as sorbent material for the development of novel SI-VA-D-μ-SPE method for the enrichment of phenolic pollutants prior to HPLC analysis. The extraction process was simplified by the injection of sorbent suspension into the sample solution, avoiding laborious weighing of small amount of solid sorbent as presented in conventional DSPE method. The satisfied recoveries and good precision for all studied analytes proved that the developed method was valid for the quantification of phenolic pollutants in different water samples. The computational study also showed good agreement with data obtained experimentally.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Ethical approval This article does not contain any studies with animals performed by any of the authors.

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Magnetic solid phase extraction of phenolic pollutants in water samples using a facile synthesized polyaniline coated zerovalent iron-silica as an efficient sorbent

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Dear Editor,

Please consider the manuscript entitled " **Magnetic solid phase extraction of phenolic pollutants in water samples using a facile synthesized polyaniline coated zerovalent iron-silica as an efficient sorbent**" for publication in **RSC Advances**. This work presents the synthesis of magnetic sorbent based on polyaniline coated zerovalent iron-silica or Fe@SiO$_2$@PANI following its application in development of magnetic solid phase extraction (MSPE). The sorbent was simply synthesized using a facile manner under low energy consumption. The developed procedure exhibits good extraction efficiency for phenolic pollutants prior to their determination by HPLC-PDA, and has been successfully utilized to the determination of phenol residues in environmental water samples.

The manuscript has not been published as well as submitted for publication elsewhere. Your consideration would be very much appreciated. Thank you very much.

Best regards,
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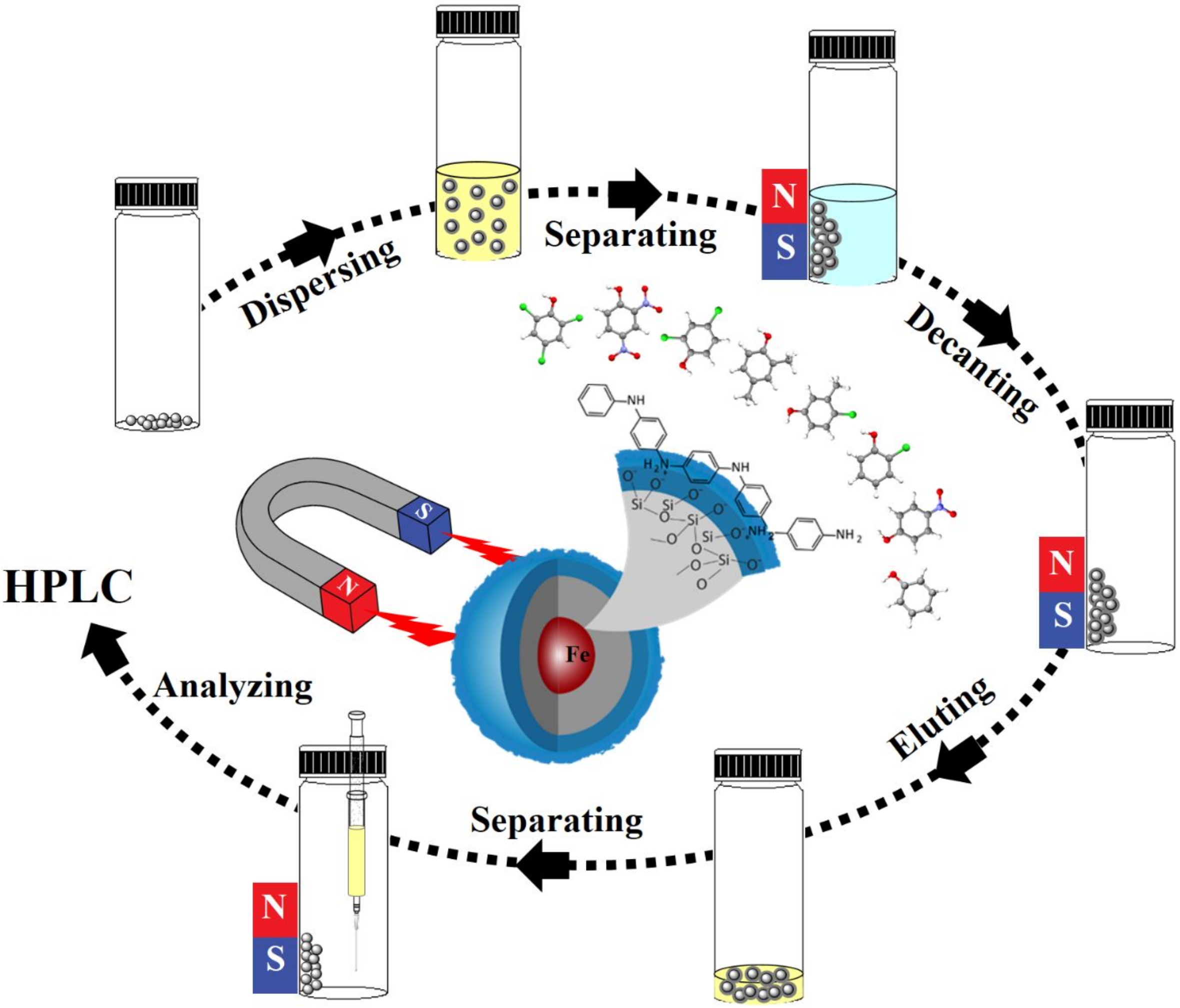
Table of content



Zerovalent iron-silica covered with polyaniline was proposed as sorbent for a simple magnetic solid phase extraction of phenolic pollutants.

Magnetic solid phase extraction of phenolic pollutants in water samples using a facile synthesized polyaniline coated zerovalent iron-silica as an efficient sorbent

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Abstract

The magnetic sorbent based on polyaniline coated zerovalent iron-silica (Fe@SiO_2@PANI) was simply synthesized using a facile manner under low energy consumption. The spherical-like shape with particle size of 235 nm was obtained. The as-prepared material was characterized and applied as sorbent for development of magnetic solid phase extraction (MSPE) of phenolic pollutants prior to their determination by HPLC-PDA. Eight phenolic compounds were selected as target analytes, including phenol, 4-nitrophenol, 2-chlorophenol, 2,4-dinitrophenol, 2,4-dimethylphenol, 4-chloro-3-methylphenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol. The main parameters influencing MSPE method, such as sorbent amount, adsorption time, sample volume, type of desorption solvent and its volume, and desorption time, were optimized. Under the selected condition, wide linear calibration curves were achieved in the concentration range of 0.020–10.000 µg mL^{-1} with the correlation coefficients above 0.9926. The limits of detection (LODs) and the limits of quantitation (LOQs) were in the ranges of 18–120 µg L^{-1} and 44–300 µg L^{-1}, respectively. The precision in term of RSDs were below than 10.8%. The determination of phenolic residues in environmental water samples showed the recoveries in the range of 83.4–118.5%. The synthesized Fe@SiO_2@PANI magnetic sorbent exhibits good adsorption affinity which can be further applied for determination of trace phenolic compounds in other sample matrices.

Keywords: zerovalent iron, polyaniline, phenol, magnetic solid phase extraction, HPLC

1. Introduction

Exposure of toxic chemicals in the environment is one of the serious issues worldwide. Phenol and its derivatives are priority pollutants classified by the United States Environmental Protection Agency (US EPA) and the European Union (EU) as they increasingly release into the aquatic environment during agricultural and industrial processes, including paper, dye, textile, plastic, and pharmaceutical production.[1–2] The presence of phenol pollutants can cause long-term damaging effects in living organisms and carcinogenic potential to humans. Therefore, monitoring the concentration of phenol compounds in the environment is of great importance and can make relevant regulations for phenol emission to prevent environmental pollution.

Separation techniques have been reported for simultaneous detection of these pollutants, including high-performance liquid chromatography (HPLC),[3–5] and gas chromatography (GC).[6–7] However, direct analysis is quite difficult due to these compounds are present at low concentration levels in the complex matrices. Hence, significant effort is paid on development of various sample pretreatment techniques for potential enrichment of the target analytes prior to instrumental analysis. The sorption-based extraction techniques have been given attention in analytical chemistry community because of some greater advantages over the liquid-phase extraction techniques, including simple procedure with short extraction time, and less consumption of toxic organic solvent. Type of solid sorbent has great impact on the efficiency of the extraction method because it determines the sorption ability to enrich the target analytes from the sample matrices.

Recently, a new sorption-based extraction method, dispersive solid phase extraction (DSPE) has been introduced. The technique is based on dispersion of the solid sorbent in a sample solution to allow the selective extraction of the analytes to the sorbent. After that, the analyte-retained sorbent was separated from the solution by centrifugation (or filtration) before eluting the analytes from the sorbent using an appropriate solvent. The DSPE technique exhibits some advantages over the conventional solid phase extraction (SPE) approach, including simple extraction process, short extraction time, high surface area, less organic solvent consumption, and no cartridge or disk needed. Recently, a novel DSPE method has been introduced based on using magnetic nanoparticles (MNPs) as sorbent, called magnetic solid phase extraction (MSPE). A unique and attractive features of MSPE is that magnetic sorbent can rapidly be isolated from sample solutions by simply applying external magnetic field outside of the extraction vessel, avoiding centrifugation or filtration of the sample. The method has the advantages of high extraction efficiency, simple separation and good reusability.[8] The efficiency of MSPE generally depends on the design of magnetic sorbent to bind well with the target analytes. Several kinds of magnetic sorbents have been synthesized and widely used for analytical applications, including magnetic carbon nanotubes,[9–10] magnetic metal organic framework (MOF),[11–13] magnetic graphene oxide,[14–15] and magnetic molecular imprinted polymer.[16–18]

Zerovalent iron nanoparticles has attracted much interest as magnetic material of choice for MSPE technique due to their high magnetization value, non-toxic, cost-effectiveness, easy preparation and modification.[19] However, the application of bare zerovalent iron in MSPE technique have some limitations, such as low selectivity toward target analytes, easy oxidation, low acid resistant and high aggregation as well as low dispersibility in sample solution.[20–21] To reduce their limitations and improve an adsorption capability for the target analytes, modification of zerovalent iron surface is intensely focused using several kinds of coating materials.[22–24] Polyaniline (PANI) is one of promising coating polymers and has attracted a great deal of attention because its layer can provide active groups (benzene rings and amine groups) on the supporting solid surface that provide possible binding sites for the target compounds, including hydrophobicity, π-π interaction, hydrogen bonding and electrostatic interaction.[25–28] Moreover, it has additional advantages, such as good environment stability, low cost monomer, and facile synthesis. On the other hand, some polymerization processes of polyaniline can directly destroy magnetic materials by oxidizing its surface with the use of chemical oxidant during polyaniline formation process, causing reduction or loss of magnetic properties. Therefore, it is very necessary to improve stability of magnetic materials before modifying with polyaniline. Silica has gained widely attention because of its easy modification and high stability as well as good dispersibility in various media.[29–30] The magnetic material using nanoscale zerovalent iron as the core and PANI as the shell (polyaniline@SiO_2@Fe) has been reported as sorbent for extraction of typical endocrine disrupting compounds, including bisphenol A, tetrabromobisphenol A and 4-nonylphenol.[31] The material shows excellent enrichment capability for the studied analytes. However, synthesis of the functionalized magnetic materials was carried out under unfavorable conditions i.e. using an autoclave, high temperature, take too long time and contains complicated steps. In addition, laborious extraction steps were not suitable for practical analysis.

Therefore, the purpose of this work was to prepare the zerovalent iron-silica covered with polyaniline and develop the simple method of MSPE for the determination of phenolic pollutants by HPLC. The silica coated zerovalent iron was simply prepared by sol-gel process with low energy consumption. Then, modification of polyaniline onto zerovalent iron-silica surface was proceeded through oxidative polymerization of aniline monomer. The morphological and magnetic properties of as-prepared sorbent were investigated. The experimental parameters influencing MSPE method, including sorbent amount, type of eluent and its volume, adsorption and desorption times, and sample volume, were studied. The developed method was applied to determine phenolic pollutant residues in various environmental water samples.

2. Experimental

2.1 Chemicals

All chemicals used in this work were at least analytical reagent grade. Ferrous sulfate heptahydrate was purchased from Carlo Erba (France). Sodium borohydride and aniline were supplied by AppliChem (India). Ethanol was purchased from Merck (Germany). Ammonium hydroxide was supplied by QRëC (New Zealand). Cetyltrimethylammonium bromide (CTAB) was obtained from Ajax Finechem Pty Ltd (Australia). Tetraethylorthosilicate (TEOS) was supplied by Sigma-Aldrich (Germany). Ammonium peroxydisulfate was obtained from Analar Normapur (Belgium). Eight phenol standards with a purity of ≥ 99% were used. 2,4-Dinitrophenol (24DNP), 2,4-dimethylphenol (24DMP), 4-chloro-3-methylphenol (4C3MP), and 2,4,6-trichlorophenol (246TCP) were supplied by Sigma-Aldrich (Germany). Phenol (Ph) was obtained from Sigma-Aldrich (USA). 4-Nitrophenol (4NP) and 2,4-dichlorophenol (2,4DCP) were purchased from Sigma-Aldrich (India). 2-Chlorophenol (2CP) was supplied by Sigma-Aldrich (China). Stock standard solutions of each phenolic compound at concentration of 1000 μg mL^{-1} were prepared using methanol as solvent. Working solutions were prepared freshly in water. Deionized water (RiOs Type I Simplicity 185 water purification system, Millipore, USA) with a resistivity of 18 MΩ·cm was used in all experiments. Acetonitrile of HPLC grade (Merck KgaA, Germany) was used for chromatographic separation.

2.2 Instrumentation

Fourier transform infrared spectra was recorded using a Perkin Elmer Spectrum One FTIR spectrometer using a standard KBr disk method with wavenumber between 400 and 4000 cm^{-1}. The crystal structure of the synthesized material was characterized by a PANalytical, EMPYREAN X-ray diffractometer (XRD) with monochromatic Cu Kα radiation ($\lambda = 0.15406$ nm) in a 2θ range of 10° to 80°. The morphology and particle size were measured using a Field Emission Scanning Electron Microscopy (FESEM) and a FEI, Tecnai G^2 20 transmission electron microscope with an accelerating voltage of 200 kV. CHN analyses were performed on a PerkinElmer PE 2400CHNS analyzer. Magnetic measurement was achieved by a VersaLab vibrating sample magnetometer (VSM) at 300 K with an applied magnetic field (H) of ± 10000 Oe.

The HPLC system consisted of an in-line degasser, a 600E quaternary pump, and a Waters 2996 photodiode array (PDA) detector (Waters, USA), using Empower software for data acquisition. The system was equipped with a Rheodyne injector with a 10-µL loop, and an ACE 5 C18 (4.6 mm×250 mm, 5 µm) (Advanced Chromatography Technologies Ltd.) analytical column. The separation was performed using acetonitrile (solvent A) and 0.1% acetic acid in water (solvent B) as mobile phase at a flow rate of 1.0 mL min^{-1}. The gradient program was as follows: 0–3 min, 45% solvent A; 3–4 min, ramped to 55% solvent A; 4–8 min, held at 55% solvent A; 8–9 min, ramped to 65% solvent A; 9–12 min, held at 65% solvent A; 12–13 min, ramped to 75% solvent A; and 13–16 min, held at 75% solvent A. After that solvent A was decreased to 45% before the next run. The detection was performed at 280 nm.

2.3 Synthesis of the sorbent

2.3.1 Preparation of zerovalent iron nanoparticles

The zerovalent iron nanoparticles were prepared via reduction of ferrous sulfate using sodium borohydride. In brief, ferrous sulfate (5.56 g) was dissolved in 400 mL water. Then, 100 mL of sodium borohydride solution (0.4 mol L^{-1}) was added with vigorous stirring for 15 min. After that, the black solid was separated by magnet, washed several times with water and ethanol, and dried in vacuum.

2.3.2 Synthesis of polyaniline coated Fe@SiO_2 particles

The Fe@SiO_2 particles were synthesized via sol-gel method using TEOS as precursor, and then polyaniline coated Fe@SiO_2 particle was prepared through oxidative polymerization of aniline in the presence of ammonium peroxydisulfate. Firstly, the zerovalent iron nanoparticles (50 mg) were dispersed in 90 mL ethanol, then 5 mL of water and 5 mL of ammonium hydroxide solution were subsequently added with sonication for 30 minutes. Next, TEOS (1 mL) was gradually dropped and the mixture was shaken for 24 hours at ambient temperature. The product was separated by external magnet, washed with ethanol until the pH became 6–7. After that, as-prepared Fe@SiO_2 particle was dispersed in 90 mL of water, then 1 mol L^{-1} HCl (2 mL) and CTAB (0.3 mmol) were slowly added with sonication for 1 hour. Subsequently, the mixture was added slowly with aniline and shaken for 1 hour in an ice bath. Finally, 10 mL of ammonium peroxydisulfate solution (0.07 mol L^{-1}) was gradually dropped and the mixture was shaken for 5 hours in ice bath. The dark green of polyaniline coated Fe@SiO_2 was collected by magnet, washed several times with water and methanol, and dried. The product was defined as Fe@SiO_2@PANI.

2.4 Samples collection

Environmental water samples were collected from different areas in northeastern Thailand. Three river water samples were taken from Nam Phong river (Khon Kaen, Thailand), Chi river (Khon Kaen, Thailand), and Mekong river (Nakhon Phanom, Thailand). Seven reservior water samples were drawn from Ubon Ratana dam (Khon Kaen, Thailand), Lam Pao dam (Kalasin, Thailand), Kud Nam Sai lake (Khon Kaen, Thailand), Kaen Nakhon lake (Khon Kaen, Thailand) and Nong Han lake (Sakon Nakhon, Thailand). All water samples were stored under cool condition (4 °C) until analysis. Each samples were filtered through 0.45 μm nylon membrane. The measured pH of all water samples were in the range of 6–7.

2.5 MSPE procedure

The MSPE process was performed as follows. First, 70 mg Fe@SiO_2@PANI sorbent was added to 25 mL aqueous sample solution in an extraction vial. The mixture was vortexed for 2 min. Then, the magnetic sorbent enriched with target analytes were collected by external magnet before decanting supernatant solution. Subsequently, desorption of analytes was carried out using 0.5 mL acetonitrile as desorption solvent and vortexed for 0.5 min. The magnet was applied to settle down sorbents and the solution was filtered through a 0.45 µm nylon membrane before further injecting into the HPLC system for analysis. The schematic diagram of the proposed MSPE is depicted in Fig. 1.

3. Results and discussion

3.1 Characterization of Fe@SiO$_2$@PANI

Modification of the functional group on solid surface was characterized by FT-IR. As shown in Fig. S1, the FT-IR spectrum of Fe exhibited the characteristic vibration peaks at 1067, 685, 562 and 470 cm^{-1}, indicating the vibration mode of γ-FeOOH-lepidocrocite, Fe–O stretching modes of the octahedral and tetrahedral sites, and maghemite (γ-Fe_2O_3), respectively.[32] In the FT-IR spectrum of Fe@SiO$_2$, the characteristic vibration peaks of both Fe and SiO_2 were observed, which located at 1629, 1097, 950, 805, and 470 cm^{-1}, assigning to Si–OH bending, Si–O–Si asymmetric stretching, Si–OH stretching, Si–O–Si symmetric bending and Si–O–Si bending, respectively.[33] In this case, weak absorption peaks at 562 cm^{-1} for Fe–O stretching mode was observed, confirming the coating of silica layer on Fe surface.[33] The FT-IR spectra of the Fe@SiO$_2$@PANI show the absorption bands at 1618, 1533 and 1275, 1097, 950, 805, 563 and 470 cm^{-1}, which can be assigned to the N–H bending, C=C stretching, C–N stretching for characteristic vibration bands of polyaniline,[34] Si–O–Si asymmetric stretching, Si–OH stretching, Si–O–Si symmetric bending, Fe–O stretching and Si–O–Si bending for vibration bands of silica and Fe. These results confirmed the successful incorporation of PANI into Fe@SiO$_2$ particle.[35]

The XRD measurements were recorded for investigation of the phase and crystal structure of the as-synthesized sorbents in the region of 10° to 80°. Fig. S2 shows the diffraction peaks of zerovalent iron at the 2θ of 45°, which were assigned to the presence of crystalline phase of zerovalent iron, according to JCPDS 87-0721. The presence of diffraction peaks at

32°, 36°, 57° and 64° corresponded to (220), (311), (511), and (440) of γ-Fe_2O_3 crystal plane, respectively (JCPDS 25-1402). This XRD pattern is in agreement with the previous report,[36] showing the covering of a very thin oxide layer on zerovalent iron surface. Considering the XRD pattern of as-synthesized Fe@SiO_2, a broad band at 2θ in the range between 10° and 30° indicated amorphous SiO_2[33,37] and the diffraction peaks at ca. 45° could be assigned to the crystalline plane of zerovalent iron. In addition, the XRD peaks due to the iron oxide phase (at 2θ of 32°, 36°, 57° and 64°) were also observed, indicating the coating of silica on zerovalent iron surface.[24] The crystal planes of (220), (311), (511), and (440) of γ-Fe_2O_3 at 2θ of 32°, 36°, 57° and 64°, respectively, were observed in the diffraction pattern of Fe@SiO_2@PANI. The broad band at 2θ of 10°–30° due to amorphous phases of both silica and polyaniline was also obviously seen.[38] However, it is noteworthy that the diffraction peak of zerovalent iron at 45° was not observed in the XRD pattern of Fe@SiO_2@PANI. This result may be due to well coating of PANI on surface of zerovalent iron silica.

The morphological structure of as-synthesized sorbents was studied by FESEM. As can be seen in Fig. 2(a) that the irregular shape of Fe with particle size of 60 nm was obtained. The inset histogram revealed the wide size distribution of Fe nanoparticles. The spherical shape of Fe@SiO_2 with particle size of 190 nm with its uniform and narrow size distribution was shown in Fig. 2(b). The SEM micrograph of Fe@SiO_2@PANI in Fig. 2(c) shows the linkage-spherical shape due to the effect of polyaniline layer coating. The particle size of 235 nm was observed. Therefore, the results of FESEM can support the formation of silica coated zerovalent iron as well as its polyaniline coated Fe@SiO_2.

The elemental analysis indicated that the sorbent contained 12.01% C, 1.72% H and 9.3% N, which confirmed the existence of polyaniline layer coated on zerovalent iron silica. In addition, the presence of Fe, Si and O contents in Fe@SiO_2 was confirmed by energy dispersive spectroscopy (EDS) technique (Fig. 2(d). The results showed that as-prepared Fe@SiO_2 contained 37.5 % O, 43.6 % Si, and 18.9 % Fe, corresponding to the existence of silica coated on zerovalent iron.

The Fe@SiO_2 and Fe@SiO_2@PANI particles were examined by TEM. The TEM images in Fig. 3(a) and Fig. 3(b) displayed the formation of spherical silica layer which coated on aggregated zerovalent iron and had silica shell thickness of 20 nm. A well-defined core-shell structure with the zerovalent iron as core, silica as first coating layer and polyaniline as top coating shell was indeed formed (see Fig. 3(c) and Fig. 3(d)). These results indicated that the Fe@SiO_2@PANI was successfully prepared.

The magnetic properties of as-prepared zerovalent iron, Fe@SiO_2 and Fe@SiO_2@PANI were measured by VSM in the field range from -10000 to +10000 Oe at room temperature. The magnetic hysteresis curves in Fig. S3 show the saturation magnetization (M_s) values around 92.05, 32.40 and 7.30 emu g^{-1} for Fe, Fe@SiO_2 and Fe@SiO_2@PANI, respectively, indicating that these materials exhibit ferromagnetic behavior at room temperature. The M_s values of as-synthesized nanoparticles are also in agreement with those reported in the previous reports.[38–40] As the diminution of the M_s values of Fe@SiO_2 and Fe@SiO_2@PANI compared with the high value of the starting Fe material, it was evident that the high contents of non-magnetic SiO_2 and PANI components coated on the Fe magnetic material which could be explained by multiple factors. One of them is the shielding of diamagnetic materials, SiO_2 and PANI, leading to the reduction of magnetic dipole moment interaction between adjacent magnetic domains.[41–42] In addition, the M_s value depends on the density of magnetic dipole moments, which corresponding to the content of magnetic material. The other factor is due to the decreasing of Fe content in as-prepared sorbents. Despite the decrease of the M_s value of modified Fe@SiO_2@PANI, the sorbent still shows fairly magnetization and is sufficient to effectively isolated from the sample matrix by means of a strong magnet.

3.2 Optimization of the MSPE condition

In this study, the synthesized Fe@SiO$_2$@PANI was used as sorbent for development of MSPE procedure for extraction of phenolic pollutants, including Ph, 4NP, 2CP, 24DNP, 24DMP, 4C3MP, 24DCP and 246TCP. Quantification of the target analytes was performed using HPLC-PDA. To achieve high extraction efficiency for all studied compounds, the effect of experimental variables, such as sorbent amount, adsorption time, sample volume, desorption solvent and its volume, and desorption time, were investigated. The optimization experiments were carried out using an aqueous solution containing 2.0 μg mL^{-1} of each phenolic pollutant. All experiments were carried out in triplicate. Peak area was used to evaluate the extraction efficiency of the proposed MSPE method.

3.2.1 Sorbent amount

The amount of sorbent materials plays a crucial role in the MSPE procedure. Insufficient sorbent amounts result in low extraction efficiency while excess sorbents result in higher consumption of sorbent materials, desorption solvent and extraction time. In this work, the amount of Fe@SiO$_2$@PANI sorbent was studied in the range of 10–90 mg, under other conditions as follows: sample volume of 10 mL, vortex adsorption time of 1 min, 1 mL acetonitrile as desorption solvent, and vortex desorption time of 1 min. The peak area of the analytes increased with increasing the sorbent amount from 10 to 70 mg, and almost kept constant afterward (see Fig. 4(a)). Thus, 70 mg of Fe@SiO$_2$@PANI was selected for further experiments.

3.2.2 Vortex adsorption time

MSPE is an equilibrium-based extraction method so that the adsorption time is optimized to ensure quantitative retention of the target analytes along with a minimal time required for sample extraction processing. In the present work, vortex agitation was applied to enhance the dispersion of the magnetic sorbents into the aqueous sample solution. The vortex time during adsorption process was tested from 1 to 5 min using the sorbent amount of 70 mg, sample volume of 10 mL, 1 mL acetonitrile as desorption solvent, and desorption time of 1 min. It could be observed that the peak area of the analytes did not changed versus vortex time (see Fig. S4). Therefore, 2 min was sufficient to perform the adsorption process.

3.2.3 Desorption time

The influence of desorption time was studied in the range of 0.5–5 min while keeping other conditions constant as follows: 70 mg Fe@SiO_2@PANI sorbent, sample volume of 10 mL, vortex adsorption time of 2 min, and 1 mL acetonitrile as desorption solvent. It illustrated that fast desorption of the analytes from the sorbent could be achieved and the desorption process was maximized for all target analytes at 0.5 min, and then remained constant (see Fig. S5). Therefore, 0.5 min vortex agitation was enough for desorption of the analytes from the synthesized sorbent.

3.2.4 Type of desorption solvent

To select the best desorption solvent for eluting the analytes from the sorbent, several organic solvents including methanol, acetonitrile and acetone, were compared. The other experimental conditions were as follows: 70 mg Fe@SiO_2@PANI sorbent, 10 mL sample volume, vortex adsorption time of 2 min, desorption solvent volume of 1 mL, and vortex desorption time of 0.5 min. As it is depicted in Fig. 4(b), the best elution of the target analytes was attained using acetonitile which was selected in this experiment.

3.2.5 Desorption solvent volume

The volume of desorption solvent also affects the sensitivity of the extraction method, as it determines the maximum enrichment factor that can be achieved for the analytes of interest. The effect of volume of acetonitrile, as the selected desorption solvent, was studied between 0.25 to 5 mL using the Fe@SiO_2@PANI sorbent amount of 70 mg, sample volume of 10 mL, vortex adsorption time of 2 min, and vortex desorption time of 0.5 min. The experimental results are summarized in Fig. 4(c). It could be seen that 0.5 mL acetonitrile is sufficient for obtaining satisfactory desorption for all analytes. Using larger desorption solvent volumes, the peak area of analytes decreased due to the dilution effect. Therefore, 0.5 mL acetonitrile was selected for extraction of the analytes from the sorbent in this work.

3.2.6 Sample volume

In order to obtain high enrichment, a sample volume was optimized. In this work, the aqueous sample solution of 10, 15, 20, 25 and 30 mL were subjected to extracted under the general procedure of using the Fe@SiO_2@PANI sorbent amount of 70 mg, vortex adsorption time of 2 min, 0.5 mL acetonitrile as desorption solvent and vortex desorption time of 0.5 min. The results are shown in Fig. 4(d). It was found that the extraction recovery of the analytes in term of peak areas increased when the sample volume increase from 10 to 25 mL, and slightly decreased with further increase of sample volume to 30 mL. This could be due to the more difficult migration of the analytes from the sample to the sorbent surface in higher volume unit of the sample. Thus, 25 mL sample solution was selected for the subsequent experiments.

3.3 Analytical performance

Under the optimum conditions, the analytical performance of the proposed MSPE method was evaluated, and the results are summarized in Table 1. The calibration curves were obtained by extracting the mixed standard solutions of eight phenolic compounds ranging from 0.020–10.000 $\mu g\ mL^{-1}$. Linearity was achieved with the correlation coefficients (r^2) in the range of 0.9926–0.9989. The limits of detection (LODs) and limit of quantifications (LOQs), which were based on signal to noise ratios of 3 and 10, respectively, were 18–120 $\mu g\ L^{-1}$ and 44–300 $\mu g\ L^{-1}$, respectively. The precision of the proposed method was evaluated by analyzing the mixed standard solutions of phenolic compounds, at concentration of 0.5 $\mu g\ mL^{-1}$ each, in one day and day-to-day. It was observed that the relative standard deviations (RSDs) of the peak area were less than 9.7% and 10.8% for intra-day (n=5) and inter-day (n=5×3), respectively. The practical demonstration of the enrichment attained by the proposed method is presented as chromatograms in Fig. 5.

Retention mechanism of the studied phenolic pollutants on Fe@SiO$_2$@PANI sorbent was expected through different kinds of interactions based on the structural features of PANI, including hydrophobicity, π-conjugated structure and polar groups. PANI can form hydrogen bond with hydroxyl group of phenols.[43–44] An electrostatic interaction between nitro group of the phenol derivatives and PANI could also be formed, which can be explained that nitrophenol rings with the positive charges can bind with polyaniline rings acting as negative charges through electrostatic interaction.[45] In addition, aromatic groups of phenol and PANI can afford abundant π-π interaction.[46]

3.4 Application to real samples

The proposed MSPE method using as-synthesized Fe@SiO$_2$@PANI as sorbent coupled with HPLC-PDA was applied to the determination of environmental water samples (collected from different rivers and reservoirs). Since the concentration of phenol pollutants in the studied samples were lower than the detection limits of the method, recovery testing was carried out to determine the accuracy of the method, by spiking real water samples with the phenolic compound standards at 2 concentration levels. The satisfactory recoveries of eight phenolic compounds were in the range of 83.4–118.5%, as summarized in Table S1.

3.5 Comparison of the Fe@SiO$_2$@PANI based MSPE with other methods

To demonstrate the potential use of the Fe@SiO$_2$@PANI as sorbent in the MSPE method, the proposed procedure was compared with some previously reported methods for the determination of phenol compounds in various sample matrices. The experimental conditions and analytical results obtained by different sample preparation procedures are listed in Table

2. The proposed method is reliable for a variety of phenol compounds. Comparing with the previous methods using PANI-based materials, the sensitivity in terms of LODs and LOQs is comparable to those obtained by the MSPE using PANI/SiO_2/Ni NPs as sorbent,[47] however, the proposed method offers lower consumption of sample volume with simple extraction conditions compared with previous report.[31] In addition, a shorter extraction time (time consumption in both adsorption and desorption processes), was another advantage of this work when compared to those reported by others.[7,31,47] Considering the Fe@SiO_2@PANI sorbent proposed in this work, it can be synthesized easily with facile condition using a simple process, and no hydrothermal or complicated equipment is required. The advantages of the developed MSPE process, together with it simple and facile preparation, give the Fe@SiO_2@PANI a choice of sorbent for pretreatment of phenol pollutants in various sample matrices.

4. Conclusion

An efficient Fe@SiO_2@PANI magnetic sorbent was successfully prepared by simple stepwise process including sol-gel followed by oxidative polymerization methods. This synthesized sorbent was characterized and applied as sorbent for development of MSPE procedure for the determination of eight phenolic pollutants. The optimum conditions for MSPE coupled with HPLC-PDA were investigated. The versatile zerovalent iron-silica particles coated with PANI exhibit multiple interactions for the target analytes showing potential feature for extraction of the phenolic pollutants from environmental water matrix. The proposed method offers good extraction recovery, high precision and accuracy with possibility of fast and simple extraction process.

Conflicts of interest

There are no conflicts to declare.

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Table 1 Analytical features of the proposed MSPE method

Analyte	Linear range (μg mL^{-1})	R^2	LOD (μg mL^{-1})	LOQ (μg mL^{-1})	RSD (%)	
					Intraday (n=5)	Interday (n=5×3)
Ph	0.020–10.000	0.9926	0.018	0.060	5.5	7.5
4NP	0.020–10.000	0.9979	0.020	0.044	9.7	7.8
2CP	0.060–10.000	0.9984	0.060	0.160	6.2	6.7
24DNP	0.030–10.000	0.9980	0.028	0.300	8.2	7.9
24DMP	0.040–10.000	0.9980	0.036	0.100	6.6	10.6
4C3MP	0.030–10.000	0.9989	0.030	0.177	5.6	6.1
24DCP	0.060–10.000	0.9959	0.060	0.182	8.2	10.8
246TCP	0.120–10.000	0.9950	0.120	0.216	5.6	5.1

Table 2 Comparison of the proposed MSPE with other reported methods

Method[Ref.]	Analytes	Sample matrix	Extraction condition	Analytical technique	Analytical performance
DMSPE[47]	2-NP, Ph, p-cresol, carvacrol, 2-tert-butylphenol, mequinol, 4-CP, resorcinol	Water	Sorbent: 20 mg PANI/SiO_2/Ni NPs Sample volume: 5 mL Adsorption: 30 s sonication + 5 min vortex Eluent: 40 μL ACN Desorption: 11.5 min sonication	GC-FID	Linear range: 0.02–100 mg L^{-1} LODs: 10–23 μg L^{-1} LOQs: 33–77 μg L^{-1} %R: 96–105 RSDs: < 4%
MSPE[31]	Bisphenol A, tetrabromobisphenol A, 4-nonylphenol	Water	Sorbent: 60 mg PANI@SiO_2@Fe Sample volume: 60 mL Adsorption: 60 min shaking on a temperature-controlled water-bath Eluent: 7.5 mL MeOH (dried with N_2 at 40°C and redissolved with 200 μL MeOH)	HPLC-UV	Linear range: 0.05–300 μg L^{-1} LODs: 0.009–0.073 μg L^{-1} %R: 92.9–98.9 RSDs: < 3.73%
SB-μ-SPE[7]	24DCP, 23DCP, 26DCP, 246TCP,	Wastewater	Sorbent: 20 mg 4-phenyl-1,2,3-triazole functionalized SBA-15 sealed inside a PP bag	GC-MS	Linear range: 1–600 μg L^{-1} LODs: 0.23–0.37 μg L^{-1} %R: 88.5–99.2

Method$^{\text{Ref.}}$	Analytes	Sample matrix	Extraction condition	Analytical technique	Analytical performance
	26DTB4MP, 4tOP, 2B4CP		Adsorption: 15 min stirring Eluent: 300 µL ethyl acetate Desorption: 20 min sonication		RSDs: 2.3–7.5 %
Online MMD-SPE[3]	4NP, 2CP, 24DNP, 2NP, 24DMP, 4C3MP, 24DCP	Groundwater	Sorbent: polyvinylidene fluoride matrix disks containing entrapped UiO-66-NH_2 MOFs Sample volume: 1.5 mL Eluent: 0.3 mL acetone Desorption flow rate: 0.5 mL min^{-1}	HPLC-DAD	Linear range: 0.5–500 µg L^{-1} LODs: 0.1–0.2 µg L^{-1} %R: 90–98 RSDs: 3.9–5.7 % (intraday), 4.7–5.7 % (interday)
In-syringe extraction[5]	Ph, 4NP, 2NP, 3MP, 4C3MP, 24DCP, 2M46DNP, 246TCP, PCP	River water	Sorbent: 5 mg graphene aerosols filled in 2-mL syringe Sample volume: 40 mL Adsorption: 20 min Eluent: 200 µL ACN	HPLC-UV	Linear range: 0.05–20 µg L^{-1} LODs: 0.016–0.075 µg L^{-1} LOQs: 0.053–0.250 µg L^{-1} %R: 96.3–102.4 RSDs: < 5.4 %

Method^Ref.	Analytes	Sample matrix	Extraction condition	Analytical technique	Analytical performance
VA-D-μ-SPE[4]	Ph, 4NP, 24DNP, 2NP, 4C3MP, 24DCP, 2M46DNP, 246TCP	Water	Sorbent: 30 mg NH_2-MIL-53(Al) MOF Sample volume: 10 mL Adsorption: 10 s vortex Eluent: 1.5 mL ACN-HOAc (9.5:0.5 v/v) Desorption: 10 s vortex	HPLC-DAD	Linear range: 0.0015–10 mg L^{-1} LODs: 0.4–13.3 μg L^{-1} LOQs: 1.3–51.9 μg L^{-1} %R: 72.3–111.4 RSDs: < 10.4%
MSPE^This study	Ph, 4NP, 2CP, 24DNP, 24DMP, 4C3MP, 24DCP, 246TCP	Water	Sorbent: 70 mg Fe@SiO_2@PANI Sample volume: 10 mL Adsorption: 2 min vortex Eluent: 0.5 mL ACN Desorption: 30 s vortex	HPLC-DAD	Linear range: 0.02–10 mg L^{-1} LODs: 18–120 μg L^{-1} LOQs: 44–300 μg L^{-1} %R: 83.4–118.5 RSDs: < 10.8 %

DMSPE: dispersive micro-solid-phase extraction; MSPE: magnetic solid phase extraction; SB-μ-SPE: stir bar-supported micro-solid-phase extraction; MMD-SPE: mixed-matrix disks solid-phase extraction

List of Figure Captions

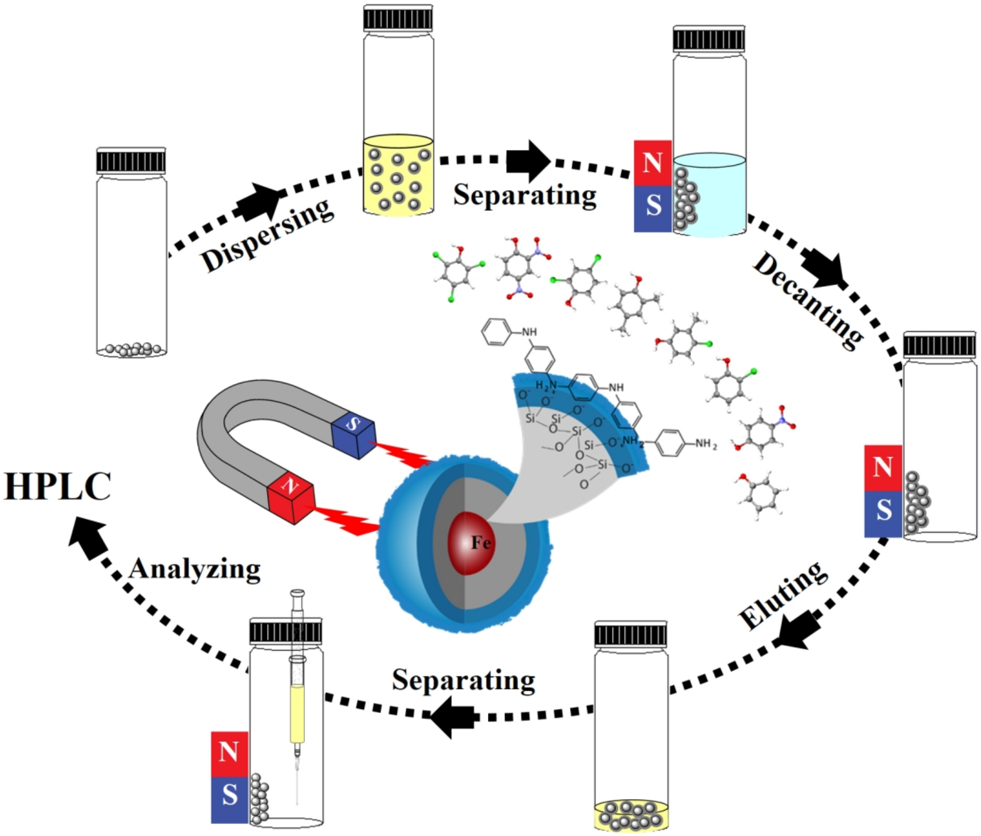
Fig. 1 Schematic diagram of the proposed MSPE procedure

Fig. 2 SEM images of (a) as-prepared Fe, (b) Fe@SiO2, (c) Fe@SiO_2@PANI and (d) EDS spectra of Fe@SiO_2. The inset histograms show size distribution of each material.

Fig. 3 TEM images of (a), (b) Fe@SiO_2 and (c), (d) Fe@SiO_2@PANI

Fig. 4 Optimization of MSPE conditions (a) sorbent amount, (b) type of desorption solvent, (c) volume of desorption solvent, and (d) sample volume

Fig. 5 Chromatograms of phenolic pollutants obtained by direct HPLC and after concentrated by MSPE procedure


Dispersing
Separating
N
S
Decanting
N
S
Eluting
Separating
N
S
Analyzing
HPLC
S
N
Fe
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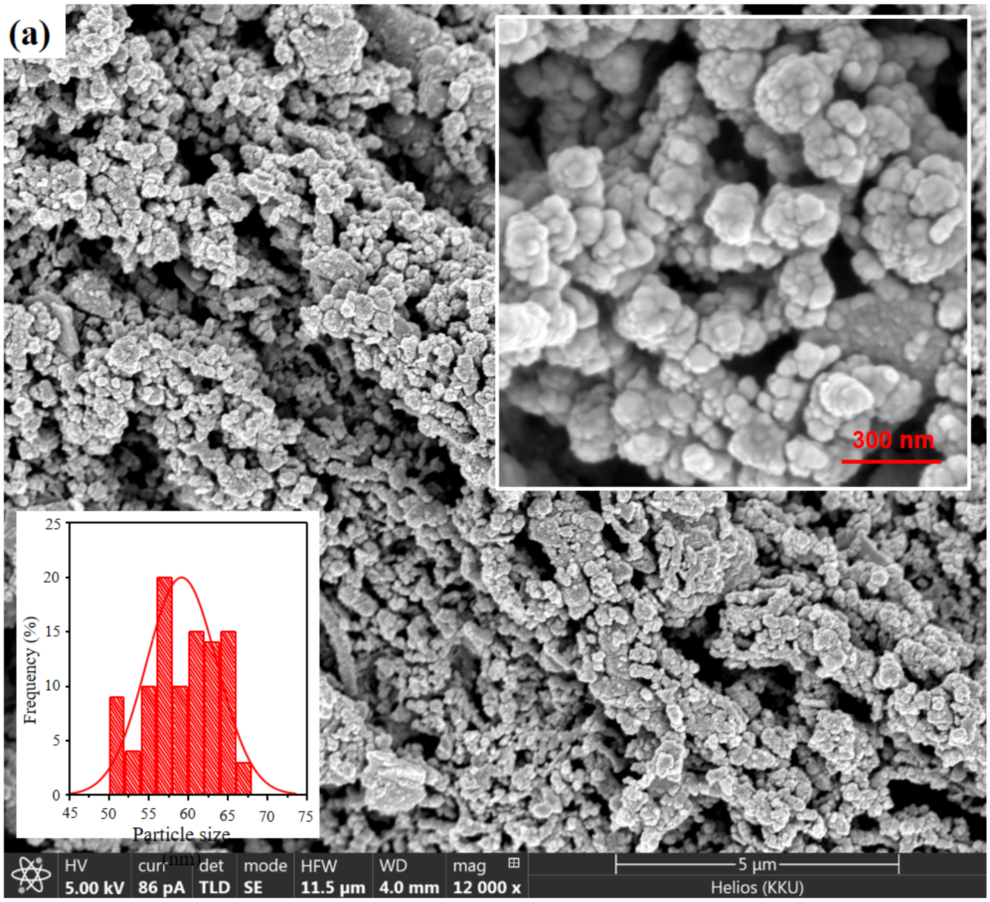
NH
NH₂
NH₂
Si
O

Fig.1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300 nm
Frequency (%)
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20
15
10
5
0
45
50
55
60
65
70
75
Particle size (nm)
HV 5.00 kV
curr 86 pA
det TLD
mode SE
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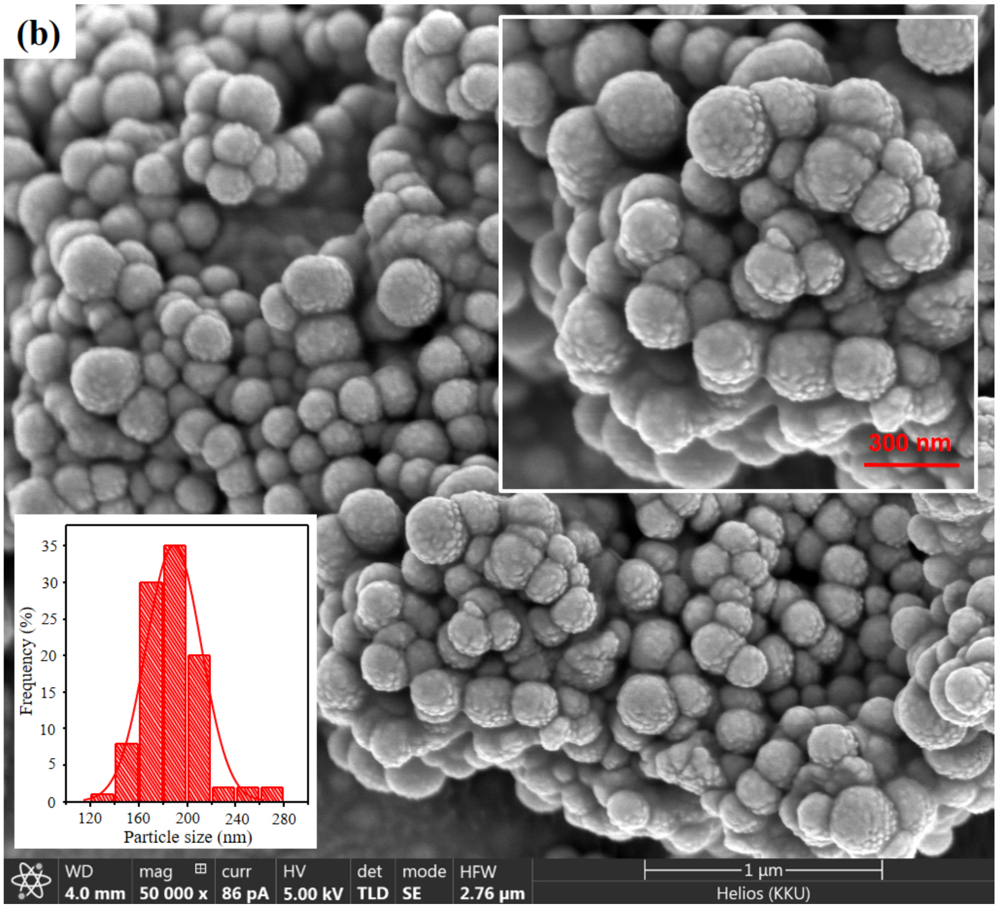
WD 4.0 mm
mag 12 000 x
5 µm
Helios (KKU)

Fig.2(a)


(b)
300 nm
Frequency (%)
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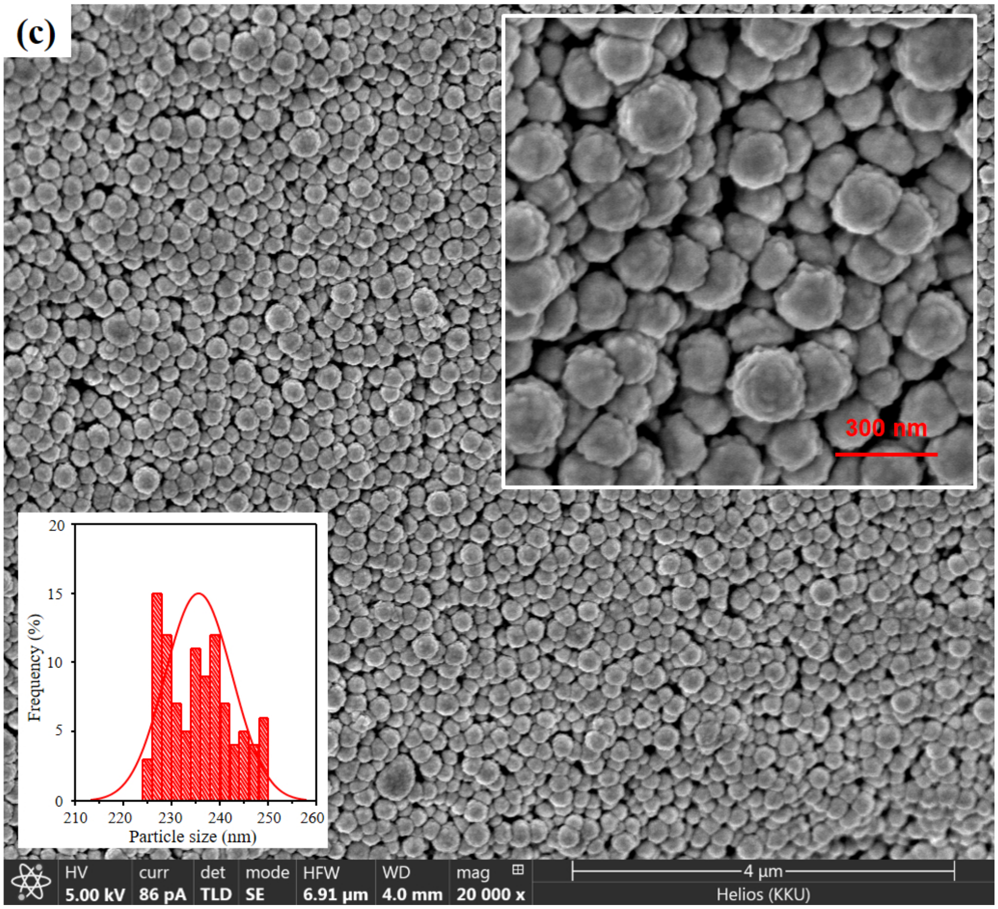
30
25
20
15
10
5
0
120
160
200
240
280
Particle size (nm)
WD 4.0 mm
mag 50 000 x
curr 86 pA
HV 5.00 kV
det TLD
mode SE
HFW 2.76 µm
1 µm
Helios (KKU)

Fig.2(b)


(c)
300 nm
20
15
10
5
0
Frequency (%)
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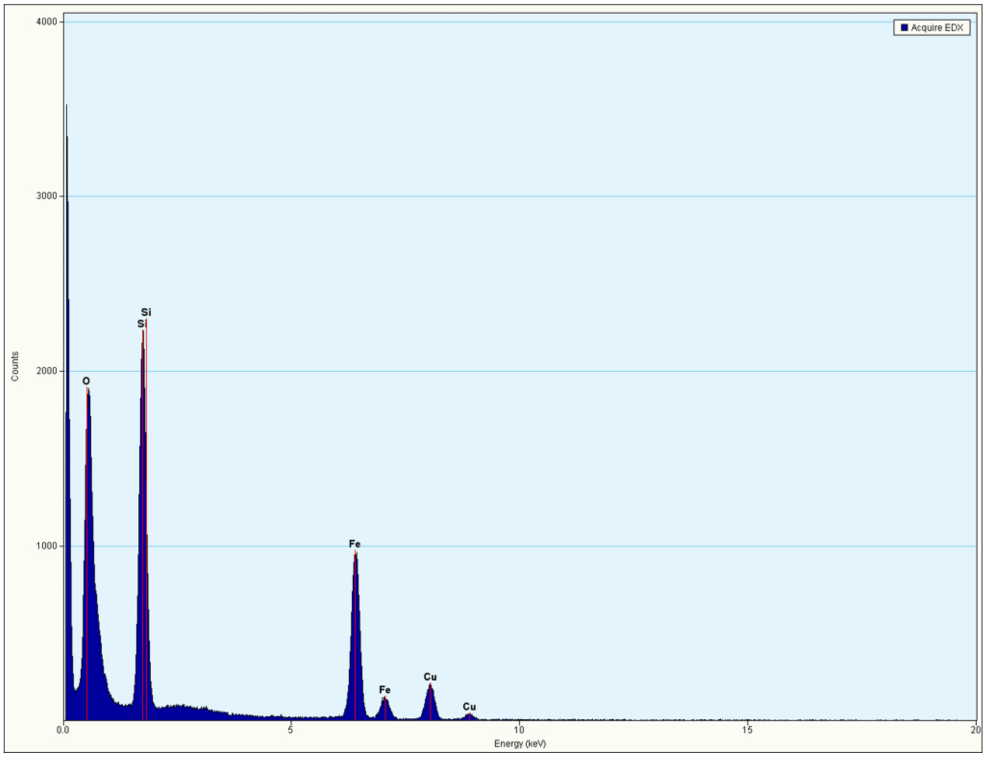
220
230
240
250
260
Particle size (nm)
HV
5.00 kV
curr
86 pA
det
TLD
mode
SE
HFW
6.91 µm
WD
4.0 mm
mag
20 000 x
4 µm
Helios (KKU)

Fig.2(c)

(d)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4000
3000
2000
1000
Counts
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Si
Si
Fe
Fe
Cu
Cu
0.0
5
10
15
20
Energy (keV)

Fig.2(d)

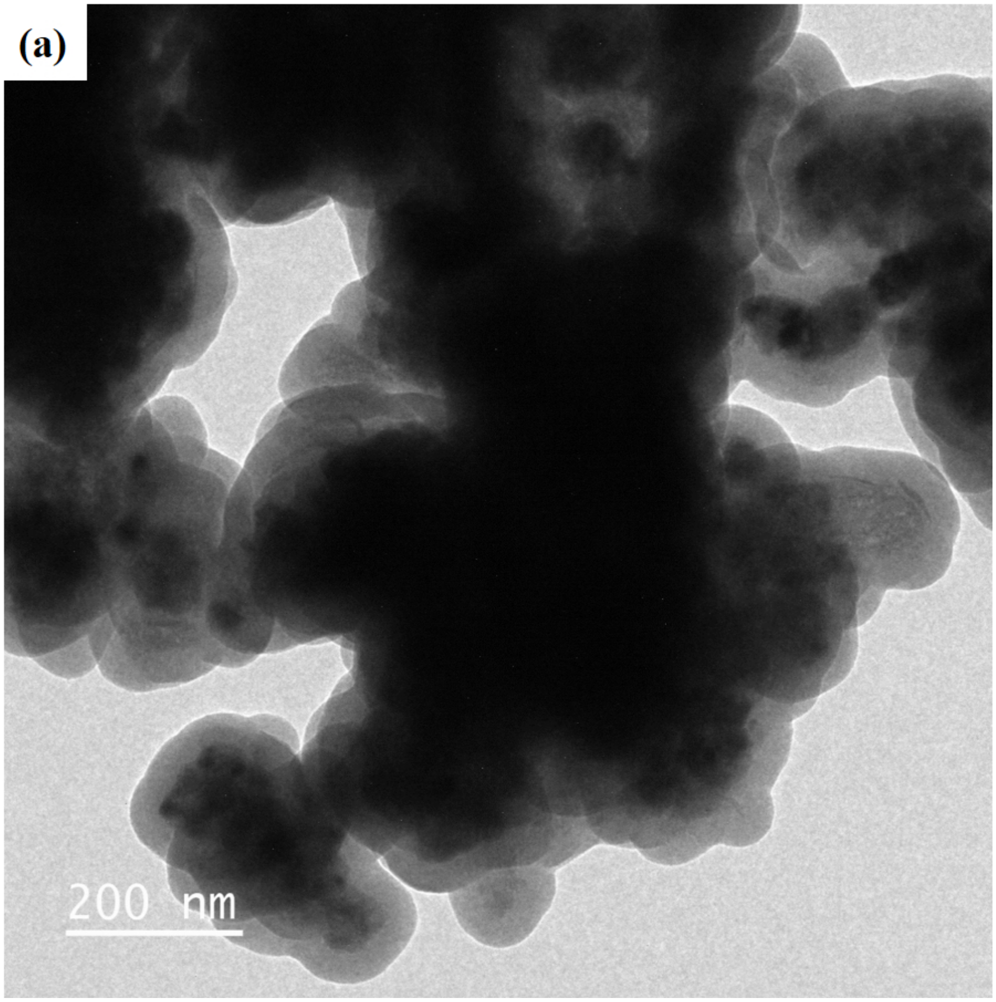


Fig.3(a)

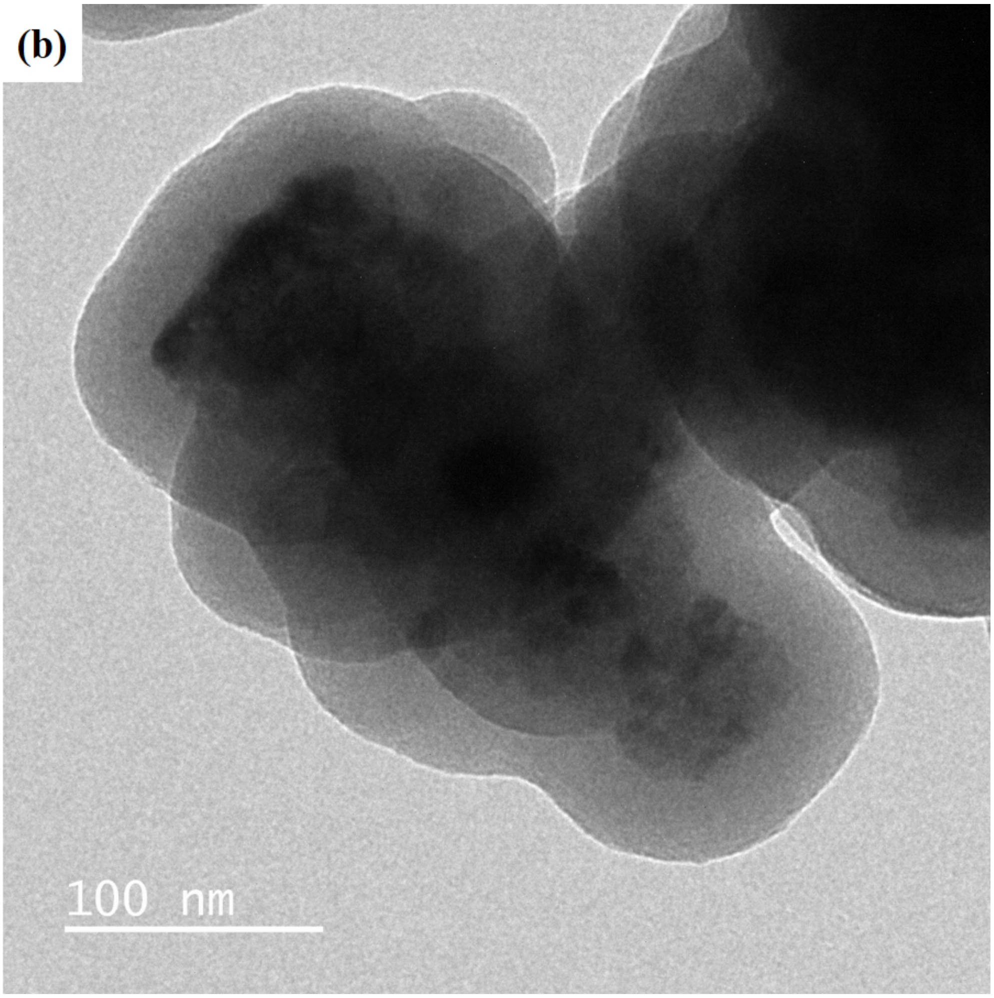
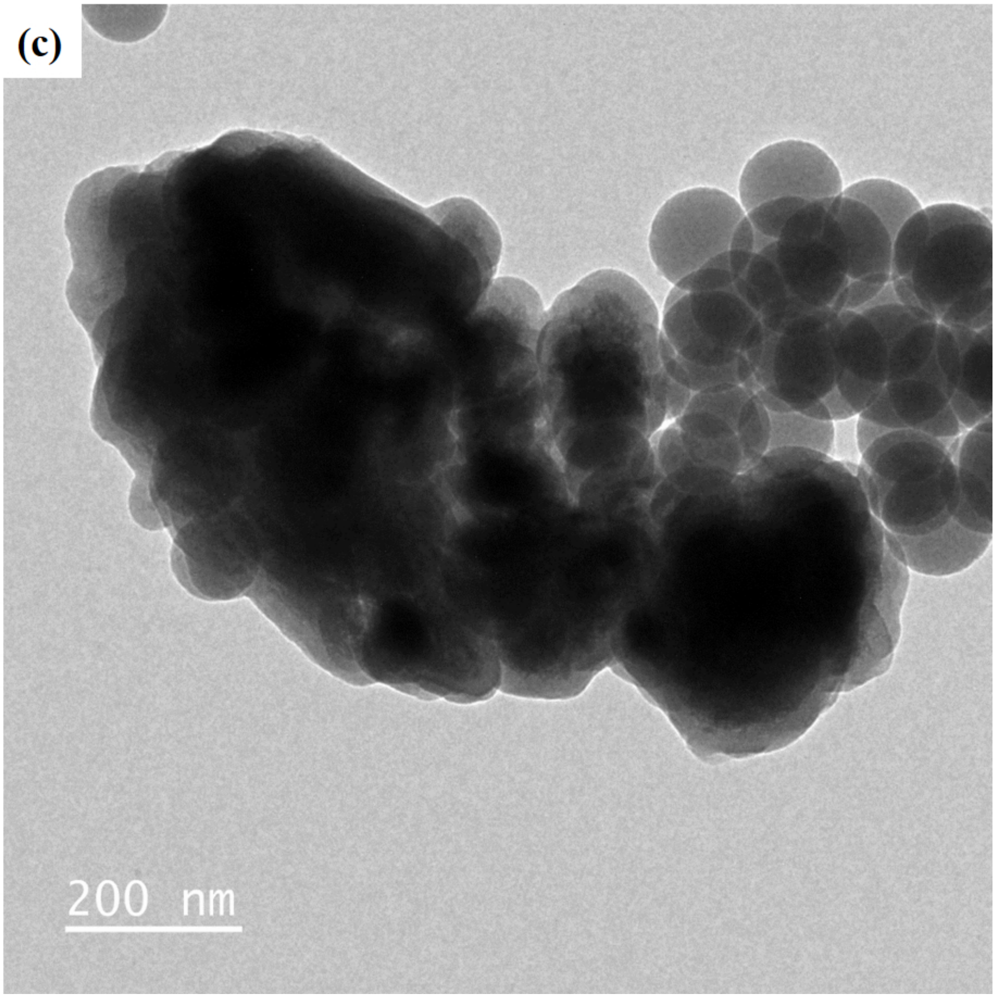


Fig.3(b)



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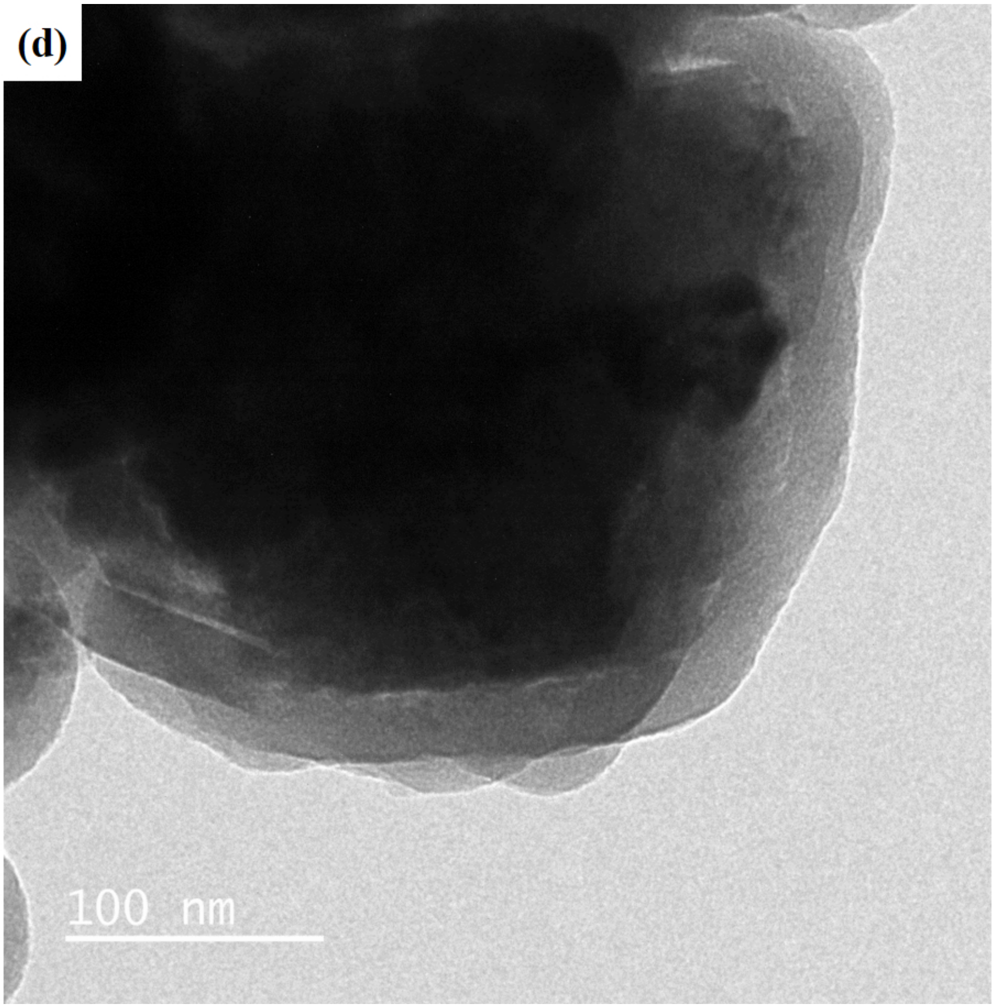

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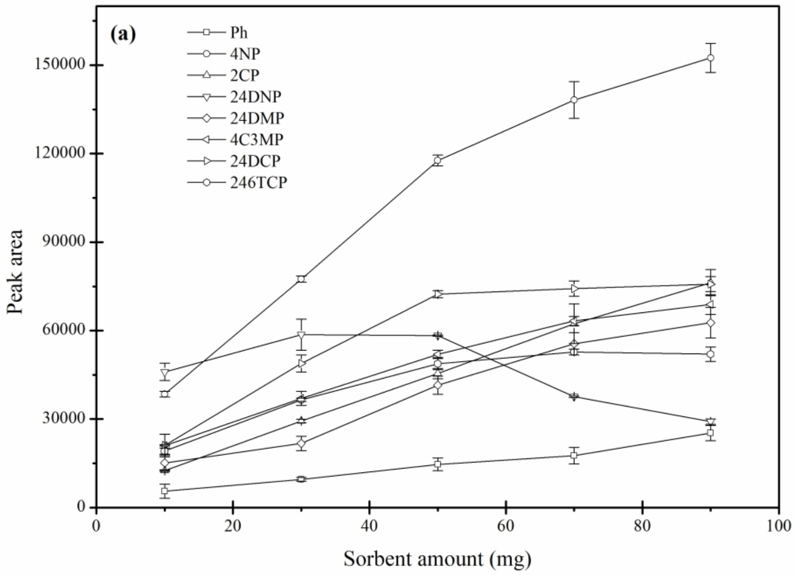

Fig.4(a)

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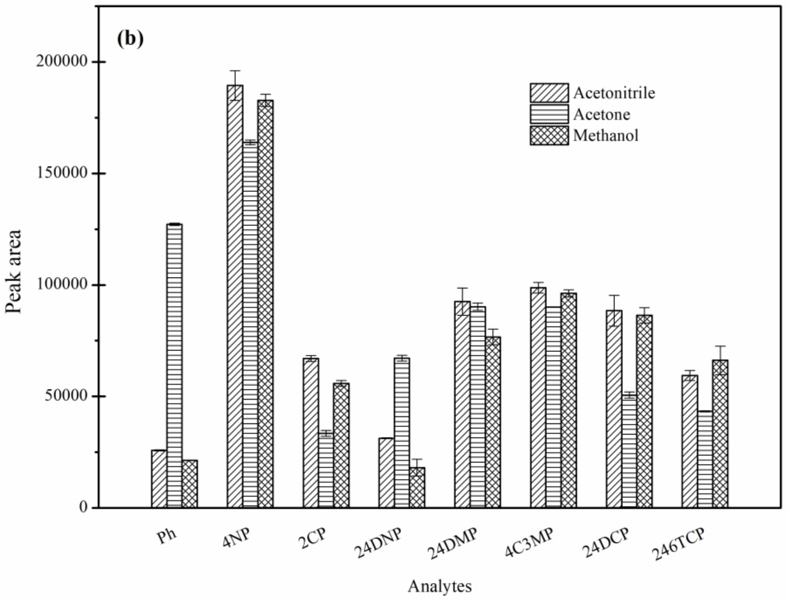

Fig.4(b)

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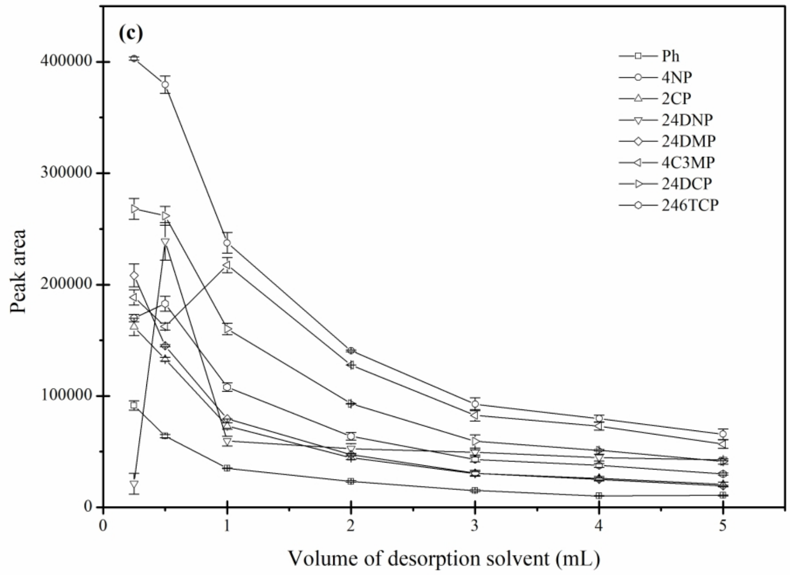

Fig.4(c)

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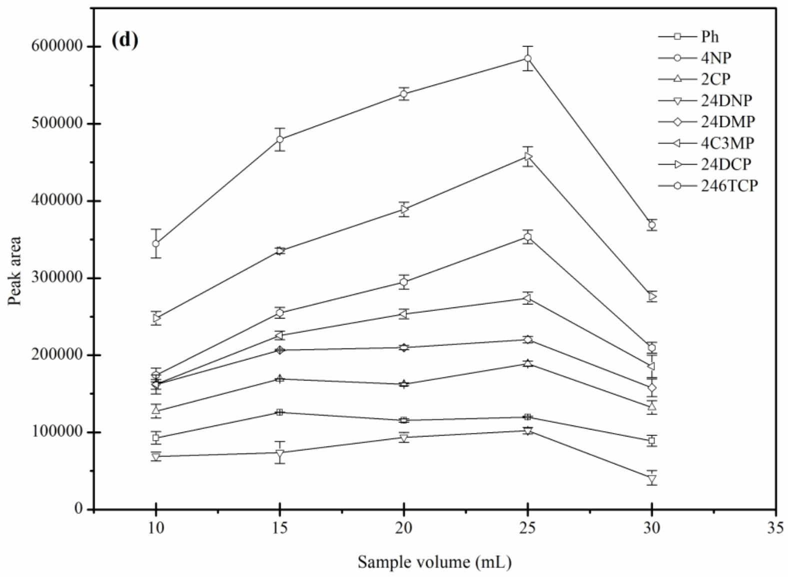
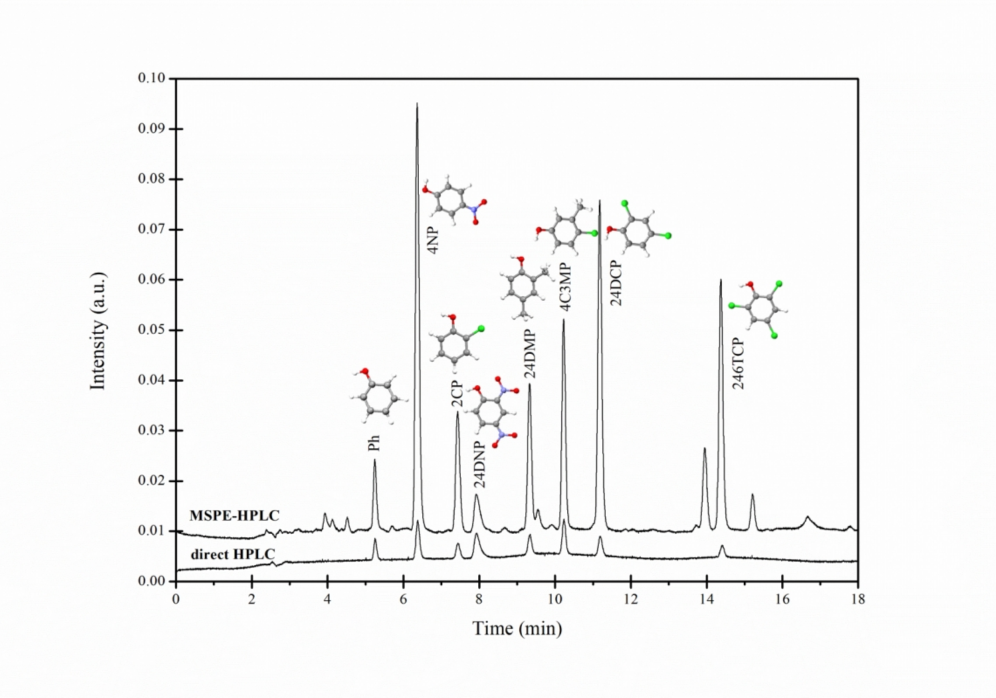


Fig.4(d)

288x201mm (300 x 300 DPI)



0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
Intensity (a.u.)
Ph
4NP
2CP
24DNP
24DMP
4C3MP
24DCP
246TCP
MSPE-HPLC
direct HPLC
0
2
4
6
8
10
12
14
16
18
Time (min)

Fig.5

Supplementary Information

Magnetic solid phase extraction of phenolic pollutants in water samples using a facile synthesized polyaniline coated zerovalent iron-silica as an efficient sorbent

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E-mail address: rodjbu@kku.ac.th

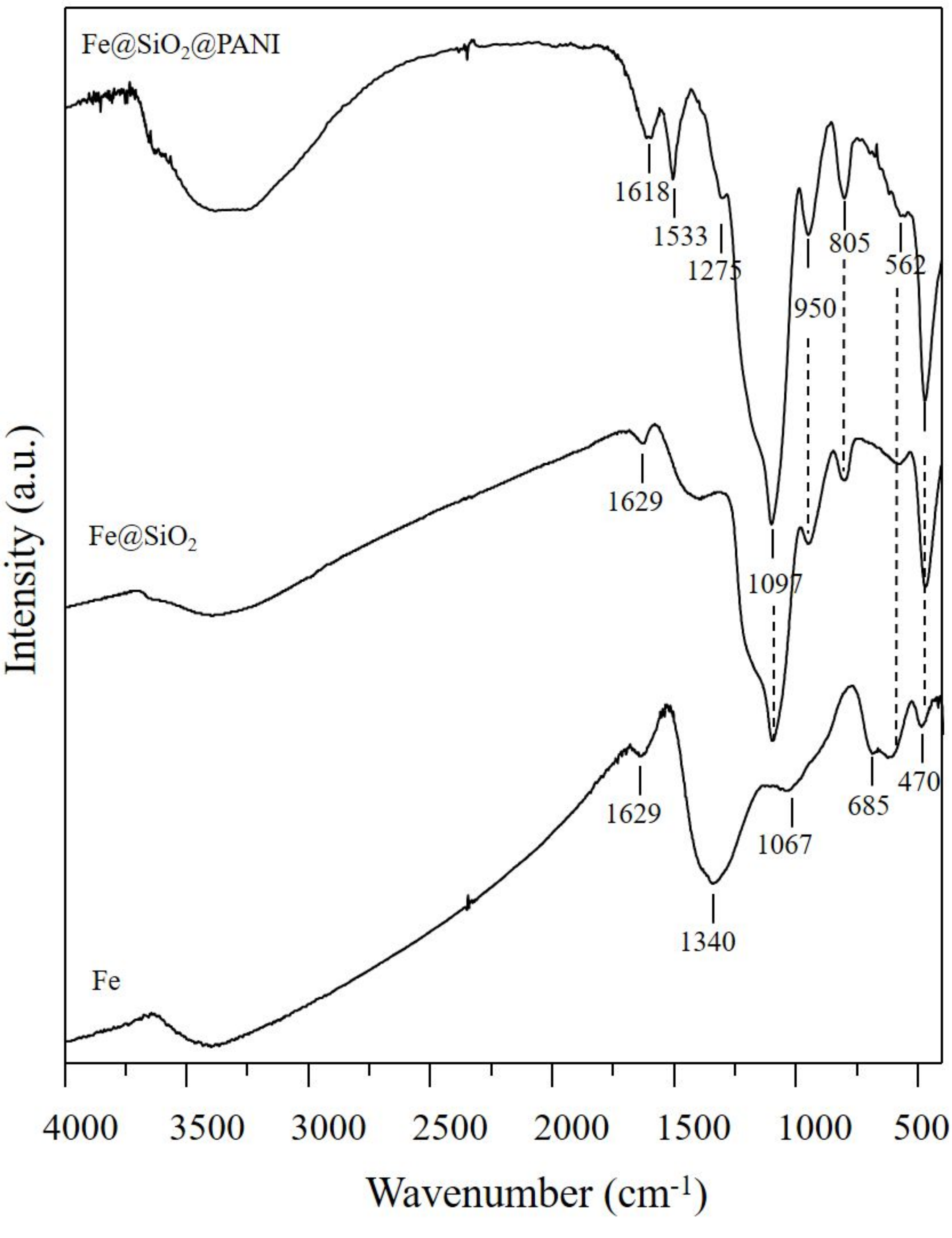

Fig. S1 FTIR spectra of the synthesized Fe, Fe@SiO$_2$ and Fe@SiO$_2$@PANI

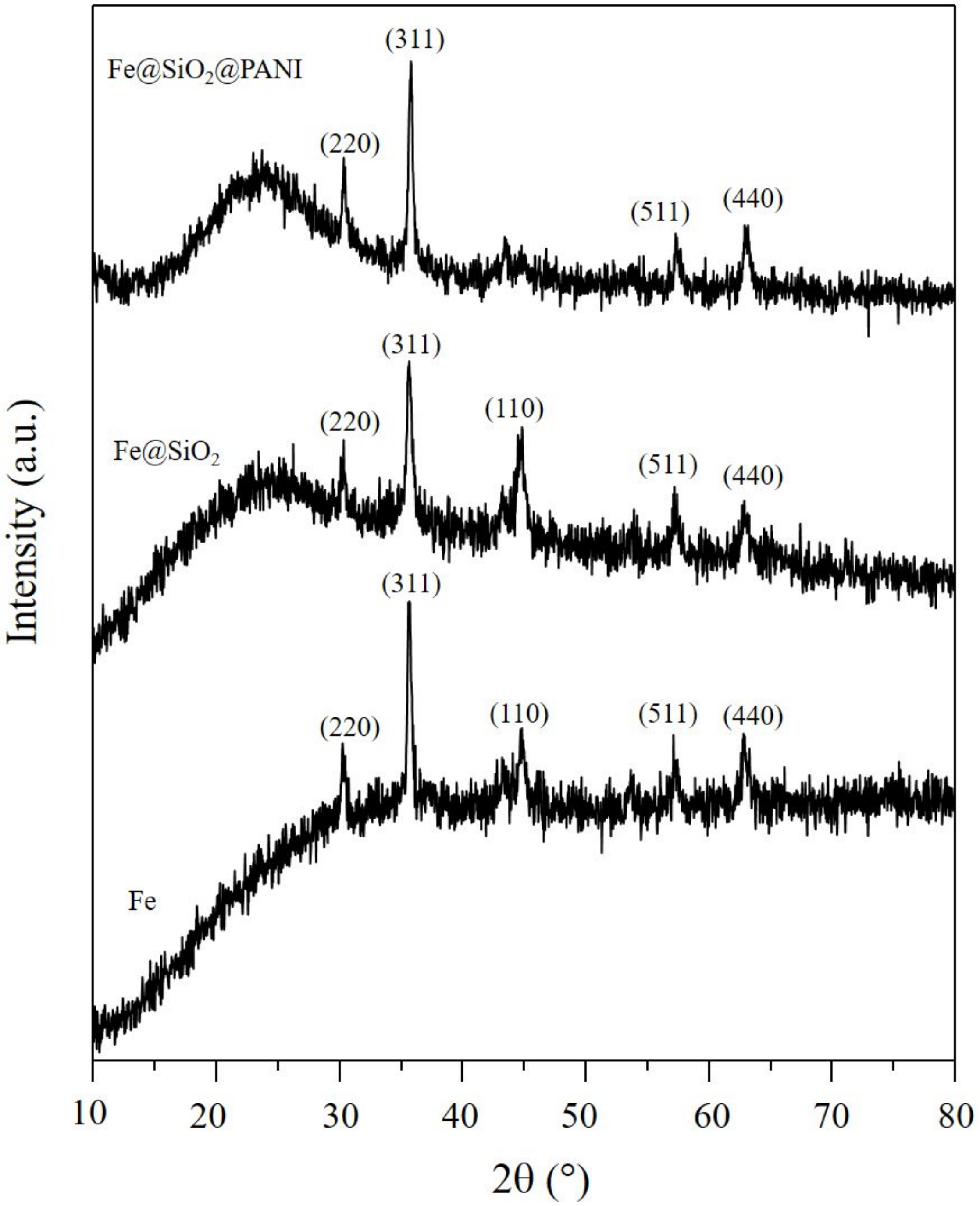

Fig. S2 XRD patterns of the synthesized Fe, Fe@SiO_2 and Fe@SiO_2@PANI

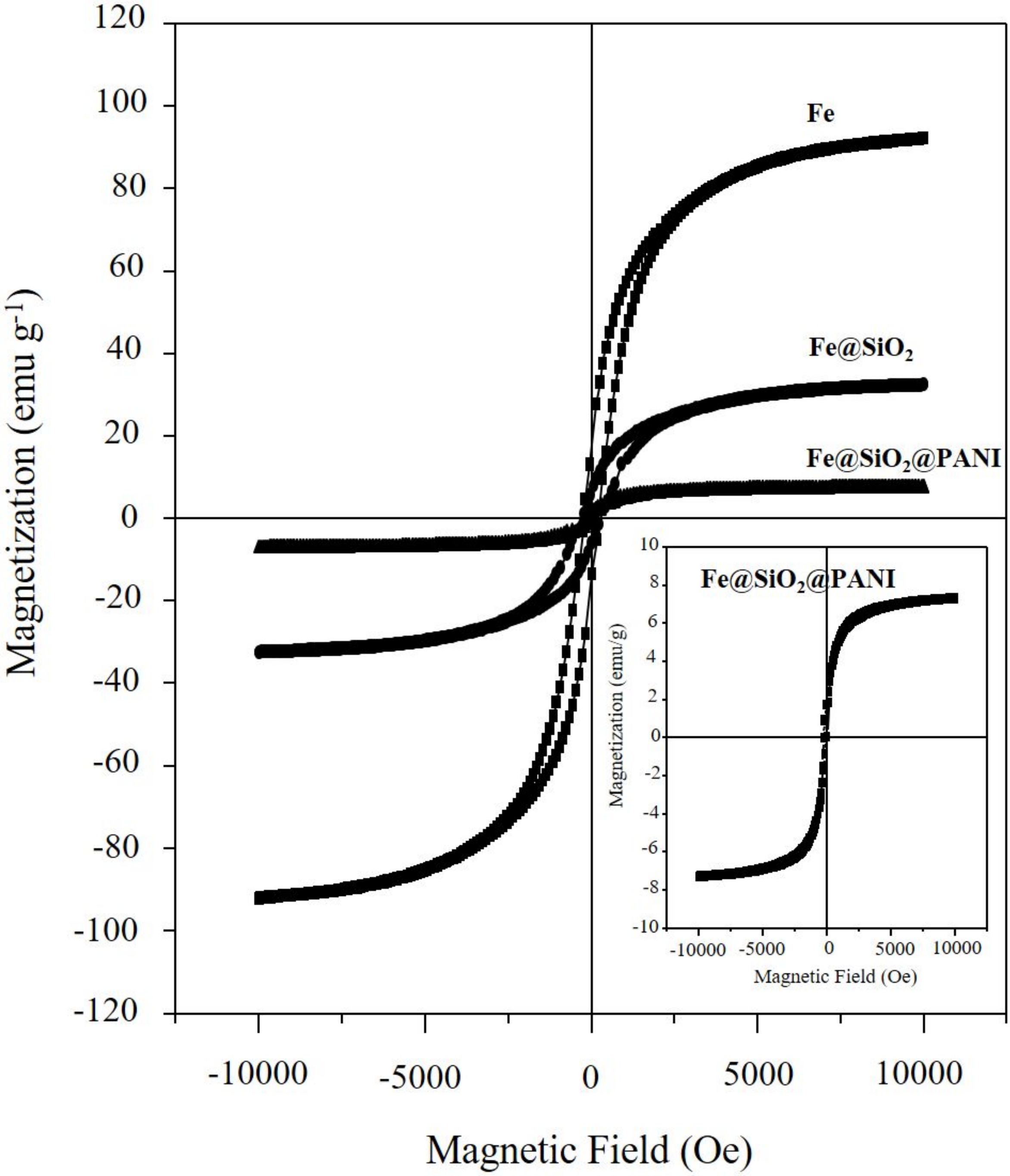

Fig. S3 M-H plot of the synthesized Fe, Fe@SiO_2 and Fe@SiO_2@PANI

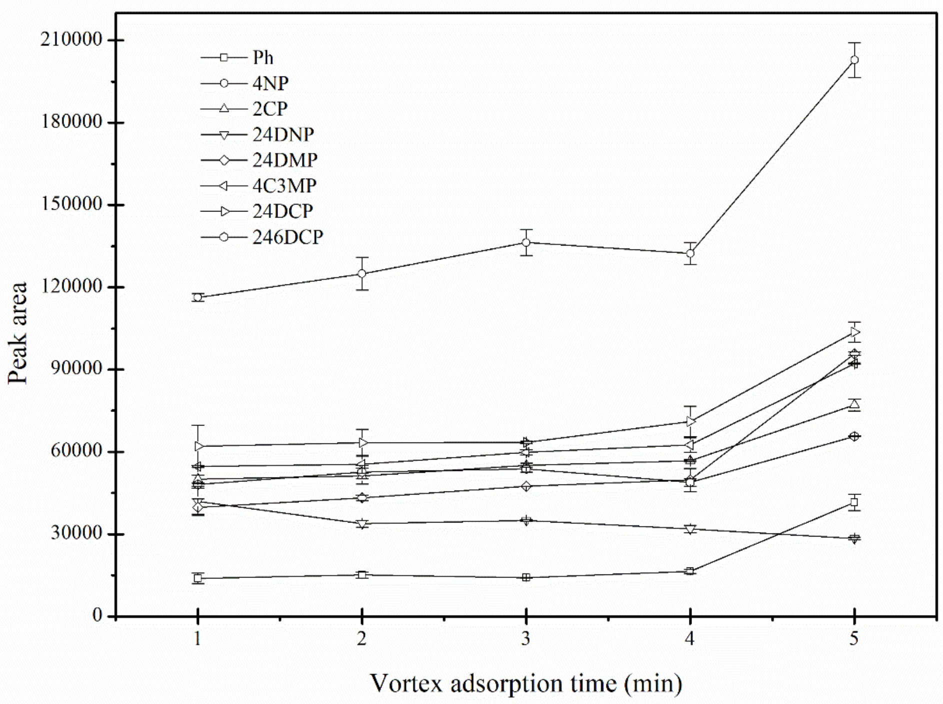

Fig. S4 Effect of vortex adsorption time

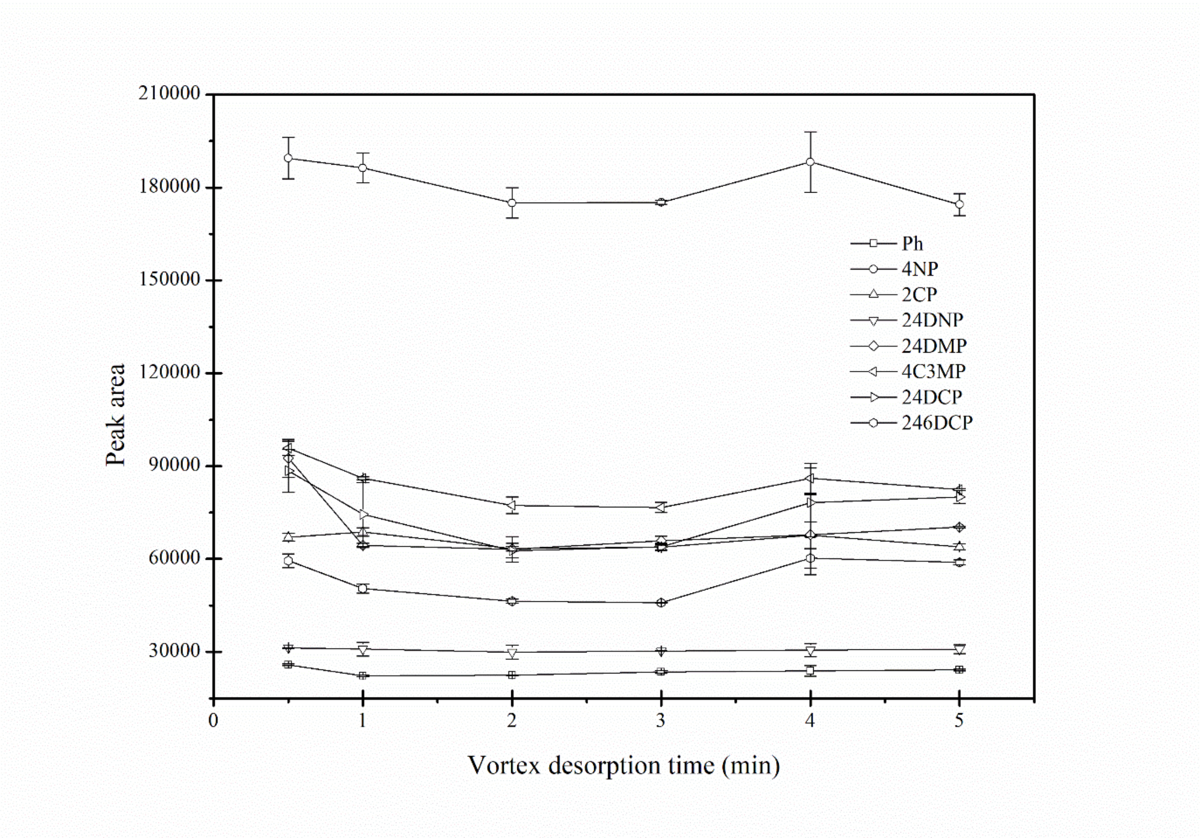

Fig. S5 Effect of vortex desorption time

Table S1 Determination of phenol residues in real samples

Sample	Ph	4NP	2CP	24DNP	24DMP	4C3MP	24DCP	246TCP
Chi river	–	–	–	–	–	–	–	–
%R1 (%RSD)	97.6 (10.7)	87.7 (4.3)	96.9 (9.6)	93.2 (11.1)	94.9 (3.0)	87.4 (2.9)	92.1 (7.5)	93.0 (1.0)
%R2 (%RSD)	98.2 (11.5)	95.7 (1.3)	108.8 (1.5)	99.6 (1.9)	102.0 (8.6)	107.6 (0.6)	86.7 (1.7)	85.9 (8.6)
Khong river	–	–	–	–	–	–	–	–
%R1 (%RSD)	101.9 (5.6)	90.3 (0.8)	97.7 (4.0)	97.0 (3.0)	96.0 (2.9)	101.2 (4.0)	90.0 (8.1)	96.2 (4.0)
%R2 (%RSD)	103.3 (1.6)	93.9 (2.5)	107.9 (1.2)	101.1 (4.2)	108.5 (2.6)	112.7 (3.3)	94.2 (5.8)	94.6 (1.6)
Ubon Ratana dam 1	–	–	–	–	–	–	–	–
%R1 (%RSD)	83.9 (0.0)	98.6 (8.9)	97.6 (6.5)	110.3 (5.2)	96.6 (4.1)	89.6 (8.1)	85.3 (3.4)	117.7 (2.8)
%R2 (%RSD)	112.6 (0.0)	102.0 (2.9)	118.5 (1.5)	103.8 (2.1)	96.3 (2.7)	105.4 (0.3)	91.9 (0.8)	100.8 (1.2)
Lam Pao dam	–	–	–	–	–	–	–	–
%R1 (%RSD)	93.1 (0.0)	87.2 (3.4)	86.4 (0.2)	103.2 (2.9)	102.4 (0.4)	84.8 (7.8)	94.5 (2.5)	88.0 (1.4)
%R2 (%RSD)	88.9 (5.3)	107.2 (0.7)	113.5 (1.2)	103.6 (3.9)	105.8 (4.2)	112.7 (11.7)	105.8 (3.3)	105.5 (2.5)
Kaen Nakhon lake	–	–	–	–	–	–	–	–
%R1 (%RSD)	99.2 (6.0)	91.5 (1.8)	90.2 (3.6)	101.3 (4.4)	93.3 (3.2)	93.0 (5.5)	95.4 (4.1)	107.4 (2.2)
%R2 (%RSD)	92.6 (6.8)	96.6 (0.3)	109.6 (6.4)	85.2 (0.3)	102.5 (7.1)	115.6 (1.6)	102.5 (1.6)	110.0 (8.4)

Sample	Ph	4NP	2CP	24DNP	24DMP	4C3MP	24DCP	246TCP
Nong Han lake	–	–	–	–	–	–	–	–
%R1 (%RSD)	102.8 (8.5)	100.6 (0.5)	96.0 (5.9)	103.2 (8.7)	91.5 (7.6)	99.1 (6.4)	88.2 (3.0)	108.6 (1.1)
%R2 (%RSD)	98.7 (2.0)	104.9 (2.5)	112.8 (2.8)	95.3 (3.7)	95.5 (1.4)	113.0 (1.8)	105.0 (2.8)	103.8 (1.6)
Nam Pong river	–	–	–	–	–	–	–	–
%R2 (%RSD)	104.0 (11.2)	93.8 (3.7)	109.5 (8.8)	94.2 (10.3)	105.5 (2.6)	116.1 (4.6)	105.7 (2.7)	103.5 (7.5)
Ubon Ratana dam 1	–	–	–	–	–	–	–	–
%R2 (%RSD)	102.8 (1.5)	103.2 (4.4)	114.7 (6.4)	98.8 (2.6)	100.0 (7.6)	111.8 (9.7)	95.5 (10.6)	98.8 (4.4)
Kut Nam Sai lake 1	–	–	–	–	–	–	–	–
%R2 (%RSD)	112.0 (9.2)	104.9 (7.8)	114.8 (4.3)	112.0 (8.6)	103.2 (7.6)	109.6 (8.4)	105.3 (9.0)	93.4 (6.6)
Kut Nam Sai lake 1	–	–	–	–	–	–	–	–
%R2 (%RSD)	110.8 (5.8)	92.5 (1.5)	112.1 (5.7)	83.4 (8.5)	100.3 (8.6)	111.8 (6.5)	70.7 (0.9)	99.5 (2.8)

– Not detected refers to values below LODs

Spiked concentrations: R1; 0.1 μg mL^{-1} Ph, 2NP and 24DMP, 0.2 μg mL^{-1} 2CP, 4C3MP and 24DCP, 0.3 μg mL^{-1} 24DNP and 246TCP;

R2; 0.5 μg mL^{-1} Ph, 2NP and 24DMP, 1.0 μg mL^{-1} 2CP, 4C3MP and 24DCP, 1.5 μg mL^{-1} 24DNP and 246TCP

Manuscript Details

Manuscript number	HELIYON_2019_3545
Title	Evaluation of metal-organic framework NH2-MIL-101(Fe) as an efficient sorbent for dispersive solid phase extraction of phenolic pollutants in environmental water samples
Article type	Original Research Article

Abstract

This work proposes an application of amine-functionalized metal-organic framework (NH2-MIL-101(Fe)) as sorbent for dispersive solid phase extraction (DSPE) of ten priority phenolic pollutants. The sorbent was simply synthesized under facile condition. The entire DSPE process was optimized by studying the effect of experimental parameters affecting the extraction recovery of the target analytes. The final extract was analyzed using high performance liquid chromatography with photodiode array detector. Under the optimum condition, the proposed procedure can be applied for wide linear calibration ranges between 1.25–5000 µg L-1 with the correlation coefficients of greater than 0.9900. The limits of detection (LODs) and limits of quantitation (LOQs) were in the ranges of 0.4–9.5 µg L-1 and 1.25–30 µg L-1, respectively. The precision evaluated in terms of the relative standard deviations (RSDs) were below 1.3% and 13.9% for retention time and peak area, respectively. High enrichment factors up to 99 were reached. The developed method has been successfully applied to determine phenol residues in environmental water samples. The satisfactory recoveries in the range of 68.4–114.4% were obtained. The results demonstrate that the NH2-MIL-101(Fe) material is promising sorbent in the DSPE of phenolic pollutants.

Keywords	Metal-organic framework; dispersive solid-phase extraction; phenol; HPLC
Taxonomy	Natural Sciences
Manuscript category	Chemistry
Manuscript region of origin	Asia Pacific
Corresponding Author	Rodjana Burakham
Corresponding Author's Institution	Khon Kaen University
Order of Authors	Tittaya Boontongto, Rodjana Burakham
Suggested reviewers	Mohammad Saraji, Veronica Pino, Manuela Schellin

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Supplementary Information_RB.docx [Supplementary Material]

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Dear Editor,

Please consider the manuscript entitled " **Evaluation of metal-organic framework NH_2-MIL-101(Fe) as an efficient sorbent for dispersive solid phase extraction of phenolic pollutants in environmental water samples**" for publication in **Heliyon**. This work presents the application of the amino-functionalized metal-organic framework NH_2-MIL-101(Fe) as sorbent material for dispersive solid phase extraction of ten priority phenolic pollutants. The sorbent was simply synthesized using a facile manner. The developed procedure exhibits good extraction efficiency for phenolic pollutants prior to their determination by HPLC-PDA, and has been successfully utilized to the determination of phenol residues in environmental water samples.

The manuscript has not been published as well as submitted for publication elsewhere. Your consideration would be very much appreciated. Thank you very much.

Best regards,
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Evaluation of metal-organic framework NH_2-MIL-101(Fe) as an efficient sorbent for dispersive solid phase extraction of phenolic pollutants in environmental water samples

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Abstract

This work proposes an application of amine-functionalized metal-organic framework (NH_2-MIL-101(Fe)) as sorbent for dispersive solid phase extraction (DSPE) of ten priority phenolic pollutants. The sorbent was simply synthesized under facile condition. The entire DSPE process was optimized by studying the effect of experimental parameters affecting the extraction recovery of the target analytes. The final extract was analyzed using high performance liquid chromatography with photodiode array detector. Under the optimum condition, the proposed procedure can be applied for wide linear calibration ranges between 1.25–5000 μg L^{-1} with the correlation coefficients of greater than 0.9900. The limits of detection (LODs) and limits of quantitation (LOQs) were in the ranges of 0.4–9.5 μg L^{-1} and 1.25–30 μg L^{-1}, respectively. The precision evaluated in terms of the relative standard deviations (RSDs) were below 1.3% and 13.9% for retention time and peak area, respectively.

High enrichment factors up to 99 were reached. The developed method has been successfully applied to determine phenol residues in environmental water samples. The satisfactory recoveries in the range of 68.4–114.4% were obtained. The results demonstrate that the NH_2-MIL-101(Fe) material is promising sorbent in the DSPE of phenolic pollutants.

Keywords: Metal-organic framework, dispersive solid-phase extraction, phenol, HPLC

1. Introduction

Metal-organic frameworks (MOFs) are inorganic-organic hybrid microporous crystalline materials constituted by metal clusters connected by organic linkers. Due to their fascinating diverse structures with tailorable chemistry, large surface areas, tunable pore sizes, good thermal stability and chemical resistance, MOFs have been demonstrated for applications in various fields such as gas storage [1–2], catalysis [3–4], chemical sensing [5], adsorption [6–7], and separation [3,8]. A large number of reports have also shown that MOFs possess great potential in a field of analytical chemistry [8–13].

Recently, MOFs have successfully been explored as sorbent materials in various sorption-based sample preparation techniques [10–13]. UiO-66, a cubic rigid 3D porous MOF-self-assembled from zirconium clusters $Zr_6O_4(OH)_4$ and terephthalate ligands, was coated on stainless steel fiber for solid-phase microextraction (SPME) of polar phenols in water samples [14]. An NH_2-MIL-53(Al) incorporated poly(styrene-divinylbenzene-methacrylic acid) monolith was efficiently applied to the in-tube solid-phase microextraction for determination of trace estrogens in human urine samples [15]. The prepared monolith showed good reproducibility up to 100 cycles of extraction. For application as sorbent materials in solid-phase extraction (SPE), MIL-101(Cr) and MIL-101(Cr) intercalated by polyaniline composite and doped with silica nanoparticles were synthesized and applied for determination of sulphonamides and thymol and carvacrol, respectively [16–17].

Nowadays, SPE-based miniaturized technique, dispersive solid-phase extraction (DSPE) is acquiring a lot of attention due to the impressive decrease in the amounts of sorbents required. DSPE is based on direct dispersion of the sorbent in a sample solution containing target analytes, extraction by sorption, separation of the sorbent with retained analytes from the solution, and following by solvent elution of the analytes. In DSPE applications involving MOFs as sorbents, the partitioning of various analytes to different MOFs was evaluated. To find a versatile MOF able to extract contaminants with different chemical and physical properties and to establish the relationships between MOF structure-analyte nature, Rocío-Bautista et al. studied the five types of MOFs, including HKUST-1, MOF-5(Zn), MIL-53(Al), UiO-64 and MOF-74(Zn), for determination of six emerging pollutants of different nature [18]. The pore size, the presence of unsaturated metal sites, and the nature of metal have a major influence in their extraction efficiencies. In addition, UiO-66, UiO66-NH_2, UiO-66-NO_2 and MIL-53(Al) were studied for determination of different aqueous organic pollutants in environmental waters [19]. The presence of functional groups in the ligands of UiO-66 influence the total efficiency of the method, particularly due to the polar character given to the organic linkers. Among the MOF-type materials used in many sample preparation applications, MILs have been utilized as promising candidates due to their superior characteristics when compared with other MOFs, including high surface-to-volume ratio, porosity, and lower costs [17]. A variety of MILs have been prepared and applied in development of DSPE methods, such as amino-functionalized MIL-53(Al) for preconcentration of phenolic pollutants [20–21], MIL-101(Cr) for phthalate esters [22], MIL-101(Cr)@GO for sulfonamides [23], Fe_3O_4@MIL-100 for polychlorinated biphenyls [24], and MIL-101 for pyrazole/pyrrole pesticides [25].

Phenol and its derivatives are one of the most toxic water pollutants, which exist in the environment due to the activity of the chemical, pharmaceutical, and petrochemical industries. Chlorophenols are the most widespread and the large group of phenols, and are formed in the environment by chlorination of mono- and polyaromatic compounds present in soil and water. Nitrophenols are formed in the reaction of phenol with nitrite ions in water under the influence of UV radiation and in the wide pH range. Methylphenols are commonly exist in the environment in considerable concentrations [26]. Owing to their high toxicity even at low concentrations, low degradable and prevalent presence in environment, the United States Environmental Protection Agency (US EPA) and the European Union (EU) have classified them as priority pollutants in aquatic environment. Therefore, determination of these compounds is of great importance for awareness and prevention of related human diseases.

Quantification of phenol and its derivatives are mainly based on selective chromatographic techniques, i.e. gas chromatography (GC) [14, 27] and high performance liquid chromatography (HPLC) [20–21, 28–29]. However, direct determination is difficult to achieve due to the complex matrices and their presence at low concentration levels. Thus, sample pretreatment is required prior to instrumental analysis. For this reason, different extraction methods have been developed. In the present work, we aimed to explore NH_2-MIL-101(Fe) as sorbent for development of DSPE for ten priority phenolic pollutants, including phenol (Ph), 4-nitrophenol (4NP), 2-chlorophenol (2CP), 2,4-dinitrophenol (24DNP), 2-nitrophenol (2NP), 2,4-dimethylphenol (24DMP), 4-chloro-3-methylphenol (4C3MP), 2,4-dichlorophenol (24DCP), 2-methyl-4,6-dinitophenol (2M46DNP), and 2,4,6-trichlorophenol (246TCP). Extraction process was accelerated using vortex agitation. The NH_2-MIL-101(Fe) was simply synthesized under facile condition when compared with other types of MOF-based materials. Experimental parameters affected the extraction efficiency of the developed procedure were carefully optimized. The method was validated and successfully applied for determination of phenol residues in surface water samples.

2. Experimental

2.1 Chemicals

Analytical phenol standards with a purity of ≥99% were used in this work. 24DNP, 4C3MP, 2M46DNP, 246TCP and 24DMP were supplied by Sigma-Aldrich (Germany). Ph was obtained from Sigma-Aldrich (USA). 4NP and 24DCP were purchased from Sigma-Aldrich (India). 2NP was supplied by Fluka (China). 2CP was supplied by Sigma-Aldrich (China). Stock standard solutions of phenols at concentration of 1000 μg mL^{-1} were prepared using methanol as the solvent. Working solutions were prepared daily by dilution with water. Deionized water (18.2 MΩ·cm) obtained by a RiOs Type I Simplicity 185 water purification system (Millipore, USA) was used in all experiments. 2-Aminoterephthalic acid (99%, Sigma-Aldrich, USA), N,N-dimethylformamide (DMF, ≥99%, Merck, Germany), and ferric chloride anhydrous (≥98%, Riedel-de Haën, Germany) were used for synthesis of amine-functionalized MOF sorbent. Acetonitrile (isocratic grade, Merck, China), methanol (gradient grade, Merck, Germany), ethanol (AR grade, Merck, Germany), acetone (AR grade, Qrëc, New Zealand) and glacial acetic acid (AR grade, Carlo Erba, Italy) were used for HPLC separation and DSPE procedure.

2.2 Apparatus

The HPLC system (Waters, USA) consisted of an in-line degasser, a 600E quaternary pump, and a Waters 2996 photodiode array (PDA) detector. Empower software was employed to acquire and analyze chromatographic data. The system was equipped with a Rheodyne injector with a 10-μL injection loop, and a Phenomenex Luna C18 (4.6 mm × 150 mm, 5 μm)

(Phenomenex, USA) analytical column. The separation was performed using acetonitrile (solvent A) and 0.1% acetic acid in water (solvent B) as mobile phase. The gradient program was as follows: 0–3 min, 40% solvent A; 3–4 min, ramped to 50% solvent A; 4–8 min, 50% solvent A; 8–9 min, ramped to 70% solvent A; 9–12 min, 70% solvent A; 12–13 min, ramped to 100% solvent A; 13–17 min, 100% solvent A; 17–18 min, decreased to 40% solvent A. A re-equilibration period of 2 min with 40% solvent A was carried out between individual runs. The detections were performed at 271 nm for Ph; 317 nm for 4NP; 258 nm for 24DNP; 276 nm for 2NP and 2CP; 280 nm for 4C3MP and 24DMP; 266 nm for 2M46DNP; 286 nm for 24DCP; and 288 nm for 246TCP.

Fourier transform infrared spectra (FTIR) were recorded on a TENSOR27 infrared scanner (Bruker, Germany) with a resolution of 2 cm^{-1} and a spectral range from 4000 to 400 cm^{-1}. The X-ray diffraction (XRD) patterns were recorded using an Empyrean X-ray diffractometer (XRD) (PANalytical, the Netherlands) with Cu Kα radiation (λ=1.5418 Å) over the 2θ range from 5° to 50°. The morphology of MIL-101 was observed on dualbeam scanning electron microscope/focused ion beam (FIB-SEM) (FEI Helios NanoLab G3 CX Dual Beam, FEI, USA)

Other instruments were used in the procedure, including a vortex mixer model G560E (50 Hz) (Scientific Industries, USA), an ultrasonic cleaner (50/60 Hz) model B-220 (Branson, USA), a rotavapor model R-200 (Buchi Labortechnik AG, Switzerland), a centrifuge model Z206A (Hermle Labortechnik, Germany) and an oven model UN110 (Memmert, Germany).

2.3 Synthesis of the sorbent

The sorbent was synthesized by solvothermal treatment adapted from the previously published procedure reported by S. Bauer et al. [30]. Briefly, a solution of 0.2250 g 2-aminoterephthalic acid in 7.5 mL DMF was mixed with a solution of 0.4050 g ferric chloride anhydrous in 7.5 mL DMF. The mixture was stirred for 10 min before thermal treatment in a stainless steel autoclave at 110 ^{o}C for 24 h. The product was filtered under vacuum, then washed with DMF and dried at room temperature.

2.4 Extraction procedure

The determination of phenolic pollutants was carried out by DSPE using amine-functionalized MOF (NH_2-MIL-101(Fe)) as sorbent followed by HPLC with photodiode array detector. For this purpose, an aliquot of 10.00 mL aqueous phenol standard or sample solution was added to a 15 mL centrifuge tube containing 50 mg of sorbent. The mixture was then placed in a vortex mixer for 10 s to accelerate the sorption of the target analytes onto the sorbent. Subsequently, the solid sorbent was isolated from the solution by centrifugation at 5000 rpm for 1 min. After that, the supernatant was discarded. Then, 2.0 mL of 0.5% acetic acid/acetonitrile mixture was added in the centrifuge tube. The analytes were desorbed by vortex mixing for 10 s. The mixture was centrifuged at 5000 rpm for 1 min. The desorption solvent which contained analytes of interest was filtered through 0.45 μm membrane and evaporated to dryness by rotary evaporator. The residue was reconstituted in 50 μL of acetonitrile before further injecting to HPLC for analysis. The proposed DSPE procedure is schematically depicted in Fig. 1.

3. Results and discussion

3.1 Sorbent characterization

The prepared NH_2-MIL-101(Fe) was characterized by XRD, SEM, and FTIR techniques. The framework structure of as-synthesized MIL-101 was identified by X-ray diffraction and the pattern is shown in Fig. S1. The XRD pattern of the as-synthesized sorbent was in good accordance with the simulated MIL-101, indicating that the pure phases were obtained. To identify the functional groups of NH_2-MIL-101(Fe), the FTIR spectroscopy was studied and the results are shown in Fig. S2. Strong bands at 1580 and 1433 cm^{-1} correspond to the presence of the symmetrical and asymmetrical C–O stretching vibrations of carboxylates and indicate the presence of 2-aminoterephthalate anions in the framework. Moreover, a shoulder at 1623 cm^{-1} attributed to the N–H bending and an absorption band at 1340 cm^{-1} assigned to the C–N stretching of aromatic amines. SEM images in Fig. S3 show the morphology of NH_2-MIL-101(Fe). The prepared material consists of hexagonal microspindle crystals with about 0.9–1.5 µm of the length, and 300–500 nm of the width. Therefore, the results of XRD, FTIR and SEM clearly confirm the formation of NH_2-MIL-101(Fe) structure.

3.2 Optimization of the DSPE condition

In the process of optimization experiments, aqueous standard solutions containing 5 mg L^{-1} of each phenol were investigated. All experiments were carried out in triplicate. Percentage of extraction recovery (%ER) was evaluated and used as the experimental response. The extraction recovery was calculated according to the following equation:

$$\%\mathrm{ER} = \left(\frac{\mathrm{V_f}}{\mathrm{V_i}}\right)\left(\frac{\mathrm{C_f}}{\mathrm{C_i}}\right) \times 100$$

Where V_i and V_f are the initial and final volumes, C_i is the initial concentration of analyte spiked in solution and C_f is the final concentration of analyte in solution that calculated from calibration curve [31].

3.2.1 Sorbent amount

In order to achieve a satisfactory extraction efficiency for the target analytes, the effect of the amount of NH_2-MIL-101(Fe) sorbent was studied by varying from 10 to 90 mg. Other experimental parameters were kept as follows: 10.00 mL sample volume, 10 s vortex adsorption time, 2 min centrifugation after adsorption, 0.5 mL of 0.5% acetic acid in acetonitrile as desorption solvent, 10 s vortex desorption time, and 1 min centrifugation after desorption. As illustrated in Fig. 2, the extraction recovery increases with the increase of sorbent amount from 10 to 50 mg, and reaches the maximum plateau afterward. Therefore, 50 mg of sorbent material was sufficient for effective extraction of the target analytes in the studied concentration, and was adopted in the further experiments.

3.2.2 Type of desorption solvent

Choice of desorption solvent is one of crucial parameters in sorbent-based extraction method. To obtain high extraction recovery for the target analytes, 0.5 mL of various solvents, including methanol, acetonitrile, acetone, 0.5% acetic acid in methanol, 0.5% acetic acid in acetonitrile and 0.5% acetic acid in acetone, were studied for desorption of phenol compounds from the Fe-MIL-101-NH_2 sorbent. Vortex was applied for 10 s during desorption step in order to ensure sufficient interaction of the sorbent containing analytes with the desorption solvent. Other experimental conditions were kept as follows: 50 mg sorbent, 10.00 mL sample volume, and 2 min centrifugation after adsorption. The results in Fig. 3 indicated that the highest extraction recoveries of most analytes were achieved using 0.5% acetic acid in acetonitrile as desorption solvent. Addition of acetic acid also resulted in significant increase of extraction recoveries for 2M46DMP and 24DNP. Therefore, the mixture of 0.5% acetic acid in acetonitrile was chosen for the desorption process.

3.2.3 Desorption solvent volume

To determine the effect of desorption solvent volume, the volume of 0.5% acetic acid in acetonitrile was varied in the range of 0.5–2.5 mL, while keeping other conditions as follows: 50 mg sorbent, 10.00 mL sample volume, 10 s vortex adsorption time, 2 min centrifugation after adsorption, 10 s vortex desorption time, and 1 min centrifugation after desorption. It should be noted that in this experiment the eluate containing desorbed analytes was subsequently injected into the HPLC system without evaporation. The results in Fig. 4 showed that the extraction recoveries of most analytes increased with increasing the volume of desorption solvent from 0.5 to 2.0 mL and remained almost constant afterward. Therefore, 2.0 mL of 0.5% acetic acid in acetonitrile was selected for further optimization.

3.2.4 Vortex adsorption time

To ensure maximum adsorption of the target analytes on the solid sorbent, vortex agitation was applied during adsorption process and the vortex time was studied from 10 to 100 s using the sorbent amount of 50 mg, 10.00 mL sample volume, 1 min centrifugation after adsorption, 2.0 mL of 0.5% acetic acid in acetonitrile as desorption solvent, 10 s vortex desorption time, and 1 min centrifugation after desorption. It was found that extraction recoveries of the studies compounds increased significantly in case of using vortex when compared with those without vortex (see Fig. S4). However, vortex time from 10 to 100 s did not contribute to any improvement of extraction efficiency. Therefore, 10 s vortex was sufficient for adsorption process.

3.2.5 Centrifugation time after adsorption

In the present work, centrifugation was performed to separate the solid sorbent from the aqueous sample solution. The centrifugation time after adsorption process was varied in the range of 1–10 min. It could be observed that centrifugation for 1 min was enough for settle down the sorbent, as shown in Fig. S5. Therefore, the mixture was centrifuged for 1 min after adsorption process before decanting the supernatant.

3.2.6 Vortex desorption time

In desorption process, the vortex time was also studied in the range from 10 to 100 s, using 50 mg sorbent, 10.00 mL sample volume, 10 s vortex adsorption, 1 min centrifugation after adsorption, 2.0 mL of 0.5% acetic acid in acetonitrile as desorption solvent, and 1 min centrifugation after desorption. The highest extraction recoveries were obtained using 10 s vortex desorption, and remained constant beyond this point. In addition, it could be observed that the higher extraction recoveries were reached when applying vortex during desorption process compared with the experiments without vortex (Fig. S6). Therefore, in this work the vortex time of 10 s was selected during desorption process.

3.2.7 Centrifugation time for desorption

Different centrifugation time in the range of 1–10 min were studied for separation of the solid sorbent from the eluent. However, longer centrifugation did not improve the extraction recovery of the target analytes (Fig. S7). Therefore, centrifugation for 1 min was found to be sufficient in this work.

In order to improve the preconcentration ability of the proposed extraction procedure, evaporation and reconstitution were performed before analysis by HPLC. In this work, the eluate was evaporated at 55 °C to dryness and the residue was reconstituted in 50 μL acetonitrile before subjecting to HPLC for further analysis. It was found that the higher enrichment factors were attained in the range of 47–99.

3.3 Analytical performance

Using the optimized conditions, the analytical performance of the proposed DSPE procedure for quantification of phenolic pollutants was investigated including linearity, sensitivity in terms of limits of detection (LODs) and limits of quantification (LOQs), precision and accuracy. The method exhibited good linearity of the calibration graphs in the range of 1.25–5000 µg L^{-1} with the correlation coefficients of greater than 0.9900. The LODs and LOQs, which were calculated based on the signal-to-noise ratios of 3 and 10, respectively, were in the ranges of 0.4–9.5 µg L^{-1} and 1.25–30 µg L^{-1}, respectively. The precision was evaluated in terms of the relative standard deviations (RSDs) of the intra- and inter-day experiments. By replicate analyses of standard mixture of the analytes with the concentration at the LOQ of each compound in a day (n=8) and several days (n=4×3), the RSDs of retention time and peak area were below 1.3% and 13.9%, respectively. The analytical features of the proposed method are summarized in Table 1. Chromatograms obtained from DSPE process was compared with that obtained by direct HPLC as shown in Fig. 5.

3.4 Application to real samples

The applicability of the proposed DSPE method was investigated by analysis of four water samples collected from different sources in northeastern of Thailand. The samples were filtered through 0.45 µm membrane filter before analysis by the proposed DSPE method. The studied samples did not contain the phenolic compounds.

To evaluate the accuracy and the matrix effect on the established method, the recovery experiments were carried out by spiking different concentrations of each phenol compound into the water samples. The results are summarized in Table 2. The range of mean recoveries was 68.4–114.4% with the RSDs of less than 15.4%.

3.5 Comparison of the proposed DSPE to other methods

The proposed DSPE method using NH_2-MIL-101(Fe) sorbent was compared to other extraction methods for determination of phenol compounds, as summarized in Table 3. The wide linear working ranges for determination of a variety of phenol compounds were observed using the developed method. The sensitivity in terms of LODs and LOQs is almost comparable to those obtained from other reports. The significant advantages of the proposed DSPE are low consumption of sample volume and short extraction time. In addition, the NH_2-MIL-101(Fe) sorbent used in this work could be simply prepared when compared with previously reported sorbents [20, 21].

4. Conclusion

In the present work, a simple and effective sample preparation procedure based on DSPE for the determination of ten phenolic pollutants was proposed. NH_2-MIL-101(Fe) material was explored as sorbent and the DSPE experimental conditions were optimized. The analytical characteristics of the method made it an appropriate sample pretreatment strategy to determine the target analytes in real samples.

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Competing interest statement

The authors declare no conflict of interest.

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List of figure captions

Fig. 1 Schematic diagram of the proposed DSPE procedure for determination of phenolic pollutants

Fig. 2 Effect of sorbent amount on DSPE of phenolic pollutants

Fig. 3 Effect of eluent type on DSPE of phenolic pollutants

Fig. 4 Effect of eluent volume on DSPE of phenolic pollutants

Fig. 5 Chromatograms obtained from direct HPLC and after DSPE process. Peak assignment: 1, Ph; 2, 4NP; 3, 2CP; 4, 24DNP; 5, 2NP; 6, 24DMP; 7, 4C3MP; 8, 24DCP; 9, 2M46DNP; 10, 246TCP

Table 1 Analytical features of the proposed DSPE-HPLC method for determination of phenolic pollutants

Analyte	**Linear range (mg L^{-1})**	**Linear equation**	**R^2**	**LOD (µg mL^{-1})**	**LOQ (µg mL^{-1})**	**EF**	**%RSD**			
							intra–day (n=8)		**inter–day (n=4×3 days)**	
							t_R	**Peak area**	**t_R**	**Peak area**
Ph	0.03–1.00	y = 434195x + 6505	0.9972	0.0095	0.03	51	0.7	12.5	0.5	10.6
	(1.00–50.00)	(y = 11005x - 4947)	(0.9988)	(0.25)	(1.00)		(0.2)	(6.4)	(0.6)	(6.2)
4NP	0.0047–0.10	y = 4171324x + 11454	0.9925	0.0015	0.0047	53	0.7	5.1	0.4	10.6
	(0.50–50.00)	(y = 62222x - 31512)	(0.9986)	(0.10)	(0.33)		(0.4)	(2.6)	(0.7)	(7.0)
2CP	0.03–1.00	y = 885032x - 11928	0.9987	0.001	0.030	69	0.4	13.9	0.4	11.0
	(2.00–50.00)	(y = 11131x - 3533)	(0.9988)	(0.50)	(1.67)		(0.6)	(3.6)	(0.6)	(7.6)
24DNP	0.015–1.00	y = 1281523x + 21419	0.9996	0.004	0.0128	88	0.6	4.6	0.5	11.9
	(0.50–50.00)	(y = 50238x - 4514)	(0.9990)	(0.10)	(0.33)		(0.7)	(5.4)	(1.0)	(7.7)
2NP	0.016–5.00	y = 2017606x - 15557	0.9900	0.005	0.016	47	0.2	8.2	0.3	10.3
	(1.00–50.00)	(y = 33243x - 24251)	(0.9976)	(0.30)	(1.00)		(0.5)	(3.1)	(0.5)	(8.2)
24DMP	0.025–3.00	y = 558122x + 6173	0.9962	0.0075	0.025	67	0.2	8.1	1.3	8.6
	(1.50–50.00)	(y = 10252x - 3358)	(0.9976)	(0.48)	(1.25)		(0.5)	(3.8)	(0.4)	(8.3)
4C3MP	0.015–1.00	y = 955857x + 10969	0.9990	0.0045	0.015	79	0.2	5.4	0.2	9.5
	(2.00–50.000)	(y = 8701x - 4742)	(0.9985)	(0.78)	(1.72)		(0.5)	(4.6)	(0.5)	(8.3)
24DCP	0.025–3.00	y = 992102x - 4502	0.9999	0.0075	0.025	67	0.2	9.3	0.3	9.4
	(2.00–50.00)	(y = 10312x - 5976)	(0.9984)	(0.58)	(1.93)		(0.5)	(3.5)	(0.5)	(4.5)
2M46DNP	0.00125–0.10	y = 5801394x + 33083	0.9950	0.0004	0.00125	97	0.1	7.3	0.2	12.2
	(0.50–50.00)	(y = 55865x - 9226)	(0.9987)	(0.11)	(0.37)		(0.8)	(4.1)	(0.7)	(2.8)
246TCP	0.0113–3.00	y = 991710x + 17020	0.9996	0.0035	0.0113	99	0.1	10.4	0.1	11.5
	(2.50–50.00)	(y = 8277x - 2452)	(0.9972)	(0.71)	(2.37)		(0.4)	(2.9)	(0.3)	(5.0)

The values in parentheses were obtained from direct HPLC.

Table 2 Determination of phenol residues in water samples

Analyte	Added (mg L^{-1})	Surface water I			Surface water II			Surface water III			River water		
		Found (mg L^{-1})	%R	%RSD	Found (mg L^{-1})	%R	%RSD	Found (mg L^{-1})	%R	%RSD	Found (mg L^{-1})	%R	%RSD
Ph	–	ND	–	–	ND	–	–	ND	–	–	ND	–	–
	0.0400	0.0390	97.6	8.6	0.0371	92.6	9.0	0.0306	77.4	7.5	0.0323	72.2	9.4
	0.2000	0.1940	97.0	7.0	0.2027	101.4	9.8	0.1503	95.6	14.0	0.1631	81.6	8.5
4NP	–	ND	–	–	ND	–	–	ND	–	–	ND	–	–
	0.0500	0.0048	96.5	8.3	0.0043	87.0	7.4	0.0055	98.0	1.0	0.0029	74.6	11.1
	0.0250	0.0259	103.5	1.8	0.0252	100.7	2.6	0.0236	90.6	8.0	0.0218	87.1	9.2
2CP	–	ND	–	–	ND	–	–	ND	–	–	ND	–	–
	0.0500	0.0464	92.8	10.5	0.0411	82.2	6.2	0.0363	85.9	12.6	0.0557	96.9	10.0
	0.2500	0.2587	103.5	9.2	0.2586	103.5	1.7	0.1712	72.6	1.0	0.2642	105.7	10.9
24DNP	–	ND	–	–	ND	–	–	ND	–	–	ND	–	–
	0.0150	0.0118	79.0	10.5	0.0153	101.9	0.7	0.0088	99.5	7.6	0.0101	100.4	9.3
	0.0750	0.0782	104.2	4.5	0.0816	108.8	1.9	0.0627	83.6	3.1	0.0523	70.1	1.3
2NP	–	ND	–	–	ND	–	–	ND	–	–	ND	–	–
	0.0200	0.0186	93.0	2.8	0.0197	98.4	6.2	0.0207	73.7	5.7	0.0296	95.1	1.8
	0.1000	0.1089	108.9	1.3	0.0982	98.2	10.1	0.0621	68.4	1.8	0.0987	98.7	15.4
24DMP	–	ND	–	–	ND	–	–	ND	–	–	ND	–	–
	0.0300	0.0261	87.1	1.1	0.0284	94.8	8.4	0.0337	91.9	6.7	0.0307	104.8	4.0
	0.1500	0.1559	108.8	5.4	0.1576	105.1	9.6	0.1341	81.8	7.5	0.1366	91.1	5.6
4C3MP	–	ND	–	–	ND	–	–	ND	–	–	ND	–	–
	0.0200	0.0169	84.6	3.2	0.0178	89.1	0.4	0.0123	94.4	2.3	0.0110	79.8	3.0

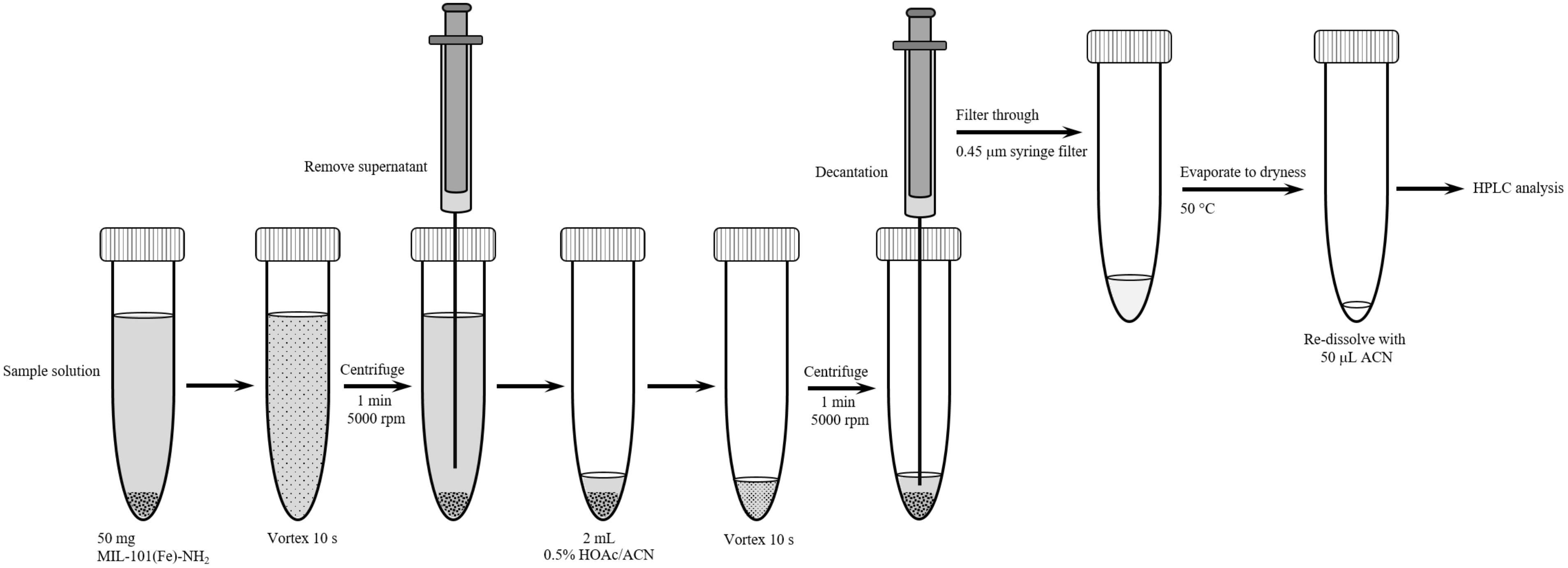
Analyte	Added (mg L^{-1})	Surface water I			Surface water II			Surface water III			River water		
		Found (mg L^{-1})	%R	%RSD	Found (mg L^{-1})	%R	%RSD	Found (mg L^{-1})	%R	%RSD	Found (mg L^{-1})	%R	%RSD
	0.1000	0.0985	98.5	1.9	0.0986	98.6	4.0	0.1111	111.1	2.4	0.0925	92.5	5.6
24DCP	–	ND	–	–	ND	–	–	ND	–	–	ND	–	–
	0.0300	0.0293	97.6	4.0	0.0263	87.6	7.8	0.0214	79.7	7.9	0.0267	88.9	5.2
	0.1500	0.1513	100.9	7.2	0.1490	99.3	4.1	0.1077	86.0	1.8	0.1140	76.0	12.5
2M46DNP	–	ND	–	–	ND	–	–	ND	–	–	ND	–	–
	0.0015	0.0014	95.7	1.7	0.0015	97.0	2.5	0.0018	114.4	8.1	0.0012	82.0	0.1
	0.0075	0.0074	98.0	7.1	0.0070	93.6	3.7	0.0057	82.3	8.5	0.0073	97.4	0.3
246TCP	–	ND	–	–	ND	–	–	ND	–	–	ND	–	–
	0.0150	0.0136	90.9	4.2	0.0141	93.7	2.4	0.0149	76.4	12.4	0.0282	70.8	14.3
	0.0750	0.0781	104.2	0.2	0.0794	105.8	1.0	0.0885	114.3	4.3	0.0781	95.8	12.5

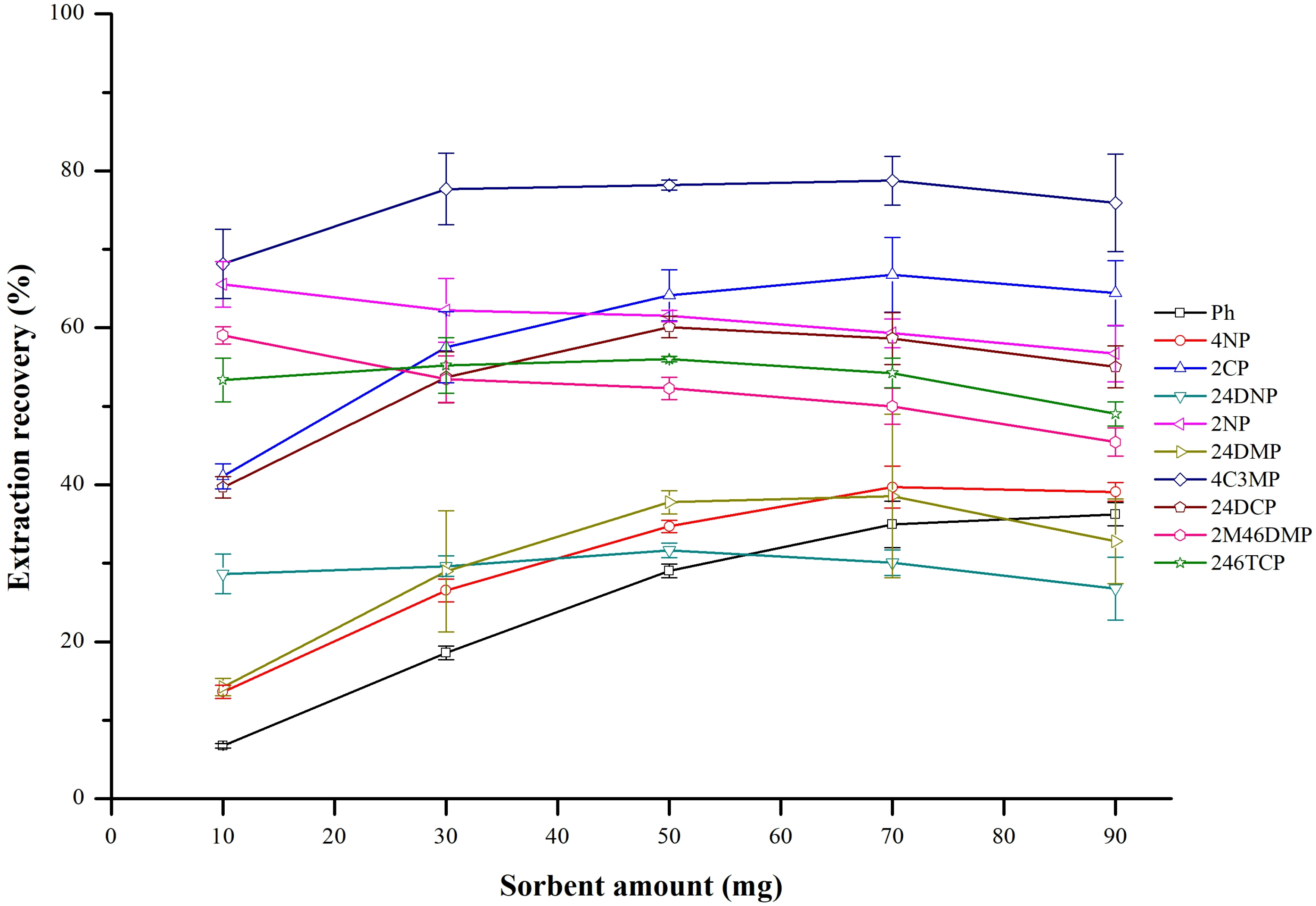
ND: not detected refers to values below detection limits.

Table 3 Comparison of the proposed DSPE to other extraction methods for determination of phenol compounds

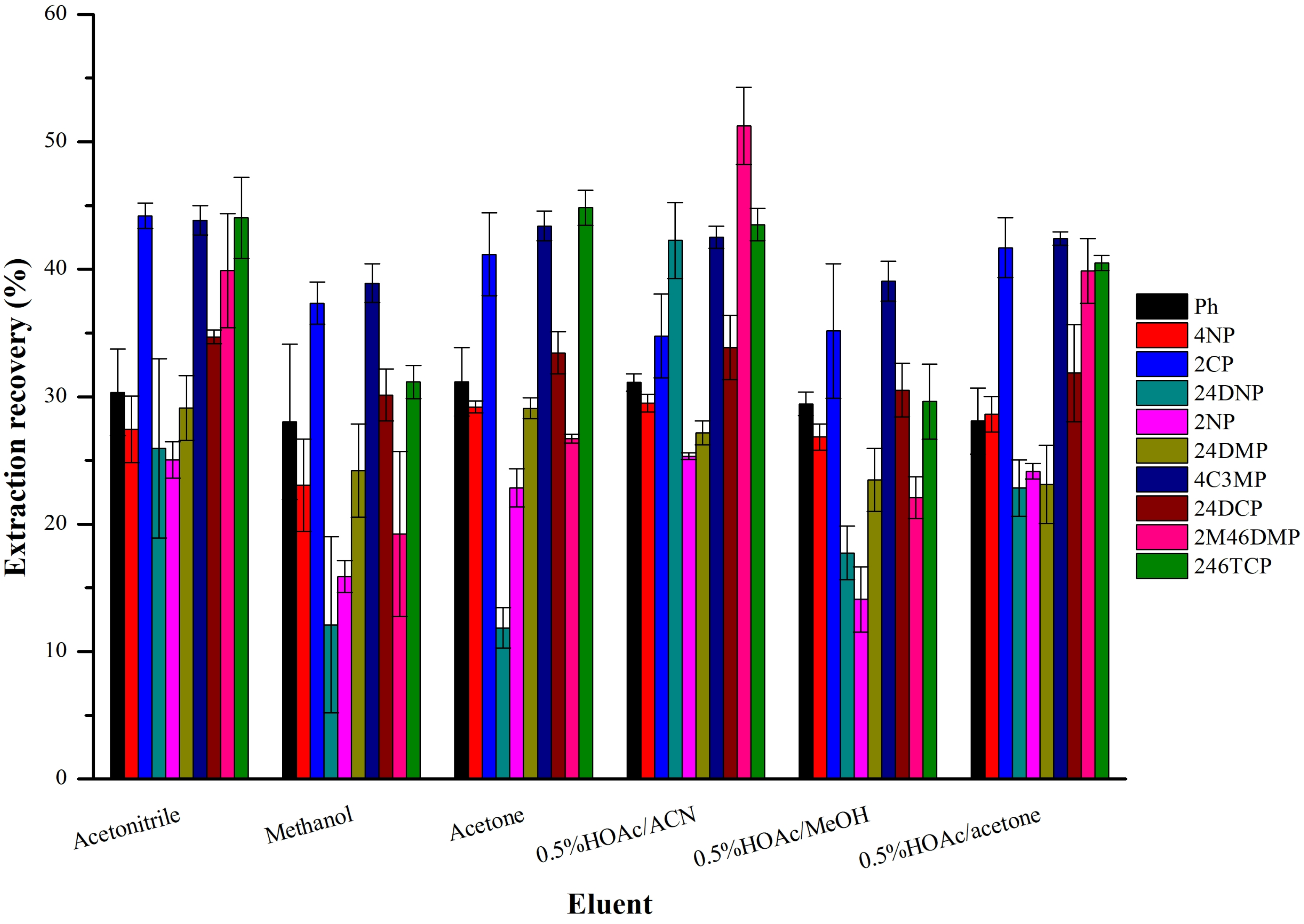
Method [Ref]	Analytes	Sample	Extraction conditions	Analytical technique	Analytical performance
VA-D-μ-SPE [20]	Ph, 4NP, 24DNP, 2NP, 4C3MP, 24DCP, 2M46DNP, 246TCP	Water	Sorbent: 30 mg NH_2-MIL-53(Al) MOF Sample volume: 10 mL Adsorption: 10 s vortex Eluent: 1.5 mL ACN-HOAc (9.5:0.5 v/v) Desorption: 10 s vortex	HPLC-DAD	Linear range: 1.5–10000 μg L^{-1} LODs: 0.4–13.3 μg L^{-1} LOQs: 1.3–51.9 μg L^{-1} EFs: 45–105 %R: 72.3–111.4 RSDs: < 10.4%
SI-VA-D-μ-SPE [21]	Ph, 2CP, 24DMP, 4C3MP, 24DCP	Water	Sorbent: NH_2-MIL-53(Al) MOF suspension (1.50 mL of 0.64 g sorbent/16 mL water) Sample volume: 10 mL Adsorption: 1 min vortex, 2 min centrifugation Eluent: 500 μL acetone	HPLC-UV	Linear range: 100–10000 μg L^{-1} LODs: 30–55 μg L^{-1} LOQs: 90–150 μg L^{-1} EFs: 5–14 %R: 83.0–122.4 RSDs: < 7.85%
In-syringe extraction [29]	Ph, 4NP, 2NP, 3MP, 4C3MP, 24DCP, 2M46DNP, 246TCP, PCP	River water	Sorbent: 5 mg graphene aerosols filled in 2-mL syringe Sample volume: 40 mL Adsorption: 20 min Eluent: 200 μL ACN	HPLC-UV	Linear range: 0.05–20 μg L^{-1} LODs: 0.016–0.075 μg L^{-1} LOQs: 0.053–0.250 μg L^{-1} %R: 96.3–102.4 RSDs: < 5.4 %
Online MMD-SPE [32]	4NP, 2CP, 24DNP, 2NP, 24DMP, 4C3MP, 24DCP	Groundwater	Sorbent: polyvinylidene fluoride matrix disks containing entrapped UiO-66-NH_2 MOFs Sample volume: 1.5 mL Eluent: 0.3 mL acetone	HPLC-DAD	Linear range: 0.5–500 μg L^{-1} LODs: 0.1–0.2 μg L^{-1} EFs: 12–20 %R: 90–98

Method [Ref]	Analytes	Sample	Extraction conditions	Analytical technique	Analytical performance
			Desorption flow rate: 0.5 mL min^{-1}		RSDs: 3.9–5.7 % (intraday), 4.7–5.7 % (interday)
DSPE [33]	Ph, 4NP, 2CP, 24DNP, 2NP, 24DMP, 4C3MP, 24DCP, 2M46DNP, 246TCP, PCP	River water	Sorbent: 6.0 mg LDO-HSs Sample volume: 100 mL Eluent: 200 µL 10% TFA	HPLC-DAD	Linear range: 0.05–40 µg L^{-1} LODs: 0.005–0.153 µg L^{-1} LOQs: 0.018–0.507 µg L^{-1} EFs: 36–459 %R: 93.9–124 RSDs: < 6.7%
MSPE [34]	2CP, 3CP, 23DCP, 34DCP	Tap water and honey tea	Sorbent: 150 mg Zn/Co$_{7:1}$-MPC Sample volume: 100 mL Extraction time: 20 min shaking Eluent: 0.4 mL of 1% alkaline methanol	HPLC-UV	Linear range: 0.5–100 µg L^{-1} LODs: 0.1–0.2 µg L^{-1} %R: 83.0–114.0 RSDs: 5.7–8.7%
DSPE [This study]	Ph, 4NP, 2CP, 24DNP, 2NP, 24DMP, 4C3MP, 24DCP, 2M46DNP, 246TCP	Surface water	Sorbent: 50 mg NH_2-MIL-101(Fe) Sample volume: 10.00 mL Adsorption: 10 s vortex, 1 min centrifugation Eluent: 2.0 mL 0.5% HOAc/ACN Desorption: 10 s vortex, 1 min centrifugation	HPLC-DAD	Linear range: 1.25–5000 µg L^{-1} LODs: 0.4–9.5 µg L^{-1} LOQs: 1.25–30 µg L^{-1} EFs: 47–99 %R: 68.4–114.4 RSDs: < 13.9%

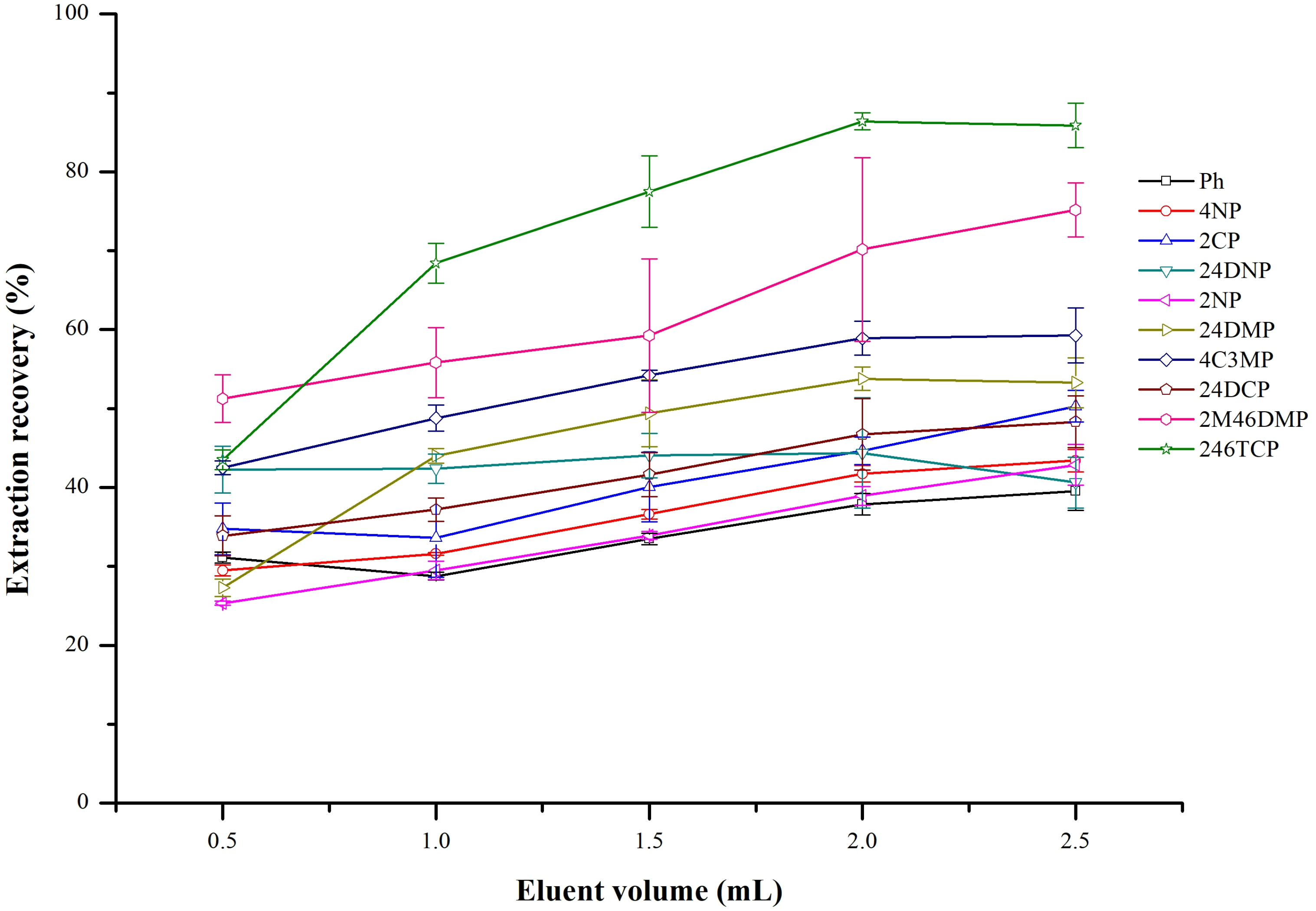

Sample solution
50 mg
MIL-101(Fe)-NH$_2$
Vortex 10 s
Centrifuge
1 min
5000 rpm
Remove supernatant
2 mL
0.5% HOAc/ACN
Vortex 10 s
Centrifuge
1 min
5000 rpm
Decantation
Filter through
0.45 μm syringe filter
Evaporate to dryness
50 °C
Re-dissolve with
50 μL ACN
HPLC analysis



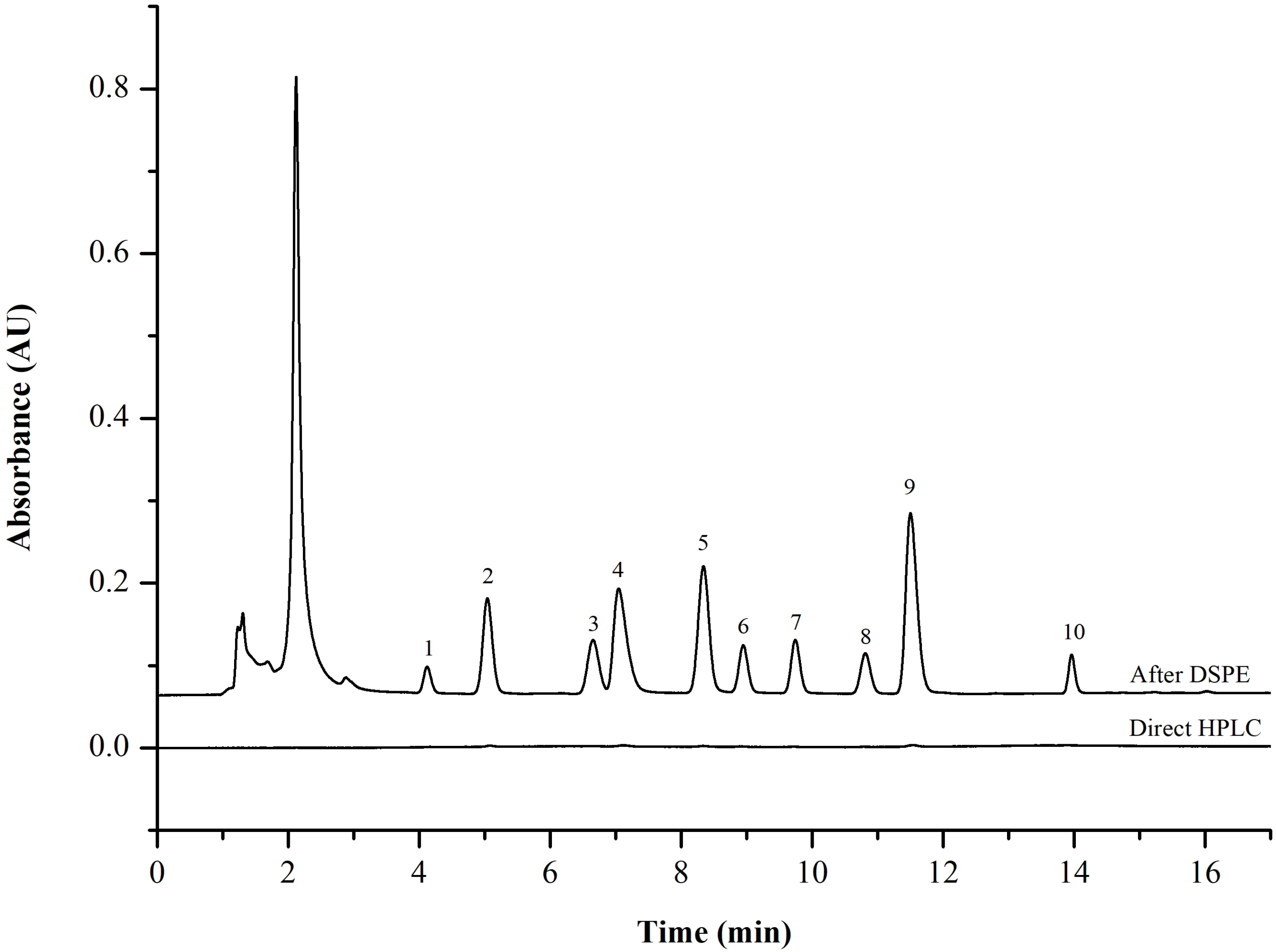
Extraction recovery (%)
Sorbent amount (mg)
0
20
40
60
80
100
0
10
20
30
40
50
60
70
80
90
Ph
4NP
2CP
24DNP
2NP
24DMP
4C3MP
24DCP
2M46DMP
246TCP



Extraction recovery (%)
0
10
20
30
40
50
60
Acetonitrile
Methanol
Acetone
0.5%HOAc/ACN
0.5%HOAc/MeOH
0.5%HOAc/acetone
Eluent
Ph
4NP
2CP
24DNP
2NP
24DMP
4C3MP
24DCP
2M46DMP
246TCP



Extraction recovery (%)
100
80
60
40
20
0
0.5
1.0
1.5
2.0
2.5
Eluent volume (mL)
Ph
4NP
2CP
24DNP
2NP
24DMP
4C3MP
24DCP
2M46DMP
246TCP


Absorbance (AU)
0.8
0.6
0.4
0.2
0.0
Time (min)
0
2
4
6
8
10
12
14
16
1
2
3
4
5
6
7
8
9
10
After DSPE
Direct HPLC

Supplementary Information

Evaluation of metal-organic framework NH_2-MIL-101(Fe) as an efficient sorbent for dispersive solid phase extraction of phenolic pollutants in environmental water samples

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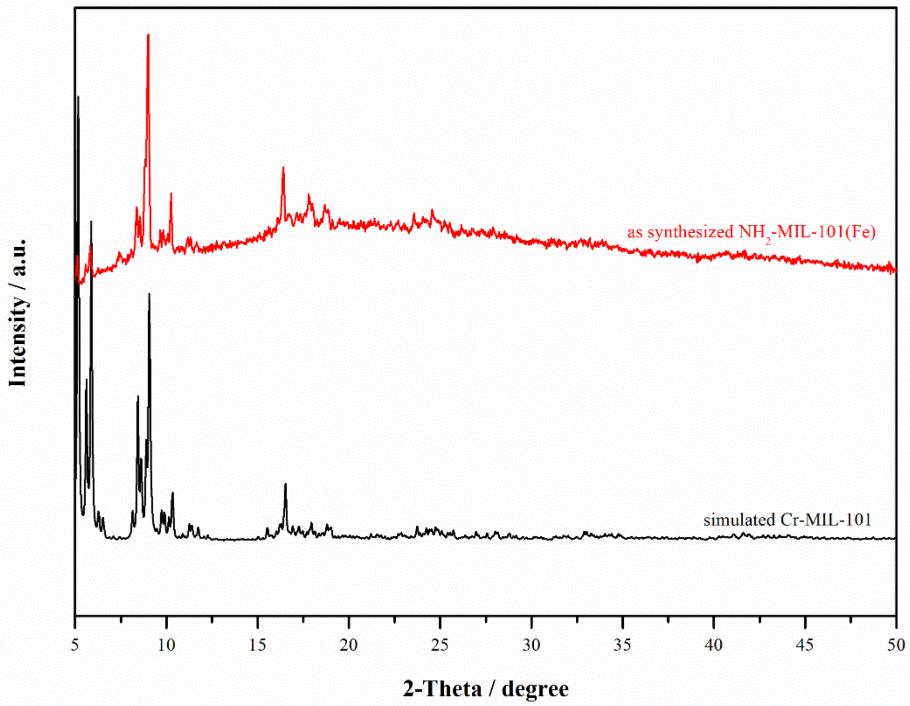

Fig. S1 XRD patterns of the synthesized NH_2-MIL-101(Fe) and simulated MIL-101

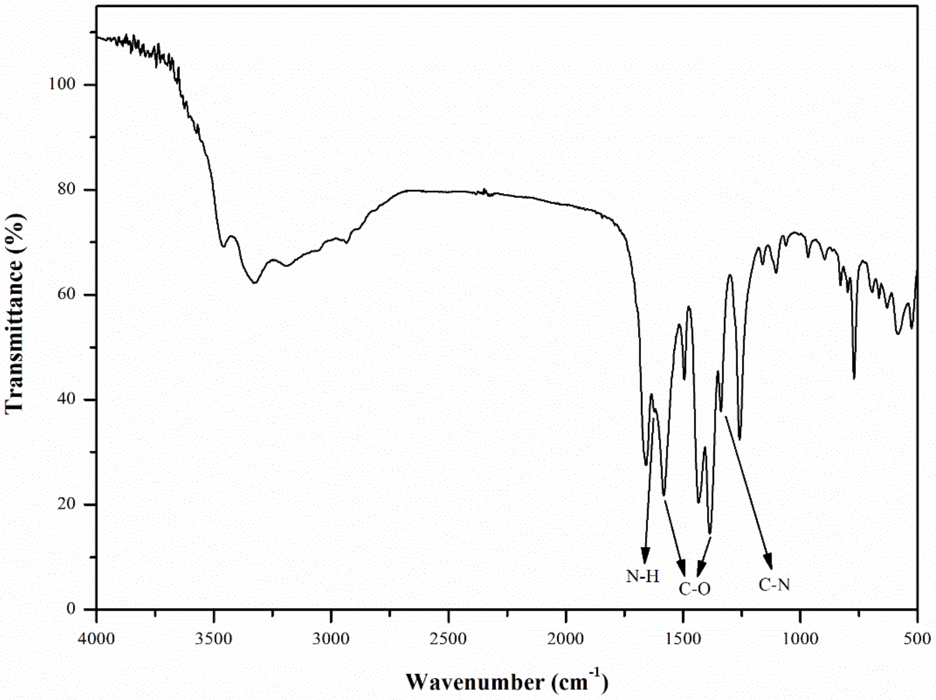

Fig. S2 FTIR spectra of the synthesized NH_2-MIL-101(Fe)

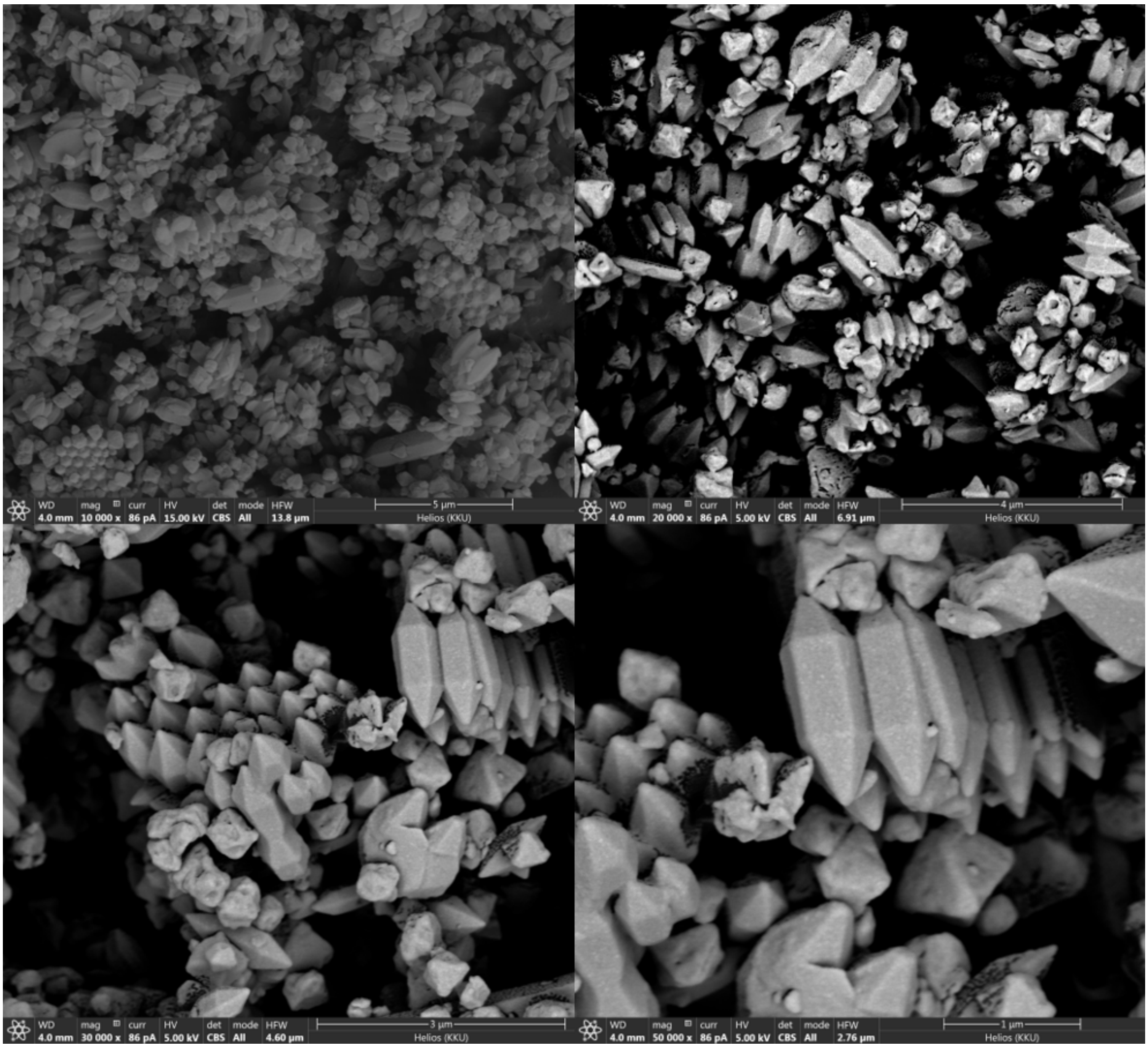

Fig. S3 SEM images of as-synthesized NH_2-MIL-101(Fe)

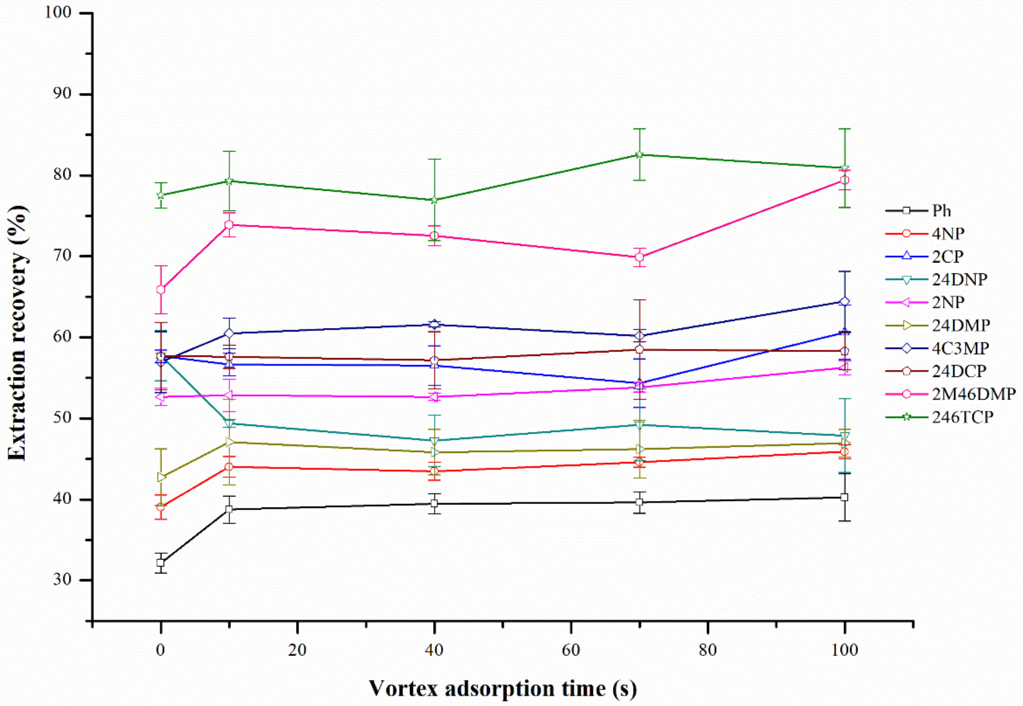

Fig. S4 Effect of vortex adsorption time on DSPE of phenolic pollutants

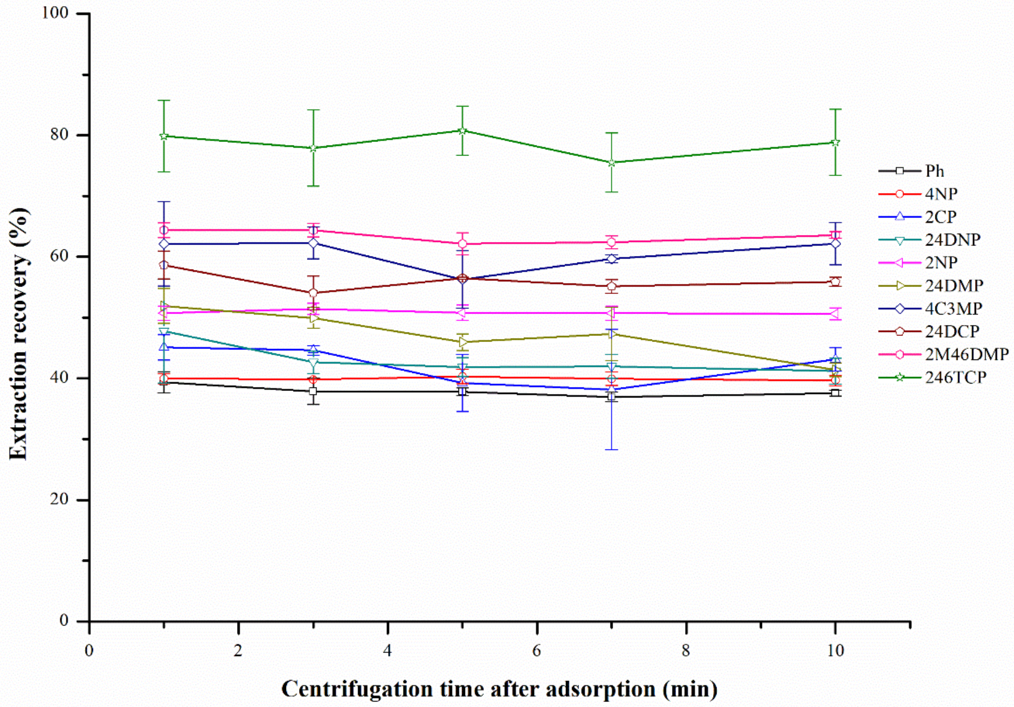

Fig. S5 Effect of centrifugation time after adsorption on DSPE of phenolic pollutants

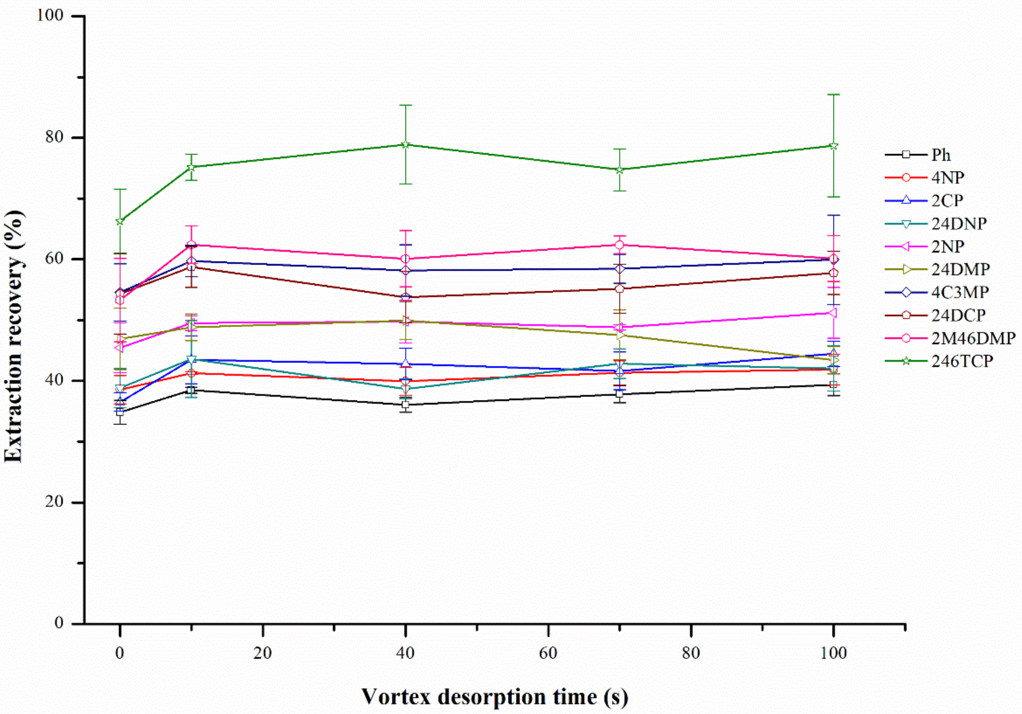

Fig. S6 Effect of vortex desorption time on DSPE of phenolic pollutants

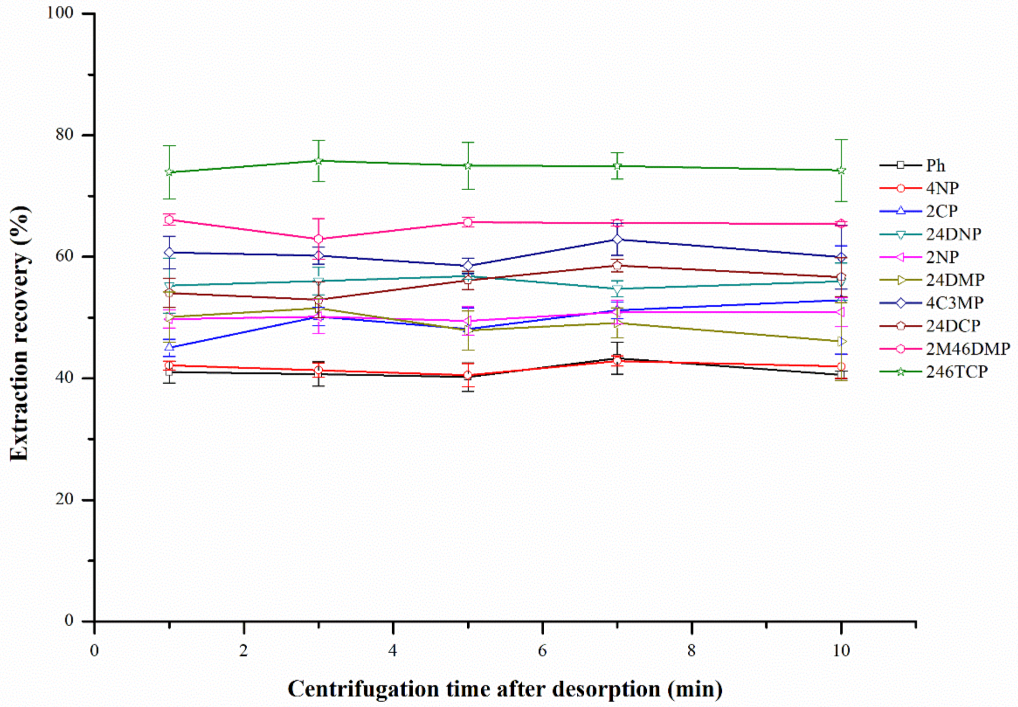

Fig. S7 Effect of centrifugation time after desorption on DSPE of phenolic pollutants

Metal-organic framework NH_2-MIL-53(Al): A new sorbent for dispersive micro-solid phase extraction of phenol residues using HPLC

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Metal–organic frameworks (MOFs) are a new class of hybrid inorganic–organic microporous materials that possess great potential for use as sorbent materials due to their framework flexibility and large surface areas. In this work, NH_2-MIL-53(Al) was prepared and applied as a sorbent in dispersive micro-solid phase extraction (D-µ-SPE) procedure coupled with high performance liquid chromatography with photodiode array detection (HPLC-PDA) for determination of eight United States Environmental Protection Agency's priority phenols in water samples. The parameters affecting the extraction efficiency, such as amount of sorbent, extraction time, type of elution solvent and its volume were optimized. Under the optimum conditions, the good linearity in the range of 0.005–10.000 µg mL^{-1} with the correlation coefficients of greater than 0.9929 was achieved. Low limits of detection (0.0004–0.0133 µg mL^{-1}) and enrichment factors up to 205 were obtained. The proposed method has been successfully applied to the determination of trace phenols in different water samples.

Keywords Dispersive micro-solid phase extraction (D-µ-SPE); Metal-organic framework (MOF); Phenols; HPLC

Sample preparation and high performance liquid chromatographic analysis of phenolic pollutants

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This research aims to develop a simple dispersive micro-solid phase extraction (DMSPE) for preconcentration of phenolic pollutants prior to high performance liquid chromatography (HPLC). In this work, NH_2-MIL-53(Al) was proposed as efficient sorbent for effective extraction of the target analytes. The experimental parameters of the DMSPE, including sorbent amount, eluent and its volume, and vortex time were studied. Under the optimum condition, the analytical performance of the method was studied. Separation was performed using an Inertsil® ODS column with gradient elution of methanol and water, at a flow rate of 1.0 mL min^{-1}. Separation of seven analytes was achieved within 15 min, the calibration graphs were linear in the range of 0.7-50.0 mg L^{-1}, with the correlation coefficient between 0.9929-0.9997. The limits of detection (LODs) and the limits of quantitation (LOQs) ranged from 0.5-2.1 mg L^{-1} and 1.4-6.0 mgL^{-1}, respectively. The precision was evaluated by performing intra-day and inter-day experiments and the obtained relative standard deviations (RSDs) of peak area were in the range of 0.62-2.07% and 0.63-2.70%, respectively.

Keywords MOFs; phenolic pollutants; DMSPE

Application of ultrasonic radiation and vortex agitation in surfactant-based microextraction techniques

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Sample preparation is generally necessary for determination of analytes in real samples. The primary objective is to clean-up and/or concentrate the analytes of interest, thus reducing or even eliminating the potential interferences from sample matrices. Recently, there is an increasing interest in the development of environmentally friendly sample preparation techniques according to the approach of green analytical chemistry. Thus miniaturization and improvement of sample handling using alternatives is a challenge that has been recently developed. The use of surfactants in low consumption organic solvent-based microextraction techniques is an important contribution to this strategy. In addition, ultrasonic irradiation and vortex agitation have been introduced to enhance the efficiency of surfactant-based microextraction techniques. A variety of new modifications, both solvent-based and sorbent-based microextraction methodologies have appeared. The presentation will describe the development of microextraction procedures based on using surfactants as extraction media in combination of applying ultrasonic irradiation or vortex agitation to accelerate the extraction efficiency. These include ultrasound-assisted surfactant-enhanced emulsification microextraction (UASEME), vortex-assisted surfactant-enhanced emulsification microextraction with solidification of floating organic droplet (VASEME-SFO), and vortex-assisted dispersive micro-solid phase extraction (VA-D-µ-SPE). Design of experimental process and effect of experimental conditions of the proposed procedures will be discussed. Application of each developed system for determination of various target analytes in real sample matrices will be demonstrated.

Acknowledgements: The Thailand Research Fund and Khon Kaen University, the Royal Golden Jubilee Ph.D. Program, PERCH-CIC and the Materials Chemistry Research Center, KKU are gratefully acknowledged.

Keywords Sample preparation; Microextraction; Surfactant; Ultrasound; Vortex

Determination of phenol residues in agricultural surface water by dispersive solid-phase extraction coupled with HPLC

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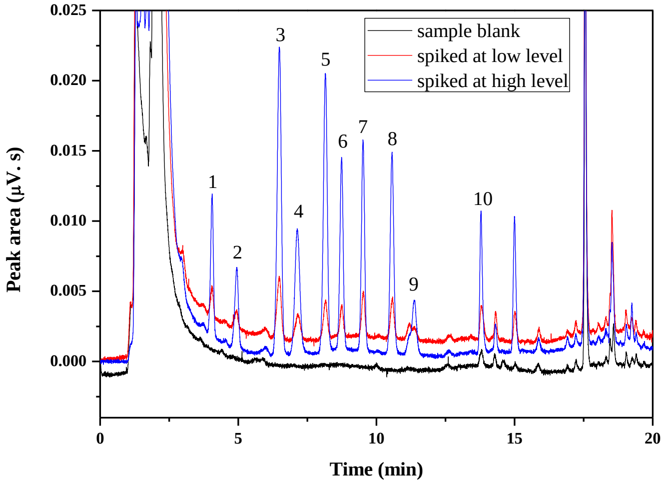
Phenols are permanent organic pollutants, which generate from human activities and various industrial processes such as the production of paper, detergents, polymers, pharmaceuticals and petrochemical products. They were classified as priority pollutants in environment because of their high toxicities even at low concentrations, effects to human being, and possible accumulation in the environment. Therefore, the sensitive and reliable analytical methods for monitoring these compound residues are usually required.

Metal–organic frameworks (MOFs) are a new class of hybrid inorganic–organic microporous materials that possess great potential for use as sorbent materials due to their framework flexibility and large surface areas. In this work, ten phenols were preconcentrated by dispersive solid phase extraction using metal-organic framework, NH_2-MIL-101 (Fe) as sorbent prior to analysis by HPLC-PDA. Factors affecting the extraction efficiency, including sorbent mass, adsorption time, elution solvent and its volume and desorption time were investigated. Under the optimum conditions, the linearity, precision, repeatability, limits of detection (LODs), limits of quantitation (LOQs) and enrichment factors (EFs) were measured to evaluate the performance of this method. To evaluate the accuracy of the method, the relative recovery was tested by spiking phenol standard solutions into the agricultural surface water samples from two rice fields.

Figure 1. Typical chromatograms of blank and spiked natural surface water sample



Under the optimum conditions, the good linearities in the range of 0.00125–5.00 µg mL^{-1} with the correlation coefficients (R^2) of greater than 0.9900 were achieved. LODs and LOQs were obtained in the range of 0.0004–0.0095 µg mL^{-1} and 0.00125–0.03 µg mL^{-1}, respectively. Enrichment factors were found to be up to 99. The proposed method has been successfully applied to the determination of trace phenols in agricultural surface water. The recoveries ranged from 79% to 109%, with the RSDs less than 11%. The results are summarized in Table 1. Figure 1 shows typical chromatograms of blank and spiked natural surface water sample at low level

Table 1. Determination of phenol residues in real Samples

Phenols	Added (ppm)	surface water from ricefiled1			surface water from ricefiled2		
		Found (ppm)	% R	%RSD	Found (ppm)	% R	%RSD
1) Phenol	0.0000	nd			nd		
	0.0400	0.0390	97.6	8.6	0.0371	92.6	9.0
	0.2000	0.1940	97.0	7.0	0.2027	101.4	9.8
2) 4-Nitrophenol	0.0000	nd			nd		
	0.0050	0.0048	96.5	8.3	0.0043	87.0	7.4
	0.0250	0.0259	103.5	1.8	0.0252	100.7	2.6
3) 2-Chlorophenol	0.0000	nd			nd		
	0.0500	0.0464	92.8	10.5	0.0411	82.2	6.2
	0.2500	0.2587	103.5	9.2	0.2586	103.5	1.7
4) 2,4-Dinitrophenol	0.0000	nd			nd		
	0.0150	0.0118	79.0	10.5	0.0153	101.9	0.7
	0.0750	0.0782	104.2	4.5	0.0816	108.8	1.9
5) 2-Nitrophenol	0.0000	nd			nd		
	0.0200	0.0186	93.0	2.8	0.0197	98.4	6.2
	0.1000	0.1089	108.9	1.3	0.0982	98.2	10.1
6) 2,4-Dinitrophenol	0.0000	nd			nd		
	0.0300	0.0261	87.1	1.1	0.0284	94.8	8.4
	0.1500	0.1559	108.8	5.4	0.1576	105.1	9.6
7) 4-Chloro-3-methylphenol	0.0000	nd			nd		
	0.0200	0.0169	84.6	3.2	0.0178	89.1	0.4
	0.1000	0.0985	98.5	1.9	0.0986	98.6	4.0
8) 2,4-Dichlorophenol	0.0000	nd			nd		
	0.0300	0.0293	97.6	4.0	0.0263	87.6	7.8
	0.1500	0.1513	100.9	7.2	0.1490	99.3	4.1
9) 2-Methyl-4,6-dinitrophenol	0.0000	nd			nd		
	0.0015	0.0014	95.7	1.7	0.0015	97.0	2.5
	0.0075	0.0074	98.0	7.1	0.0070	93.6	3.7
10) 2,4,6-Trichlorophenol	0.0000	nd			nd		
	0.0150	0.0136	90.9	4.2	0.0141	93.7	2.4
	0.0750	0.0781	104.2	0.2	0.0794	105.8	1.0

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Polyaniline covering zerovalent iron-silica magnetic particle for magnetic solid phase extraction of trace phenolic compounds

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Abstract: The creation of specific sorbent to preconcentrate trace toxic analytes from water resources is one of interesting research. In this work, the fabrication of new magnetic sorbents with high specific binding interaction, high stability and rapid separation was extremely focused. The magnetic solid phase extraction (MSPE) based on zerovalent iron–silica coated with polyaniline (ZVI@SiO_2@PANI) magnetic sorbent coupled with high-performance liquid chromatography (HPLC) was proposed to determine eight phenolic compounds, including phenol, 4-nitrophenol, 2-chlorophenol, 2,4-dinitrophenol, 2,4-dimethylphenol, 4-chloro-3-methylphenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol. The synthesis of zerovalent iron (Fe) was carried out through borohydride reduction method. The ZVI@SiO_2@PANI magnetic sorbent was simply prepared via sol-gel method followed by oxidative polymerization of aniline. The morphology of as-prepared magnetic sorbent showed polyaniline layer covering 180 nm of spherical zerovalent iron–silica particle. The important parameters influencing MSPE method were optimized. The ZVI@SiO_2@PANI magnetic sorbent had good adsorption affinity (%adsorption $\geq$ 50%). Furthermore, the 4-chloro-3-methylphenol exhibited highly sorption capacity (76 %adsorption) on magnetic sorbent in comparison with other phenolic compounds due to it could form more binding sites and stronger interaction to sorbent.

Keywords: Zerovalent iron; Polyaniline; Phenolic compound; Magnetic solid phase extraction; HPLC

Determination of priority phenolic pollutants by vortex-assisted dispersive micro-solid phase extraction via sorbent injection and HPLC

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Abstract: An amine-functionalized metal-organic framework based on aluminium (NH_2-MIL-53(Al)) was synthesized and applied as a sorbent for extraction of priority phenolic pollutants prior to HPLC analysis. A new designed vortex-assisted dispersive micro-solid phase extraction via sorbent injection was proposed in which the sorbent suspension was precisely injected into the sample solution instead of weighing of small amount of sorbent for each determination as presented in conventional DSPE procedure. The experimental parameters affecting the extraction efficiency were optimized, including sorbent volume, vortex agitation time, eluent type and its volume, and sample volume. Good linearity was obtained in the concentration range of 0.1–10.0 mg L^{-1} with the correlation coefficients in the range of 0.9970–0.9981. The LODs and LOQs were in the ranges of 0.030–0.055 mg L^{-1} and 0.090–0.150 mg L^{-1}, respectively. Good precision of peak area with the relative standard deviation (RSD) values of better than 5.8% and 7.8% were obtained for intra- and inter-day experiments, respectively. The developed method has been successfully applied to determine phenolic residues in water samples. The satisfactory recoveries were obtained in the range of 83.0–122.4% with the RSDs of less than 12.9%.

Keywords: Metal-organic frameworks; sorbent injection; dispersive solid phase extraction; phenol; HPLC

Magnetic solid phase extraction of trace phenolic pollutants using polyaniline modified zerovalent iron-silica magnetic particle as sorbent

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This work aims to develop new materials with high specific binding interaction and stability for rapid enrichment of phenolic pollutants. The zerovalent iron-silica coated with polyaniline (ZVI@SiO_2@PANI) magnetic sorbent was designed and synthesized. The synthesis of zerovalent iron (Fe) was carried out through borohydride reduction method. The ZVI@SiO_2@PANI magnetic sorbent was simply prepared via sol-gel method followed by oxidative polymerization of aniline. The morphology of as-prepared magnetic sorbent showed polyaniline layer (~180 nm) covering spherical zerovalent iron–silica particle. The synthesized sorbent was applied for magnetic solid phase extraction (MSPE) technique. Eight phenolic compounds, including phenol, 4-nitrophenol, 2-chlorophenol, 2,4-dinitrophenol, 2,4-dimethylphenol, 4-chloro-3-methylphenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol, were selected as model analytes and determination of these compounds was carried out using HPLC with photodiode array detector. The important parameters influencing MSPE method were optimized. Good analytical performance was obtained using the optimum conditions as follows: 30 mg Fe@SiO_2-CTAB@PANI as sorbent amount, sample volume of 25 mL, adsorption time of 2 min, 0.5 mL acetonitrile as desorption solvent and desorption time of 30 sec. The linear range between 0.01–10.00 mg L^{-1} was obtained with the limits of detection (LODs) and limits of quantitation (LOQs) in the ranges of 0.01–0.12 mg L^{-1} and 0.04–0.12 mg L^{-1}, respectively. The method was applied to determine phenolic pollutants in water samples.

Keywords: Zerovalent iron; Polyaniline; Phenolic compound; Magnetic solid phase extraction; HPLC

Sorbent materials for preconcentration of toxic residues using solid-phase extraction and liquid chromatography: Offline and online approaches

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Abstract

Monitoring of toxic residues in the different matrices is of great importance due to their harmful impacts not only on human but also on ecological systems. Sample preparation is generally necessary for determination of target analytes in real samples. The primary objective is to clean-up and/or concentrate the analytes of interest, thus reducing or even eliminating the potential interferences from sample matrices. There is an increasing interest in the development of sample preparation techniques using sorbent materials. The use of sorbent-based extraction can make one avoid a number of major drawbacks of liquid-phase extraction e.g. consumption of large toxic organic solvents, incomplete phase separation, low quantitative recoveries, and time consumption. Recently developments in this research field have been achieved with the aid of new materials along with the introduction of novel extraction procedures. The presentation will describe the development of sample preparation procedures based on using new sorbent materials coupling with liquid chromatography, both offline and online approaches. These include the use of surfactant-modified mineral oxides, metal-organic frameworks, and conductive polymer as sorbent for extraction of pesticides and phenolic pollutants. Design of experimental processes and effect of experimental conditions of the proposed procedures will be discussed. Application of each developed system for determination of target analytes in various real sample matrices will be demonstrated.

Keywords: Solid-phase extraction, Sorbent materials, Sample preparation, Chromatography, Online

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Green perspective in sample preparation methods for chromatographic analysis

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ABSTRACT

Sample preparation is necessary for determination of analytes in real samples. For chromatographic analysis, most of sample preparation methods typically consist of an extraction/preconcentration procedure that results in the isolation and enrichment of analytes of interest from a sample matrix. Recently, there is an increasing interest in the development of environmentally friendly sample preparation techniques according to the approach of green analytical chemistry. Thus miniaturization and improvement of sample handling using alternatives is a challenge that has been recently developed. The use of surfactants in low consumption organic solvent-based microextraction techniques is an important contribution to this strategy. A variety of new modifications, both solvent-based and sorbent-based microextraction methodologies have been reported. The presentation will describe the development of microextraction procedures, both liquid-phase and solid-phase extraction, based on using surfactants. These include ultrasound-assisted surfactant-enhanced emulsification microextraction (UASEME) and vortex-assisted dispersive micro-solid phase extraction (VA-D-μ-SPE). Design of experimental process and effect of experimental conditions of the proposed procedures will be discussed. Application of each developed extraction procedures for chromatographic determination of various target analytes in real sample matrices will be demonstrated.

Metal organic frameworks as dispersive micro-solid-phase extraction sorbent for the extraction and determination of phenols from surface waters

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Metal-organic frameworks (MOFs) are a new class of hybrid inorganic-organic microporous crystalline materials composed of metal ions and organic ligands. The unique structures and properties of MOFs, such as high surface area, tunable pore size, and good thermal stable make them attractive materials for diverse applications including gas storage, sensing, catalysis, adsorption, separation and also possess great potential for use as sorbent materials for sample pretreatment. Phenols are permanent organic pollutants, which generate from human activities and various industrial processes. They were classified as priority pollutants in environment by United States Environmental Protection due to their high degree of toxicity even at low levels. Here, we report the application of Fe-MIL-101-NH_2 as a dispersive micro-solid-phase extraction (D-µ-SPE) sorbent to extract ten phenols from aqueous samples prior to analysis by high performance liquid chromatography with photodiode-array detection (HPLC-PDA). The parameters affecting the extraction efficiency, such as amount of sorbent, extraction time, type of elution solvent and its volume were optimized. Under the optimum conditions, the good linearities in the range of 0.00125–5.00 µg mL^{-1} with the correlation coefficients of greater than 0.9929 were achieved. Low limits of detection (0.0004–0.0095 µg mL^{-1}) and enrichment factors up to 99 were obtained. To evaluate the accuracy of the method, the relative recoveries were tested by spiking phenol standard solutions into the samples. The proposed method has been successfully applied to the determination of trace phenols in agricultural surface water with recoveries ranged from 79% to 109% and the RSDs less than 11%.

Fabrication of polyaniline coated on zerovalent iron silica magnetic sorbent for determination of trace phenols in environmental water resources

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Phenolic compounds are one of serious pollutants, causing potential toxic and carcinogenic effects on humans. The determination of phenolic compounds from water resources is interesting work for environmental fields. In this work, the synthesis of specific magnetic sorbents with various binding interaction, high stability and fast separation was extremely focused. The magnetic solid phase extraction (MSPE) based on zerovalent iron-silica covered with polyaniline (Fe@SiO_2@PANI) magnetic sorbent coupled with high performance liquid chromatography (HPLC) was proposed to assay eight phenolic compounds, including phenol, 4-nitrophenol, 2-chlorophenol, 2,4-dinitrophenol, 2,4-dimethylphenol, 4-chloro-3-methylphenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol. The zerovalent iron was simply synthesized by borohydride reduction method. The Fe@SiO_2@PANI magnetic sorbent was prepared by sol-gel method followed by oxidative polymerization of aniline. The morphology of as-prepared magnetic sorbent was spherical shape with particle size of 235 nm, and its magnetic property exhibited ferromagnetic behavior with saturated magnetization value of 7.30 emu/g. The main parameters effecting MSPE method such as sorbent amount, eluent type, adsorption time, desorption time, sample and eluent volume were optimized. Wide linear calibration graphs with the correlation coefficients above 0.993 were obtained. The limits of detection (LODs) were in the range of 0.02-0.12 mg/L, the limits of quantitation (LOQs) were in the range of 0.06-0.30 mg/L, and RSDs were below 10.80% (n = 5). The determination of phenolic compounds in varieties environmental waters showed that phenolic compounds contaminating in all water resource were not found and their recoveries were in the range of 98.82-111.79% (n = 3). As-design magnetic sorbent served high adsorption affinity, rapid separation and reusability. Additionally, it can further apply for analysis of trace phenolic compounds in various samples.

Sorbent-based microextraction systems for monitoring of toxic residues

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Sample preparation is a crucial step during an analytical work-flow dealing with the determination of residues presented at very low concentration in complex matrices. This step will help in the achievement of the desirable limits of detection/quantification, elimination of possible interferences in a dirty matrix and provide the target analytes enrichment. Comparatively, solid-phase extraction (SPE) method provides good recovery, short extraction time, high enrichment factor, low-cost and consumption of less organic solvent than liquid-based extraction methods. A variety of sorbent materials have been introduced for the selective and specific extraction and enrichment of the target analytes. Recently development in this research field has been achieved with the aid of new materials along with the introduction of novel microextraction procedures. The presentation will describe the development of sample preparation procedures based on using new sorbent materials for various target toxic residues. These include the use of surfactant-modified mineral oxides, metal-organic frameworks, conductive polymer and magnetic materials as sorbent. Design of experimental processes and effect of experimental conditions of the proposed procedures will be discussed. Application of each developed system for determination of different target analytes in various real sample matrices will be demonstrated.

Keywords: sample preparation, solid-phase extraction, sorbent materials, microextraction

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