Development and Application of Sample Preparation Techniques for the Determination of Trace Organic Contaminants in Environment and Food

Piyaluk Nurerk

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Chemistry
Prince of Songkla University
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I hereby certify that this work has not been accepted in substance for any degree, and is not being currently submitted in candidature for any degree.

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ชื่อวิทยานิพนธ์ การพัฒนาและการประยุกต์ใช้เทคนิคการเตรียมตัวอย่างสำหรับวิเคราะห์สารปนเปื้อนอินทรีย์ปริมาณน้อยในสิ่งแวดล้อมและอาหาร
ผู้เขียน นางสาวปิยะลักษณ์ หนูฤกษ์
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บทคัดย่อ

วิทยานิพนธ์นี้มีจุดประสงค์เพื่อพัฒนาและประยุกต์ใช้เทคนิคการเตรียมตัวอย่างสำหรับวิเคราะห์สารปนเปื้อนอินทรีย์ปริมาณน้อยในสิ่งแวดล้อมและอาหาร โดยแบ่งออกเป็น 2 ส่วน คือการสกัดด้วยตัวดูดซับของแข็งและการสกัดด้วยของเหลวปริมาณน้อย

ส่วนแรกเป็นการพัฒนาตัวดูดซับของแข็งและตัวดูดซับของแข็งอนุภาคแม่เหล็ก โดยประกอบด้วย 5 งาน งานวิจัยแรกคือการพัฒนาตัวดูดซับของแข็งในลักษณะวัสดุโครงข่ายโลหะอินทรีย์สำหรับประยุกต์ใช้ในการสกัดและเพิ่มความเข้มข้นของสารกรองรังสียูวีในตัวอย่างน้ำและวิเคราะห์ด้วยเทคนิคแก๊สโครมาโทกราฟี แทนเดม แมสสเปกโทรเมตรี การประยุกต์ใช้วัสดุรูพรุนโครงข่ายโลหะอินทรีย์ซึ่งพื้นที่ผิวสัมผัสสูงและมีความสามารถในการดูดซับสารกรองรังสียูวีโดยอันตรกิริยาแบบ π-π และไฮโดรโฟบิก ภายใต้สภาวะที่เหมาะสมวิธีที่พัฒนาขึ้นให้ช่วงความเป็นเส้นตรงตั้งแต่ 0.5 ถึง 100 ไมโครกรัมต่อลิตร และขีดจำกัดการตรวจวัดอยู่ในช่วง 1.0 ถึง 11.7 นาโนกรัมต่อลิตร ได้ประยุกต์ใช้วิธีที่พัฒนาขึ้นในการวิเคราะห์หาปริมาณสารกรองรังสียูวีในตัวอย่างน้ำในสิ่งแวดล้อมและสระว่ายน้ำ โดยให้ค่าร้อยละการได้กลับคืนที่ดีในช่วง 82 ถึง 105 และค่าร้อยละเบี่ยงเบนมาตรฐานสัมพัทธ์ในช่วง 0.9 ถึง 9.7 งานวิจัยที่สองคือการพัฒนาตัวดูดซับของแข็งก้นกรองบุหรี่เคลือบพอลิอะนิลีน สำหรับประยุกต์ใช้ในการสกัดด้วยตัวดูดซับของแข็งในการสกัดและเพิ่มความเข้มข้นสารโพลีไซคลิกอะโรมาติกไฮโดรคาร์บอนในตัวอย่างน้ำ และวิเคราะห์ด้วยเทคนิคโครมาโทกราฟีของเหลวสมรรถนะสูงร่วมกับตัวตรวจวัดฟลูออเรสเซนต์ โดยก้นกรองบุหรี่มีรูพรุนสูง ลดปัญหาการอุดตันของตัวดูดซับ ทำให้ของเหลวสามารถไหลผ่านตัวดูดซับได้เร็ว การเคลือบก้นกรองบุหรี่ด้วยพอลิอะนิลีน เพื่อเพิ่มพื้นที่ผิวสัมผัสในการดูดซับสารโพลีไซคลิกอะโรมาติกไฮโดรคาร์บอนโดยสามารถเกิดอันตรกิริยาแบบ π-π ภายใต้สภาวะที่เหมาะสมวิธีที่พัฒนาขึ้นให้ช่วงความเป็นเส้นตรงตั้งแต่ 0.0005 ถึง 10 ไมโครกรัมต่อลิตร และขีดจำกัดการตรวจวัดเท่ากับ 0.5 นาโนกรัมต่อลิตร ได้ประยุกต์ใช้วิธีที่พัฒนาขึ้นในการวิเคราะห์หาปริมาณสารโพลีไซคลิกอะโรมาติกไฮโดรคาร์บอนในตัวอย่างน้ำ โดยให้ค่าร้อยละการได้กลับคืนที่ดีในช่วง 85 ถึง 98 และค่าร้อยละเบี่ยงเบนมาตรฐานสัมพัทธ์ในช่วง 3.5 ถึง 8.8 ตัวดูดซับที่พัฒนาขึ้นสามารถเตรียมได้ง่าย ราคาถูก เป็นมิตรต่อสิ่งแวดล้อม ให้ค่าการเตรียมซ้ำที่ดี และสามารถใช้ซ้ำได้อย่างน้อย 18 ครั้ง งานวิจัยที่สามคือการพัฒนาตัวดูดซับของแข็งคาลิกซารีนคอมโพสิทแกรฟีนออกไซด์ปรับปรุงผิวก้นกรองบุหรี่เคลือบพอลิ-

โดพามีน สำหรับประยุกต์ใช้ในการสกัดสารอะฟลาทอกซินในข้าวโพดและวิเคราะห์ด้วยเทคนิคโครมาโทกราฟีของเหลวสมรรถนะสูงร่วมกับตัวตรวจวัดฟลูออเรสเซนต์ โดยการประยุกต์ใช้คาลิกซารีน แกรฟีนออกไซด์ และพอลิโดพามีน เพื่อเพิ่มพื้นที่ผิวสัมผัสในการดูดซับสารอะฟลาทอกซิน ซึ่งสามารถเกิดพันธะไฮโดรเจน อันตรกิริยาแบบ π-π และไฮโดรโฟบิก ภายใต้สภาวะที่เหมาะสมวิธีที่พัฒนาขึ้นให้ช่วงความเป็นเส้นตรงตั้งแต่ 0.01 ถึง 10 ไมโครกรัมต่อกิโลกรัม และขีดจำกัดการตรวจวัดเท่ากับ 0.01 ไมโครกรัมต่อกิโลกรัม สำหรับการตรวจวิเคราะห์อะฟลาทอกซินบี 1 ให้ช่วงความเป็นเส้นตรงตั้งแต่ 0.02 ถึง 10 ไมโครกรัมต่อกิโลกรัม และขีดจำกัดการตรวจวัดเท่ากับ 0.02 ไมโครกรัมต่อกิโลกรัม สำหรับการตรวจวิเคราะห์อะฟลาทอกซินบี 2 และให้ช่วงความเป็นเส้นตรงตั้งแต่ 0.05 ถึง 10 ไมโครกรัมต่อกิโลกรัม และขีดจำกัดการตรวจวัดเท่ากับ 0.05 ไมโครกรัมต่อกิโลกรัม สำหรับการตรวจวิเคราะห์อะฟลาทอกซินจี 1 และอะฟลาทอกซินจี 2 ได้ประยุกต์ใช้วิธีที่พัฒนาขึ้นในการวิเคราะห์หาปริมาณสารอะฟลาทอกซินในตัวอย่างข้าวโพด โดยให้ค่าร้อยละการได้กลับคืนที่ดีในช่วง 83 ถึง 107 และค่าร้อยละเบี่ยงเบนมาตรฐานสัมพัทธ์ในช่วง 0.20 ถึง 14.7 ตัวดูดซับที่พัฒนาขึ้นเตรียมได้ง่าย ราคาถูก และสามารถใช้ซ้ำได้ถึง 17 ครั้ง งานวิจัยที่สี่และห้าเป็นการพัฒนาตัวดูดซับสำหรับการสกัดด้วยตัวดูดซับของแข็งอนุภาคแม่เหล็ก ในลักษณะอนุภาคแม่เหล็กคอมโพสิทอัลจิเนตเคลือบด้วยพอลิอะนิลีนและพอลิไพโรล สำหรับประยุกต์ใช้ในการสกัดและเพิ่มความเข้มข้นสารโพลีไซคลิกอะโรมาติกไฮโดรคาร์บอนและสารรบกวนการทำงานของต่อมไร้ท่อ ได้แก่ เอสไตรออล เบต้า-เอสตราไดออล และ บิสฟีนอล เอ ในตัวอย่างน้ำ และวิเคราะห์ด้วยเทคนิคโครมาโทกราฟีของเหลวสมรรถนะสูงร่วมกับตัวตรวจวัดฟลูออเรสเซนต์ โดยการประยุกต์ใช้อนุภาคแม่เหล็กช่วยให้แยกตัวดูดซับออกจากสารตัวอย่างได้ง่ายและรวดเร็วด้วยแท่งแม่เหล็ก การกักอนุภาคแม่เหล็กในเม็ดอัลจิเนตเพื่อช่วยเพิ่มการกระจายตัวของตัวดูดซับในตัวอย่างน้ำและเพิ่มพื้นที่ผิวในการเคลือบพอลิอะนิลีนและพอลิไพโรล ซึ่งพอลิอะนิลีนช่วยในการดูดซับสารโพลีไซคลิกอะโรมาติกไฮโดรคาร์บอน ด้วยอันตรกิริยาแบบ π-π และพอลิไพโรลช่วยในการดูดซับสารรบกวนการทำงานของต่อมไร้ท่อด้วยอันตรกิริยาแบบ π-π และพันธะไฮโดรเจน ภายใต้สภาวะที่เหมาะสมวิธีที่พัฒนาขึ้นให้ช่วงความเป็นเส้นตรงตั้งแต่ 0.040 ถึง 50 ไมโครกรัมต่อลิตร และขีดจำกัดการตรวจวัดเท่ากับ 0.010 ไมโครกรัมต่อลิตร สำหรับการตรวจวิเคราะห์สารโพลีไซคลิกอะโรมาติกไฮโดรคาร์บอน และให้ช่วงความเป็นเส้นตรงตั้งแต่ 0.50 ถึง 100 ไมโครกรัมต่อลิตร และขีดจำกัดการตรวจวัดเท่ากับ 0.50 ไมโครกรัมต่อลิตร สำหรับการตรวจวิเคราะห์สารรบกวนการทำงานของต่อมไร้ท่อ ได้ประยุกต์ใช้ตัวดูดซับของแข็งอนุภาคแม่เหล็กคอมโพสิทอัลจิเนตเคลือบพอลิอะนิลีนเพื่อตรวจวิเคราะห์หาปริมาณสารโพลีไซคลิกอะโรมาติกไฮโดรคาร์บอนในตัวอย่างน้ำในสิ่งแวดล้อม โดยให้ค่าร้อยละการได้กลับคืนที่ดีในช่วง 86 ถึง 98 และค่าร้อยละเบี่ยงเบนมาตรฐานสัมพัทธ์ในช่วง 3.1 ถึง 8.3 และประยุกต์ใช้ตัวดูดซับของแข็งอนุภาคแม่เหล็กคอมโพสิทอัลจิเนตเคลือบพอลิไพโรลเพื่อตรวจวิเคราะห์หาปริมาณสาร

รบกวนการทำงานของต่อมไร้ท่อในตัวอย่างน้ำในสิ่งแวดล้อม โดยให้ค่าร้อยละการได้กลับคืนที่ดีในช่วง 91 ถึง 98 และค่าร้อยละเบี่ยงเบนมาตรฐานสัมพัทธ์ในช่วง 3.0 ถึง 7.2 ตัวดูดซับที่พัฒนาขึ้นสามารถเตรียมได้ง่าย ใช้งานสะดวก ราคาถูก ให้ค่าการเตรียมซ้ำที่ดี และเป็นมิตรต่อสิ่งแวดล้อม

ในส่วนที่สองเป็นการพัฒนาเทคนิคการสกัดด้วยของเหลวปริมาณน้อยด้วยลวดสแตนเลสของลูกสูบในเข็มฉีดขนาดเล็ก งานวิจัยสุดท้ายคือการพัฒนาการกัดกร่อนลวดสแตนเลสของลูกสูบที่เป็นมิตรต่อสิ่งแวดล้อม โดยใช้สารละลายผสมระหว่างเฟอร์ริกคลอไรด์และกรดไฮโดรคลอริกเป็นสารกัดกร่อนแทนการใช้กรดไฮโดรฟลูออริก การกัดกร่อนทำได้โดยจุ่มเส้นลวดสแตนเลสของลูกสูบลงในสารกัดกร่อนในขั้นตอนเดียว โดยการประยุกต์ใช้ลวดสแตนเลสที่กัดกร่อนซึ่งมีพื้นผิวขรุขระช่วยในการพยุงตัวทำละลายอินทรีย์ในการสกัดสารโพลีไซคลิกอะโรมาติกไฮโดรคาร์บอนโดยการจุ่มโดยตรงลงไปในตัวอย่างน้ำ หลังจากการสกัดนำไปคายการดูดซับด้วยความร้อนที่ส่วนหัวฉีดของเครื่องแก๊สโครมาโทกราฟเพื่อการวิเคราะห์ ภายใต้สภาวะที่เหมาะสมวิธีที่พัฒนาขึ้นให้ช่วงความเป็นเส้นตรงตั้งแต่ 0.01 ถึง 50 ไมโครกรัมต่อลิตร และขีดจำกัดการตรวจวัดอยู่ในช่วง 0.006 ถึง 0.058 ไมโครกรัมต่อลิตร ให้ค่าการเตรียมซ้ำที่ดี โดยมีค่าร้อยละเบี่ยงเบนมาตรฐานสัมพัทธ์ในช่วง 4.2 ถึง 12.7 วิธีการกัดกร่อนที่เป็นมิตรต่อสิ่งแวดล้อมที่พัฒนาขึ้นสามารถทำได้ง่าย รวดเร็วในขั้นตอนเดียว และได้ประยุกต์ใช้วิธีที่พัฒนาขึ้นในการสกัดและเพิ่มความเข้มข้นสารโพลีไซคลิกอะโรมาติกไฮโดรคาร์บอนในตัวอย่างน้ำ โดยให้ค่าร้อยละการได้กลับคืนที่ดีในช่วง 84 ถึง 102 และค่าร้อยละเบี่ยงเบนมาตรฐานสัมพัทธ์ในช่วง 1.0 ถึง 9.5

โดยสรุปผลของการศึกษาแสดงให้เห็นว่าเทคนิคการเตรียมตัวอย่างที่พัฒนาขึ้นสามารถประยุกต์ใช้ในการตรวจวิเคราะห์สารปนเปื้อนอินทรีย์ปริมาณน้อยในสิ่งแวดล้อมและอาหารได้อย่างมีประสิทธิภาพ สามารถทำได้ง่าย ใช้งานสะดวก ราคาถูก และเป็นมิตรต่อสิ่งแวดล้อม นอกจากนี้ตัวดูดซับที่พัฒนาขึ้นสามารถนำไปประยุกต์ใช้ในการสกัดสารปนเปื้อนอินทรีย์อื่น ๆ ในสิ่งแวดล้อมและอาหาร โดยใช้ร่วมกับเทคนิควิเคราะห์ทางโครมาโทกราฟี

Thesis title	Development and Application of Sample Preparation Techniques for the Determination of Trace Organic Contaminants in Environment and Food
Author	Miss Piyaluk Nurerk
Major Program	Chemistry
Academic year	2019

ABSTRACT

This thesis aimed to develop and apply sample preparation techniques for the determination of trace organic contaminants in environment and food. Two parts based on extraction phase were performed, including sorbent-based extraction and liquid phase-microextraction.

In the first part focused on the development of solid-phase extraction (SPE) and magnetic solid-phase extraction (MSPE) for sorbent-based extraction techniques. Five sub-projects were carried out. The first sub-project was a metal organic frameworks material of MIL-101. It was successfully synthesized and utilized as a SPE adsorbent for the extraction and preconcentration of UV filters followed by gas chromatography-tandem mass spectrometry (GC-MS/MS). The high porous of MIL-101 adsorbent has large surface area and strong adsorption ability of UV filters through π-π and hydrophobic interactions. Under the optimum conditions, the developed method provided the linear in the range of 0.5 – 100 μg L^{-1} with the low limits of detection in the range of 1.0 – 11.7 ng L^{-1}. This method has been successfully applied for the extraction and quantification of UV filters in environmental and recreational water samples. The developed MIL-101 adsorbent provided good recoveries in a range of 82 – 105% with a relative standard deviations (%RSDs) in the range of 0.9 – 9.7%. The second sub-project was polyaniline coated cigarette filters which were successfully synthesized and employed as the SPE adsorbent for the extraction and enrichment of polycyclic aromatic hydrocarbons (PAHs) in environmental water samples and quantified by high-performance liquid chromatography with fluorescence detector (HPLC-FLD). The high porosity and large surface area of cigarette filters helped to reduce the back pressure allowing extraction

process at the high sample flow rate without loss of extraction ability. The coating of polyaniline facilitated the strong adsorption of PAHs via π-π interaction. Under the optimum conditions, the linearity was in the range of 0.005 – 10 µg L^{-1} with a low detection limit of 0.5 ng L^{-1}. This method provided a high enrichment factor and good recoveries in the range of 85 – 98% with RSDs in the range of 3.5 – 8.8%. The developed adsorbent is easy to prepare, cost-effective, environmentally friendly, reproducible and could be reused up to 18 times. The third sub-project was a hybrid adsorbent of calix[4]arene functionalized graphene oxide onto polydopamine-coated cigarette filters. This adsorbent was applied for the SPE and clean-up aflatoxins in corn samples followed by HPLC-FLD. This porous adsorbent included the combination of polydopamine, graphene oxide and calix[4]arene for the fabrication of a hybrid adsorbent which facilitated the highly efficient adsorption of aflatoxins via hydrogen bonding, hydrophobic and π-π interactions. Under the optimum conditions, the developed adsorbent provided a linear response in the range of 0.01 – 10 µg kg^{-1} with a detection limit of 0.01 µg kg^{-1} for aflatoxin B1, 0.02 – 10 µg kg^{-1} with a detection limit of 0.02 µg kg^{-1} for aflatoxin B2 and 0.05 – 10 µg kg^{-1} with a detection limit of 0.05 µg kg^{-1} for aflatoxin G1 and aflatoxin G2. This method was successfully applied for the determination of aflatoxins from corn samples with satisfactory recoveries from 83 to 107% with the RSDs ranging from 0.20 to 14.7%. The developed adsorbent is simple to prepare, low cost and could be reused up to 17 times. The fourth and fifth sub-project were polyaniline and polypyrrole coated magnetite nanoparticles incorporated in alginate beads. The magnetic adsorbents were successfully synthesized and used as MSPE adsorbent for the extraction and preconcentration of PAHs and endocrine-disrupting compounds (EDCs) including estriol, β-estradiol and bisphenol A in water samples followed by HPLC-FLD. The magnetite nanoparticles provided a simple and fast separation of the adsorbent from the sample solution using an external magnet. An alginate hydrogel helped to entrap the magnetite nanoparticles for increasing of dispersibility and enhancing the surface area for coating. The large surface areas of polyaniline coated alginate/magnetite composite helped to increase the extraction yield of PAHs via π–π interaction and polypyrrole coating facilitated the high adsorption of EDCs through hydrogen bonding, π–π and hydrophobic interactions. The developed method provided a wide linear range from 0.040 to 50 µg L^{-1} with a low detection limit

of 0.010 µg L^{-1} for PAHs and from 0.50 to 100 µg L^{-1} with a low detection limit of 0.50 µg L^{-1} for EDCs. The developed adsorbent of polyaniline coated magnetite nanoparticles entrapped in alginate beads were applied for the extraction and preconcentration of PAHs in environmental water samples with a good recovery of 86 – 98% and the RSDs in the range of 3.1 – 8.3%. The developed adsorbent of polypyrrole coated magnetite nanoparticles entrapped in alginate beads were effectively applied for the extraction and determination of EDCs in environmental water samples with a good recovery of 91 – 98% and the RSD in the range of 3.0 – 7.2%. The developed adsorbents are simple to prepare, convenient, cost-effective, good reproducibility and environmentally friendly.

In the second part focused on the development of liquid phase-microextraction approach called plunger-in-needle liquid phase-microextraction (PIN-LPME). The last sub-project was environmentally friendly method of etching a stainless steel plunger wire using ferric chloride-hydrochloric acid ($FeCl_3$-HCl) solution as the etchant, replacing the conventional hydrofluoric acid use. The etching procedure was operated in one-step by immersing a stainless steel plunger wire directly into the etchant. The etched plunger wire provided rough surface, allowing stable organic solvent holder for PIN-LPME and then directly expose into water samples for the extraction of PAHs. The extract was subsequently subjected to thermal desorption in injector port of gas chromatograph for analysis. Under the optimal conditions, the developed method provided good linearity in the range of 0.01 – 50 µg L^{-1}, low detection limits in the range of 0.006 – 0.058 µg L^{-1} and good reproducibility with RSDs in the range of 4.2 – 12.7%. The environmentally friendly etching method is simple, fast and one-step approach and successfully applied for extraction and enrichment of PAHs in water samples with good recovery of 84 – 102% and RSDs in the range of 1.0 – 9.5%.

In conclusion, the sample preparation techniques were successfully developed and applied for the determination of trace organic contaminants in environment and food. These developed methods provided good analytical performance with several advantages, including simple to prepare, convenient, cost-effective and environmentally friendly. The developed methods have the potential to apply for the extraction and determination of others trace organic contaminant in environment and food samples coupled with chromatography for analysis.

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Piyaluk Nurerk

THE RELEVANCE OF THE RESEARCH WORK TO THAILAND

The purpose of this Doctor of Philosophy Thesis in Chemistry is to develop and apply sample preparation techniques for trace organic contaminants in environment and food coupled to chromatography for analysis. These developed methods provided good analytical performance, simple to prepare, convenient, cost-effective and environmentally friendly. They can be applied for the determination of UV filters, polycyclic aromatic hydrocarbons, aflatoxins and endocrine-disrupting compounds in real samples, including corn, environmental and recreational water. Furthermore, the developed methods have the potential to apply for the determination of others trace organic contaminants and can be used as alternative analytical methods in several governmental organizations and private sectors in Thailand.

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LIST OF ABBREVIATIONS

BI-SDME	Bubble-in-single drop microextraction
DLLME	Dispersive liquid–liquid microextraction
EDCs	Endocrine disrupting compounds
EU	European Union
FLD	Fluorescence detector
GC	Gas chromatography
GOx	Graphene oxide
HPLC	High-performance liquid chromatography
LLE	Liquid-liquid extraction
LPME	Liquid phase-microextraction
MCLs	Maximum contaminant level
MOFs	Metal organic frameworks
MRLs	Maximum residue limits
MS	Mass spectrometry
MSPE	Magnetic solid-phase extraction
PAHs	Polycyclic aromatic hydrocarbons
PIN-LPME	Plunger-in-needle liquid phase-microextraction
SBSE	Stir bar sorptive extraction
SDME	Single drop microextraction
SPE	Solid-phase extraction
SPME	Solid-phase microextraction
US EPA	United states Environmental Protection Agency

List of Publications

This thesis is divided into two parts based on extraction phase of sample preparation techniques, including sorbent-based extraction and liquid phase-microextraction. The following papers are referred to in the text by their Roman numerals.

Paper I	**Nurerk, P**., Llompart, M., Donkhampa, P., Bunkoed, O., Dagnac, T., Solid-phase extraction based on MIL-101 adsorbent followed by gas chromatography tandem mass spectrometry for the analysis of multiclass organic UV filters in water. *Journal of Chromatography A* (2019) https://doi.org/10.1016/j.chroma.2019.460564.
Paper II	Bunkoed, O., Rueankaew, T., **Nurerk, P.**, Kanatharana, P., Polyaniline-coated cigarette filters as a solid-phase extraction sorbent for the extraction and enrichment of polycyclic aromatic hydrocarbons in water samples. *Journal of Separation Science* 39 (2016) 2332-2339.
Paper III	**Nurerk, P.**, Bunkoed, W., Kanatharana, P., Bunkoed, O., A miniaturized solid-phase extraction adsorbent of calix[4]arene-functionalized graphene oxide/polydopamine-coated cellulose acetate for the analysis of aflatoxins in corn. *Journal of Separation Science* 41 (2018) 3892-3901.
Paper IV	**Nurerk, P.**, Kanatharana, P., Bunkoed, O., Polyaniline-coated magnetite nanoparticles incorporated in alginate beads for the extraction and enrichment of polycyclic aromatic hydrocarbons in water samples. *International Journal of Environmental Analytical Chemistry* 97(2) (2017) 145-158.

Paper V	Bunkoed, O., **Nurerk, P.**, Wannapob, R., Kanatharana, P., Polypyrrole-coated alginate/magnetite nanoparticles composite sorbent for the extraction of endocrine-disrupting compounds. *Journal of Separation Science* 39 (2016) 3602-3609.
Paper VI	**Nurerk, P.**, Liew, C.S.M., Bunkoed, O., Kanatharana, P., Lee, H.K., Environmentally friendly etching of stainless steel wire for plunger-in-needle liquid-phase microextraction of polycyclic aromatic hydrocarbons. *Talanta* 197 (2019) 465-471.

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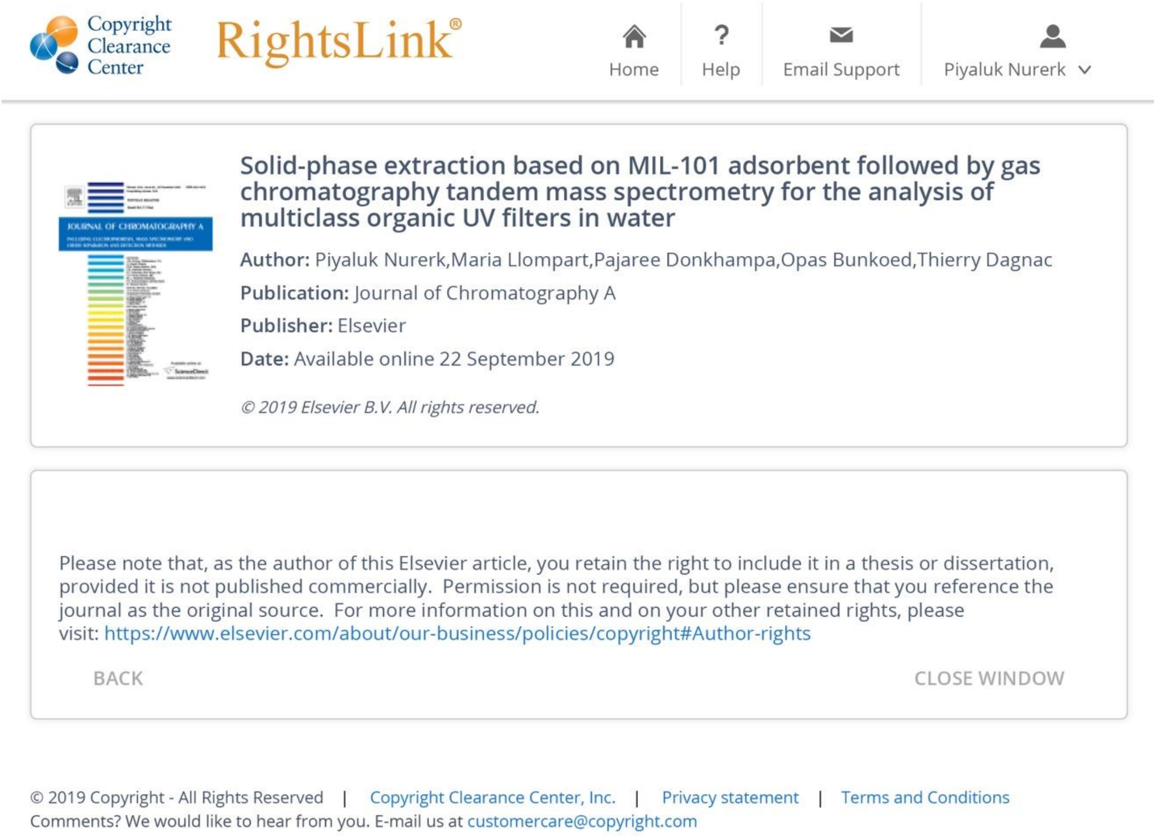

Solid-phase extraction based on MIL-101 adsorbent followed by gas chromatography tandem mass spectrometry for the analysis of multiclass organic UV filters in water

Author: Piyaluk Nurerk,Maria Llompart,Pajaree Donkhampa,Opas Bunkoed,Thierry Dagnac

Publication: Journal of Chromatography A

Publisher: Elsevier

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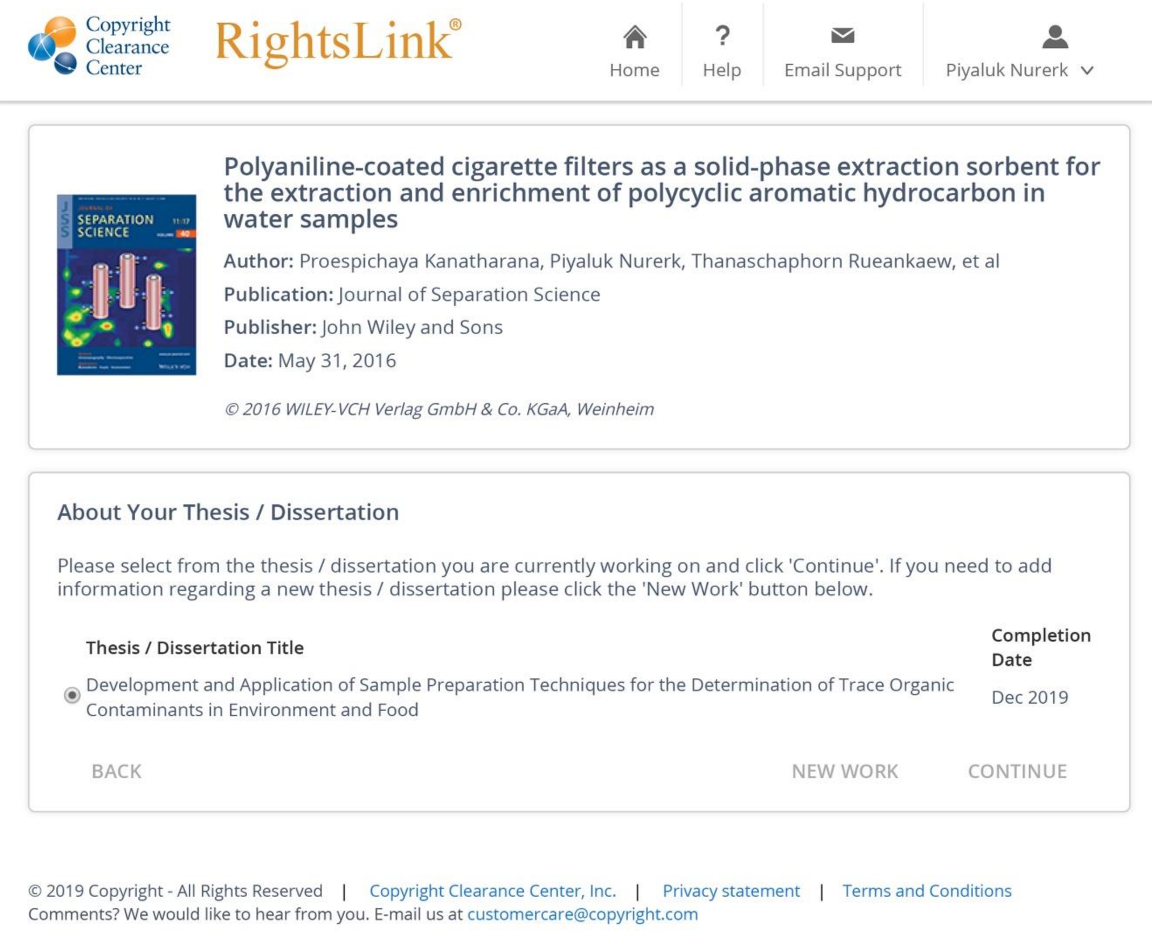

Polyaniline-coated cigarette filters as a solid-phase extraction sorbent for the extraction and enrichment of polycyclic aromatic hydrocarbon in water samples

Author: Proespichaya Kanatharana, Piyaluk Nurerk, Thanaschaphorn Rueankaew, et al

Publication: Journal of Separation Science

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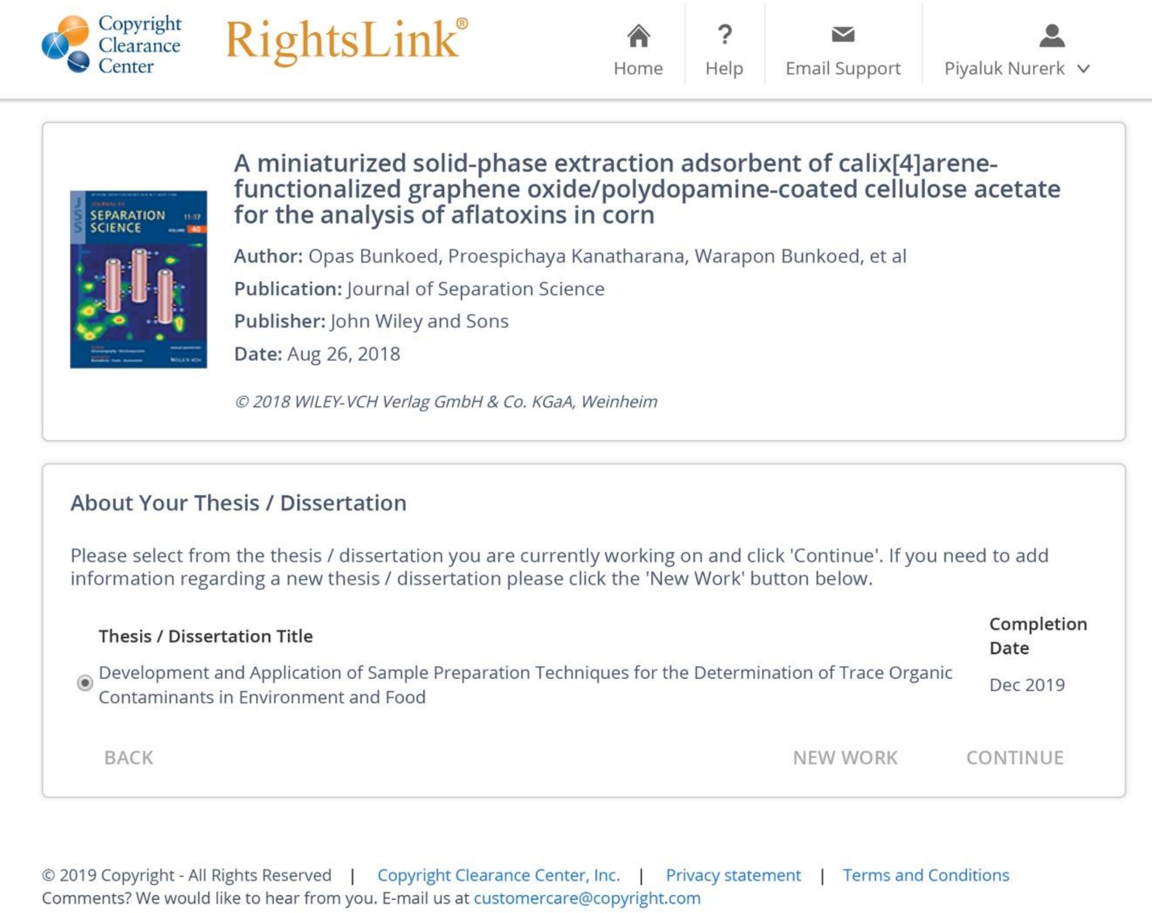

A miniaturized solid-phase extraction adsorbent of calix[4]arene-functionalized graphene oxide/polydopamine-coated cellulose acetate for the analysis of aflatoxins in corn

Author: Opas Bunkoed, Proespichaya Kanatharana, Warapon Bunkoed, et al

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Paper IV

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Polyaniline-coated magnetite nanoparticles incorporated in alginate beads for the extraction and enrichment of polycyclic aromatic hydrocarbons in water samples

Author: Piyaluk Nurerk, , Proespichaya Kanatharana, et al

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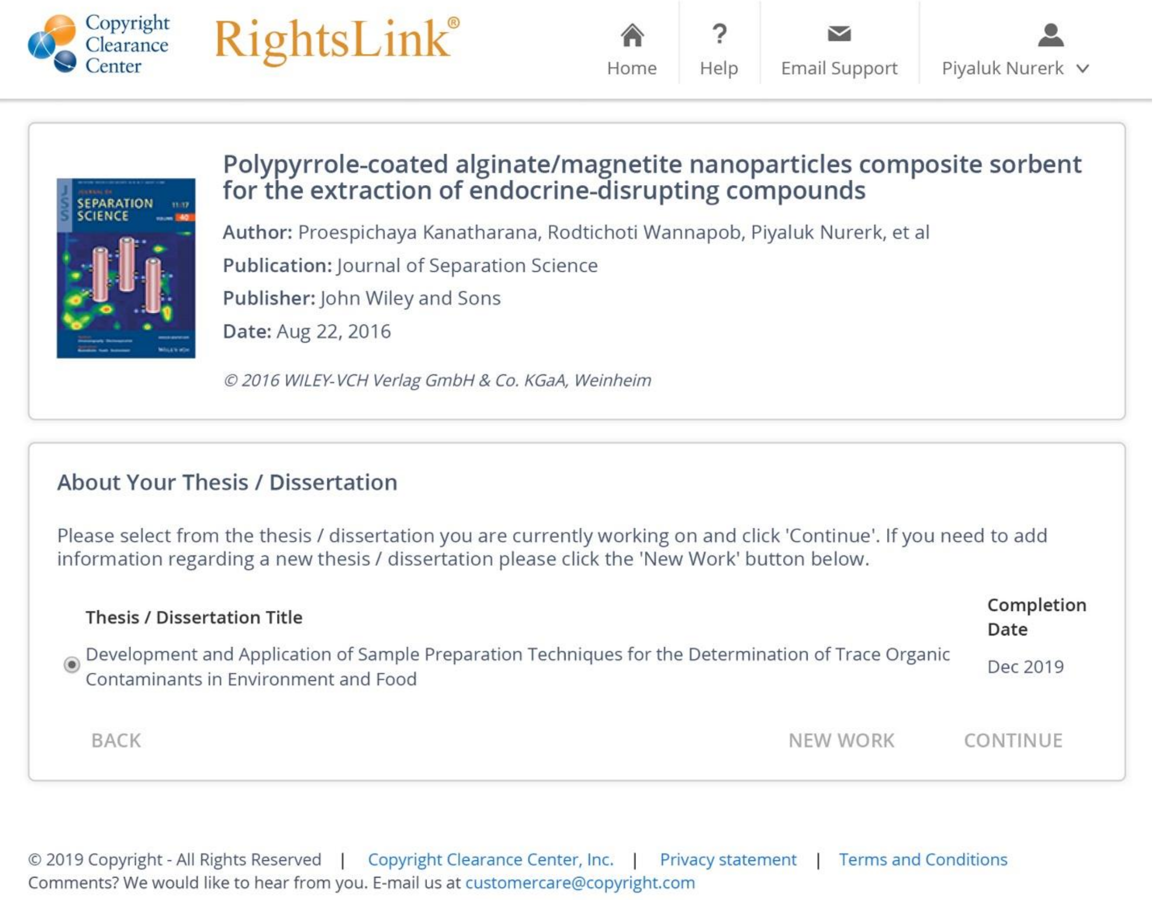

Polypyrrole-coated alginate/magnetite nanoparticles composite sorbent for the extraction of endocrine-disrupting compounds

Author: Proespichaya Kanatharana, Rodtichoti Wannapob, Piyaluk Nurerk, et al

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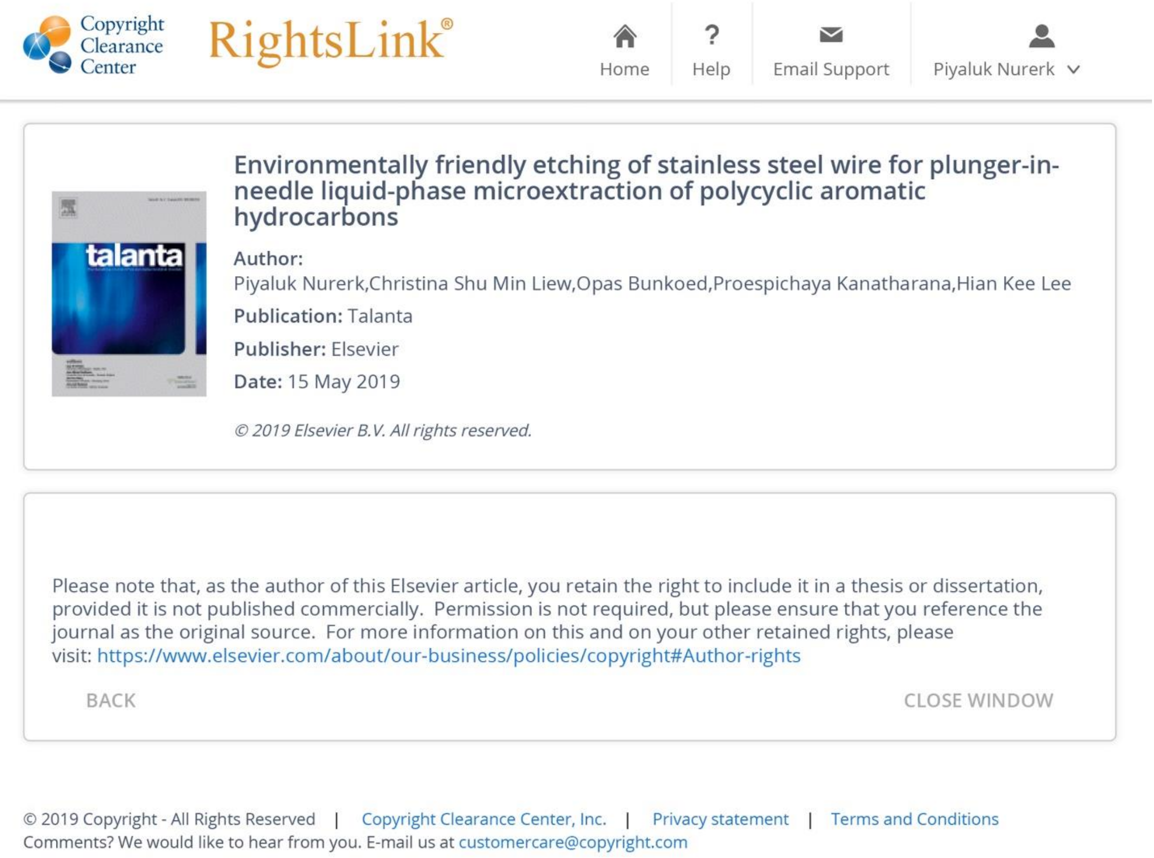

Environmentally friendly etching of stainless steel wire for plunger-in-needle liquid-phase microextraction of polycyclic aromatic hydrocarbons

Author:
Piyaluk Nurerk,Christina Shu Min Liew,Opas Bunkoed,Proespichaya Kanatharana,Hian Kee Lee

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1. Introduction

1.1 Background and rationale

Recently, the increasing of organic contaminants emerged in the environment and food is a problem of great concern to human health and ecological systems. These contaminants are produced from both synthetic compounds with agriculture, industry, transport, domestic activities and natural chemicals by hormones excretion (Dimpe and Nomngongo, 2016; Fernández-Ramos *et al.*, 2014; Geissen *et al.*, 2015). Typical organic contaminants, including polycyclic aromatic hydrocarbons (PAHs), UV filters, bisphenol A, estrogens and aflatoxins, are widespread released in environmental and food matrices. They can enter the food chain and cause harm to the human health and other organisms, even at trace (parts per billion or parts per trillion) levels (Mueller *et al.*, 2003; Schlumpf *et al.*, 2008; Wang *et al.*, 2015a; Wen and Zhu, 2014). The occurrence of emerging contaminants in environmental matrices, such as PAHs, UV filters, bisphenol A and estrogens, can cause adverse effect on endocrine disruption and they have potential to be mutagen and carcinogen. (Gorga *et al.*, 2014; Plagellat *et al.*, 2006; Schlumpf *et al.*, 2004; Yao *et al.*, 2015). The contamination of highly toxic aflatoxins in food can cause cancer for human and also agricultural damage (Akiyama *et al.*, 2001; Hussein and Brasel, 2001; IARC, 2002).

To ensure human health and food safety, several organizations have set the legislative limits for these organic contaminants in environment and food. Environmental Protection Agency (US EPA) has listed PAHs as priority pollutants, and established the maximum contaminant level (MCLs) for some of PAHs in water, included Benzo(a)anthracene 0.1 µg L^{-1}, Benzo(b)fluoranthene and Benzo(a)pyrene 0.2 µg L^{-1} (EPA, 2008). The European Union (EU) has listed 2-Ethylhexyl methoxycinnamate as priority pollutant in European monitoring water policy (EU, 2015). The EU has set maximum residue limits (MRLs) of total aflatoxins in cereals of 4.0 µg kg^{-1} and 2.0 µg kg^{-1} for aflatoxins B1 (EU, 2006). Therefore, to assess the risk of human health and control food safety, the determination of these organic contaminants in environment and food is crucial.

Analytical techniques which are generally used to determine the organic contaminants including gas chromatography (GC) and high-performance liquid chromatography (HPLC) with various detectors. These techniques provide high sensitivity, good selectivity and simultaneous analysis of multiple analytes using separation column (Nascimento *et al.*, 2015; Yang *et al.*, 2011; Zhao *et al.*, 2016a). However, the organic contaminants are usually present at trace levels with the complex matrices, a suitable sample preparation is required to concentrate the target analytes and clean-up the sample before instrumental analysis (Tobiszewski *et al.*, 2009; Xu *et al.*, 2016).

The recent trend of sample preparation for the determination of trace organic compounds attempts to miniaturize the extraction process, being environmentally friendly method (Armenta *et al.*, 2019; Ribeiro *et al.*, 2014). Regarding to the extraction phase, sorbent-based extraction is an interesting sample preparation technique because of its highly efficient extraction and preconcentration (Azzouz *et al.*, 2018). Solid-phase extraction (SPE) is a sample preparation technique based on sorbent-based extraction which is the most extensively used for the extraction and determination of organic contaminants due to its good extraction efficiency and simplicity (Andrade-Eiroa *et al.*, 2016a; Azzouz *et al.*, 2018). Commercially packed SPE cartridges have been used for the extraction of organic contaminant such as C18 bonded silica and copolymer. However, the commercially available adsorbents are expensive, and the cartridge clogging can occur due to their packed particulate matter (Noosang *et al.*, 2015; Nurerk *et al.*, 2018). To overcome these drawbacks, the porous adsorbent and porous supporting materials, which composited/modified with adsorption materials, have been applied as SPE adsorbents, such as metal organic frameworks, cigarette filters and alginate hydrogel bead (Bunkoed *et al.*, 2016b; Nurerk *et al.*, 2017; Nurerk *et al.*, 2019b).

Besides, a new SPE mode based on the magnetic adsorbent called magnetic solid-phase extraction (MSPE) has been developed. The magnetic adsorbent can be easily and fast separated from the sample solution using an external magnetic field

(Herrero-Latorre *et al.*, 2015; Speltini *et al.*, 2016). To improve adsorption ability and stability of the magnetic adsorbent, the high affinity materials and porous supporting materials have been composited or modified onto the magnetic adsorbent (Bunkoed *et al.*, 2016a; Deng *et al.*, 2013; Nurerk *et al.*, 2017). Therefore, the propose of the first part of this thesis is to develop the SPE and MSPE adsorbents which are high extraction capability, simple to prepare and cost-effective for the extraction and determination of UV filters **(Paper I)**, PAHs **(Paper II, IV)** and aflatoxins **(Paper III)**, endocrine disrupting compounds (EDCs) including estrogens and bisphenol A **(Paper V)**.

Based on liquid-based extraction, liquid-liquid extraction (LLE) is a traditional sample preparation method for the extraction of organic contaminants. The LLE procedure has several limitations such as large amounts of toxic organic solvent and sample use, tedious operation and time-consuming. (Hyötyläinen and Riekkola, 2008; Sarafraz-Yazdi and Amiri, 2010). By the current trend of miniaturized and environmentally friendly sample preparation techniques, liquid phase-microextraction (LPME) is an alternative approach to minimize the solvent consumption. The LPME uses microliters of extraction solvent to extract and preconcentrate the target analytes in one-step (Kokosa, 2013; Spietelun *et al.*, 2014; Stanisz *et al.*, 2014). LPME has been developed in several modes such as single drop microextraction (SDME) (Jain and Verma, 2011; Psillakis and Kalogerakis, 2002), bubble-in-single drop microextraction (BI-SDME) (Guo *et al.*, 2016) and hollow fiber LPME (Ratola *et al.*, 2008; Sibiya *et al.*, 2013). Nevertheless, the SDME and BI-SDME are lack of stability of solvent drop, as well as the formation of air bubbles in the hollow fiber, leading to poor reproducibility (Charalabaki *et al.*, 2005; Płotka-Wasylka *et al.*, 2016). Consequently, the second part of this thesis is focused on the development of the new approach of LPME based on the simple, fast and environmentally friendly method for the extraction and preconcentration of PAHs **(Paper VI)**

1.2 Objective

The objective of this thesis is to develop sample preparation techniques for the extraction and determination of trace organic contaminants in environment and food. Two parts based on extraction phase consisting of sorbent-based extraction and liquid phase-microextraction were studied as follows.

Part I: Sorbent-based extraction

Sub-project I: A metal organic frameworks material of MIL-101 was synthesized and used as a SPE adsorbent for extraction and determination of UV filters compounds in environmental and recreational water samples **(Paper I)**.

Sub-project II: Polyaniline coated cigarette filters were synthesized and used as a SPE adsorbent for the extraction and preconcentration of PAHs in environmental water samples **(Paper II)**.

Sub-project III: The hybrid SPE adsorbent consisting of calix[4]arene functionalized graphene oxide onto polydopamine coated cigarette filters was synthesized and used for the extraction and preconcentration of aflatoxins in corn samples **(Paper III)**.

Sub-project IV: The MSPE adsorbent of polyaniline coated magnetite nanoparticles entrapped in alginate beads was prepared and applied for the extraction and preconcentration of PAHs in environmental water samples **(Paper IV)**.

Sub-project V: The magnetite nanoparticles incorporated into alginate beads and coated with a polypyrrole adsorbent were synthesized and used as MSPE adsorbent for the extraction and preconcentration of EDCs including estriol, β-estradiol and bisphenol A in environmental water samples **(Paper V)**.

Part II: Liquid phase-microextraction

Sub-project VI: The environmentally friendly method of etching a stainless steel plunger wire for plunger-in-needle LPME was developed and applied for the extraction and preconcentration of PAHs in environmental water samples **(Paper VI)**.

2. Sample preparation techniques

The contamination of organic compounds usually presents at the trace level within a complex matrix. Thus, sample preparation is an important step before instrumental analysis which can eliminate the interferences and preconcentrate the target analytes. In addition, it can improve the limits of detection of the analytical method (Pyrzynska, 2018; Tobiszewski *et al.*, 2009; Xu *et al.*, 2016). By the recent trend of miniaturized and environmentally friendly sample preparation techniques, a number of sample preparation techniques, both sorbent-based extraction and liquid-based extraction techniques, have been developed and applied for the extraction of trace organic contaminants in various samples such as solid-phase extraction (SPE) (Liu *et al.*, 2004; Liu *et al.*, 2013; Wang *et al.*, 2007), magnetic solid-phase extraction (MSPE) (Hashemi *et al.*, 2014; Sukchuay *et al.*, 2015; Zhang *et al.*, 2010a), stir bar sorptive extraction (SBSE) (Magi *et al.*, 2012; Noroozian and Rahimi, 2015), solid-phase microextraction (SPME) (Pang and Liu, 2012; Yang *et al.*, 2006), liquid–liquid extraction (LLE) (Rodil *et al.*, 2009; Tavakoli *et al.*, 2008), dispersive liquid–liquid microextraction (DLLME) (Campone *et al.*, 2011; Fernández *et al.*, 2015) and liquid phase-microextraction (LPME) (Charalabaki *et al.*, 2005; Loh *et al.*, 2013).

Among them, solid-phase extraction (SPE), magnetic solid-phase extraction (MSPE) and liquid phase-microextraction (LPME) are particularly interesting techniques due to their simplicity, convenience, less amount of solvent and sample use, low-cost operation and enabled high throughput determination. (Andrade-Eiroa *et al.*, 2016a; Armenta *et al.*, 2019; Ribeiro *et al.*, 2014; Sanagi *et al.*, 2012).

2.1 Sorbent-based extraction

Sorbent-based extraction has attracted much attention as a sample preparation technique due to its ability to efficiently clean-up the sample and preconcentrate the target analytes based on the adsorption of the target analytes onto the adsorbent (Andrade-Eiroa *et al.*, 2016a; Azzouz *et al.*, 2018).

2.1.1 Solid-phase extraction (SPE)

Solid-phase extraction (SPE) is the most widely used sample preparation method for the extraction and determination of organic compounds due to its extraction capacity with high recovery, high enrichment factor and ease of operation (Andrade-Eiroa *et al.*, 2016b; Azzouz *et al.*, 2018). The basic principle of solid-phase extraction is based on the partitioning of the analytes from the sample matrix (liquid) into a solid phase (adsorbent). SPE procedure usually involves four steps as demonstrated in Figure

1. First, the SPE adsorbent is conditioned with the suitable organic solvent to remove impurities on the surface of sorbents for the subsequent loading the sample, in this step the analytes are adsorbed on the surface of the sorbent. The adsorbent is then washed to remove the interferences and eluted the retained analytes with an appropriate eluting solvent (Buszewski and Szultka, 2012; Camel, 2003).

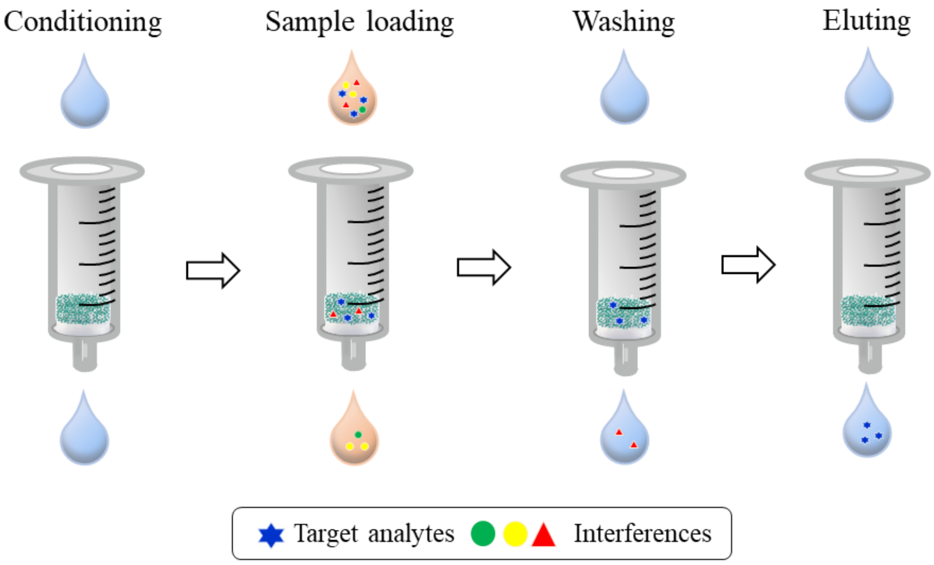

Figure 1 Schematic of solid-phase extraction procedure

The selection of adsorbent is a key parameter to obtain good extraction efficiency and enrichment capability of the target analytes. Various commercial SPE adsorbents have been used for the extraction of trace organic compounds such as C18 bonded silica (Abdel-Azeem *et al.*, 2015; Díaz-Cruz *et al.*, 2012), copolymer hydrophilic-lipophilic balance (HLB) (Liu *et al.*, 2011b; Ventura *et al.*, 2004) and graphitized carbon black (GCB) (Cavaliere *et al.*, 2007; Gentili *et al.*, 2002). However, shortcomings of these commercial adsorbents include cartridge clogging and expensiveness (Bunkoed *et al.*, 2016b; Noosang *et al.*, 2015). In recent years, the new porous materials have received extensive attention to obtain better extraction efficiency, minimize SPE method and reduce analytical cost. Several porous materials have been applied for SPE as an adsorbent and supporting material such as carbon nanomaterials

(Cai *et al.*, 2003; Liu *et al.*, 2011a; Yu *et al.*, 2013a), metal organic framework (Wang *et al.*, 2013b, **Paper I**), cryogel (Chullasat *et al.*, 2017; Noosang *et al.*, 2015) and cigarette filters **(Paper II, III)**. Moreover, high affinity materials have been coated or composited with supporting material to enhance their extraction efficiency and enrichment capability. Various adsorption materials, such as polymers **(Paper I-II)**, graphene oxide and calixarene **(Paper III)** have been used for sample enrichment. The extraction efficiency of the developed SPE adsorbents were comparable or better than commercial SPE adsorbent (Figure 2). However, the developed adsorbents were lower cost and could be reused. This result indicated that the developed adsorbents can be used as alternative adsorbents for the extraction and determination of trace organic contaminants.

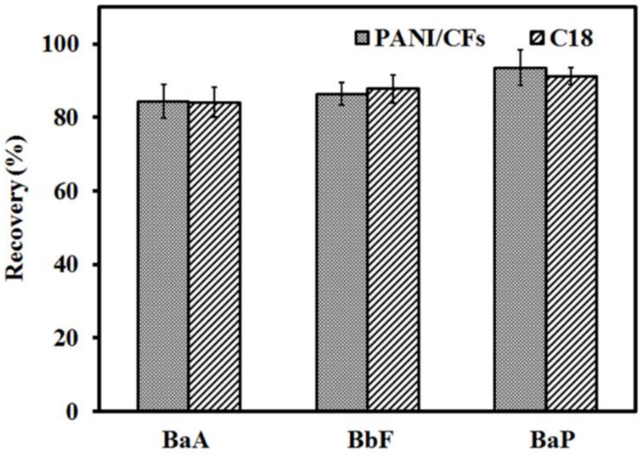

Figure 2 Comparison between the developed PANI/CFs sorbent and the commercial C18 sorbent for extraction of the PAHs from spiked deionized water (Reprinted form Bunkoed and coworkers, 2016; copyright with permission form Wiley Online Library) (Bunkoed *et al.*, 2016b)

2.1.2 Magnetic solid-phase extraction (MSPE)

Magnetic solid-phase extraction (MSPE) is a modified mode of SPE. This method employs the magnetic adsorbent to extract the target analytes by direct dispersion into sample matrix which facilitates the adsorption capability between adsorbents and analytes through their interactions. This extraction method also provides rapid magnetic separation avoiding centrifugation or filtration, and convenient operation (Herrero-Latorre *et al.*, 2015; Speltini *et al.*, 2016; Wang *et al.*, 2013a). The MSPE procedure is carried out as shown in Figure 3. The adsorbents are directly dispersed into sample solution, performing the adsorption with suitable extraction time under stirring. After adsorption, the adsorbents with adsorbed target analytes are separated from the sample solution using an external magnet. Subsequently, the adsorbed analytes are eluted with a desorption solvent and quantified. Furthermore, the adsorbents can be reused which can reduce analysis cost and time (Herrero-Latorre *et al.*, 2015; Wierucka and Biziuk, 2014).

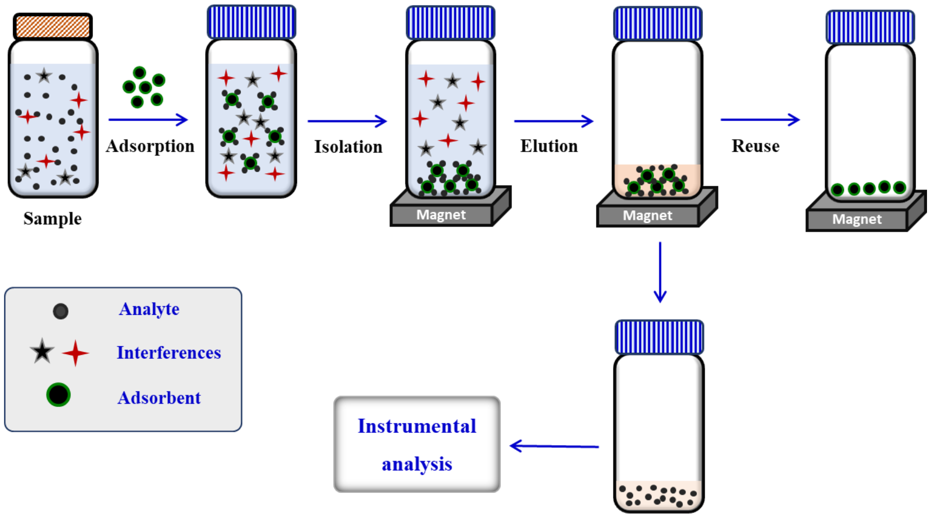

Figure 3 Schematic of magnetic solid-phase extraction procedure

Various magnetic nanoparticles (MNPs) have been used as MSPE adsorbent such as iron, nickel, cobalt, and their oxides, (Li *et al.*, 2013; Li *et al.*, 2015b; Yu *et al.*, 2019). However, pure MNPs are prone to aggregate, leading to low dispersibility and loss of their surface contact area towards the target analytes (Pinsrithong and Bunkoed, 2018; Yu *et al.*, 2019). To overcome these shortcomings, the MNPs are normally modified with suitable materials e.g. silica (Hakami *et al.*, 2012) and surfactants (Zhao *et al.*, 2008), or incorporated into porous polymeric hydrogel e.g. alginate, chitosan and gelatin (Figure 4). The modification of MNPs can improve their durability and adsorption affinity by enhancing the dispersion. (Hao *et al.*, 2015; Nurerk *et al.*, 2017; Yu *et al.*, 2013b).

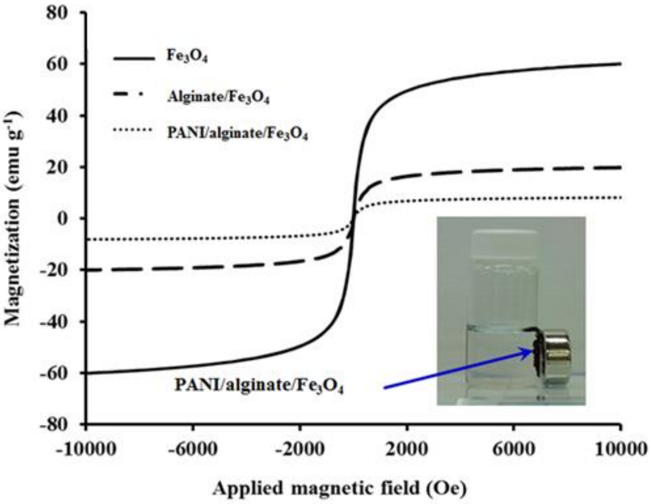

Figure 4 The hysteresis loops of Fe_3O_4, Alginate/Fe_3O_4 and PANI/alginate/Fe_3O_4. The inset represents the PANI/alginate/Fe_3O_4 beads separated by a magnet (Reprinted form Nurerk and coworkers, 2017; copyright with permission form Taylor & Francis Online) (Nurerk *et al.*, 2017)

In addition, a wide variety of high affinity coating materials have been modified onto or composited with the magnetic adsorbent to improve their extraction efficiency. These adsorption materials include multiwall carbon nanotubes (Bunkoed and Kanatharana, 2015), graphene oxide (Deng *et al.*, 2013) and polymers **(Paper IV, V)**.

2.1.3 Supporting materials

2.1.3.1 Cigarette filters

Cigarette filters are an interesting porous supporting material. They are made from cellulose acetate fibers which provide three-dimensional porous structure (Figure 5) allowing an easy flow of the sample solution at a high rate with low back pressure (Liu *et al.*, 2015a; Nascimento *et al.*, 2016) and they are also cost-effective and convenient to use. cigarette filters have been successfully applied as a supporting material of adsorbent for the preconcentration of various compounds such as metal ions

(Li *et al.*, 2009b; Li *et al.*, 2015a), ketoconazole (Andrade *et al.*, 2015), PAHs **(Paper II)** and aflatoxins **(Paper III)** in environmental, biological and food samples.

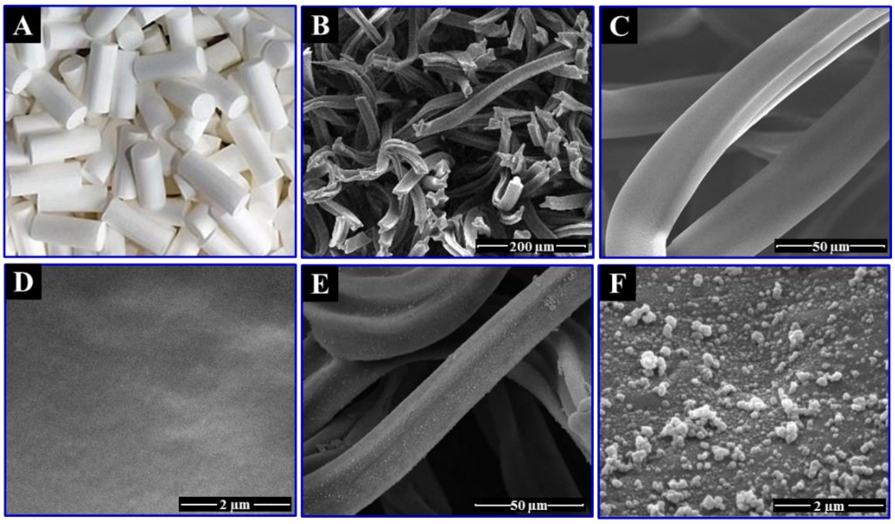

Figure 5 Photo of cigarette filters (A) and SEM image of highly porous structure cigarette filters at 200x magnification (B); 1000x magnification (C); 20000x magnification (D) and calix[4]arene-GO/PDA-CFs adsorbent at 1000x (E); 20000x magnification (F) (Reprinted form Nurerk and coworkers, 2018; copyright with permission form Wiley Online Library) (Nurerk *et al.*, 2018)

2.1.3.2 Alginate hydrogel

Alginate is a biopolymer containing the linear chain of D-mannuronic acid (M) and L-guluronic acid (G) units in a pyranose form (Jiao *et al.*, 2016). The hydrogel form process is performed by the simple cross-linking reaction between alginate and divalent cations, such as calcium ions (Ca^{2+}) and barium ions (Ba^{2+}), to form egg-box model (Figure 6) (He *et al.*, 2016; Serrano-Aroca *et al.*, 2018; Zheng, 1997).

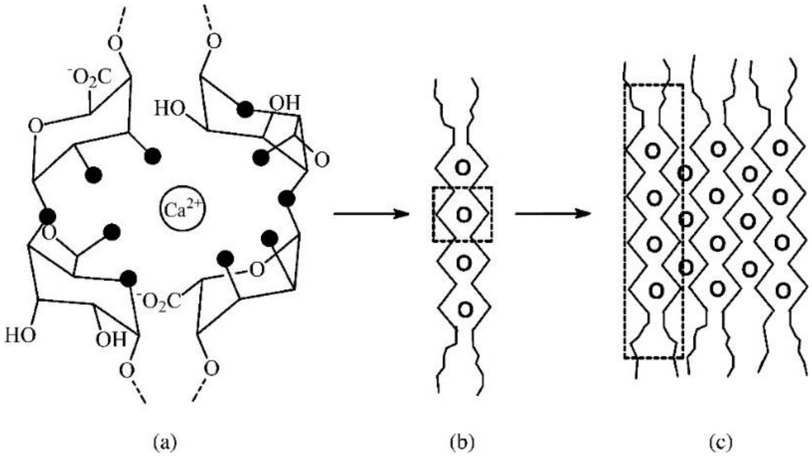

Figure 6 Schematic representation of the hierarchical structure of egg-box junction zones in alginate/calcium gels: (a) coordination of Ca^{2+} in a cavity created by a pair of guluronate sequences along alginate chains; (b) egg-box dimer, and (c) laterally associated egg-box multimer. The black solid circles represent the oxygen atoms possibly involved in the coordination with Ca^{2+}. The open circles represent Ca^{2+} ions (Reprinted form Fang and coworkers, 2007; copyright with permission form ACS Publications) (Fang *et al.*, 2007)

The alginate hydrogel has insoluble gel network, biodegradability and cost-effectiveness, it is greatly useful to entrap several materials such as nanoparticles, carbon nanomaterials, and its porosity can help the target analytes to diffuse into the pore and come in contact with the adsorption material (Figure 7). It also has a hydrophilicity which can improve the dispersibility of the adsorbent in the sample solution, thus reducing the extraction time (Algothmi *et al.*, 2013; Bezbaruah *et al.*, 2009; Bunkoed and Kanatharana, 2015; Jiao *et al.*, 2016; Zare *et al.*, 2016). Furthermore, the modification of high affinity materials is commonly required to obtain efficient and selective adsorbent. Many adsorption materials have been modified by compositing or coating onto the alginate hydrogel bead and employed as the MSPE adsorbent, including octadecyl silica (Zhang *et al.*, 2010b), multiwalled carbon nanotubes (Bunkoed and Kanatharana, 2015) and polymer **(Paper II, III)**.

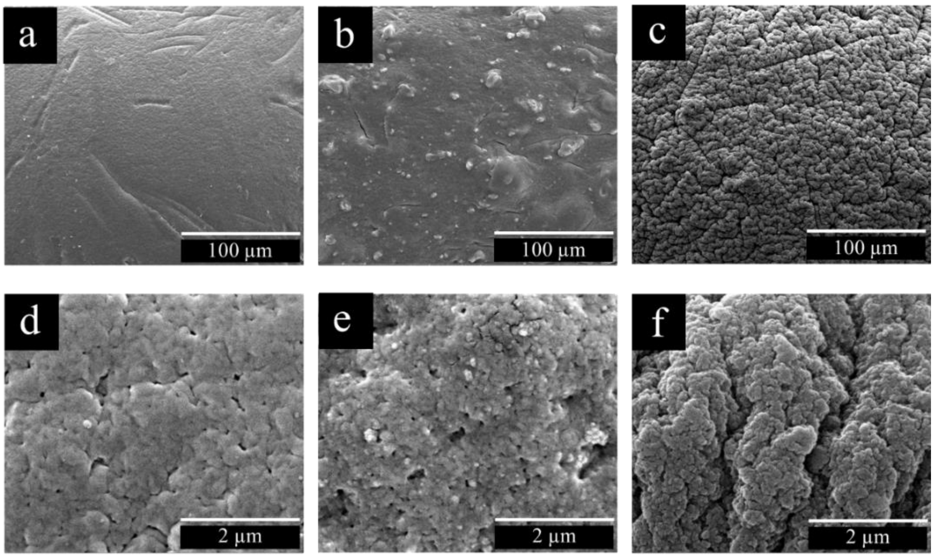

Figure 7 SEM image of alginate (a = 500x, b = 20,000x), Fe_3O_4/alginate (c = 500x, d = 20,000x) and PANI/alginate/Fe_3O_4 (e = 500x, f = 20,000x) (Reprinted form Nurerk and coworkers, 2017; copyright with permission form Taylor & Francis Online) (Nurerk *et al.*, 2017)

2.1.4 Adsorption materials

2.1.4.1 Metal organic frameworks

Metal organic frameworks (MOFs), known as a porous coordination polymer, are a class of crystalline porous materials formed via assemble coordination bond of metal ions and organic linker ligands (Gu *et al.*, 2010; Zhou *et al.*, 2012). MOFs have much interesting adsorption materials due to their distinctive properties including high surface area, high porosity, and good chemical and thermal stability (Lian *et al.*, 2018; Zhou *et al.*, 2017). Various types of MOFs, for example, zeolitic imidazolate framework (ZIFs) family, Hong Kong University of Science and Technology (HKUST) family Materials of Institute Lavoisier (MIL) family (Figure 8) have been applied in many applications such as gas storage (Li *et al.*, 2009a), chemical sensors (Kreno *et al.*, 2012), drug delivery (Horcajada *et al.*, 2009) and sample preparation (Li *et al.*, 2019; Wang *et al.*, 2018).

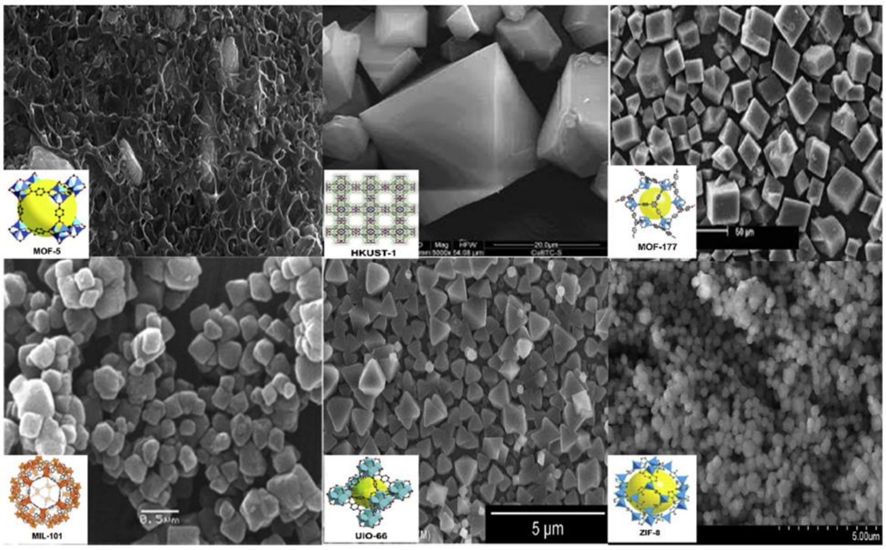

Figure 8 Representative MOFs (Reprinted form Safaei and coworkers, 2019; copyright with permission form Elsevier) (Safaei *et al.*, 2019)

For the application of MOFs as the adsorbents for sample preparation, despite the different types of MOFs, they possess porous structure which can improve the diffusion of target analytes into the adsorbent. Furthermore, hydrophobic properties and π–π interaction endow MOFs with high affinity and selectivity for the target analytes. (Ahmed and Jhung, 2014; Khan and Jhung, 2017; Rowsell and Yaghi, 2004; Wang *et al.*, 2018). They have been applied to extract various hydrophobic compounds in complex matrices such as PAHs (Rocío-Bautista *et al.*, 2016; Zhou *et al.*, 2017), phthalate esters (Liu *et al.*, 2015b; Wang *et al.*, 2015b) and UV filters **(Paper I)**. The extraction efficiency of the MOFs was investigated by comparing to available commercially adsorbent including C18 SPE adsorbent and Hydrophilic-Lipophilic Balance (HLB) commercial (Figure 9). The results showed that the MOFs provided higher extraction efficiency due to its larger surface area, resulting in the improvement of the extraction capability to target analytes.

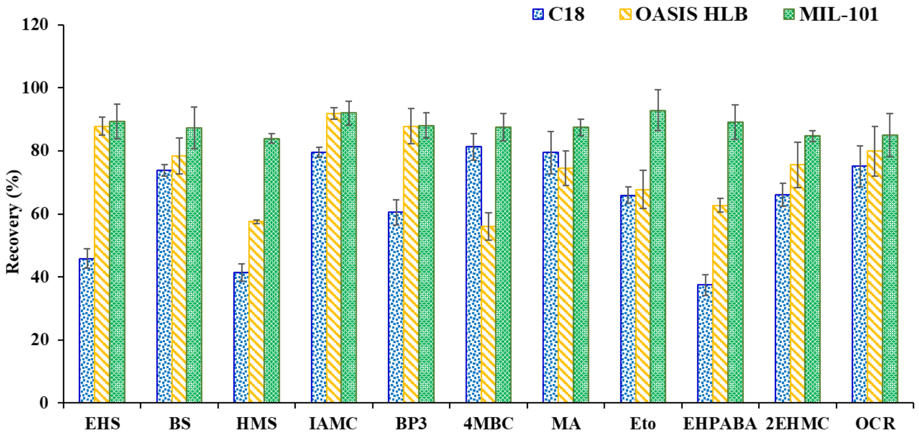

Figure 9 Comparison of the extraction efficiency between the MIL-101 adsorbent and two commercial SPE cartridges (Reprinted form Nurerk and coworkers, 2019; copyright with permission form Elsevier) (Nurerk *et al.*, 2019b)

2.1.4.2 Polymer

Polymer has attracted enormous interest as an adsorption material class due to its versatile properties. Various kinds of polymer have been applied as the high affinity material for sample preparation such as polydopamine, polyaniline and polypyrrole. They possess π-conjugated structure and multifunctional groups (Figure 10), including amine and catechol groups, which contribute strong interactions included π–π, hydrophobic and hydrogen bonding, to adsorb a wide range of organic compounds. (Bunkoed *et al.*, 2016a; McCullum *et al.*, 2014; Nurerk *et al.*, 2017; Wang *et al.*, 2013c). Moreover, they can be easily synthesized under mild conditions with a defined shape of the supporting materials. They also have large surface areas, good thermal and chemical stability (Asiabi *et al.*, 2015; Bagheri *et al.*, 2013; Hou *et al.*, 2015). Polymers are extensively used for the extraction of various compounds including sulfonamides (Sukchuay *et al.*, 2015), pesticides (Arnnok *et al.*, 2017), phthalate esters (Zhao *et al.*, 2016a), PAHs **(Paper II, IV)** and endocrine-disrupting compounds **(Paper V)**.

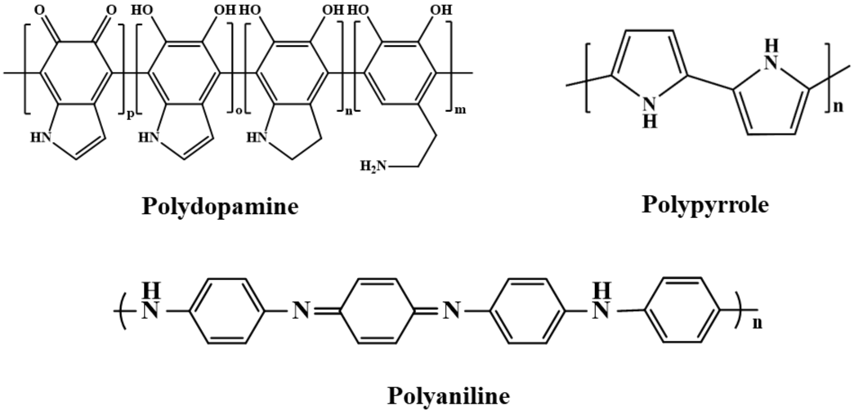

Figure 10 Structure of polydopamine, polyaniline and polypyrrole

In addition, polymers have been combined with another adsorption materials, such as graphene oxide, octadecyl silica and calixarene, and applied as the hybrid adsorbents. The integration of materials with their prominently different properties has much attention to enhance efficient extraction. The hybrid adsorbents provided better adsorption capability due to the combination of multiple adsorption affinity and larger surface areas, thus increase in extraction capability (Figure 11) (Chullasat *et al.*, 2017; Klongklaew *et al.*, 2018; Nurerk *et al.*, 2018; Pinsrithong and Bunkoed, 2018).

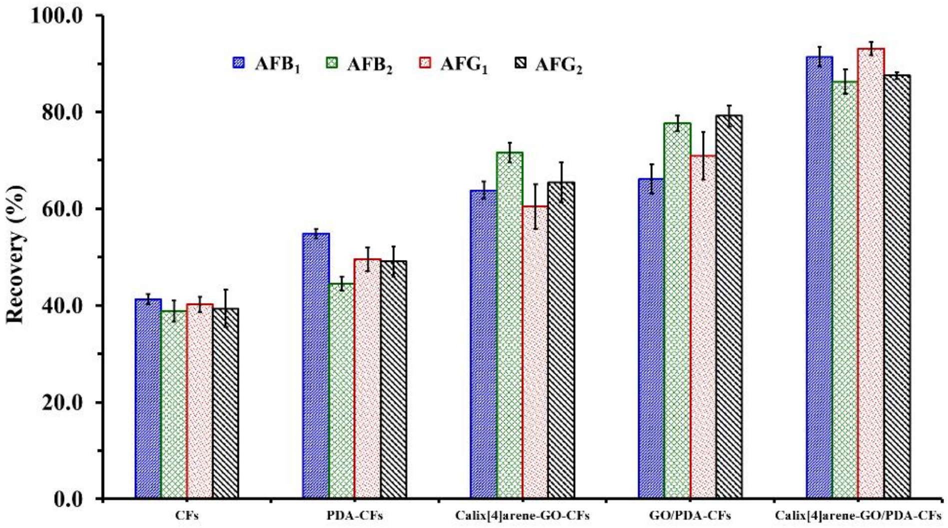

Figure 11 The efficiency of extraction of aflatoxins by CFs, PDA/CFs, calix[4]arene-GO/CFs, GO/PDA-CFs and the calix[4]arene-GO/PDA-CFs adsorbent (Reprinted

form Nurerk and coworkers, 2018; copyright with permission form Wiley Online Library) (Nurerk *et al.*, 2018)

2.1.4.3 Graphene oxide

Graphene oxide (GO) is a carbon nanomaterial oxidized form of graphene. The structure of GO consists of a two-dimension (2D) layer of sp^2 hybridized carbon atom and multifunctional groups including epoxy, hydroxyl, and carboxyl on its basal plane and edge (Figure 12) (Dreyer *et al.*, 2010; Kabiri and Namazi, 2014). Regarding its structure, GO can form strong π-π and hydrophobic interaction with the benzenoid compounds, as well as its multifunctional group can adsorb the target analytes through hydrogen bonds. Moreover, it has high specific surface area, good thermal and chemical stability (Dahaghin *et al.*, 2017; Mahpishanian and Sereshti, 2014; Wen *et al.*, 2014). Owing to these excellent adsorption abilities, GO has been applied as the adsorbent for the extraction both polar and non-polar contaminants in different matrices, for example, EDCs (Naing *et al.*, 2016), pesticides (Wu *et al.*, 2011), aflatoxins (Wu *et al.*, 2011) and sulfonamides (Gao *et al.*, 2018).

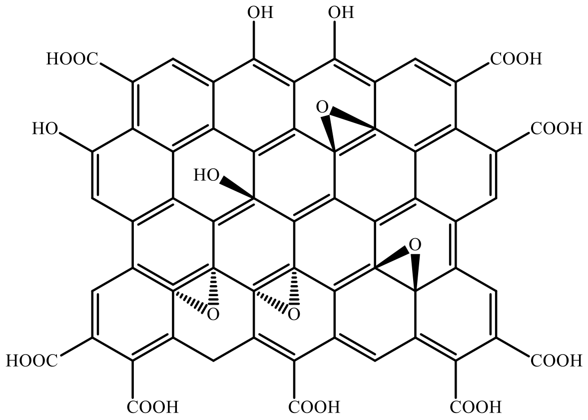

Figure 12 Structure of graphene oxide

2.1.4.4 Calixarene

Calixarene is a macrocyclic phenol molecule linked via methylene bridges (Figure 13). The cyclic can be formed by the reaction of para-substituted phenols with formaldehyde via cyclic condensation (Li *et al.*, 2004b; Zhang *et al.*, 2016; Zhou *et al.*, 2013). Calixarene is an interesting adsorption material owing to its high affinity to the aromatic compounds through π-π and hydrophobic interactions. Furthermore, it has supramolecular recognition ability which can form host−guest complexes with target molecules to increase the selectivity. It also can be modified with more polar functional group for a wide range of application (Hu *et al.*, 2012; Li *et al.*, 2016; Li *et al.*, 2004b; Zhao *et al.*, 2016b). Calixarene has been developed as the adsorption material for the extraction and preconcentration of several compounds from complex matrices, including, aliphatic amines in fish (Li *et al.*, 2004c), phthalate esters in plastic packaging bags (Li *et al.*, 2004a) and pesticide in fruit samples. (Li *et al.*, 2016)

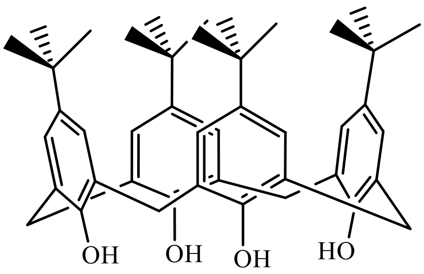

Figure 13 Structure of calixarene

2.2 Liquid phase-microextraction (LPME)

Liquid phase-microextraction (LPME) is a miniaturized sample preparation technique which is introduced to overcome the drawbacks of conventional LLE including large amount of organic solvents consumption, large sample volume use and long-time analysis with tedious operation. (Hyötyläinen and Riekkola, 2008; Sarafraz-Yazdi and Amiri, 2010). The LPME extraction is based on the equilibrium partitioning of target analytes between the water-immiscible solvent (extractant/acceptor) and the aqueous sample (donor phase). LPME is performed microliters of acceptor phase which can be directly exposed into or hanged over the donor phase for headspace extraction. This technique integrates extraction and preconcentration in one step, allowing high enrichment factor and low limit of detection. (Kokosa, 2013; Spietelun *et al.*, 2014; Stanisz *et al.*, 2014). LPME has been applied for the extraction of several organic compounds from water samples, such as PAHs (Sibiya *et al.*, 2013), pesticides

(Lambropoulou and Albanis, 2005; Shen and Lee, 2002) and estrogens (Goh and Lee, 2017).

2.2.1 Plunger-in-needle liquid phase-microextraction (PIN-LPME)

Plunger-in-needle liquid phase-microextraction (PIN-LPME) is a new approach of LPME combined with a commercially plunger-in-needle microsyringe. The PIN microsyringe has been develop as the home-made extraction device (Figure 14) because its stainless steel plunger wire provides an advantage as an ultra-low volume (Nurerk *et al.*, 2019a; Zhang *et al.*, 2014).

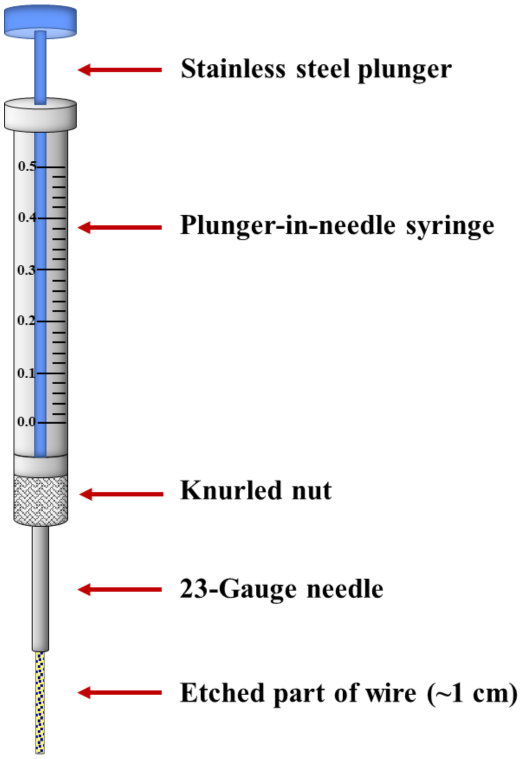

Figure 14 Schematic of the PIN-LPME device

In the PIN-LPME procedure, the plunger wire is firstly etched to produce a rough and microporous structure, which utilizes as the solvent holder for LPME. After solvent coating steps, the etched part of plunger wire is directly immersed into sample solution for extraction and subsequently subjected to thermal desorption (Zhang *et al.*, 2014). The etched plunger wire can enhance the extraction efficiency due to its increase the contact area between solvent and aqueous sample.

However, the etching process still requires the toxic and corrosive hydrofluoric acid as the etchant. Thus, the environmentally friendly etching method has been developed for PIN-LPME **(Paper VI)**. The plunger wire was etched by immersion into the aqueous ferric chloride-hydrochloric acid solution ($FeCl_3$-HCl) with one-step and simple approach. The etched wire also provided the rough surface which allows the stable hold of coated solvent (Figure 15).

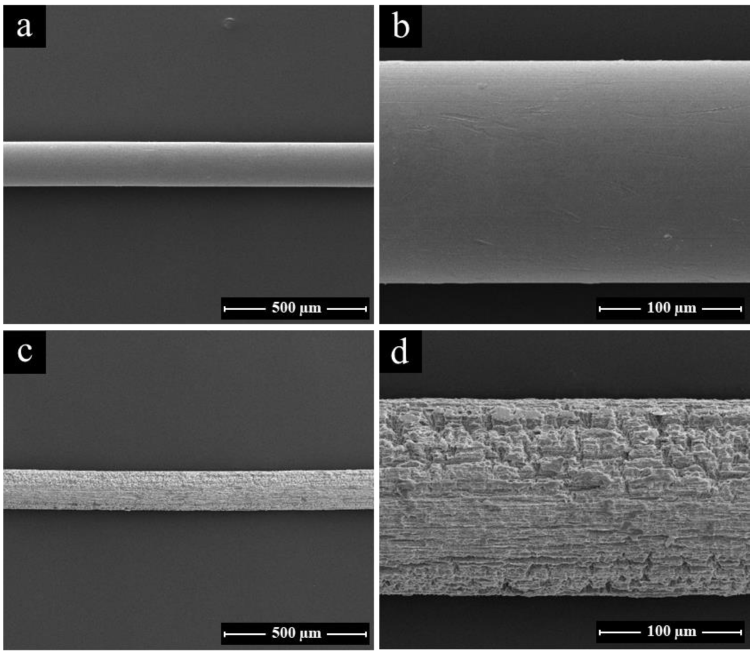

Figure 15 Scanning electron micrographs of plunger wire before (a = 100 ×; b = 500 ×), and after etching (c = 100 ×; d = 500 ×) (Reprinted form Nurerk and coworkers, 2019; copyright with permission form Elsevier) (Nurerk *et al.*, 2019a)

The extraction capability of the etched stainless steel plunger wire has been investigated by comparing to non-etched wire (Figure 16). The results showed that the etched wire with solvent coating could be improved extraction capability of the target compounds. The developed method was applied for the extraction of several PAHs in different water samples.

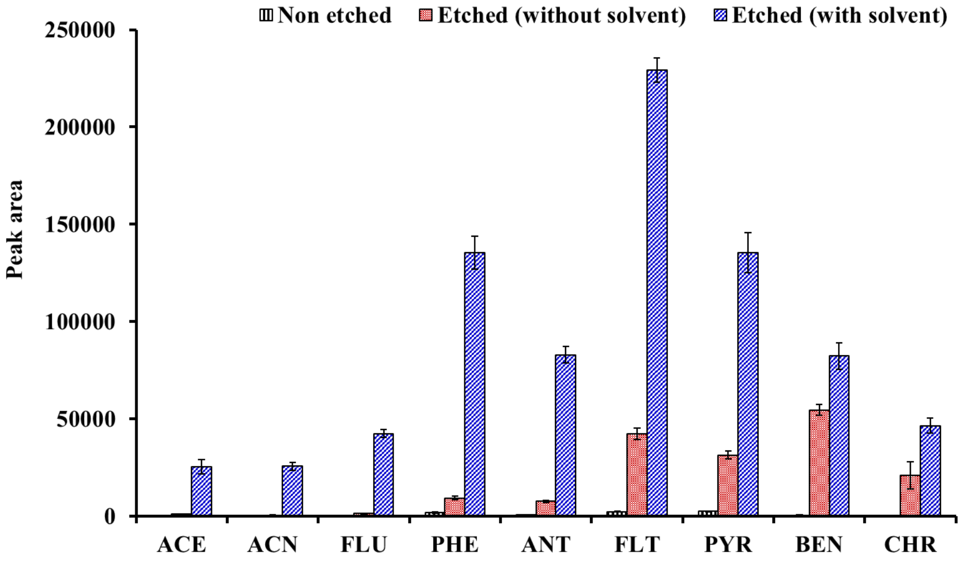

Figure 16 The comparison of non-etched, etched wire, without and with solvent (cyclohexane) for PIN-LPME of PAHs (Reprinted form Nurerk and coworkers, 2019; copyright with permission form Elsevier) (Nurerk *et al.*, 2019a)

3. Analytical performance criteria

Under the optimum conditions of developed methods, the analytical characteristics were evaluated in terms of linearity, limit of detection (LOD), limit of quantification (LOQ), accuracy, precision, reproducibility and reusability.

3.1 Linearity

Linearity of analytical method is its ability to provide the results which are directly proportional to the concentrations of the analyte in a sample (ICH) (ICH, 2005). The linearity is performed with triplication of at least 4 different concentration levels of the analytes. Then, the linear ranges are plotted between the average values of response versus the concentration of analytes, the linear regression is acquired when the coefficient of determination (R^2) is greater than 0.99 (Peris-Vicente *et al.*, 2015). In this thesis, the linearity was plotted between the peak areas versus the corresponded concentration of UV filters (in µg L^{-1} range) **(Paper I)**, PAHs (in µg L^{-1} range) **(Paper II, IV and VI)**, aflatoxins (in µg kg^{-1} range) **(Paper III)** and EDCs (in µg L^{-1} range)

(Paper V). All sub-projects provided a good linearity with coefficient of determination more than 0.99.

Table 1 Linear range and coefficients of determination (R^2) of six sub-projects

Analytical method	Sample preparation	Sample	Target analytes	Linearity (μg L^{-1}/ μg kg^{-1})	R^2	Reference
GC-MS/MS	SPE (MIL-101)	Water	UV filters	0.5-100	0.9973-0.9999	**Paper I**
HPLC-FLD	SPE (PANI/CFs)	Water	PAHs	0.0005-10.0	0.9991-0.9999	**Paper II**
HPLC-FLD	SPE (Calix[4]arene-GO/PDA-CFs)	Corn	Aflatoxins	0.01-10.0	0.9981-0.9987	**Paper III**
HPLC-FLD	MSPE (PANI/alginate/ Fe_3O_4)	Water	PAHs	0.040-50.0	0.9991-0.9997	**Paper IV**
HPLC-FLD	MSPE (PPY/alginate/ Fe_3O_4)	Water	EDCs	0.50-100	0.9943-0.9991	**Paper V**
GC-MS	PIN-LPME	Water	PAHs	0.010-50.0	0.9915-0.9987	**Paper VI**

3.2 Limit of detection and limit of quantification

Limit of detection (LOD) is the lowest concentration of an analyte which can be reliably detected under the optimum conditions of the developed method and limit of quantification (LOQ) is the lowest concentration which can be quantitatively determined (Peris-Vicente *et al.*, 2015). There are several approaches to calculate the LOD and LOQ. In this thesis, two approaches were used to estimate the LOD and LOQ. The LOD and LOQ were calculated based on a signal-to-noise (S/N) ratio as a recommendation of International Conference of Harmonization (ICH) (ICH, 2005) for the determination of PAHs **(Paper II, IV and VI)**, aflatoxins **(Paper III)** and EDCs **(Paper V)**. The LOD was calculated based on the concentration which provided signal-to-noise ratio equal or greater than 3 ($S/N \geq 3$) and LOQ was calculated based on the concentration which provided signal-to-noise ratio equal or greater than 10 ($S/N \geq 10$).

In another approach, the LOD and LOQ were calculated based on the blank determination as a recommendation of EURACHEM guideline (Magnusson and Örnemark, 2014) for the determination of UV filters **(Paper I)**, as following equation:

$$LOD = \bar{X}_{bl} + 3S_{bl}$$

$$LOQ = \bar{X}_{bl} + 10S_{bl}$$

Where $\bar{X}_{bl}$ is the mean concentration of the blank and S_{bl} is the standard deviation of the blank.

Table 2 LODs and LOQs of six sub-projects

Analytical method	Sample preparation	Target analytes	LOD (µg L^{-1}/ µg kg^{-1})	LOQ (µg L^{-1}/ µg kg^{-1})	Reference
GC-MS/MS	SPE (MIL-101)	UV filters	0.001-0.012	0.0035-0.040	**Paper I**
HPLC-FLD	SPE (PANI/CFs)	PAHs	0.0005	0.0020	**Paper II**
HPLC-FLD	SPE (Calix[4]arene-GO/PDA-CFs)	Aflatoxins	0.010-0.050	0.040-0.20	**Paper III**
HPLC-FLD	MSPE (PANI/alginate/ Fe_3O_4)	PAHs	0.010	0.040	**Paper IV**
HPLC-FLD	MSPE (PPY/alginate/ Fe_3O_4)	EDCs	0.5	2.0	**Paper V**
GC-MS	PIN-LPME	PAHs	0.006-0.058	0.023-0.281	**Paper VI**

3.3 Accuracy

The accuracy of an analytical method can be defined as the degree of the closeness of agreement between the true value or an accepted reference value and the experimental value (ICH, 2005). Accuracy of the method is studied in term of recovery which was studied by spiking different concentration levels of the analytes into the real sample (at least three replicates) and calculated by the following equation (AOAC, 2016):

$$\text{Recovery (\%)} = \frac{C_F - C_U}{C_A} \times 100$$

Where C_F is the concentration of analyte measured in fortified sample or spiked sample, C_U is the concentration of analyte measured unfortified sample and C_A is the concentration of analyte added in the sample.

The recoveries were investigated at 0.1, 1.0 and 10 µg L^{-1} of UV filters for the SPE adsorbent of MIL-101 **(Paper I)**, 0.005, 0.020, and 0.10 µg L^{-1} of PAHs for the SPE adsorbent of polyaniline coated cigarette filters **(Paper II)**, 0.1, 0.5 and 2.0 µg kg^{-1} of aflatoxins for the hybrid SPE adsorbent **(Paper III)**, 0.10, 0.50 and 2.0 µg L^{-1} of PAHs for the MSPE adsorbent polyaniline coated magnetite nanoparticles entrapped in alginate beads **(Paper IV)**, 2.0, 5.0 and 20.0 µg L^{-1} of EDCs for the MSPE adsorbent polypyrrole coated magnetite nanoparticles entrapped in alginate beads **(Paper V)** and 0.5 and 5.0 µg L^{-1} of PAHs for the PIN-LPME **(Paper VI)**. Satisfactory recoveries were obtained in the range of 82 – 107% **(Paper I – VI)** which were acceptable as recommended by the Association of Analytical Communities (AOAC) (60 – 115% at the concentration lower than 10 µg L^{-1}) (AOAC, 2016).

3.4 Precision

The precision of an analytical method can be defined as the closeness of agreement of the replication measurement under optimum conditions (AOAC, 2016). The precision is usually determined by the percentage relative standard deviation (% RSD) of the response from different spiked concentrations of the analytes into the real sample with five replications for each concentration. The relative standard deviation is calculated by the following equation (AOAC, 2016):

$$\text{RSD (\%)} = \underline{\;\text{SD}\;} \times 100$$

$$\frac{}{\bar{X}}$$

Where SD is standard deviation and $\bar{X}$ is the mean of n measurement (n=5). In this thesis, the relative standard deviations were less than 15% **(Paper I – VI)** which were acceptable recommendation for precision at µg L^{-1} level (the AOAC recommends precision less than 21% as satisfactory) (AOAC, 2016).

3.5 Reproducibility

Reproducibility defines as the closeness of individual measures of the analytes under the same preparing conditions. In this thesis, the reproducibility of the developed method was evaluated in terms of lot-to-lot reproducibility. Six different lots of adsorbent were prepared at different times and used them to extract analytes from the spiked samples under the same conditions **(Paper II - VI)**. The relative standard deviations (RSDs) were lower than 6%, and these were better than the acceptable values recommended by the AOAC (<16%) (AOAC, 2016). The developed PIN-LPME method for the determination of PAHs **(Paper V)**, the RSDs of wire-to-wire reproducibility of three different wires were less than 13% which were also satisfactory as recommended by the AOAC.

3.6 Reusability

The reusability is a factor for evaluating the performance of the developed adsorbents, since this can reduce in both preparation time and analysis cost. After the desorption of the analytes from the adsorbent, to eliminate the memory effect, they are washed with desorption solvent and water before performing the next extraction. In this thesis, the developed adsorbents could be reused ranging from 6 to 18 times with the recoveries of the analytes still higher than 80% **(Paper II – V)**. This demonstrated that the developed adsorbent exhibited good stability during the extraction procedure.

4. Concluding remarks

This thesis successfully developed sample preparation techniques including sorbent-based extraction and liquid phase-microextraction followed by chromatography for identification and quantification. The sample preparation techniques based on sorbent-based extraction consisted of SPE and MSPE. The new approach of LPME was developed as plunger-in-needle liquid phase-microextraction (PIN-LPME). The great performance of these developed methods was successfully applied for the extraction and determination of trace organic contaminants in environment and food.

In the first part, the effective adsorbents were developed and used as SPE and MSPE adsorbents. The first sub-project was a metal organic frameworks material of MIL-101 which was utilized as a SPE adsorbent followed by GC-MS/MS for the extraction and simultaneous analysis of multiclass UV filters including benzophenone-derivatives, salicylates, cinnamates, and others from environmental and recreational water samples **(Paper I)**. The high porous of MIL-101 adsorbent had large contact area and strong adsorption ability with the target analytes. The validated method exhibited good sensitivity with low limits of detection (1.0 – 11.7 ng L^{-1}), good adsorption ability (82 – 105%), good repeatability and enabled high throughput. The second sub-project is polyaniline coated cigarette filters which were used as a SPE adsorbent for the extraction and preconcentration of PAHs in environmental water samples and quantified by HPLC-FLD **(Paper II)**. The coated polyaniline helped to enhance the extraction capability due to its high affinity to the target analytes. The high porosity and large surface area of cigarette filters allowed performing at the high sample flowrate with low back pressure, resulting in shorter extraction process time. The developed method provided good extraction efficiency (85 – 98%), good sensitivity with low detection limit (0.5 ng L^{-1}) and high enrichment factor. The developed adsorbent was easy to prepare, cost-effective, good reusability. The third sub-project is the hybrid adsorbent of calix[4]arene functionalized graphene oxide onto polydopamine coated cigarette filters. This developed adsorbent was applied for the SPE and clean-up aflatoxins in corn samples followed by HPLC-FLD **(Paper III)**. The hybrid adsorbent not only had high porosity, but also exhibited the strong adsorption ability due to its integration of high affinity materials. The developed method provided effective extraction (83 – 107%), good accuracy, good reproducibility and good reusability.

The fourth and fifth sub-project is the development of MSPE adsorbent consisting of polyaniline coated magnetite nanoparticles incorporated in alginate beads for the extraction and enrichment of PAHs in environmental water samples **(Paper IV)** and polypyrrole coated magnetite nanoparticles entrapped in alginate beads for the extraction and preconcentration of EDCs including estriol, β-estradiol and bisphenol A in environmental water samples followed by HPLC-FLD **(Paper V)**. The magnetite nanoparticles facilitated the simple and fast separation of the adsorbent from the sample solution. The alginate helped to increase the dispersibility and the surface contact area. The polyaniline and polypyrrole could enhance the extraction efficiency because of their high adsorption ability through the target analytes. The developed methods exhibited good extraction capability, good stability and good reproducibility. The developed magnetic adsorbents were simple to prepare, convenient and cost-effective.

The second part is the development of environmentally friendly method of etching a stainless steel plunger wire, replacing the conventional hydrofluoric acid etching. The etching was performed by immersing a stainless steel plunger directly into the etchant of ferric chloride-hydrochloric acid solution. The etching was simple, fast and one-step procedure. The etched plunger wire was used as the organic solvent holder for the PIN-LPME followed by GC-MS and applied for extraction and preconcentration of PAHs in environmental water samples **(Paper VI)**. The developed method demonstrated high enrichment factor, low detection limits (0.006 – 0.058 µg L^{-1}), good extraction ability (84 – 102%) and good precision.

These developed methods were successfully applied for the extraction and determination of trace organic contaminants in real samples, including different environmental water (tap, river, lake, reservoir, wastewater and seawater), recreational water (swimming pool) and corn. The good performance of the developed methods has the potential to apply for the future extraction and preconcentration of others trace organic contaminant in environment and food samples.

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Appendices

Paper I

Nurerk, P., Llompart, M., Donkhampa, P., Bunkoed, O., Dagnac, T., Solid-phase extraction based on MIL-101 adsorbent followed by gas chromatography tandem mass spectrometry for the analysis of multiclass organic UV filters in water. *Journal of Chromatography A*

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Solid-phase extraction based on MIL-101 adsorbent followed by gas chromatography tandem mass spectrometry for the analysis of multiclass organic UV filters in water

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ABSTRACT

A metal organic framework material MIL-101 was developed as an effective solid-phase extraction adsorbent for the extraction of eleven UV filters compounds. The MIL-101 adsorbent was packed into a polypropylene cartridge and connected at the outlet tip with the Visiprep^{TM} vacuum manifolds allowing process up to 12-port SPE samples, simultaneously. The extracted UV filters were quantified by gas chromatography-tandem mass spectrometry. Several parameters affecting the extraction efficiency of the target analytes, i.e. desorption conditions, sample pH, the addition of salt and sample volume were optimized by ANOVA analysis followed by a multifactorial design. The sample breakthrough volume of the developed method was also evaluated. The SPE-GC–MS/MS method was validated in terms of linearity ($R^2 \geq 0.9973$), accuracy (with satisfactory recovery from 82% to 105%), precision (relative standard deviation of less than 10%) and limits of detection ranging from 1.0 to 11.7 ng L^{-1}. The validated method was successfully applied for the extraction and quantification of the target UV filters in different types of water samples, including lake, river, seawater and swimming pool waters. The most often found UV filters were octocrylene, 4-methylbencylidene camphor and homosalate that also came out with the highest concentrations, up to 4000 ng L^{-1}, particularly in swimming pool waters.

1. Introduction

In recent years, the concern of the adverse effects of ultraviolet radiation has significantly increased. UV filters are substances which are intended to protect human skin against UV radiation (320–400 nm for UVA and 290–320 for UVB) [1,2]. For this reason, they are increasingly added to cosmetic formulations, both in sunscreens and in many other leave-on daily personal care products. UV filters are usually added to these products in combination (2–6 compounds) to cover a broad range of UV spectrum [3,4]. The presence of UV filters in the aquatic environment is directly or indirectly related to discharges during bathing and washing activities through domestic wastewater [2,5]. Many of these compounds are lipophilic, therefore they can bioaccumulate and biomagnify through the food chain, and they cause adverse effects like estrogenic activity on biota and human beings [6,7]. Consequently, the monitoring methods for UV filters in the environment is of vital importance. Some groups of UV filters have been detected in environmental samples at concentrations up to 300 ug L^{-1}. However, these concentrations were generally ranging from the ng L^{-1} to the ug L^{-1} levels [8,9]. Therefore, a sample preparation is normally required to isolate and pre-concentrate the target analytes from sample matrices prior to instrumental analysis.

Several sample preparation methods have been reported for the analysis of UV filters, including solid-phase extraction (SPE) [4,10,11], solid-phase microextraction (SPME) [12], stir bar sorptive extraction (SBSE) [13], and magnetic solid phase extraction (MSPE) [14,15]. Among these methods, SPE has attracted more attention due to its extraction capacity, high enrichment factor, and simplicity [16,17]. For the SPE method, the adsorbent plays an important role in both extraction efficiency and selectivity, thus different types of adsorbent materials are studied. For example, Díaz-Cruz et al. used 500 mg of commercial C18 bonded silica as the SPE

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adsorbent for the extraction of UV filters in tap water and other clean waters [2]. Liu et al. applied the 500 mg of copolymer hydrophilic-lipophilic balance (HLB) SPE adsorbent for the extraction of UV filters in tap and wastewater [11]. Piovesana et al. [15] developed a graphitized carbon black-based magnetic material for the extraction of UV filters in environmental lake and river. Moreover, new adsorptive materials have been introduced to improve extraction efficiency and miniaturize the SPE approach. Metal organic frameworks (MOFs) are a class of porous materials prepared by self-assembly of metal ions with organic linker ligands via coordination bonds [18]. MOFs possess their unique properties, including large specific surface area and tunable surface function via the choice of various of metal ions or organic bridging ligands [19]. Due to their special characters, various types of MOFs, such as zeolitic imidazolate framework-8 (ZIF-8) [20,21], Materials of Institute Lavoisier (MIL)-100 [22,23] as well as MIL-101 [24–26] have been successfully used as adsorbents for the sample enrichment. Considered one of the most prominent MOFs, MIL-101 has been successfully used as adsorbent due to its advantages of large surface area, high porosity, excellent chemical stability and cost-effective [24,27]. In addition, MIL-101 can adsorb the target analytes through π–π interaction and hydrophobic effect [26]. Zhou et al. have synthesized MIL-101 modified zero valent iron nanoparticles and applied them for the extraction of polycyclic aromatic hydrocarbons from environmental water [24]. Zang et al. developed MIL-101 coated fiber for headspace SPME of volatile aromatic compounds [25]. In addition, Jia et al. [26] adopted the MIL-101 composite for conducting dispersive µ-SPE of sulfonamides.

This is the first time that MIL-101 is proposed as an on-column SPE adsorbent and that is applied for the extraction and enrichment of UV filters compounds. Thus, the aim of this study is to develop a SPE method based on MIL-101 adsorbent followed by gas chromatography-tandem mass spectrometry (GC–MS/MS), for the simultaneous analysis of different chemical classes UV filters (benzophenone-derivatives, salicylates, cinnamates, and others), The experiments include 2-Ethylhexyl methoxycinnamate (2EHMC) which was listed as priority pollutant in the aquatic environment [28] from different natural and recreational water samples.

2. Experimental

2.1. Chemicals, materials and samples

Ethylhexyl salicylate (EHS), homosalate (HMS), ethylhexyl dimethyl PABA (EHPABA) and octocrylene (OCR) were purchased from Sigma-Aldrich (Saint Louis, MO, USA). Benzyl salicylate (BS) and menthyl anthranilate (MA) were obtained from Fluka (Saint Louis, MO, USA). 4-Methylbencylidene camphor (4MBC) was supplied by Alfa Aesar (Karlsruhe, Germany). Benzophenone-3 (BP3), isoamyl methoxycinnamate (IAMC) and etocrylene (Eto) were acquired from TCI (Tokyo, Japan). 2-Ethylhexyl methoxycinnamate (2EHMC) was purchased from Ehrenstorfer (Augsburg, Germany).

Hydrochloric acid (HCl), acetone and methanol were supplied by Merck (Darmstadt, Germany). Ethyl acetate, acetonitrile and hexane were obtained from Sigma-Aldrich Chemie GmbH (Steinheim, Germany). Sodium thiosulphate was purchased from Panreac (Barcelona, Spain).

Individual stock solutions were prepared in ethyl acetate. Mixture in methanol were prepared to spike water sample. All solutions were stored at −20 °C.

The samples employed were Mili-Q water, mineral water, river water, wastewater, swimming pool water and sea water, taken in the summer and spring seasons. Water samples were collected in 200 mL glass bottles, added 50 mg of sodium thiosulfate and kept at 4 °C until their analysis.

2.2. Preparation of MIL-101 adsorbent and solid phase extraction procedure

The preparation procedure is depicted in Fig. 1. First, the MIL-101 adsorbent was synthesized under hydrothermal method according to the previous method [27], with minor modification. Briefly, chromium nitrate nonahydrate (2.0 g), terephthalic acid (0.80 g) and sodium acetate (0.10 g) were added to 25 mL of ultrapure water and mixed in a Teflon-lined stainless steel vessel, sealed and heated at 200 °C for 12 h. After cooling down to ambient temperature, the green color suspension of MIL-101 was washed with deionized water and dimethylformamide. Then, the MIL-101 was purified by adding 25 mL of ethanol in the Teflon-lined stainless steel vessel and heated up at 100 °C for 10 h to remove unreacted terephthalic acid. The final product was filtered, washed by deionized water and dried at 80 °C for 24 h.

Afterward, 50 mg of MIL-101 adsorbent was packed into a 2.0 mL polypropylene cartridge and connected at the outlet tip with the SPE manifold (Visiprep^{TM}, Supelco, USA). Before loading the sample, the adsorbent was conditioned with 1.0 mL of ethyl acetate followed by 1.0 mL of ultrapure water. Different volumes of the samples were loaded through the adsorbent using vacuum. Afterwards, the concentrated UV filters were eluted with 2.0 mL of ethyl acetate by gravity flow. The eluent was evaporated to dryness by nitrogen purging and reconstituted with 200 µL of ethyl acetate before being injected into the GC–MS/MS system.

2.3. Instrumentation

The X-ray diffraction (XRD) patterns were recorded using a X'Pert-MPD (Philips, Netherlands). The morphology of the developed adsorbent was observed by a JSM-5200 SEM (JEOL, Tokyo, Japan). Fourier transform infrared (FT-IR) spectra were obtained using a Spectrum BX FTIR spectroscope (PerkinElmer, Waltham, MA, USA).

The GC–MS/MS analysis was performed using a Thermo Scientific Trace 1310 gas chromatograph coupled to a triple quadrupole mass spectrometer (TSQ 8000) and IL 1310 autosampler from Thermo Scientific (San Lose, CA, USA). Separation was carried out on a Zebron ZB-Semivolatiles capillary column (30 m × 0.25 mm I.D. × 0.25 µm film thickness) supplied by Phenomenex (Torrance, CA, USA). Helium (purity 99.999%) was used as carrier gas at a constant column flow of 1.0 ml min^{-1}. The GC oven temperature was programmed from 100 °C (held for 1 min) to 290 °C at 25 °C min^{-1} (held for 6 min). The total run was 15 min. The injector temperature was set at 260 °C and injections were operated in the splitless mode (200 kPa, held 1 min). The injection volume was 1.0 µL.

The mass spectrometer was operated in the electron ionization positive mode (+ 70 eV). The temperatures of the transfer line and the ion source were set at 290 and 350 °C, respectively. Selected reaction monitoring (SRM) acquisition mode was applied monitoring two or three transitions per compound. The retention times and the SRM transition are shown in Table S1. The system was operated by Xcalibur 2.2 and quantification was performed using the Trace Finder^{TM} 3.2 software.

The chromatographic conditions were optimized to achieve the effective separation and identification of the 11 studied UV filters. These conditions were adapted from previous studies [3,12].

2.4. Statistic analysis

Basic and descriptive statistics, as well as experimental design analysis, were performed using Statgraphics Centurion XVI 16.1.15 (Manugistics, Rockville, MD, USA) as software package. An experimental design methodology was applied for the optimization of

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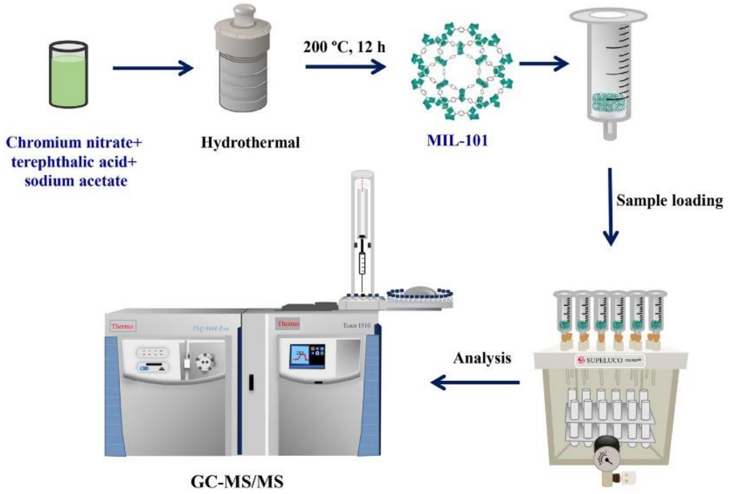

Fig. 1. Schematic of the preparation of MIL-101 adsorbent and analytical workflow for the developed SPE-GC–MS/MS method.

the SPE process to evaluate the simultaneous effects of the experimental parameters.

3. Results and discussion

3.1. Characterization of the adsorbent

The crystalline property was investigated by XRD. Fig. 2a showed the XRD pattern of MIL-101, which is in good agreement with the previous reports [27,29]. The surface morphology of the MIL-101 adsorbent was characterized by SEM and, as shown in Fig. 2b, the adsorbent showed crystalline structures and high porosity. FT-IR spectroscopy was also performed to investigate the functional groups of the adsorbent. The MIL-101 FT-IR spectrum (Fig. 2c) exhibited two bands at 1410 cm^{-1} and 1514 cm^{-1} that were attributed to the C–O stretching of dicarboxylate and C=C stretching of benzene indicating the presence of organic linker. The absorption bands at 1018 cm^{-1} and 750 cm^{-1} were attributed to the deformation vibration of C–H in benzene [27,30]. These characterization results indicated that a MIL-101 was successfully synthesized as adsorbent.

3.2. Optimization of the SPE

The parameters that potentially affected the SPE procedure were optimized to achieve the best extraction efficiency. In this study, the desorption conditions, including the type and volume of solvent used, were first evaluated. Once the desorption conditions were selected, the other parameters i.e. sample pH, ionic strength and sample volume were optimized by means of a multifactor experimental design.

3.2.1. Study of desorption conditions

Considering the physico-chemical properties of studied UV filters (Table S1), as well as their interactions with the adsorbent, various protic and aprotic solvents with different polarities were investigated: acetonitrile (ACN), methanol (MeOH), ethyl acetate (AcOEt), hexane:acetone (1:1, v/v) and hexane.

To this purpose, a spiked ultrapure water (10 µg L^{-1}) containing eleven target compounds was employed and the extracted UV filters were eluted twice with 1.0 mL of each solvent. As expected, the results depicted in Fig. S1 clearly show that the different solvents eluted the target analytes with different desorption efficiency. Moreover, the obtained recoveries from the second

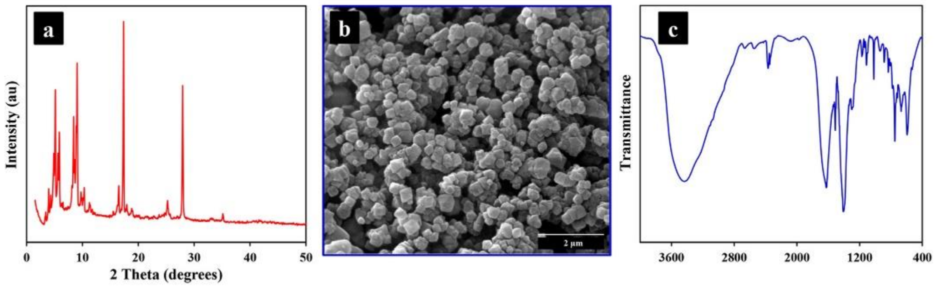

Fig. 2. XRD pattern (a), SEM image (b) and FT-IR spectrum (c) of MIL-101 adsorbent.

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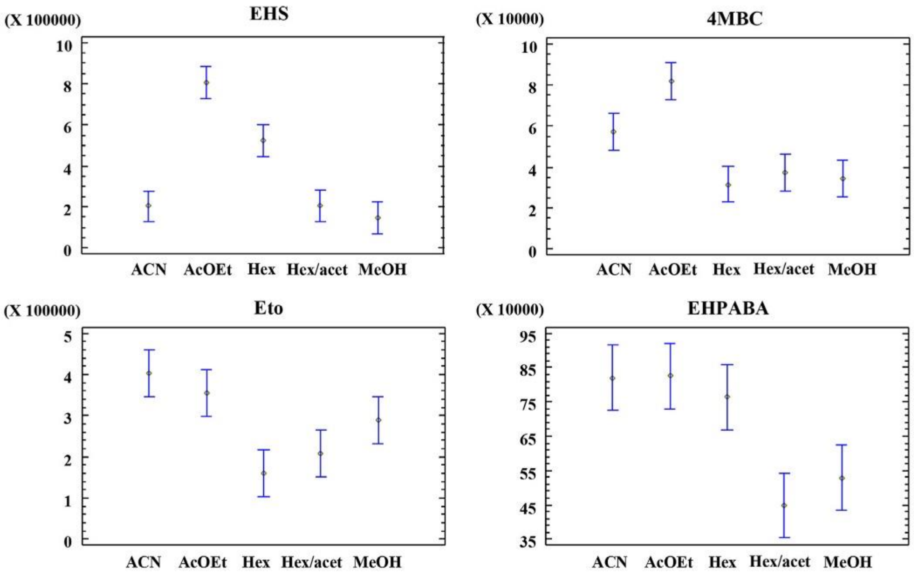

Fig. 3. Mean plots for some representative UV filter compounds obtained in the one-way ANOVA study.

elution were in the range of 15–33% for all solvents (average recovery 19.7 ± 4.1), indicating that the analytes still retained on the adsorbent after first elution. Thus, 2.0 mL of each solvent was selected for conducting the subsequent experiments. The output of the selection of type of desorption solvents were also analyzed by one-way analysis of variance (ANOVA) and summarized in Table S2. For all compounds, excluding OCR, the desorption solvent factor was statistically significant. The results are depicted in the mean value charts shown in Fig. 3 for some representative analytes. As suggested by the charts in Fig. S1, it was confirmed that ethyl acetate, an aprotic solvent with intermediate polarity, provided the highest responses for most of compounds (EHS, BS, HMS, IAMC, BP3 and 4MBC), whereas hexane and the mixture hexane/acetone (1:1, v/v), the most apolar solvents, provided the worst recoveries, especially for EHS, BS and HMS. Acetonitrile provided the best results for only three compounds (MA, Eto and EHMC), while both ethyl acetate and acetonitrile provided comparable response for EHPABA. Acetonitrile and methanol, the two most polar solvents, gave very low recoveries for EHS, BS and HMS. Consequently, ethyl acetate appeared as the most suitable solvent and was selected as desorption solvent for subsequent experiments.

3.2.2. Optimization of the extraction process (pH, NaCl, volume)

The influence of the main variables potentially affecting the SPE were optimized, as well. Several factors such as the sample pH, salt addition and sample volume were investigated. A multifactorial design was conducted to simultaneously assess the influence of these three factors. As shown in Table S3, the sample pH (A) was assessed at three levels (3.0, 4.5 and 6.0), the addition of NaCl (B) at three levels (0.0, 7.5 and 15% (w/v)) and the sample volume (C) at three levels (10, 15 and 20 mL). The chromatographic peak areas were used as experimental responses of the implemented categorical multifactorial design 2^3 (plus 2 central points), which gave rise to 10 experiments.

The results for the multifactor ANOVA study are shown in Table 1. The F-ratio measures the contribution of each factor or interaction on the variance of the response and the *p*-value tests the statistical significance of each factor and interaction. Factor A (pH) was the most influential variable, resulting statistically significant

Table 1
ANOVA summary table obtained for the MIL-101 based SPE process.

Compounds	pH (A)		NaCl (B)		Volume (C)		AB		AC		BC	
	F	*p*	F	*p*	F	*P*	F	*p*	F	*p*	F	*p*
EHS	8.77	0.060	0.53	0.518	0.05	0.843	2.73	0.197	0.56	0.509	0.49	0.533
BS	12.19	***0.040***	0.70	0.465	0.19	0.693	4.35	0.128	0.26	0.647	0.12	0.754
HMS	12.40	***0.039***	0.25	0.649	0.16	0.720	2.05	0.247	1.16	0.360	2.68	0.200
IAMC	9.56	0.054	2.95	0.184	1.69	0.284	3.22	0.170	1.10	0.371	0.09	0.785
BP3	17.62	***0.025***	3.31	0.166	0.69	0.467	6.92	0.078	2.32	0.225	0.04	0.850
4MBC	5.79	0.095	5.26	0.106	2.29	0.227	2.89	0.188	0.22	0.669	0.27	0.638
MA	9.91	0.051	0.01	0.946	1.44	0.316	4.36	0.128	3.33	0.165	6.27	0.087
Eto	4.22	0.132	1.38	0.325	1.04	0.383	5.83	0.095	1.46	0.314	0.07	0.813
EHPABA	12.36	***0.039***	0.02	0.891	1.67	0.287	1.28	0.340	3.77	0.147	3.77	0.148
EHMC	1.90	0.262	2.30	0.227	3.01	0.181	8.23	0.064	0.40	0.570	3.59	0.155
OCR	12.65	***0.038***	0.96	0.400	0.00	0.999	0.44	0.553	1.65	0.289	2.86	0.190

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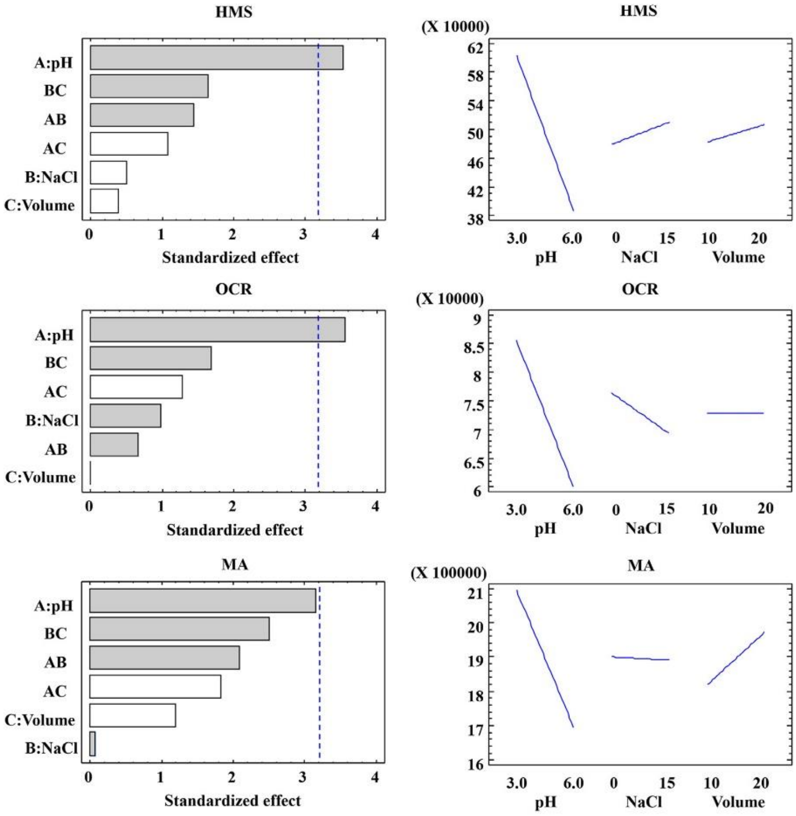

Fig. 4. Pareto charts and main effects plot showing the significant factors (95%) for some of the target UV filters.

for half analytes. pH affects the chemical form with which the analytes interact with the adsorbent and then it can significantly affect their extraction yield. The other factors as well as their interactions were no significant (p > 0.05).

Fig. 4 show the Pareto charts and the main effect plots for some representative analytes (HMS, OCR and MA). In the Pareto charts, the standardized effects are plotted in decreasing order of absolute magnitude, thus making easier to see which ones are the most important factors and interactions. In addition, the vertical line in the chart represents the statistically significant bound at the 95% confidence level. Main effect plots show how the response varies when each factor switches from its low level to its high level, while all other factors are held at the center of the experimental domain.

In the Pareto charts, factor A clearly exceeds the significance limit (vertical line in the graphs) for HMS and OCR and it is close to the line for MA, whereas the other factors are no significant. The main effect plots demonstrate how higher response was achieved when the sample was adjusted to pH 3.0. The other two factors, the addition of NaCl and sample volume, did not significantly affect the responses obtained.

In view of the results, it was possible to define a general method for the simultaneous extraction of the UV filters. The selected conditions implied the adjustment of the sample pH to 3.0, without adding NaCl to the sample solution and employing 20 mL as sample volume for the further experiments.

3.3. Sample breakthrough volume

The sample breakthrough volume was studied to evaluate the largest sample volume that could be loaded through the adsorbent without the loss of the analytes [31,32]. In this study, several sample volumes were investigated: 10, 20, 40, 60, and 80 mL. As shown in Fig. 5, the recoveries decreased when the sample volume was greater than 40 mL, this volume being then selected to perform the extractions, achieving in this way a maximum enrichment.

3.4. Method performance evaluation

To evaluate the analytical performance of the developed method for the extraction of UV filters, the linearity, limit of detection (LOD), accuracy and precision were investigated (Table 2). Under the optimal conditions, the method showed good linearity with the coefficients of determination (R^2) of $\geq$0.9973 for all of the UV filters studied. The LODs, calculated as the concentration corresponding to the signal of the blank plus three times its standard deviation, ranged from 1.0 to 11.7 ng L^{-1}. The method precision was evaluated within a day ($n = 3$) and among days ($n = 6$),

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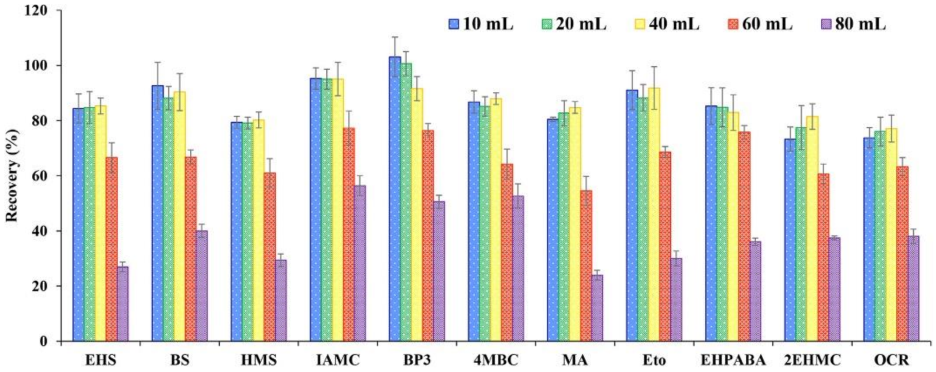

Fig. 5. Study of sample breakthrough volume on SPE efficiency for the target UV filters.

Table 2
Method performance, linear range, coefficients of determination (R^2), LODs, precision and accuracy.

UV filters	Instrumental linearity (μg L^{-1})	R^2	LODs (ng L^{-1})	Precision, RSD (%)		Recovery (%)	
				Intra-day[a]	Inter-day[b]	Mean[c]	RSD[d]
EHS	0.5–100	0.9984	8.0	1.3	4.3	82–100	1.3–6.3
BS	0.5–100	0.9995	3.2	5.3	7.2	87–100	1.3–8.7
HMS	0.5–100	0.9999	3.1	6.2	4.9	84–98	1.8–7.6
IAMC	0.5–100	0.9991	2.8	6.0	8.2	90–101	1.1–7.6
BP3	0.5–100	0.9991	5.2	3.0	2.0	87–99	0.9–9.2
4MBC	0.5–100	0.9973	1.6	3.1	6.4	88–98	1.2–6.9
MA	0.5–100	0.9999	8.5	4.6	3.8	83–105	1.6–8.6
Eto	0.5–100	0.9993	1.0	6.4	5.1	88–101	1.3–7.0
EHPABA	0.5–100	0.9999	1.4	6.6	6.1	85–105	1.3–7.3
2EHMC	0.5–100	0.9995	11.7	5.9	5.1	84–102	1.1–7.8
OCR	0.5–100	0.9988	7.7	5.8	9.2	85–104	1.1–8.0

[a] $n = 3$.
[b] $n = 6$.
[c] mean recovery of UV filters in difference matrices at three different concentration levels (0.1, 1.0 and 10 μg L^{-1}).
[d] %RSD values of the recovery.

by adding 10 μg L^{-1} of the studied UV filters into ultrapure water. The RSD values ranged from 1.3% to 6.6% and from 2.0% to 9.2% in terms of intra-day and inter-day precisions, respectively.

Six different water matrices including ultrapure, mineral water, river, wastewater, swimming pool and seawater were employed to evaluate the suitability of the proposed method. Recoveries were performed at three different fortification levels, 0.1, 1.0 and 10 μg L^{-1} of the target UV filters in the six water samples. The results are summarized in Table S4. Quantitative recoveries and satisfactory precision were achieved in all cases. Recoveries were between 82 and 105% and RSD values ranged from 0.9% to 9.7%. In addition, the UV filters recovery achieved in ultrapure water was not different from that achieved in the other water matrices, suggesting that no significant matrix effect was occurring. Therefore, external calibration with standard of UV filters dissolved in ethyl acetate was used for quantitative purpose.

3.5. Comparison between the MIL-101 adsorbent and commercial SPE cartridge

The extraction efficiency of the developed MIL-101 adsorbent was compared to that of a commercial C18 and a Hydrophilic-Lipophilic Balance (HLB) SPE adsorbents, filled with the same amount of sorbent (50 mg). As shown in Fig. S2, the developed adsorbent enabled reaching higher UV filter recoveries (up to 6.0–52%) than the commercial C18 SPE sorbent in all cases. The likely adsorption of the target UV filters on MIL-101 through both π–π and hydrophobic interactions may explain this greater efficiency, since only hydrophobic interactions are possible between UV filters and the C18 sorbent.

The recoveries obtained from MIL-101 were comparable with those achieved with HLB for five compounds (BS, OCR, EHS, IAMC, and BP3). However, for the remaining six compounds, the developed material allowed a much higher extraction efficiency. In addition, the porous framework provided larger surface area, leading to improve the extraction ability to UV filters.

3.6. Comparison with other methods

The analytical performance of the developed MIL-101 based method was compared with that of other reported methods based on IL-USA-DLLME-HPLC-UV [33], PIN-SPME-GC–MS [34], SBSE-HPLC-APCI-MS/MS [13], μ-SPE-GC–MS [35], MSPE-HPLC-MS [14], MSPE-UHPLC-MS/MS [15], SPE-GC–MS/MS [11], SPE (Online)-LC-MS/MS [4] and SPE-UHPLC-ESI-MS/MS [10] (Table 3). It can be seen that the MIL-101 method performance shows very competitive parameters, often better than those achieved using the other methods. Moreover, the MIL-101 based method only requires 40 mL of sample volume, few mL of extracting solvent and a total extraction time of 20 min, being one of the fastest methods. The quantification of the developed method could be easily performed by external standard calibration, making unnecessary obtaining calibration curves for each water matrix by repeating the whole extraction process. This miniaturized SPE approach involves low

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Table 3

Comparison of the performance parameters of the proposed MIL-101 SPE-GC–MS/MS method with other methods developed for the determination of UV filters in water samples.

Extraction Method[a]	Analytical technique[b]	Extractant	No. of analytes	Water	Sample volume (mL)	Extraction process time (min)	Desorption solvent	LOD (ng L^{-1})	Recovery (%)	RSD (%)	Ref.
IL-USA-DLLME	HPLC-UV	Ionic liquid	3	Tap, river, swimming pool	10	8	Methanol	200–5000	71–118	4.0–6.3	[33]
PIN-SPME	GC–MS	Graphene based sol–gel coating	3	River	7	55	–	0.5–6.8	99–114	5.7–11.3	[34]
SBSE	HPLC-APCI-MS/MS	Polydimethyl-siloxane coated stir bar	6	Wastewater, river, sea	50	360	Methanol	0.6–114	64–85	3–8	[13]
MSPE	HPLC-MS	Magnetic polydopamine (Fe_3O_4@PDA)	4	Tap water, wastewater	10	21	Acetonitrile	89–127.7	98–104	2.1–2.9	[14]
MSPE	UHPLC-MS/MS	Fe3O4 graphitized carbon blacks (mGCB)	3	Lake, river	50	45	Acetonitrile 0.05% formic acid	1–2	85–98	6–15	[15]
µ-SPE	GC–MS	MWCNTs packed polypropylene membrane	5	Drinking, tap, river, dam, wastewater	50	28	Dichloromethane	3–18	67–116	6.2–15	[35]
SPE	GC–MS/MS	HLB	3	Tap, effluent wastewater	1000	100	methanol/ dichloromethane (50:50; v/v)	0.3–6.5	71–150	1–19	[11]
SPE (Online)	LC-MS/MS	Cross-linked styrenedivinyl-benzene polymer (PLRP-s)	2	Ground, river, effluent wastewater	5	5	Acetonitrile	4.0–6.0	96–111	0–11	[4]
SPE	UHPLC-ESI-MS/MS	Graphitized carbon black	4	Tap, lake	200	12	Dichloromethane/ methanol	1.2–3.5	84–115	1–11	[10]
SPE	GC–MS/MS	MIL-101	11	Mineral, river, wastewater, swimming pool, sea	40	20	Ethyl acetate	1.0–11.7	82–105	0.9–9.7	This work

[a] IL-USA-DLLME, ionic liquid-based ultrasound-assisted dispersive liquid–liquid microextraction; PIN-SPME, plunger-in-needle solid-phase microextraction; SBSE, stir bar sorptive extraction; MSPE, Magnetic solid-phase extraction; µ-SPE, micro-solid-phase extraction.

[b] HPLC, high-performance liquid chromatography; UHPLC, ultra-high-performance liquid chromatography; LC, liquid chromatography.

Table 4

Concentration (µg L^{-1}) of the studied UV filters in the lake, river, seawater and recreational water samples.

Sample	EHS	BS	HMS	IAMC	BP3	4MBC	MA	Eto	EHPABA	2EHMC	OCR
LW		0.023 ± 0.001	0.021 ± 0.001	0.017 ± 0.001		0.076 ± 0.008			0.018 ± 0.001		0.116 ± 0.011
RW1						0.060 ± 0.011	0.045 ± 0.010			0.076 ± 0.009	0.084 ± 0.001
RW2			0.013 ± 0.001								
RW3						0.120 ± 0.007		0.017 ± 0.001	0.007 ± 0.001		0.082 ± 0.001
SW1		0.010 ± 0.001	0.025 ± 0.009			0.044 ± 0.006	0.034 ± 0.024			0.117 ± 0.005	0.083 ± 0.011
SW2			0.016 ± 0.002			0.067 ± 0.016					
SW3		0.011 ± 0.001	0.023 ± 0.002	0.024 ± 0.001		0.394 ± 0.031		0.101 ± 0.007	0.024 ± 0.001		0.026 ± 0.001
SW4		0.064 ± 0.004	0.024 ± 0.002	0.049 ± 0.003	0.015 ± 0.001	0.879 ± 0.043		0.38 ± 0.24	0.100 ± 0.006		0.256 ± 0.014
SP1	1.13 ± 0.45	0.023 ± 0.015	4.4 ± 1.3	0.20 ± 0.30	0.44 ± 0.14	1.321 ± 0.013		0.018 ± 0.010		0.46 ± 0.20	2.66 ± 0.31
SP2											0.063 ± 0.014
SP3	0.200 ± 0.017		1.587 ± 0.017								0.86 ± 0.34
SP4		0.058 ± 0.004	0.115 ± 0.008	0.057 ± 0.003	0.023 ± 0.001	0.192 ± 0.006		0.298 ± 0.019	0.043 ± 0.003		0.239 ± 0.019
SP5	0.028 ± 0.002	0.052 ± 0.005	0.386 ± 0.028	0.016 ± 0.001	0.020 ± 0.003	3.43 ± 0.18		0.257 ± 0.020	0.025 ± 0.002		0.318 ± 0.027

LW: lake water, RW: river water, SW: Seawater, SP: Swimming pool water, blank spaces: below LOD.

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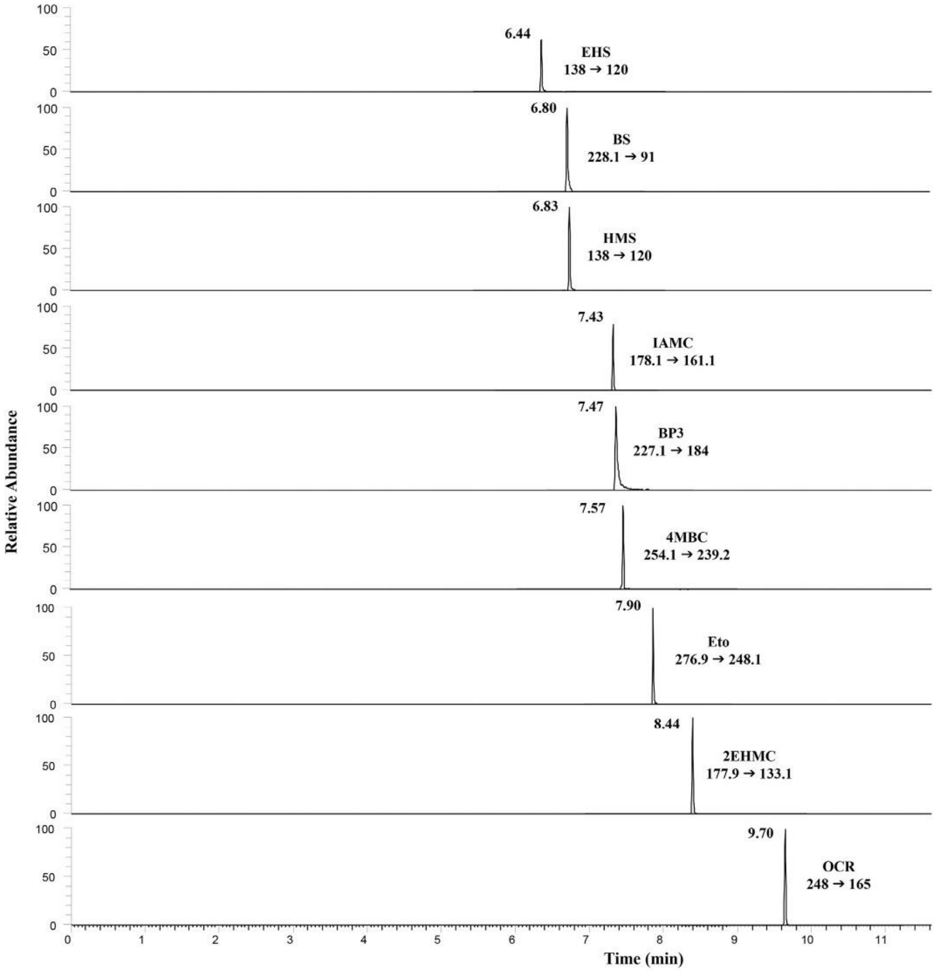

Fig. 6. SRM reconstructed chromatogram for a swimming pool water sample; SP1 (see concentration in Table 4).

environmental impact since the residue generation is strongly minimized. In addition, low amounts of toxic solvent and adsorbent have been used, and low-energy consumption was required to perform the extraction process.

3.7. Application to real samples

The developed MIL-101 SPE-GC–MS/MS method was applied for the extraction and determination of UV filters in real water samples, including natural (lake, river and seawater) and recreational (swimming pool) water.

Fig. 6 exhibits a GC–MS/MS reconstructed chromatogram for a swimming pool sample (SP1) where nine UV filters were found.

Quantification was performed by external standard calibration curve employing a standard solution of eleven target compounds prepared in ethyl acetate. As shown in Table 4, the eleven target UV filters were detected in the analyzed samples, with average concentrations ranging from 34 to 661 ng L^{-1} (BS, HMS). The most often found compounds were OCR (eleven out of thirteen samples), 4MBC and HMS (ten out of thirteen samples), these three UV filters being the most employed, alone or in combination, in sunscreen and other cosmetic products [6]. In addition, as expected, the largest concentrations were found in swimming pool (up to 4400 ng L^{-1} for HMS), where people protect their skin against solar rays with sunscreens.

Swimming pool sample 1 even contained 9 out of 11 target UV filters with four of them showing concentrations higher than 1000 ng L^{-1}.

It is worth noting that 2EHMC, which was listed as priority pollutant in aquatic environment [28] was quantified in three samples (two natural waters and one recreational waters), in the concentration range 76–460 ng L^{-1}.

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4. Conclusions

An analytical methodology based on a solid-phase extraction with a MIL-101 adsorbent followed by gas chromatography tandem mass spectrometry was developed for the determination of eleven multiclass organic UV filters in different water samples. The optimized method provided low limits of detection (1.0–11.7 ng L^{-1}), good adsorption/desorption ability of UV filters (recovery 82–105%) and good repeatability (RSD lower than 10%).

Owing to the reduced extraction time of 20 min and considering the possibility of eluting several cartridges at the same time, the developed method enabled high throughput. Moreover, the absence of significant matrix effect implies that the UV filters quantification can be easily performed by external calibration. The developed method was successfully applied for the extraction and determination of UV filters in different real samples, including environmental (lake, river and seawater) and recreational (swimming pool) waters, where the eleven target compounds were detected with average concentrations ranging from 34 to 661 ng L^{-1}. The great performance of the developed method makes possible its application for the future determination of other hydrophobic emerging contaminants in water.

Declaration of Competing Interest

None.

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Supplementary materials

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Supporting information

Solid-phase extraction based MIL-101 adsorbent followed by gas chromatography tandem mass spectrometry for the analysis of multiclass organic UV filters in water

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Table S1 Experimental GC–MS/MS parameters for the analysis of the target UV filters and some physico-chemical properties.

Acronym	INCI[a] name	MW[b] (g mol^{-1})	Log K_{ow}[c]	pKa	RT (min)	MS/MS transitions[d]	CE[e]
EHS	Ethylhexyl salicylate	250.33	5.8	8.1	6.44	120 → 92	10
						138 → 120	10
						250.1 → 120	15
BS	Benzyl salicylate	228.24	4.0	8.1	6.80	91 → 65	15
						228.1 → 91	10
HMS	Homosalate	262.34	5.8	8.1	6.83	120 → 92	10
						138 → 120	10
						262.2 → 120	15
IAMC	Isoamyl p-methoxycinnamate	248.32	4.1	-	7.43	161 → 133	10
						178.1 → 161.1	10
						248.1 → 178	10
BP3	Benzophenone-3	228.24	3.6	7.6	7.47	151 → 95	10
						227.1 → 127.9	35
						227.1 → 184	20
4MBC	4-methylbenzylidene camphor	254.37	4.9	-	7.57	127.9 → 102	20
						170.6 → 128.1	15
						254.1 → 239.2	10
MA	Menthyl anthranilate	275.39	6.3	2.2	7.77	119 → 91.8	10
						137 → 119	10
						275.2 → 137	10
Eto	Etocrylene	277.32	4.0	-	7.90	231.9 → 176.5	20
						248 → 164.9	25
						276.9 → 248.1	10
EHPABA	Ethylhexyl dimethyl PABA	277.40	6.1	2.4	8.27	148 → 104.2	25
						165.1 → 148.6	25
						277.2 → 164.9	10
2EHMC	2-Ethylhexyl methoxycinnamate	290.40	5.7	-	8.44	161 → 133.1	10
						177.9 → 133.1	20
						290.2 → 178.1	10
OCR	Octocrylene	361.48	7.5	-	9.70	232 → 203	20
						248 → 165	30
						360.2 → 276.1	20

[a] International Nomenclature of Cosmetic Ingredients, [b] Molecular weight, [c] Octanol-water partition coefficient, [d] Underlined values correspond to the quantification transition, [e] CE: Collision energy (eV).

Table S2 F-ratios and *p*-values obtained in the ANOVA study of the desorption solvent[a].

Compounds	F-ratios	*p*-values
EHS	32.85	0.000
BS	61.47	0.000
HMS	27.86	0.000
IAMC	8.04	0.004
BP3	7.84	0.004
4MBC	13.84	0.000
MA	7.60	0.004
Eto	7.77	0.004
EHPABA	8.63	0.003
2EHMC	9.74	0.002
OCR	2.37	0.122

[a] *p*-values lower than 0.05 indicate statistical significance.

Table S3 Experimental factors and level studied in the experimental design.

Factor	Code	Low level	Intermediate level	High level	Continuous
pH	A	3.0	4.5	6.0	Yes
NaCl (%w/v)	B	0.0	7.5	15	Yes
Volume (mL)	C	10	15	20	Yes

Table S4 Recoveries of UV filters in different water matrices.

Sample	UV filters	Recovery (%RSD), n=3		
		0.1 μg L^{-1} spiking level	1.0 μg L^{-1} spiking level	10 μg L^{-1} spiking level
Ultrapure water	EHS	92.3 ± 6.2	96.0 ± 3.2	94.2 ± 1.3
	BS	90.7 ± 7.5	92.9 ± 2.8	91.9 ± 5.3
	HMS	94.5 ± 1.8	96.9 ± 4.9	87.5 ± 6.2
	IAMC	92.0 ± 4.1	91.8 ± 1.9	92.6 ± 6.0
	BP3	88.0 ± 4.5	94.9 ± 1.6	95.2 ± 3.0
	4MBC	87.6 ± 5.0	96.1 ± 3.5	97.4 ± 3.1
	MA	87.5 ± 3.0	93.4 ± 5.6	95.5 ± 4.6
	Eto	92.8 ± 7.0	93.9 ± 1.9	93.8 ± 6.4
	EHPABA	89.1 ± 6.2	92.5 ± 5.7	93.1 ± 6.6
	2EHMC	85.5 ± 2.0	93.3 ± 1.8	85.3 ± 5.9
	OCR	88.1 ± 7.6	90.9 ± 5.4	87.6 ± 5.8
Mineral water	EHS	86.9 ± 4.6	92.2 ± 3.7	89.9 ± 5.1
	BS	87.0 ± 7.5	96.6 ± 1.3	95.9 ± 4.4
	HMS	96.5 ± 2.4	89.9 ± 7.6	86.6 ± 4.8
	IAMC	95.4 ± 5.4	96.7 ± 3.9	91.6 ± 4.1
	BP3	92.5 ± 4.3	96.3 ± 2.4	95.2 ± 8.9
	4MBC	94.4 ± 6.9	91.9 ± 6.6	89.3 ± 2.3
	MA	88.8 ± 4.0	94.0 ± 4.5	83.1 ± 3.2
	Eto	90.7 ± 3.7	87.7 ± 2.8	91.9 ± 1.8
	EHPABA	93.7 ± 2.1	90.6 ± 4.0	98.8 ± 4.6
	2EHMC	97.8 ± 5.1	101.6 ± 4.2	97.0 ± 2.2
	OCR	91.8 ± 7.8	94.0 ± 5.3	93.9 ± 5.5
River water	EHS	89.3 ± 6.2	88.7 ± 5.5	90.2 ± 3.3
	BS	87.3 ± 7.5	92.1 ± 5.7	87.0 ± 8.7
	HMS	83.9 ± 1.8	91.5 ± 2.1	84.0 ± 3.7
	IAMC	92.0 ± 4.1	89.9 ± 7.0	92.5 ± 3.8
	BP3	88.0 ± 4.5	90.8 ± 7.3	92.8 ± 1.8
	4MBC	87.6 ± 5.0	97.5 ± 1.8	89.3 ± 2.3
	MA	87.5 ± 3.0	92.8 ± 6.1	95.7 ± 1.6
	Eto	92.8 ± 7.0	94.0 ± 2.6	95.6 ± 7.0
	EHPABA	89.1 ± 6.2	86.9 ± 1.3	84.7 ± 6.4
	2EHMC	84.7 ± 2.0	87.7 ± 7.8	83.6 ± 1.1
	OCR	85.0 ± 8.0	91.2 ± 4.2	85.0 ± 5.7

Sample	**UV filters**	**Recovery (%RSD), n=3**		
		0.1 µg L^{-1} spiking level	**1.0 µg L^{-1} spiking level**	**10 µg L^{-1} spiking level**
Wastewater	EHS	87.1 ± 2.4	90.9 ± 2.9	89.2 ± 3.8
	BS	93.6 ± 3.4	100.1 ± 3.4	91.3 ± 4.3
	HMS	94.6 ± 2.3	92.3 ± 4.2	92.9 ± 4.8
	IAMC	90.1 ± 6.0	92.9 ± 3.8	97.0 ± 6.2
	BP3	91.0 ± 6.3	91.2 ± 0.9	93.9 ± 1.3
	4MBC	94.7 ± 3.5	94.5 ± 1.2	90.1 ± 1.9
	MA	92.0 ± 5.9	89.8 ± 8.6	85.1 ± 6.0
	Eto	89.7 ± 2.7	87.5 ± 2.3	90.7 ± 6.2
	EHPABA	94.7 ± 4.8	88.3 ± 7.3	96.9 ± 6.3
	2EHMC	91.1 ± 2.1	87.3 ± 3.1	89.6 ± 1.3
	OCR	98.5 ± 3.9	89.6 ± 5.9	100.7 ± 5.8
Swimming pool water	EHS	82.4 ± 1.8	86.2 ± 2.7	94.6 ± 3.6
	BS	94.1 ± 2.7	90.6 ± 4.1	88.0 ± 4.0
	HMS	95.8 ± 3.7	93.5 ± 2.3	91.7 ± 4.9
	IAMC	96.8 ± 4.8	95.5 ± 1.5	97.5 ± 1.1
	BP3	86.9 ± 9.2	87.3 ± 4.4	97.1 ± 3.3
	4MBC	89.2 ± 6.5	95.8 ± 1.6	90.8 ± 2.6
	MA	91.7 ± 2.6	105.3 ± 7.5	98.9 ± 4.2
	Eto	90.1 ± 6.3	94.7 ± 5.1	92.8 ± 1.3
	EHPABA	93.3 ± 2.9	95.0 ± 6.4	89.2 ± 3.4
	2EHMC	90.1 ± 3.9	99.6 ± 5.6	95.0 ± 3.2
	OCR	103.5 ± 4.5	98.1 ± 7.5	100.6 ± 7.1
Sea water	EHS	100.3 ± 3.6	85.9 ± 2.7	97.4 ± 6.3
	BS	100.0 ± 1.9	95.4 ± 6.0	88.6 ± 2.5
	HMS	98.0 ± 4.8	89.5 ± 4.2	91.6 ± 2.1
	IAMC	94.6 ± 7.6	99.7 ± 1.7	100.9 ± 7.3
	BP3	96.6 ± 5.3	95.3 ± 2.6	99.4 ± 5.1
	4MBC	92.7 ± 1.7	97.8 ± 2.4	98.0 ± 3.1
	MA	95.1 ± 3.7	102.9 ± 4.4	92.4 ± 2.4
	Eto	100.4 ± 6.1	88.0 ± 4.8	97.6 ± 4.6
	EHPABA	96.8 ± 3.3	92.1 ± 3.2	104.7 ± 5.5
	2EHMC	94.7 ± 3.6	95.2 ± 3.8	91.5 ± 4.4
	OCR	96.4 ± 5.9	90.4 ± 9.7	94.4 ± 1.1

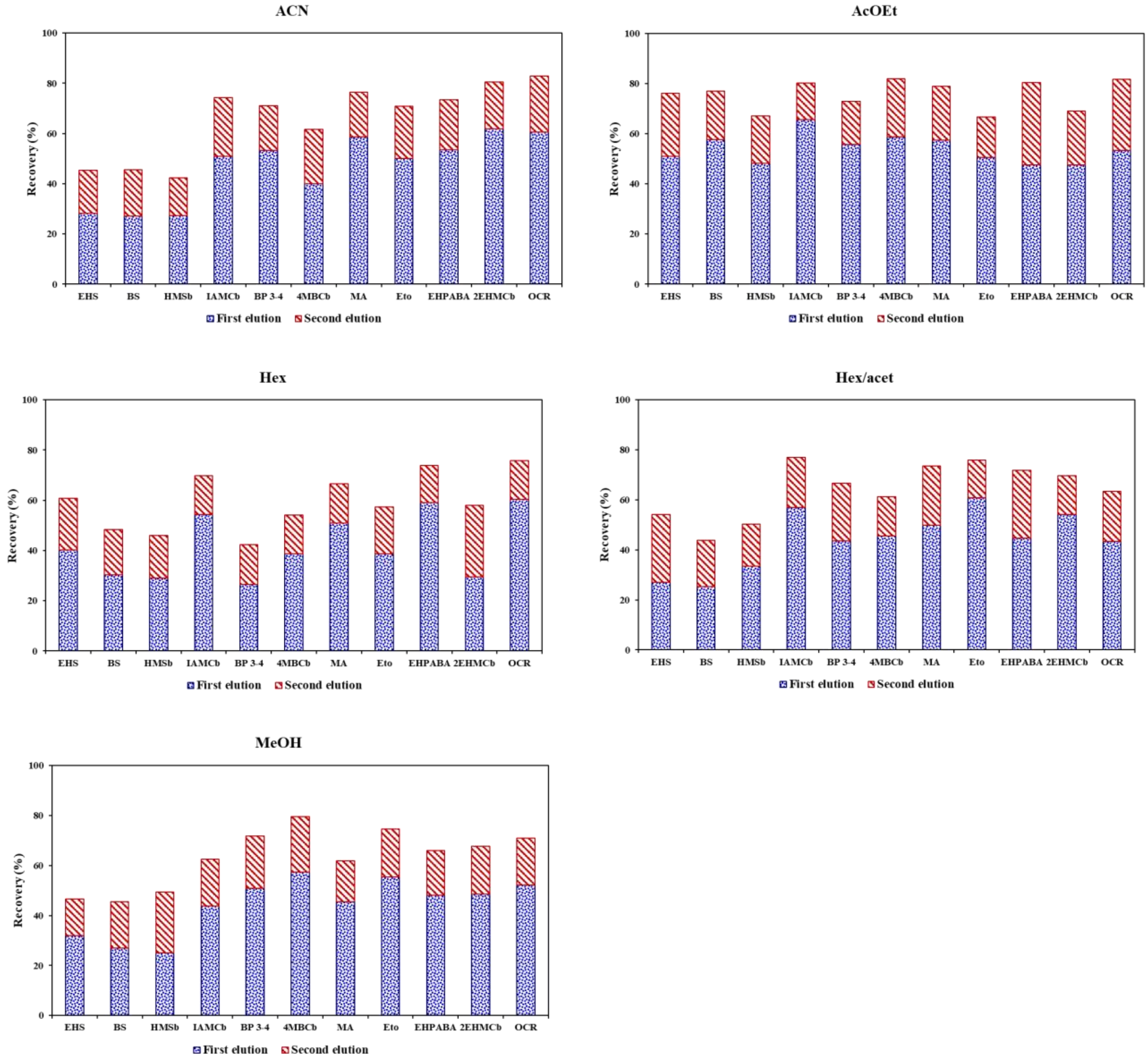

Fig. S1 Effect of the desorption solvent and volume on SPE efficiency for UV filters.

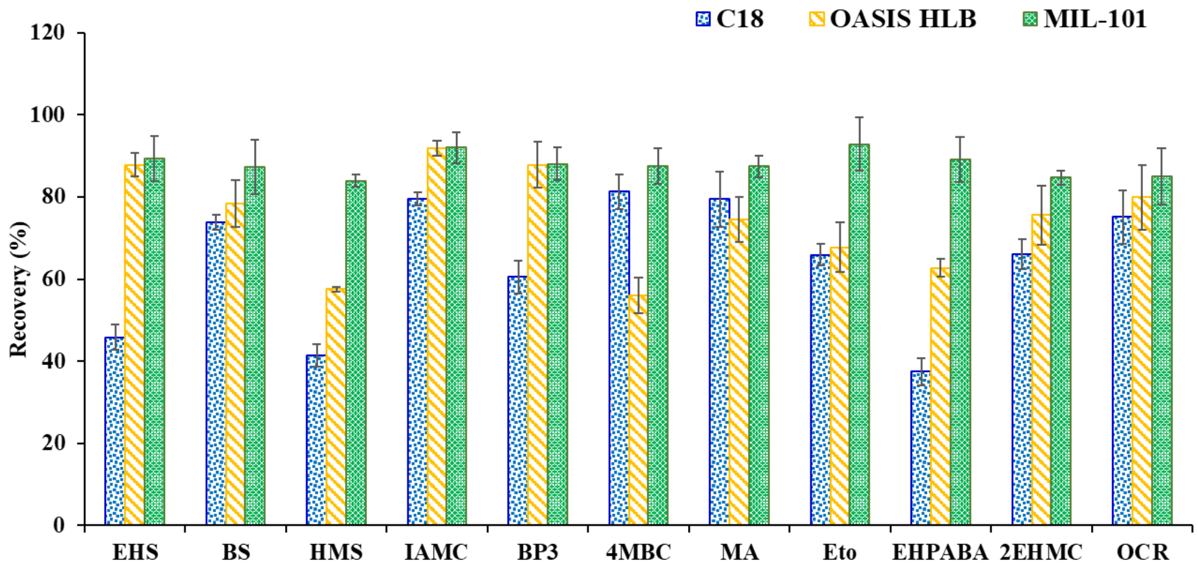

Fig. S2 Comparison of the extraction efficiency between the MIL-101 adsorbent and commercial SPE cartridges.

Paper II

Bunkoed, O., Rueankaew, T., **Nurerk, P.**, Kanatharana, P., Polyaniline-coated cigarette filters as a solid-phase extraction sorbent for the extraction and enrichment of polycyclic aromatic hydrocarbons in water samples. *Journal of Separation Science* 39 (2016) 2332-2339.

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Research Article

Polyaniline-coated cigarette filters as a solid-phase extraction sorbent for the extraction and enrichment of polycyclic aromatic hydrocarbon in water samples

Polyaniline coated cigarette filters were successfully synthesized and used as a solid-phase extraction sorbent for the extraction and preconcentration of polycyclic aromatic hydrocarbons in water samples. The polyaniline helped to enhance the adsorption ability of polycyclic aromatic hydrocarbons on the sorbent through π–π interactions. The high porosity and large surface area of the cigarette filters helped to reduce backpressure and can be operated with high sample flow rate without loss of extraction efficiency. The developed sorbent was characterized by Fourier transform infrared spectroscopy and scanning electron microscopy. The parameters that affected the extraction efficiencies, i.e. polymerization time, type of desorption solvent and its volume, sample flow rate, sample volume, sample pH, ionic strength, and organic modifier were investigated. Under the optimal conditions, the method was linear over the range of 0.5–10 μg/L and a detection limit of 0.5 ng/L. This simple, rapid, and cost-effective method was successfully applied to the preconcentration of polycyclic aromatic hydrocarbons from water samples. The developed method provided a high enrichment factor with good extraction efficiency (85–98%) and a relative standard deviation <10%.

Keywords: Cigarette filters / Polyaniline / Polycyclic aromatic hydrocarbons / Solid-phase extraction
DOI 10.1002/jssc.201600285

Additional supporting information may be found in the online version of this article at the publisher's web-site

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are some of the most dangerous contaminating pollutants in the environment [1]. The presence of these pollutants in the environment results from the incomplete combustion of organic matter [2]. They enter into the surface water by atmospheric fallout, leaching of municipal effluents, vehicle emission, and by oil spills [3, 4]. Due to their mutagenic and carcinogenic activity, the World Health Organization (WHO) has set maximum permissible concentrations for most of the PAHs in drinking water at 0.2 μg/L [5]. Therefore, the determination of PAHs in water is very important. HPLC has been widely used for the determination of PAHs due to its high sensitivity, selectivity, and good precision [6, 7]. However, PAHs are usually present at trace levels in water samples and together with the complexity of the matrices, a suitable extraction and preconcentration technique is generally required before instrumental analysis.

Many sample preparation methods have been reported for the extraction of PAHs such as LLE [8], hollow-fiber LPME [9], SPE [10], SPME [11,12], stir bar sorptive extraction [13], stir rod sorptive extraction [14], and magnetic SPE [15,16]. Among these methods, SPE is the most widely used due to its high extraction efficiency, high enrichment factor, low solvent consumption, and ease of operation [17, 18]. For SPE, the selection of adsorbent is one of the most important factors since this affects the extraction efficiency of the target analytes. Various commercial sorbents such as C_{18} [18], oasis HLB [19] have been used as SPE sorbents for the extraction and preconcentration of PAHs. However, commercial SPE sorbents are expensive, packed SPE particle could result in high backpressure and the clogging of the cartridge by particulate matter. To overcome these limitations, cellulose fibers have been a good choice of adsorbent due to their high porosity that leads to low backpressure and they are also cost-effective [20, 21]. Cellulose acetate fibers have been successfully used as the

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Abbreviations: BaA, benzo(a)anthracene; **BaP**, benzo(a)pyrene; **BbF**, benzo(b)fluoranthene; **CF**, cigarette filter; **PAH**, polycyclic aromatic hydrocarbon; **PANI**, polyaniline

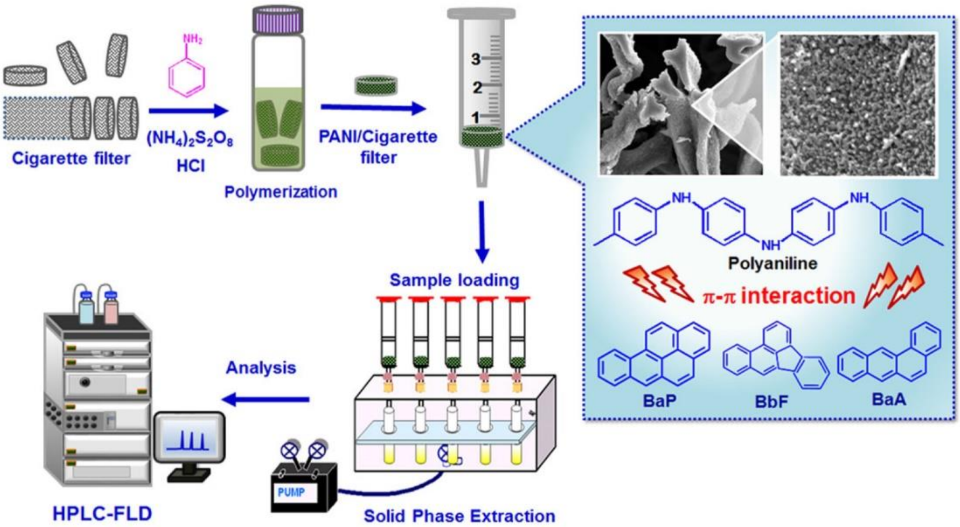

Figure 1. Schematic diagram of the preparation of PANI-coated CFs and the SPE procedure.

adsorbent for the preconcentration of some metal ions [22, 23]. However, to increase the extraction efficiency of the sorbent for PAHs, the surface of the cigarette filters (CFs) needs to be modified or coated with higher affinity materials. Polyaniline (PANI) is a popular conductive polymer that has attracted much attention in separation sciences due to its versatile properties such as hydrophobicity, large π-conjugated structure, polar functional groups, and good thermal and chemical stability [24, 25]. In previous work PANI has been used as an SPME coating material [26–28], however, it could result in a low extraction capacity and can require a long extraction time to reach an extraction equilibrium [29].

In this work, we used PANI coated onto the surface of CFs made from cellulose acetate fiber to enhance the adsorption ability for PAHs due to its large surface area, the ability to establish π interactions between sorbent and the analytes. The PANI-coated CFs (PANI/CFs) sorbent was then applied to extract and preconcentrate PAHs from water samples and then the adsorbed PAHs were detected by HPLC with a fluorescent detector. Benzo(a)anthracene(BaA), benzo(a)pyrene (BaP), and benzo(b)fluoranthene (BbF), because of their toxicity, were selected as the test compounds to investigate the performance of the developed sorbent.

2 Materials and methods

2.1 Chemicals and reagents

Hydrochloric acid, acetonitrile, methanol, and toluene were from Merck (Darmstadt, Germany). Aniline and ammonium persulfate were from Sigma–Aldrich (Steinheim, Germany). Hexane was from J. T. Baker (Philipsburg, NJ, USA). BaA (99% purity), BaP (99% purity), and BbF (99% purity) were from Restek, USA. Ultrapure water was obtained from a Maxima ultrapure system (ELGA, Buckinghamshire, UK)

2.2 Instrumentation

Chromatographic analysis was performed using a Hewlett-Packard 1100 series HPLC system with a fluorescence detector (Agilent Technologies, Germany). The separations of PAHs were performed on a RP VertiSep C_{18} column (Vertical Chromatography, Thailand). The mobile phase was acetonitrile/ water (95:5, v/v) at a flow rate of 1.0 mL/min and the column temperature was set at 30°C. The PAHs were detected by a fluorescence detector with the following excitation (Ex) and emission (Em) wavelengths; BaA: Ex = 290, Em = 410; BbF: Ex = 266, Em = 450; and BaP: Ex = 270, Em = 410 nm. The morphology of the prepared sorbent was observed by SEM (JSM 5200, JOEL, Japan). The FTIR spectra were determined by an FTIR spectrometer from PerkinElmer (MA, USA)

2.3 Preparation of the PANI-coated CFs and the SPE procedure

The CF was obtained from Thailand tobacco monopoly (Bangkok, Thailand). It was first cut into a small piece (0.20 cm) and washed with a proper amount of methanol and water, respectively. The polymerization is shown in Fig. 1; the CFs were added into a beaker containing 1.0 M of HCl, 0.10 M ammonium persulfate, and 0.3 M of aniline monomer. The polymerization was completed by stirring at 500 rpm for 2 h at 25°C. After polymerization, the PANI-coated CFs sorbent was

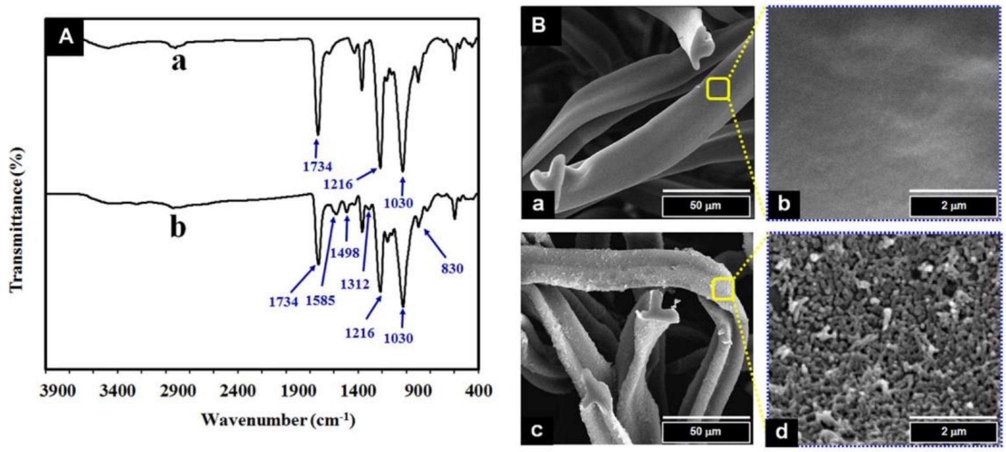

Figure 2. (A) FTIR spectra of the CFs (a) and PANI-coated CFs (b); and (B) scanning electron micrographs of the CFs at 1000 magnification (a), 20 000 magnifications (b), the PANI-coated CFs at 1000 magnification (c), and 20 000 magnification (d).

washed three times with 20 mL of methanol and deionized water, respectively. The PANI/CFs sorbent were then packed into a 1.0 mL polypropylene cartridge and the outlet tip of the cartridge was connected to the SPE manifold, while the inlet of the cartridge was connected to the PTFE tube whose other end was inserted into the sample solution. Before extraction, the PANI/CFs sorbent was precondition with 1.0 mL of methanol and 5.0 mL of deionized water, respectively. Extraction of PAHs was carried out by passing 200 mL of sample solution through the PANI/CFs sorbent under a vacuum at a certain flow rate. The concentrated PAHs were eluted with 2.0 mL of methanol, and the eluent was evaporated to dryness at 50°C, and redissolved with 1.0 mL of mobile phase. Finally, a volume of 20 µL was injected into the HPLC system with the fluorescence detector.

3 Results and discussion

3.1 Characterization of PANI-coated CFs sorbent

The FTIR spectra of the CFs and the PANI-coated CFs are shown in Fig. 2A. CFs showed a characteristic peak at 1734 cm^{-1} (O–C=O stretching) and 1216 cm^{-1} (C–O stretching) that corresponded to the acetyl group. An absorption peak at 1585 cm^{-1} (C=C stretching of the quinoid ring), 1498 cm^{-1} (C=C stretching of the benzenoid ring), 1312 cm^{-1} (C–N stretching of an aromatic amine), and 830 cm^{-1} (C–H out of plane of the quinoid ring) all indicated the successful coating of the PANI onto the surface of the CFs. SEM images of the CFs and PANI-coated CFs are shown in Fig. 2B. It can be seen that the PANI was uniformly distributed on the CFs. The nanostructure of the film provided a high surface area and a high extraction capacity toward aromatic compounds.

3.2 Effect of the polymerization time

To obtain the highest extraction efficiency of the PANI/CFs sorbent, the effect of the polymerization time was investigated between 0 and 12 h (Supporting information Fig. S1). Not coating with PANI provided a low recovery. The recoveries increased when the polymerization time was increased and the highest recovery was obtained at 2 h. This indicated that PANI helped to increase the adsorption capability of PAHs on the sorbent. However, when the polymerization time was further increased to 6 and 12 h, the recovery decreased. This may be because the PANI layers became too thick, so the adsorption and desorption abilities of the analytes were reduced during the extraction and desorption process. At the longer polymerization times of 6 and 12 h, the PANI layer became unstable and showed a lower adhesion to the surface of the CFs. Therefore, the polymerization time of 2 h was employed for preparation of the PANI/CFs sorbent. The surface characteristics of the prepared PANI/CFs sorbent at different polymerization times were further investigated by the SEM. As shown in Fig. 3, the PANI layers after 1 and 2 h polymerization were nearly spherical in shape and had a uniform distribution of particle size, however, after 6 and 12 h PANI was shown to agglomerate and thus had reduced surface and adsorption areas.

3.3 Optimization of the SPE procedure

The parameters that affected the extraction efficiency of the PANI/CFs sorbent were optimized to obtain the best extraction efficiency, using the smallest amount of organic solvent and shortest analysis time, i.e. type of eluting solvent and its volume, sample flow rate, sample volume, organic modifier, sample pH, and ionic strength.

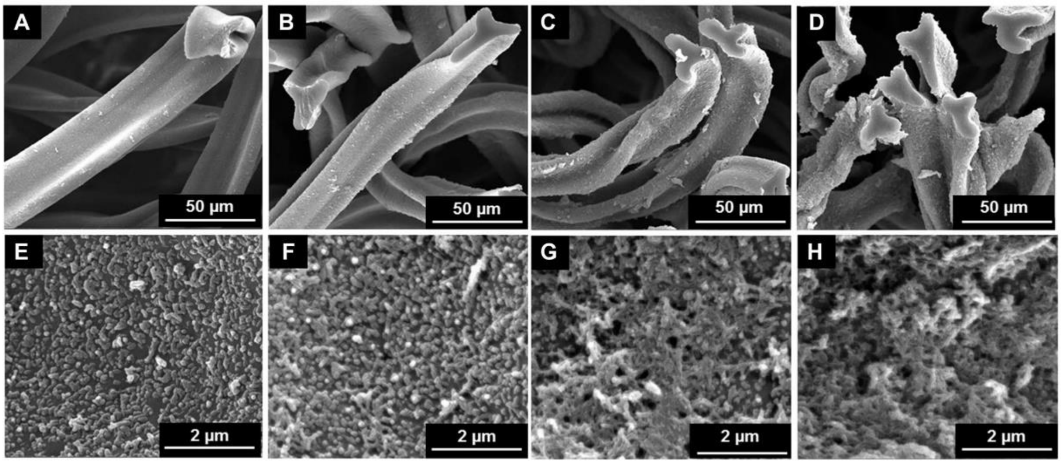

Figure 3. Scanning electron micrographs of PANI-coated CFs with different polymerization times and magnification, 1 h = ×1000 (A), ×20 000 (E); 2 h = ×1000 (B), ×20 000 (F); 6 h = ×1000 (C), ×20 000 (G); 12 h = ×1000 (D), ×20 000 (H).

3.3.1 Type of eluting solvent and its volume

The eluting solvent must have a strong affinity for the PAHs to elute them from the PANI/CFs sorbent with the smallest volume. Since PAHs are nonpolar compounds and the adsorption of PAHs onto the PANI/CFs sorbent were based on π–π interactions, therefore, an eluting solvent with different polarities were evaluated and the results are shown in Supporting information Fig. S2; the desorption efficiency was significantly affected by the eluent; however, acetonitrile provided the highest recovery for BaA, but low recovery for BaP (57 ± 3%). Methanol provided the highest recovery for BaP and the recovery of BbF and BaA were acceptable (>80%). Therefore, methanol was selected as the eluting solvent for further experiments.

The optimum volume of eluting solvent was also evaluated due to the need to use the smallest volume but that may not be sufficient to elute all the analytes efficiently while a larger volume will increase the waste, reagent cost, and analysis time. The results indicated that all analytes could be completely eluted from the PANI/CFs sorbent with 2.0 mL of methanol (Supporting information Fig. S3). Therefore, to minimize the amount of organic solvent 2.0 mL of methanol was chosen for further experiments.

3.3.2 Sample flow rate and sample volume

The flow rate of the sample solution through the sorbent was another important parameter due to its effects on the retention of analytes [30], at higher flow rate of sample, nonequilibrium process can lead to lower retention of the analytes while a lower flow rate requires a longer analysis time. The influence of the sample flow rate was investigated over the range of 4.0–14.0 mL/min. As shown in Supporting information Fig. S4, the results indicated that between 4.0 and 10.0 mL/min the recoveries of all analytes were not significantly different and the recoveries of PAHs decreased with the increase of the sample flow rates to 12 mL/min. Thus, 10 mL/min was chosen as the optimum value. This was due to the high porosity of the PANI/CFs sorbent, therefore, a higher sample flow rate can be operated without sorbent clogging and low backpressure. This is much faster than using a traditional SPE cartridge so the total analysis time could be reduced.

In the SPE technique, the sample volume needed to be optimized because it could affect the retention of the analytes on the sorbent which affected the extraction efficiency [31]. To study the effect of the sample volume, a series of volumes of spiked water (50–500 mL) were investigated. The results indicated that when the sample volume increased to 500 mL, the recoveries decreased and insufficient recoveries were obtained (<80%; Supporting information Fig. S5). Therefore, after considering the enrichment factor, LODs, and extraction efficiency, a sample volume of 200 mL was utilized in the following experiments.

3.3.3 Organic modifier

Due to the low solubility of PAHs in water, it was necessary to add an organic modifier to the water sample to prevent the adsorption of PAHs on the glass wall and during the SPE procedure [18, 32]. To evaluate the effect of the modifier on the extraction efficiency, different percentages of acetonitrile ranging from 0 to 20% were added to a spiked deionize water and the results are shown in Supporting information Fig. S6. The recoveries of the PAHs in the absence of organic modifiers ranged from 65 to 81%, which is not sufficient for real sample applications. The addition of the organic modifier results in an increase in the recoveries of all the analytes

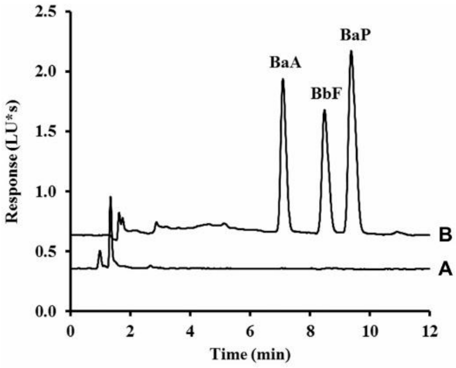

Figure 4. Chromatograms of spiked water sample (0.05 µg/L) without extraction (A) and with extraction using PANI/CFs sorbent (B) under the optimum sample preparation conditions.

and the maximum recoveries were obtained at an acetonitrile content of 2.0%. Therefore, 2% of acetonitrile was used to enhance the recovery.

3.3.4 Effect of the sample pH and ionic strength

The effect of sample pH on the extraction efficiency of PAHs was studied by adjusting the sample pH with hydrochloric acid and sodium hydroxide solutions. As shown in Supporting information Fig. S7, the recoveries did not significantly change over the sample pH range of 3.0–11.0. The reason for this was because the PAHs existed as neutral molecules and were not influenced by any change to the sample pH. Therefore, there was no need to adjust the sample pH before the SPE procedure due to all the water samples being within this pH range.

The mechanism of mass transfer of the analytes in the SPE technique can be influenced by ionic strength [33]. Thus, the effect of the ionic strength on the extraction efficiency of PAHs was investigated. By increasing the concentration of NaCl from 0 to 5% w/v, there was no significant change in the extraction efficiency of PAHs (Supporting information Fig. S8). Therefore, no addition of salt to the water sample was needed.

3.4 Comparison of PANI-coated CFs with a commercial SPE sorbent

The extraction efficiencies of PANI/CFs sorbent was compared to a commercial C_{18} SPE sorbent. Recoveries of PAHs ranged from 84 to 93% for the PANI/CFs sorbent and from 84 to 91% for a C_{18} cartridge (Supporting information Fig. S9). The average recoveries of both sorbents were comparable in the statistic *t*-test, so there were no significant differences between the two sorbents ($P < 0.05$). However, the developed PANI/CFs sorbent showed some advantages over the commercial C_{18} sorbent since the sample flow rate was faster so the analysis time was reduced. This is because of the high porosity of the PANI/CFs sorbent. Moreover, the developed sorbent can be reused 18 times, whereas a commercial sorbent cannot be reused. Therefore, the PANI/CFs sorbent can be used as an alternative sorbent for the extraction and preconcentration of PAHs.

3.5 Reproducibility and reusability

To evaluate the reproducibility of the PANI/CFs sorbent, the sorbent was synthesized in six different batches and used to extract PAHs from spiked deionized water (0.05 µg/L) under the same conditions. The averages of the recoveries of the six preparation times were: BaA 84.3 ± 2.0, BbF 90 ± 2.0, and BaP 93.3 ± 2.4% with the RSDs < 5% (Supporting information Fig. S10). The results indicated that there was no significant difference between the six different preparation times. It also established that the synthesized PANI/CFs sorbent had good reproducibility.

Reusability is an important factor for evaluating the performance of the developed sorbent. After use, the sorbent was washed with 2.0 mL of methanol and 5.0 mL of deionized water. After washing, there was no carryover of the analytes on the sorbent detected. As shown in Supporting information Fig. S11, the sorbent could be reused 18 times while maintaining recoveries of PAHs > 80%. This good reusability indicated that this PANI/CFs sorbent was stable during the extraction procedure.

3.6 Method performance

Analytical performance of the developed method, i.e. linearity, LOD, and LOQ, were evaluated under the optimum conditions and the results are summarized in Supporting information Table S1. To obtain the method linearity, the spiked water samples from 0.0005 to 50 µg/L were extracted by the PANI/CFs sorbent and analyzed by HPLC–FID. The method showed a wide linearity from 0.0005 to 10 µg/L, the coefficient of determination (R^2) was >0.999. The linearity was sufficient for the determination of trace level concentrations of PAHs in water sample. LODs ($S/N \geq 3$) were 0.5 ng/L and LOQs ($S/N \geq 10$) were 2 ng/L. This method can therefore be effective to extract and determine PAHs in water sample since its LOD and LOQ values were much lower than their maximum acceptable contamination level in surface water, i.e. 0.1 µg/L for BaA, and 0.2 µg/L for BbF and BaP, respectively.

3.7 Application of the developed PANI-coated CFs sorbent to real water samples

Under optimum conditions, the developed method using PANI/CFs was successfully applied to the determination of PAHs in water samples, i.e. tap, river, and wastewater. The

Table 1. Comparison of the developed method with other methods for the determination of PAHs

Extraction method	Detection	Sorbent	LOD (μg/L)	Recovery (%)	RSD (%)	References
MES	HPLC-FLD	PANI/Zn-film/stainless steel stick	0.05	82–110	2.3–9.7	[26]
SBS	HPLC-FLD	Poly(pyrrole-co-phenol) film	0.02–0.12	69–113	2.4–12.0	[37]
SPME	GC-MS	Polymeric ionic liquid on a silica-coated stainless steel wire	0.05–0.25	50–110	9.0–29.0	[12]
MSPE	HPLC-FLD	Fe_3O_4/MWCNTs/alginate composite sorbent	0.005	92–98	1.5–3.5	[15]
MSPE	GC-MS	Fe_3O_4 magnetic nanoparticle graphene (Fe_3O_4 MNG)	0.009–0.018	80–100	0.1–1.3	[36]
MSPE	GC-MS	Magnetic nanoparticles featured with divinylbenzene and sulfonate functionalities (Fe_3O_4–DVB–SO_3^-)	0.0006–0.002	80–115	3.3–16.5	[35]
SPE	HPLC-UV	Multiwalled carbon nanotubes	0.005–0.058	78–115	0.5–7.4	[31]
SPE	HPLC-FLD	PANI/CFs sorbent	0.0005	85–98	3.5–8.8	This work

MSE, microextractor stick; SBS, stir bar sorptive; MSPE, magnetic SPE.

chromatograms of the spiked water sample with and without extraction using PANI/CFs are shown in Fig.4. The quantitative results are shown in Supporting information Table S2. PAHs levels were found to be between 0.012 and 0.16 μg/L in river and wastewater. However, these were still lower than the maximum contaminant level allowed for surface water, 0.1 μg/L for BaA, and 0.2 μg/L BbF and BaP, respectively. These results proved that the developed method was a powerful technique for monitoring the PAHs at very low concentrations in water samples. The presence of PAHs in river water may be due to incomplete combustion from vehicle exhaust emission deposited into the river water [34], while, the contamination of PAHs in wastewater may be due to the formation of PAHs during cooking then discharged into the effluent. The recoveries of PAHs in spiked water sample at three concentration levels ranged from 85 to 98% with the RSDs of <10% (Supporting information Table S3). The recoveries were acceptable by the United States Environmental Protection Agency (US EPA) (70–130%) and indicated that there were no interferences from the matrix of the water samples. It can be concluded that the PANI/CFs sorbent was suitable for the extraction and preconcentration of trace PAHs in water samples.

3.8 Comparison of the PANI-coated CFs sorbent with other reported methods

Many methods have been developed for the determination of PAHs. To further demonstrate the advantages of this new method, the figures of merit of the developed method were compared with some other work and these are summarized in Table 1. The LODs of the developed method were much lower than some others, despite the fact that some of them have used MS detection [12, 35]. This indicated that the newly developed method was highly sensitive for the detection of PAHs. In the case of the recoveries, the values from this work were within the same range [15, 26, 35, 36] or better than some previous work [12, 31, 37]. In addition, the RSD values of the developed method were lower than the previous methods, to indicate again that this method has a better repeatability than any other previous methods. This may be because the developed sorbent is simple to prepare, used only one step for the preparation while other methods required complicated preparation and time. Thus, it is clear that the developed method has a high extraction efficiency and sensitivity and can be used for the ultratrace analysis of PAHs in water samples. The other advantages are that the sample can be operated at a high flow rate (10 mL/min) that greatly reduced the analysis time. Moreover, it can be reused at least 18 times. All the results have shown that the developed method is a good sample preconcentration technique that can be used as an alternative method for ultratrace analysis of PAHs in water samples.

4 Conclusion

The coating of PANI onto the surface of CFs helped to increase the adsorption ability of PAHs on the sorbent by π–π interactions. The developed method showed good extraction efficiency and had a high enrichment factor. This method provided for a very low detection limit at 0.5 ng/L for BaA, BbF, and BaP that was much lower than the maximum acceptable contamination levels set by the US-EPA. In addition, the faster sample loading of the PANI/CFs sorbent compared to the traditional SPE cartridges led to a reduced sample preparation time and no cartridge clogging. The developed PANI/FCs sorbent was simple to prepare, cost-effective, and the sorbent could be reused for at least 18 times, so that would help to reduce the costs of analysis and it was environmentally friendly. The sorbent has the potential for use to extract and preconcentrate other less polar molecules from water samples.

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The authors have declared no conflict of interest.

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Supporting Information

Polyaniline coated cigarette filters as a solid phase extraction sorbent for the extraction and enrichment of polycyclic aromatic hydrocarbon in water samples

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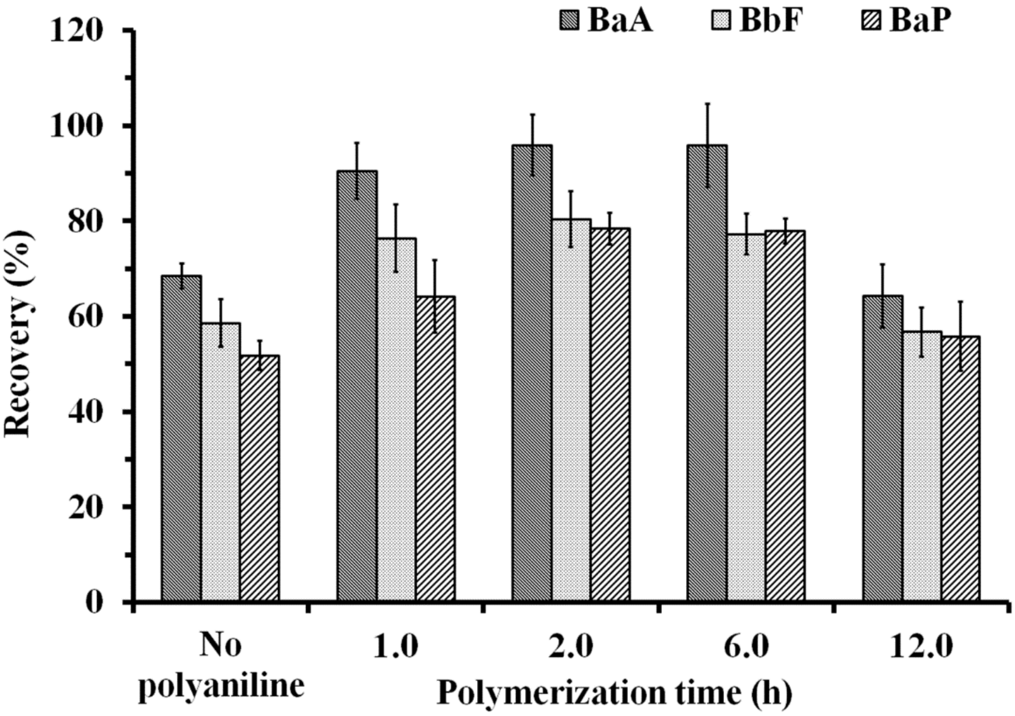

Fig S1. Effect of polymerization times on the recovery of PAHs

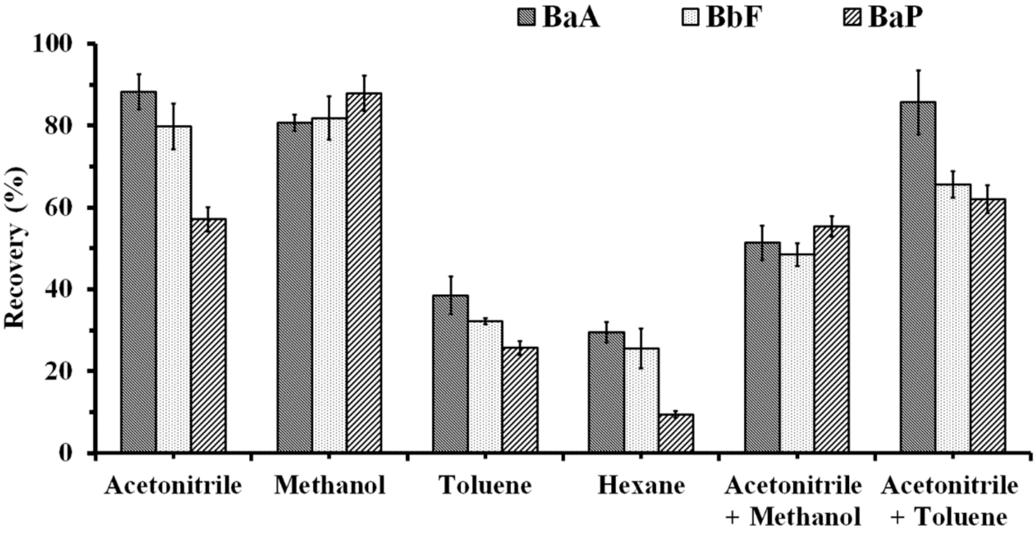

Fig S2. Effect of the type of eluting solvent on the recovery of PAHs

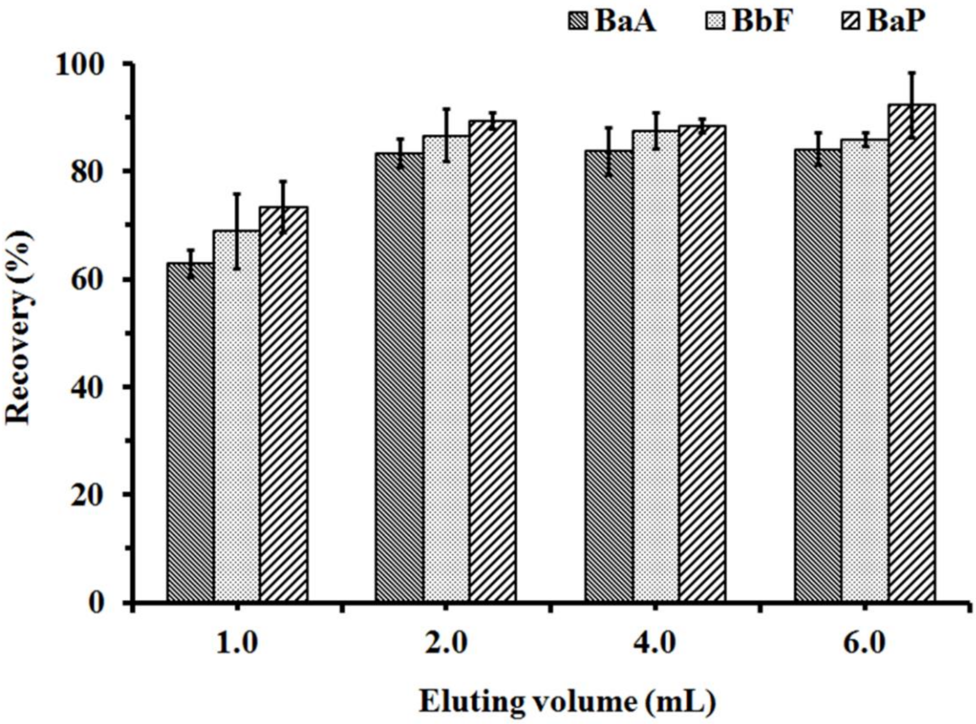

Fig. S3 Effect of the volume of methanol on the recovery of PAHs using the PANI/CFs sorbent

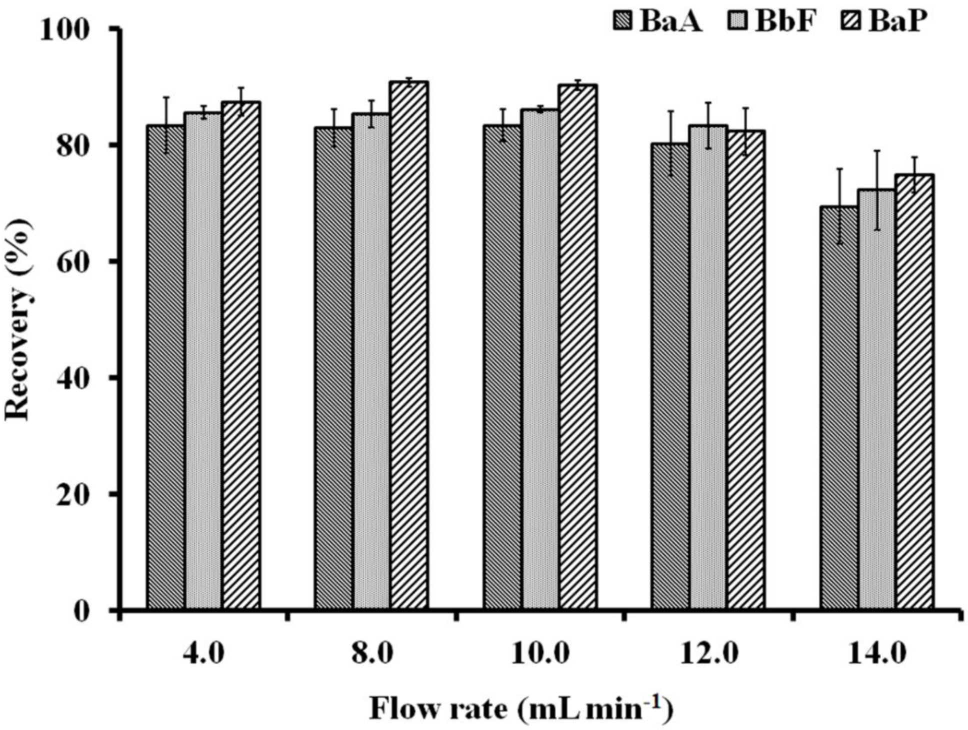

Fig. S4 Effect of the sample flow rate on the recoveries of PAHs using the PANI/CFs sorbent

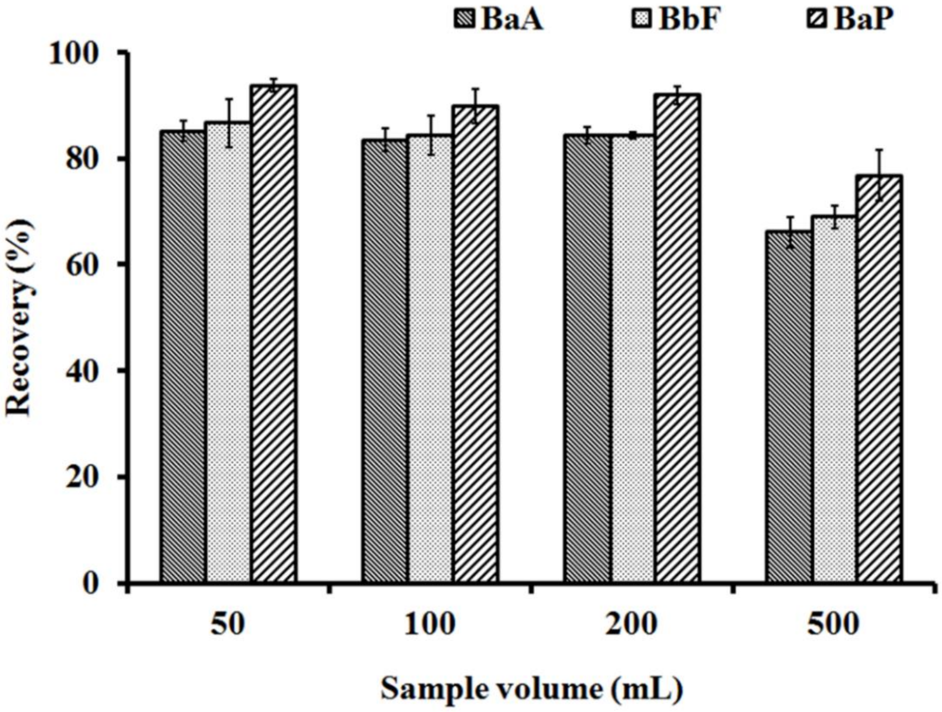

Fig. S5 Effect of the sample volume on the recoveries of PAHs using the PANI/CFs sorbent

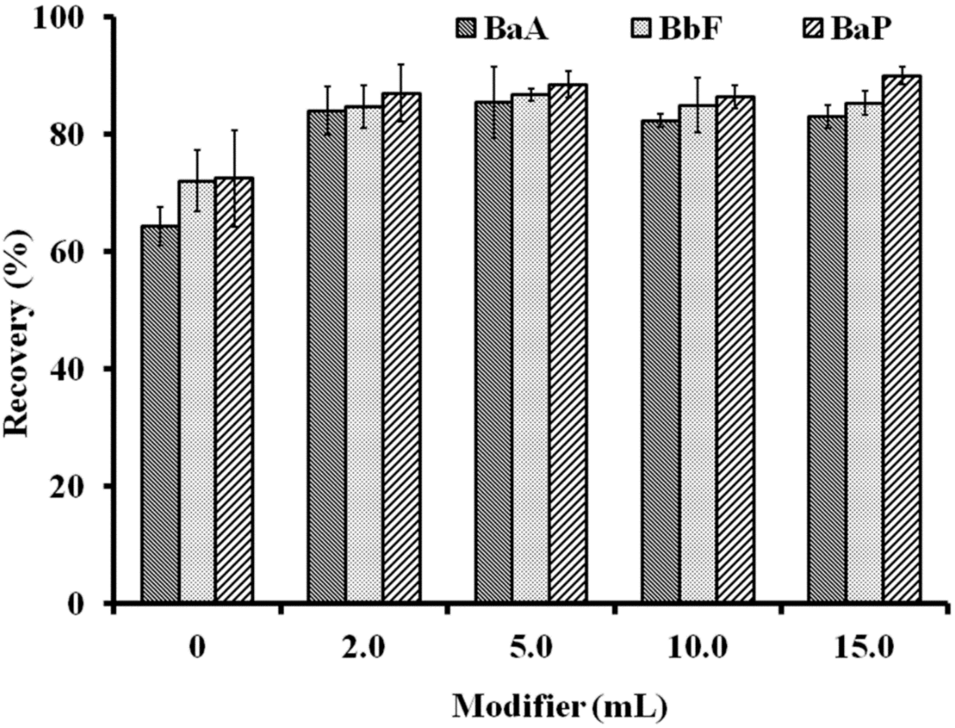

Fig. S6 Effect of a modifier content in the water sample on the recovery of PAHs using the PANI/CFs sorbent

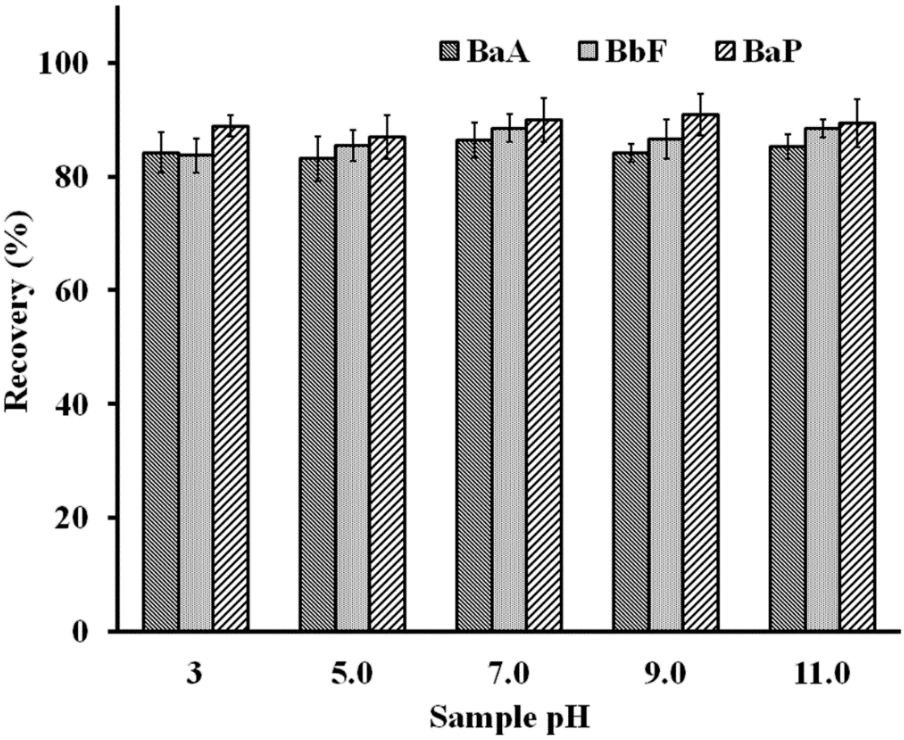

Fig. S7 Effect of sample pH on the recoveries of PAHs using the PANI/CFs sorbent

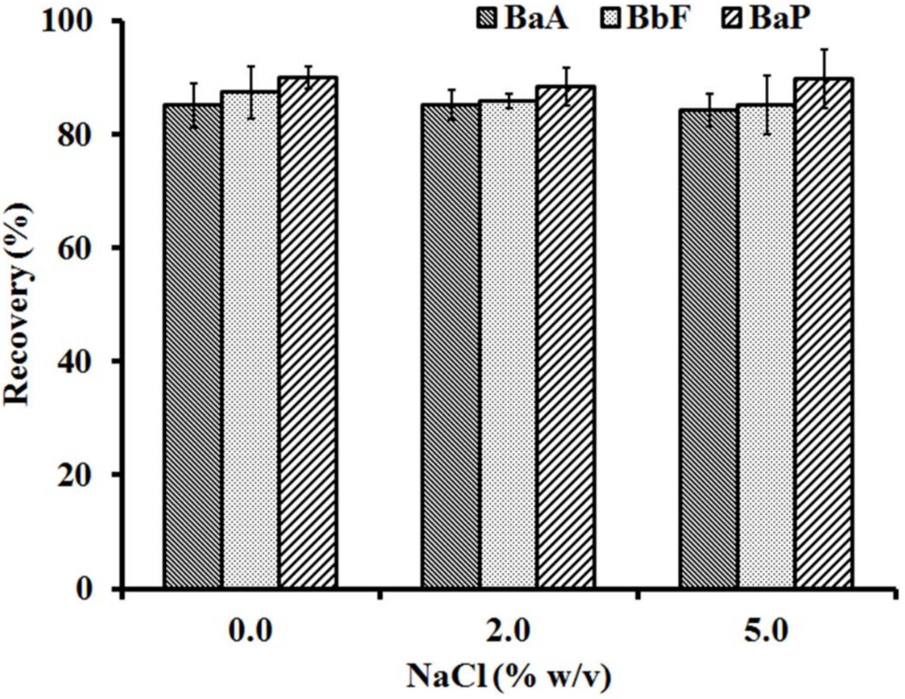

Fig. S8 Effect of ionic strength on the recovery of PAHs using the PANI/CFs sorbent

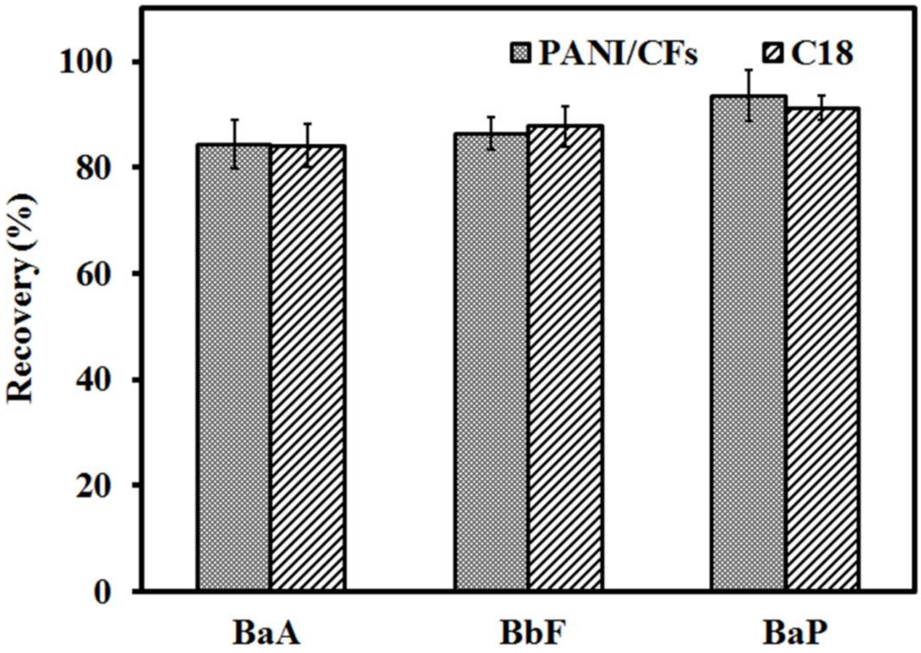

Fig. S9 Comparison between the developed PANI/CFs sorbent and the commercial C18 sorbent for extraction of the PAHs from spiked deionized water

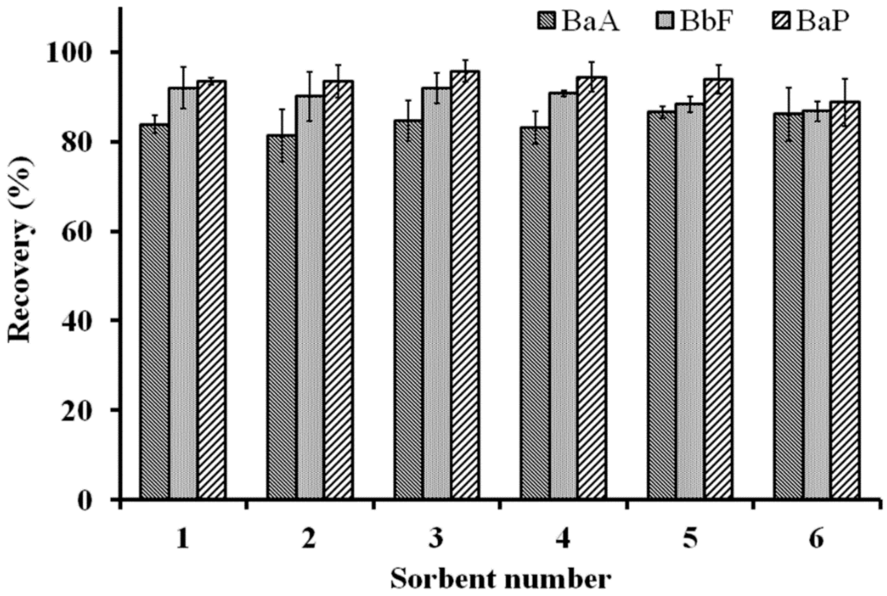

Fig. S10 The reproducibility of the PANI/CFs sorbent that were prepared using the same conditions but at different times

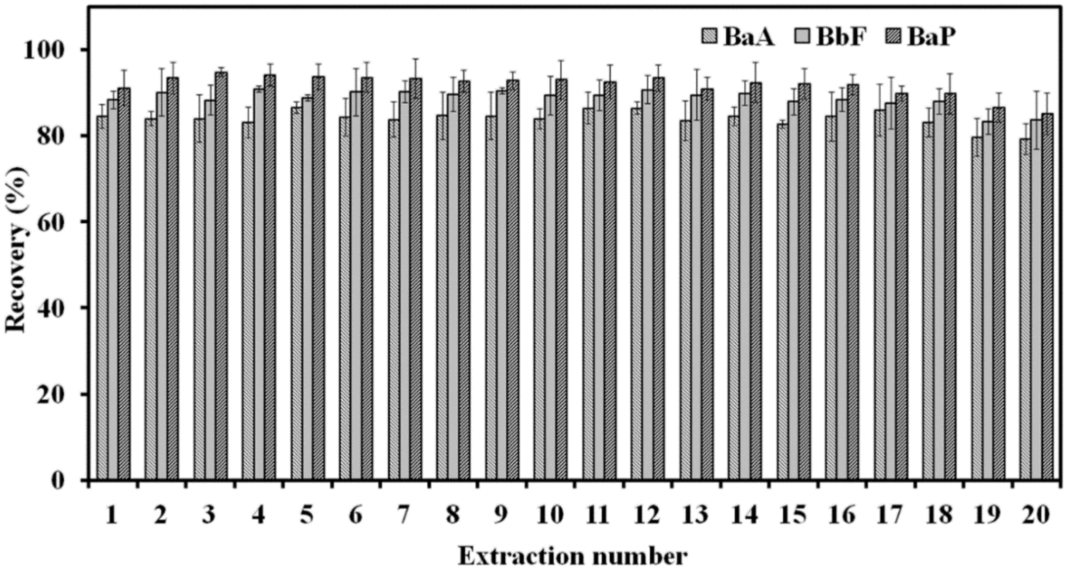

Fig. S11 Reusability of the PANI/CFs sorbent for extraction of PAHs from spiked water sample (n=5)

Table S1. Analytical performance of the PANI/CFs sorbent

PAHs	Linear range (µg L^{-1})	Regression line equation	R^2	LOD (µg L^{-1})	LOD (µg L^{-1})
BaA	0.0005-10.0	y = (281.9 ± 2.9)X + (13.7±10.4)	0.9998	0.0005	0.002
BbF	0.0005-10.0	y = (320.7 ± 1.3)X + (6.5±4.5)	0.9999	0.0005	0.002
BaP	0.0005-10.0	y = (504.4 ± 2.5)X + (9.4±9.0)	0.9991	0.0005	0.002

Table S2. Concentration of PAHs in water samples (n=5)

Water sample	Concentration (µg L^{-1})		
	BaA	BbF	BaP
Tap water 1	ND	ND	ND
Tap water 2	ND	ND	ND
Tap water 3	ND	ND	ND
River water 1	0.028 ± 0.006	0.048 ± 0.005	0.021 ± 0.006
River water 2	0.028 ± 0.003	0.038 ± 0.005	0.014 ± 0.001
River water 3	0.25 ± 0.005	0.032 ± 0.006	0.018± 0.004
Wastewater 1	0.079 ± 0.005	0.159 ± 0.007	0.059 ± 0.006
Wastewater 2	0.019 ± 0.003	0.024 ± 0.005	0.012 ± 0.002
Wastewater 3	0.053 ± 0.006	0.042 ± 0.006	0.035 ± 0.005

ND= not detected

Table S3. Recoveries of PAHs in spiked water samples

Water sample	Added ($\mu g\ L^{-1}$)	Recovery (%)		
		BaA	BbF	BaP
Tap water	0.005	89.7 ± 7.0	95.0 ± 6.0	97.2 ± 5.2
	0.020	87.6 ± 6.0	94.0 ± 4.7	95.2 ± 6.3
	0.10	85.6 ± 3.5	93.0 ± 6.2	94.2 ± 5.3
River water	0.005	88.3 ± 6.0	93.0 ± 5.5	98.2 ± 8.1
	0.020	87.3 ± 6.8	91.4 ± 4.5	96.2 ± 5.4
	0.10	85.7 ± 4.0	91.0 ± 6.5	94.7 ± 7.4
Wastewater	0.005	88.7 ± 6.2	96.0 ± 8.8	98.2 ± 5.2
	0.020	87.3 ± 4.3	92.0 ± 6.5	97.2 ± 5.4
	0.10	86.6 ± 6.4	92.7 ± 5.6	97.0 ± 4.8

Paper III

Nurerk, P., Bunkoed, W., Kanatharana, P., Bunkoed, O., A miniaturized solid-phase extraction adsorbent of calix[4]arene-functionalized graphene oxide/polydopamine-coated cellulose acetate for the analysis of aflatoxins in corn. *Journal of Separation Science* 41 (2018) 3892-3901.

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RESEARCH ARTICLE

JOURNAL OF SEPARATION SCIENCE

A miniaturized solid-phase extraction adsorbent of calix[4]arene-functionalized graphene oxide/polydopamine-coated cellulose acetate for the analysis of aflatoxins in corn

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A calix[4]arene-functionalized graphene oxide/polydopamine-coated cellulose acetate adsorbent was fabricated for the pre-concentration of aflatoxins. The highly porous developed adsorbent does not produce the high backpressure that normally occurs in particle-packed cartridges and its large surface area helps to improve adsorption. The highly efficient adsorption of aflatoxins by the hybrid adsorbent is facilitated via hydrogen bonding and hydrophobic and π-π interactions. Polymerization time, amount of calix[4]arene-functionalized graphene oxide, type and volume of desorption solvent, sample pH, sample volume, and sample flow rate were optimized. The linearity of aflatoxin B1 was in the range of 0.01–10.0 μg/kg, aflatoxin B2 was in the range of 0.02–10.0 μg/kg and aflatoxin G1 and aflatoxin G2 were in the range of 0.050–10.0 μg/kg. The limits of detection were 0.01 μg/kg for aflatoxin B1, 0.02 μg/kg for aflatoxin B2 and 0.05 μg/kg for aflatoxin G1 and aflatoxin G2. The developed calix[4]arene-functionalized graphene oxide/polydopamine-coated cellulose acetate adsorbent was successfully utilized for the analysis of aflatoxins from corn samples and the extraction efficiency was satisfactory with obtained recoveries from 83.0 to 106.7%. Moreover, fabricated adsorbent is easy to prepare, inexpensive, and can be reused.

KEYWORDS
aflatoxins, calix[4]arene, cellulose acetate, graphene oxide, polydopamine

1 | INTRODUCTION

Aflatoxins (AFs) are one of a group of harmful mycotoxins produced mainly by *Aspergillus flavus* and *Aspergillus parasiticus*. The four major aflatoxin compounds are aflatoxin B1 (AFB_1), aflatoxin B2 (AFB_2), aflatoxin G1 (AFG_1), and aflatoxin G2 (AFG_2) [1]. AFs are carcinogenic, highly toxic, mutagenic compounds, especially AFB_1, which is classified as a Group I human carcinogen by the International Agency of Research on Cancer [2]. These substances can contaminate agricultural products such as corn, nuts, wheat, rice, milk, and soybeans [3–5]. The contamination of food and animal feed by AFs can cause several health problems in humans and animals, as well as economic losses. To ensure food safety, the European Union has established maximum residue limits (MRLs) of total AFs in cereals of 4.0 μg/kg and 2.0 μg/kg for AFB_1 [6]. Due to their high toxicity, the determination of AFs in agricultural products is crucial and the contamination of corn, in particular, by AFs is of great concern because corn is the major food for humans and feed

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Article Related Abbreviations: AF, aflatoxin; AFB_1, aflatoxin B1; AFB_2, aflatoxin B2; AFG_1, aflatoxin G1; AFG_2, aflatoxin G2; calix[4]arene-GO/PDA-CFs, calix[4]arene-graphene oxide/polydopamine-coated cellulose acetate fibre; CF, cellulose acetate fibre; GO, graphene oxide; MRL, maximum residue limit; PDA, polydopamine for livestock throughout the world [7]. Various analytical techniques have been developed and utilized for the analysis of AFs. These techniques included TLC [8], ELISA [9] and HPLC [10,11]. HPLC is the most extensively used technique due to its high sensitivity, good selectivity, which can separate and identify target analytes, and versatility in the analysis of the complex matrices of AFs [10,12]. Typically, the matrices in agricultural products are complex and AFs are present in relatively low amounts. Therefore, an effective sample preparation step is necessary prior to instrumental analysis.

Several extraction and clean-up methods have been reported for the analysis of AFs. SPE [13,14], dispersive liquid-liquid microextraction [11,15], SPME [16,17], and magnetic solid phase extraction [18,19] have all been used. However, SPE is the most frequently used method for clean-up and preconcentration of target analytes due to its extraction capacity, high enrichment factor, and simplicity [20]. However, commercially packed SPE cartridges have some limitations, including cartridge clogging and cost [21]. In the fabrication of SPE adsorbents, cellulose acetate fiber (CFs) is an interesting porous supporting material with the potential to overcome these limitations. Its three dimensional porous structure can flow the sample at a high rate with low back pressure [22]. It has been used as an adsorbent for the separation of compounds such as ketoconazole [23], polycyclic aromatic hydrocarbons [24], and oil-water [22]. To improve the efficiency of the separation of AFs, attention has been given to surface modification of the adsorbent with a combination of materials with inherently different properties. An interesting combination of materials for the fabrication of a hybrid adsorbent is polydopamine (PDA), calix[4]arene, and graphene oxide (GO). PDA has multifunctional groups including amino and catechol groups [25] and GO consists of a wide range of functional groups such as epoxy, hydroxyl, and carboxyl [26]. Meanwhile, calix[4]arene is a macrocyclic molecule which consists of phenol units linked via methylene bridges [27]. Together, they can adsorb AFs through hydrogen bonding, and hydrophobic and π-π interactions.

In this work, a hybrid porous adsorbent of calix[4]arene-functionalized GO/PDA-coated CFs (calix[4]arene-GO/PDA-CFs) was developed and used as an effective miniaturized SPE adsorbent which can reduce the amount of adsorbent and organic solvent in the system. The adsorbent can help to reduce back pressure and can load the sample solution at a high flow rate due to the high porosity of the CFs. The large active surface areas of composite calix[4]arene-GO and PDA can improve the adsorption of AFs. The calix[4]arene-GO/PDA-CFs adsorbent was applied to extract AFs (AFB_1, AFB_2, AFG_1, AFG_2) from corn samples before analysis with HPLC coupled with a fluorescence detector.

2 | MATERIALS AND METHODS

2.1 | Chemicals and reagents

The CF was obtained from the Krongthip company (Bangkok, Thailand). Dopamine hydrochloride, acetonitrile, methanol, 4-tert-butylcalix[4]arene, hydrazine hydrate, and GO were from Sigma–Aldrich (Steinheim, Germany). Ammonia solution was from JT Baker (Bangkok, Thiland). Sodium chloride was from Lobachemie (Mumbai, India). Tris (hydroxymethyl) aminomethane, ethanol ($\geq$98%), and trifluoroacetic acid (TFA) were purchased from Merck (Frankfurt, Germany). AFB_1, AFB_2, AFG_1, and AFG_2 were obtained from Romer Labs (Tulln, Austria). Deionized water was produced using a Maxima ultra-purification system (ELGA, Buckinghamshire, UK).

2.2 | Instrumentation

HPLC analysis used a Hewlett-Packard 1100 coupled with a fluorescence detector. The data were acquired and evaluated using Chemstation software (Agilent Technologies, Germany). The AFs were separated in a Vertisep^{TM} UPS C_{18} column (5 µm particles size, 15.0 × 0.46 cm I.D.) (Vertical chromatography, Bangkok, Thailand). The morphology of the developed adsorbent was observed with a JSM-5200 SEM (JEOL, Tokyo, Japan). The N_2 adsorption and desorption isotherms were produced using Quantachrome Autosorb 1 (Quantachome Instruments, USA).

2.3 | HPLC conditions

The mobile phase was composed of (A) water and (B) acetonitrile with gradient elution as follows; initial B 25% at 0 min, increased B to 35% at 2–6 min and holding for 4 min, and further decreased B to 25% at 10–18 min and holding for 5 min. The mobile phase was delivered to the system at a constant flow rate of 0.8 mL/min and the injection volume was 20 µL. The excitation and emission wavelengths of all AFs were established at 365 and 450 nm, respectively.

2.4 | Preparation of calix[4]arene-GO/PDA-coated CFs adsorbent

To fabricate the miniaturized calix[4]arene-GO/PDA-CFs adsorbent, the CFs were cut into small lengths (0.20 cm). Subsequently, the PDA was coated on the surface of CFs via self-polymerization [28]. Briefly, dopamine hydrochloride (180 mg) was dissolved in 100 mL of 0.010 M tris buffer (pH 8.5), and the CFs were added to the solution and stirred at 500 rpm for 4 h at 27 ± 1°C. Meanwhile, the calix[4]arene-GO was synthesized by adapting previous methods [29]. Briefly, 40 mg of GO and 20 mg of 4-tert-butylcalix[4]arene were dissolved in deionized water (40 mL) and stirred at 27 ± 1°C for 12 h. Then, 200 μL of hydrazine hydrate and 200 μL of ammonia solution were added into the mixture solution and stirred at 70°C for 12 h. The fabricated PDA-CFs were washed with deionized water and then immersed in the calix[4]arene-GO solution and stirred for 6 h. The calix[4]arene-GO was strongly adsorbed and entrapped in the as-prepared porous PDA-CFs adsorbent. The prepared calix[4]arene-GO/PDA-CFs adsorbent was removed from the solution and placed into a polypropylene tube (1 mL) connected at the outlet with the SPE manifold (Supleco, USA). The adsorbent was then washed with 2.0 mL of methanol followed by 5.0 mL of deionized water. The fabrication procedure is depicted in Figure 1.

2.5 | Sample preparation, solid phase extraction procedure and adsorption capacity investigation

Corn samples were homogenized to powder with a blender. AFs were extracted from corn samples using ultrasonication before preconcentration and clean-up with the as-prepared calix[4]arene-GO/PDA-CFs adsorbent. In a polypropylene centrifuge tube, 1.0 g of corn sample and 0.10 g of NaCl were mixed and 10.0 mL of a mixture solution of methanol and deionized water (80:20 % v/v) was added for the extraction of AFs. The extraction was performed by ultrasonication at 30°C for 20 min and centrifugation at 5000 rpm for 10 min. The supernatant was separated and evaporated to dryness at 55°C. The residue was re-dissolved in 5.0 mL of deionized water and further cleaned up with the developed calix[4]arene-GO/PDA-CFs adsorbent.

The calix[4]arene-GO/PDA-CFs adsorbent was conditioned with methanol (1.0 mL) followed by deionized water (1.0 mL) before loading the samples for clean-up. The

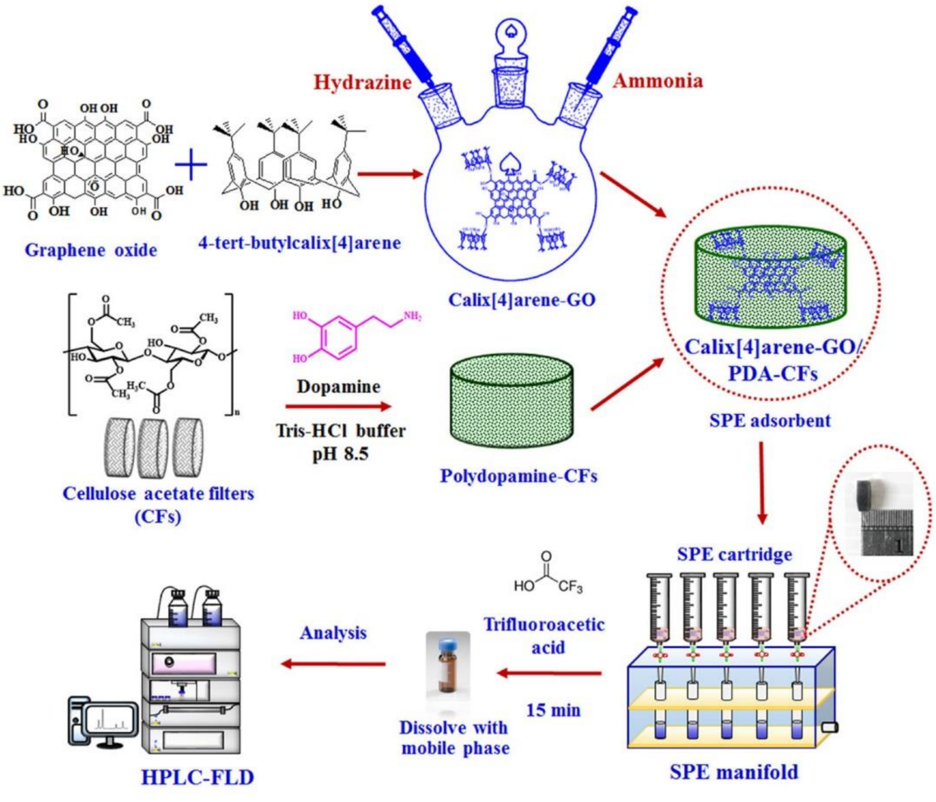

FIGURE 1 The fabrication procedure of calix[4]arene-GO/PDA-CFs adsorbent and the SPE procedure

extracted sample in aqueous solution was loaded through the adsorbent at a flow rate of 6.0 mL/min and the interferences were removed by washing with 2.0 mL of deionized water. Subsequently, the adsorbed AFs were eluted from the adsorbent with 1.0 mL of methanol and the eluent was evaporated to dryness at 50°C. Then, 100 µL of trifluoroacetic acid (derivatizing agent) were added and the solution was kept at room temperature (25°C) for 15 min in the absence of light before dilution in 900 µL of mobile phase (water/acetonitrile; 75:25 v/v). Finally, the sample solution was filtered through a 0.22 µm nylon syringe filter prior to HPLC analysis.

The adsorption capacity (q_e) was calculated as following equation:

$$q_e = \frac{(C_0 - C_e)\,V}{m} \qquad (1)$$

where q_e is the adsorption capacity (µg/g), C_0 and C_e are the initial and final AFs concentrations (µg/L), V is the sample volume (L) and m is the adsorbent mass (g).

3 | RESULTS AND DISCUSSION

3.1 | Characterization of the adsorbent

The morphologies of the CFs and calix[4]arene-GO/PDA-CFs adsorbent were investigated by scanning electron microscopy. The surface of the CFs was smooth (Figure 2A,B), whereas the surface of the calix[4]arene-GO/PDA-CFs adsorbent was rough. PDA particles are uniformly distributed over the surface of the CFs (Figure 2C,D). The images illustrate the successful modification of the surface of the CFs in the hybrid adsorbent. The Brunauer-Emmett-Teller (BET) specific surface areas of the CFs and the calix[4]arene-GO/PDA-CFs adsorbent were calculated by N_2 adsorption-desorption isotherms as 0.8685 and 5.0741 m^2/g, respectively. These results indicate that modification of the CFs increased the active surface area for the adsorption of target analytes in the hybrid calix[4]arene-GO/PDA-CFs adsorbent. The adsorption capacities of the calix[4]arene-GO/PDA-CFs adsorbent for AFB_1, AFB_2, AFG_1 and AG_2 were calculated as 53.56, 51.33, 47.27, and 52.70 µg/g, respectively.

3.2 | Optimization of adsorbent preparation and solid phase extraction

In order to achieve the best extraction efficiency with short extraction time and low solvent consumption, the following parameters were optimized: the type of adsorbent, polymerization time, concentration of calix[4]arene-GO, sample pH, ionic strength, desorption conditions, sample volume, and sample flow rate. The extraction efficiency of the developed method was appraised from the obtained recovery and all the experiments were performed in triplicate.

3.2.1 | Type of adsorbent

The extractions of AFs by CFs, PDA-CFs, calix[4]arene-GO/CFs, GO/PDA-CFs, and the calix[4]arene-GO/PDA-CFs adsorbent were investigated for comparison. The recoveries obtained by CFs, PDA-CFs, calix[4]arene-GO-CFs, GO/PDA-CFs, and the calix[4]arene-GO/PDA-CFs adsorbent were in the range of 35–41%, 45–55%, 60–72%, 63–82% and 86–94%, respectively (Supporting Information Figure S1). The hybrid calix[4]arene-GO/PDA-CFs adsorbent clearly provided the highest recovery. These results demonstrate that the modification of the CFs with the hybrid materials increased the efficiency of the adsorbent in the separation of AFs through hydrophobic and π-π interactions and hydrogen bonding, (Supporting Information Figure S2). Therefore, the hybrid calix[4]arene-GO/PDA-CFs adsorbent was used for the extraction and pre-concentration of AFs prior to analysis with HPLC.

3.2.2 | Polymerization time of PDA

Since the polymerization time of PDA during fabrication of the adsorbent may affect extraction efficiency, the effect of polymerization time was investigated. The polymerization times during sorbent preparation were varied at 2.0, 4.0, 6.0, and, 12.0 h. The extraction efficiency increased when the polymerization time increased from 2.0 to 4.0 h (Figure 3A). This result indicated that PDA can help to improve the extraction efficiency of the adsorbent. However, the recoveries subsequently decreased at polymerization times above 4.0 h. This might be because the PDA layer was too dense and too thick, which reduced the active surface area for the adsorption of AFs (Supporting Information Figure S3). Therefore, 4.0 h was selected as the optimized time for the polymerization of PDA.

3.2.3 | Concentration of calix[4]arene-GO

The concentration of calix[4]arene-GO also influenced the extraction efficiency. The extraction efficiency of the adsorbent increased when the concentration of calix[4]arene-GO increased from 0.05 to 0.30 % w/v. Extraction efficiency then remained almost constant at higher concentrations (Figure 3B). The increased extraction efficiency was due to the higher number of adsorption sites available for the adsorption of AFs. Thus, 0.20% w/v was chosen as the optimized concentration of calix[4]arene-GO.

3.2.4 | Sample pH

The sample pH is a crucial factor which affects the adsorption process of analytes on an adsorbent [16,30]. Thus, the

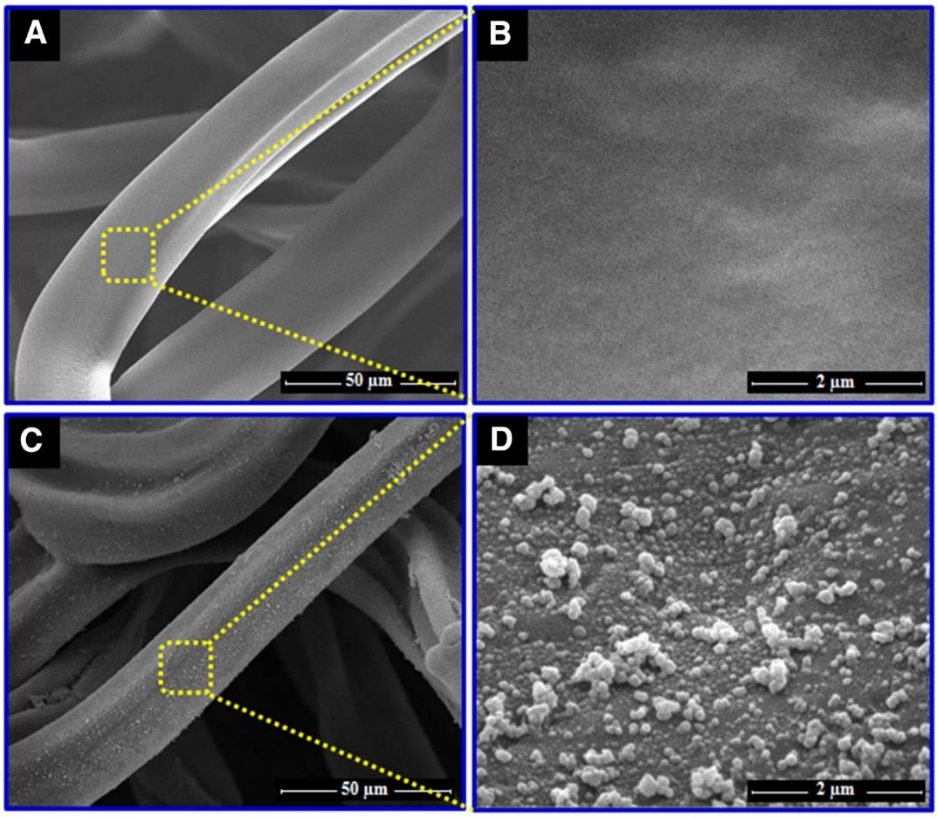

FIGURE 2 SEM images of CFs at (A) 1000x magnification; (B) 20000x magnification and calix[4]arene-GO/PDA-CFs adsorbent (C) 1000x magnification; (D) 20000x magnification

effect of sample pH on the adsorption efficiency of the developed adsorbent was examined by adjusting sample pH from 3.0 to 11.0 with 0.1 M hydrochloric acid or 0.1 M sodium hydroxide. The results are depicted in Figure 3C. The highest extraction efficiency was obtained within a pH range of 3.0–9.0. Since the pKa of AFs are equal to 10.09 ± 0.20, the AFs in the sample maintained their neutrality within this pH range [10,31]. The recoveries decreased at higher pH than 9.0 because deprotonation would disturb the hydrogen bonding between AFs and the calix[4]arene-GO/PDA-CFs adsorbent, resulting in a reduced efficiency of adsorption. In addition, AFs decompose in strong acidic conditions at pH lower than 3 [16]. Since, in this work, the extracted sample was re-dissolved in deionized water with a pH between 5.5 and 6.0, the sample solution can be directly loaded through the developed adsorbent without adjusting the sample pH.

3.2.5 | Desorption conditions

The type of desorption solvent is also an important factor in achieving high recoveries. The effect of type of desorption solvent with different polarity was evaluated dichloromethane, ethyl acetate, methanol, and acetonitrile. The polarity index of these solvents are 3.1 for dichloromethane, 4.4 for ethyl acetate, 5.1 for methanol and 5.8 for acetonitrile, respectively. Methanol produced the highest extraction efficiency (Figure 3D). The least polar solvent (dichloromethane) produced the lowest recovery because it could not break the hydrogen bonding between AFs and the calix[4]arene-GO/PDA-CFs adsorbent. While, the high polar solvent could not completely break the π-π interaction. Consequently, methanol was employed to elute AFs from the adsorbent and the optimal volume of methanol was then determined within the range of 0.5–3.0 mL. The results indicated that 1.0 mL of methanol was sufficient for the elution of all AFs from the

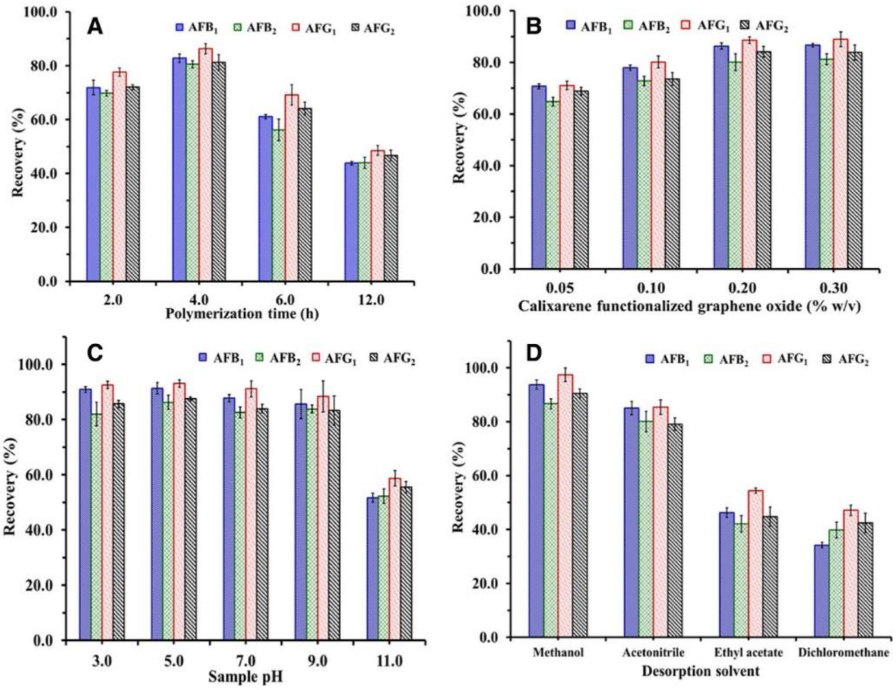

FIGURE 3 Effect of polymerization time (A), concentration of calix[4]arene-functionalized graphene oxide (B), sample pH (C) and type of desorption solvent (D) on the efficiency of extraction of aflatoxins by the calix[4]arene-GO/PDA-CFs adsorbent

calix[4]arene-GO/PDA-CFs adsorbent (Supporting Information Figure S4).

3.2.6 | Sample volume and its flow rate

The performance of sample volumes of 2.0, 5.0, and 10.0 mL were investigated. The extraction efficiency of the adsorbent decreased at a sample volume of 10.0 mL (Supporting Information Figure S5). This was maybe because the high sample volume also contained more matrix interferences which disturbed the interaction between AFs and the adsorbent surface. Therefore, 5.0 mL was selected as the optimal sample volume for further experiment.

The sample flow rate also affects extraction recoveries and analysis time [32]. It was investigated in the range of 2.0–10.0 mL/min. The results are shown in Supporting Information Figure S6. The recoveries decreased at sample flow rates faster than 6.0 mL/min because the analytes were not able to completely adsorb at higher flow rates. Hence, a sample flow rate of 6.0 mL/min was chosen for subsequent experiments. The calix[4]arene-GO/PDA-CFs adsorbent allowed for higher flow rates than particles packed cartridge adsorbents (1.0 mL/min) due to its higher porosity and lower back pressure.

3.3 | Analytical performance

The performance of the analytical method was validated by determining the linear range, LOD, and LOQ (Supporting Information Table S1). The linearity was investigated using fortified corn samples spiked with standard AFs at different concentrations. The linearity of the developed method was in the range of 0.01–10.0 μg/kg for AFB_1, 0.02–10.0 μg/kg for AFB_2, and 0.05–10.0 μg/kg for AFG_1 and AFG_2. The LODs and LOQs were in the range of 0.01–0.05 and 0.04–0.20 μg/kg, respectively. The results imply that the developed method has a good sensitivity, its LODs and LOQs were much lower than the MRLs established by the EU (2.0 μg/kg for AFB_1 and 4.0 μg/kg for total AFs). Therefore, the developed method can be safely used for the preconcentration, clean-up, and analysis of AFs in complex samples.

3.4 | Reproducibility, reusability and adsorption capacity

The reproducibility of the fabricated calix[4]arene-GO/PDA-CFs adsorbent was evaluated by preparing six batches of the calix[4]arene-GO/PDA-CFs adsorbent at different times and using them to extract AFs from spiked corn samples (1.0 µg/kg) under the same conditions. The average recoveries of the six different adsorbents were 95.5 ± 1.2 for AFB_1, 93.1 ± 1.3 for AFB_2, 90.2 ± 2.1 for AFG_1 and 86.9 ± 1.8 for AFG_2 (Supporting Information Figure S7). The RSDs of six AFs (1.2–2.1%) were satisfactory as recommended by the Association of Analytical Communities (AOAC) (>30% at the concentration 1.0 µg/kg) [33]. These results indicated that the fabrication of the calix[4]arene-GO/PDA-CFs adsorbent has a good reproducibility.

The reusability of the calix[4]arene-GO/PDA-CFs adsorbent was also investigated. After extraction and desorption of the first cycle, the used calix[4]arene-GO/PDA-CFs adsorbent was washed with 2.0 mL of methanol. If no carry-over of the analytes was detected, it was reused for the next cycle. As shown in Supporting Information Figure S8, the adsorbent could be reused up to 17 times with the recoveries of AFs still higher than 80%. The results demonstrate that the calix[4]arene-GO/PDA-CFs adsorbent exhibited good stability during the extraction and desorption process.

3.5 | Comparison of the calix[4]arene-GO/PDA-coated CFs with a commercial solid phase extraction adsorbent

The extraction efficiency of the calix[4]arene-GO/PDA-CFs adsorbent was compared to the efficiency of an Hydrophilic-Lipophilic Balance (HLB) commercial C18 SPE adsorbent (Supporting Information Figure S9). The recoveries obtained from the developed adsorbent for AFB_1, AFB_2, AFG_1 and AFG_2 were 97.0 ± 2.1, 93.0 ± 1.3, 90.3 ± 2.0, and 88.6 ± 3.9, respectively. The recoveries obtained from the commercial C18 SPE adsorbent for AFB_1, AFB_2, AFG_1, and AFG_2 were 91.0 ± 0.8, 94.7 ± 1.3, 89.9 ± 1.5, and 88.0 ± 4.1%, respectively. The average recoveries of the two adsorbents were not significantly different when compared by t-test [34]. The calix[4]arene-GO/PDA-CFs adsorbent can be operated at a higher sample flow rate (6.0 mL/min) and can be reused at least 17 times. The commercial particles packed cartridge can load the sample at only 1.0 mL/min and it cannot be reused.

3.6 | The determination of AFs in corn samples

The developed calix[4]arene-GO/PDA-CFs adsorbent was applied for the preconcentration of AFs and clean-up of corn samples. AFs were detected in corn samples in the range of not-detectable to 0.305 µg/kg (Supporting Information Table S2) which are lower than the MRLs established by the EU (4.0 µg/kg for total AFs and 2.0 µg/kg for AFB_1). The accuracy of the developed method was also evaluated by spiking corn samples with standard solutions at three different concentrations: 0.1, 0.5, and 2.0 µg/kg. The recoveries of AFs ranged from 83.0 to 106.7% with RSDs between 0.20 and 14.7% (Supporting Information Table S3). An acceptable intra-day (n = 6) and inter-day (n = 6) precisions were obtained with RSDs ranging from 1.3 to 14.8 % and 3.9 to 15.0 %, respectively. Figure 4 shows the chromatograms of a corn sample and a corn sample spiked with AFs at a concentration of 1.0 µg/kg after clean-up with calix[4]arene-GO/PDA-CFs adsorbent. These results imply that the calix[4]arene-GO/PDA-CFs adsorbent coupled with HPLC-FD is a reliable system for the extraction and analysis of trace AFs in corn and other food and feed samples.

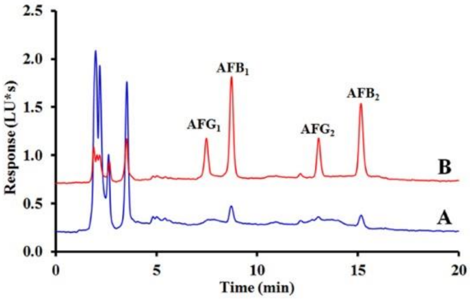

FIGURE 4 Typical chromatograms of corn sample (A) and spiked corn sample at 1.0 µg/kg (B) after the extraction using the calix[4]arene-GO/PDA-CFs adsorbent

3.7 | Comparison of the developed method with other methods

The analytical performance of the calix[4]arene-GO/PDA-CFs adsorbent coupled with HPLC analysis was compared with other works (Table 1). The LOD of this method was lower than the other methods [11,13,16,31,35] with the exception of a method which used a highly sensitive and expensive detector that provided a lower LOD [17]. In the case of extraction ability, the recoveries of the developed method were better than those of some methods [11,16,17,35] and comparable with other methods [12,13,31]. The developed method demonstrated a high sensitivity and efficient extraction and clean-up and therefore can be used for the determination of trace AFs in food samples. In addition, the calix[4]arene-GO/PDA-CFs adsorbent can operate at a fast sample flow rate and be reused for a minimum of 17 cycles which reduces the analysis costs and sample preparation time.

TABLE 1 Comparison of the developed method with other methods for the quantitative analysis of aflatoxins

Detection	Extractant	Sample	Sample pretreatment	LOD (μg/kg)	Recovery (%)	References
HPLC-FD	Organic solvent	Cereal products	DLLME	0.01-0.17	67–92	[11]
HPLC-PDA	Carbon nanotube Reinforced sol–gel hollow fiber	Peanut, rice, wheat	SPME	0.06-0.07	47–107	[16]
LC-MS	Zorbax Eclipse XDB-C8	Nut, cereal, dried fruit, spice	In tube-SPE	0.0021-0.0023	81–109	[17]
HPLC-FD	Antibody-free modified magnetic nanoparticles	Corn, rice	MSPE	0.013-0.041	90–97	[12]
HPLC-FD	Graphene oxide	Peanut	DSPE	0.08-0.65	85–101	[13]
UPLC-MS	C18	Corn	DSPE	0.05	68–120	[35]
HPLC-FD	Hyperbranched polymers	Cereal	SPE	0.012-0.12	83–103	[31]
HPLC-FD	Calix[4]arene-GO/PDA-CFs	Corn	SPE	0.01-0.05	83–107	This work

DLLME = Dispersive liquid–liquid microextraction
MSPE = Magnetic solid phase extraction
DSPE = Dispersive solid phase extraction

4 | CONCLUDING REMARKS

A calix[4]arene-GO/PDA-CFs adsorbent was successfully fabricated and utilized for the extraction, clean-up, and analysis of AFs in corn samples. The fabricated hybrid porous adsorbent adsorbs AFs through hydrogen bonding and hydrophobic and π-π interactions, which enable the developed analytical method to provide a good extraction efficiency (83.0 ± 11.2 to 106.7 ± 10.5%) with low detection limits ranging from 0.01 to 0.05 μg/kg. The developed calix[4]arene-GO/PDA-CFs adsorbent is simple to prepare and cost effective (0.3 USD/cartridge). In addition, the adsorbent could be operated at a high sample flow rate (6.0 mL/min) without cartridge clogging and can be reused at least 17 times, which would help to reduce analysis costs and adsorbent fabrication time.

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CONFLICT OF INTEREST

The authors have declared no conflict of interest.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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Supporting Information

A miniaturized solid phase extraction adsorbent of calix[4]arene-functionalized graphene oxide/polydopamine-coated cellulose acetate for the analysis of aflatoxins in corn

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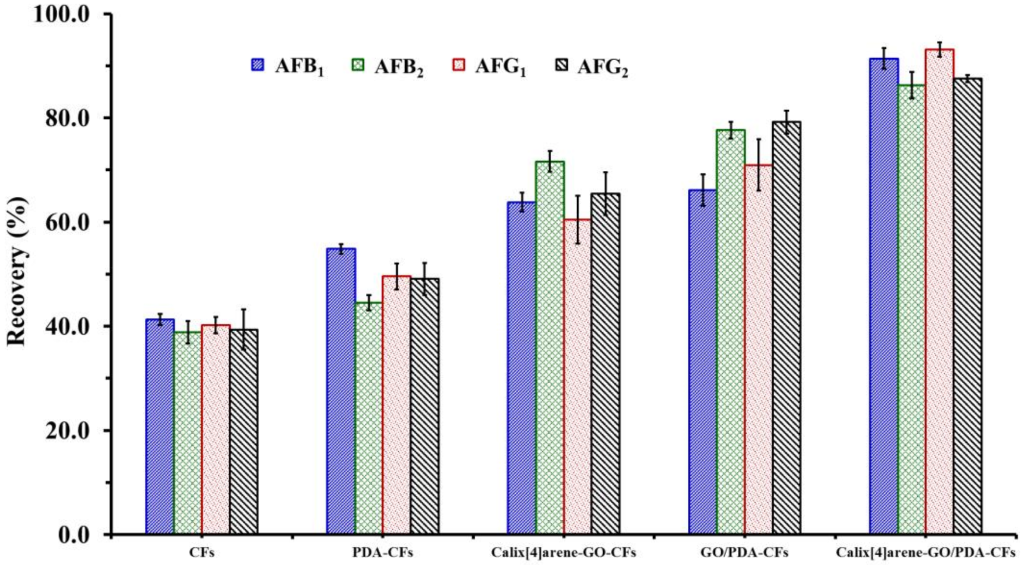

Fig. S1 The efficiency of extraction of aflatoxins by CFs, PDA/CFs, calix[4]arene-GO/CFs, GO/PDA-CFs and the calix**[4]**arene**-**GO**/**PDA**-**CFs adsorbent.

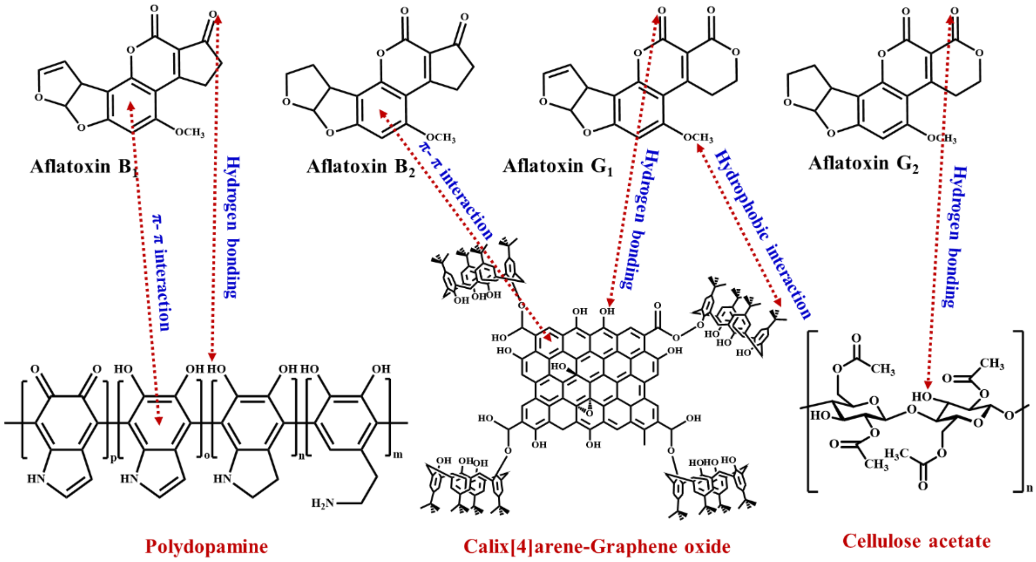

Fig. S2 The interactions between the calix[4]arene-GO/PDA-CFs adsorbent and aflatoxins.

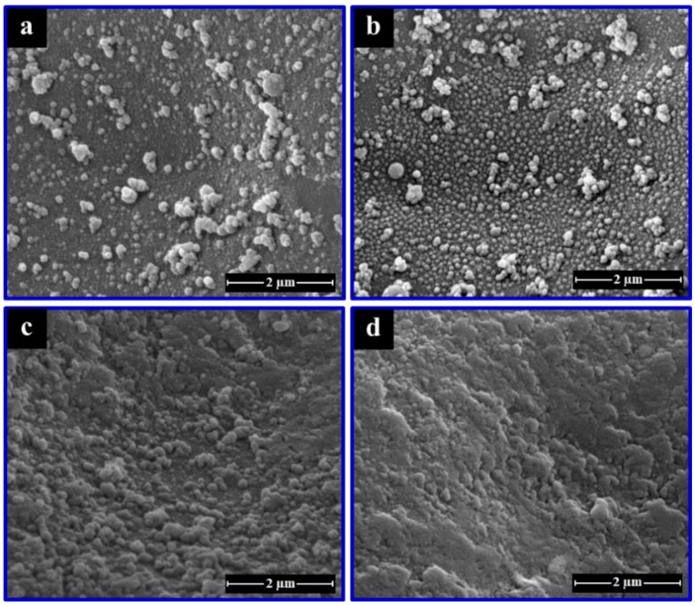

Fig. S3 SEM images of calix[4]arene-GO/PDA-CFs adsorbent with polydopamine polymerization times of 2 h (a), 4 h (b), 6 h (c) and 12 h (d).

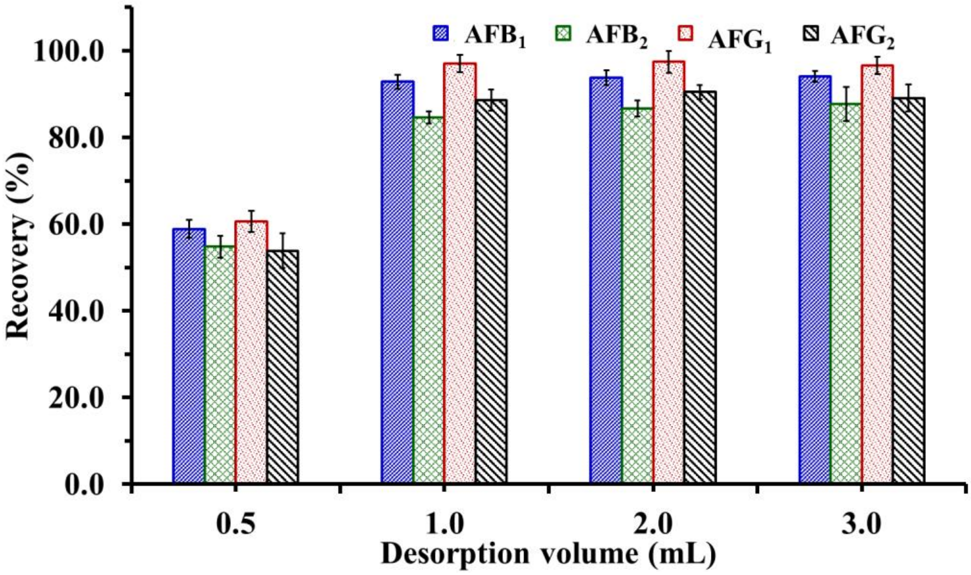

Fig. S4 Effect of desorption solvent volume on the efficiency of extraction of aflatoxins using the calix[4]arene-GO/PDA-CFs adsorbent.

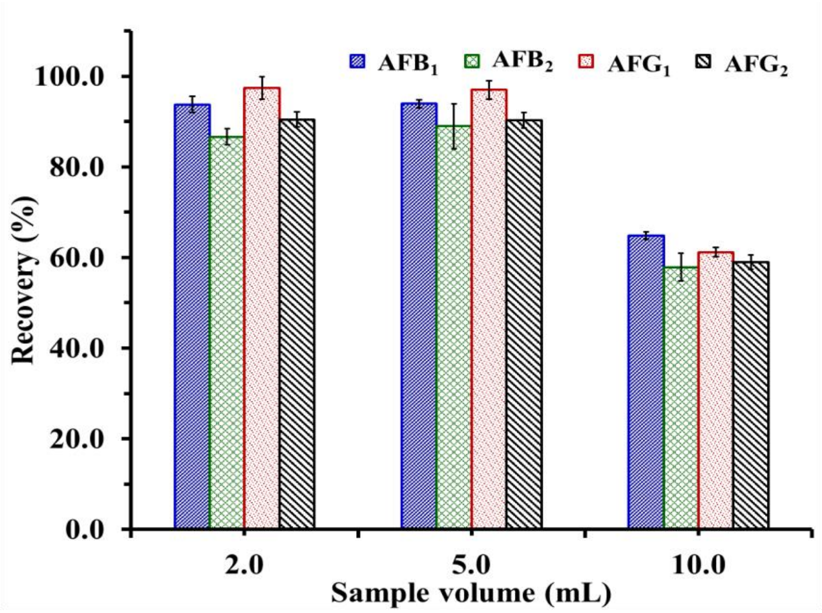

Fig. S5 Effect of sample volume on the efficiency of extraction of aflatoxins using the calix**[**4**]**arene**-**GO/PDA**-**CFs adsorbent.

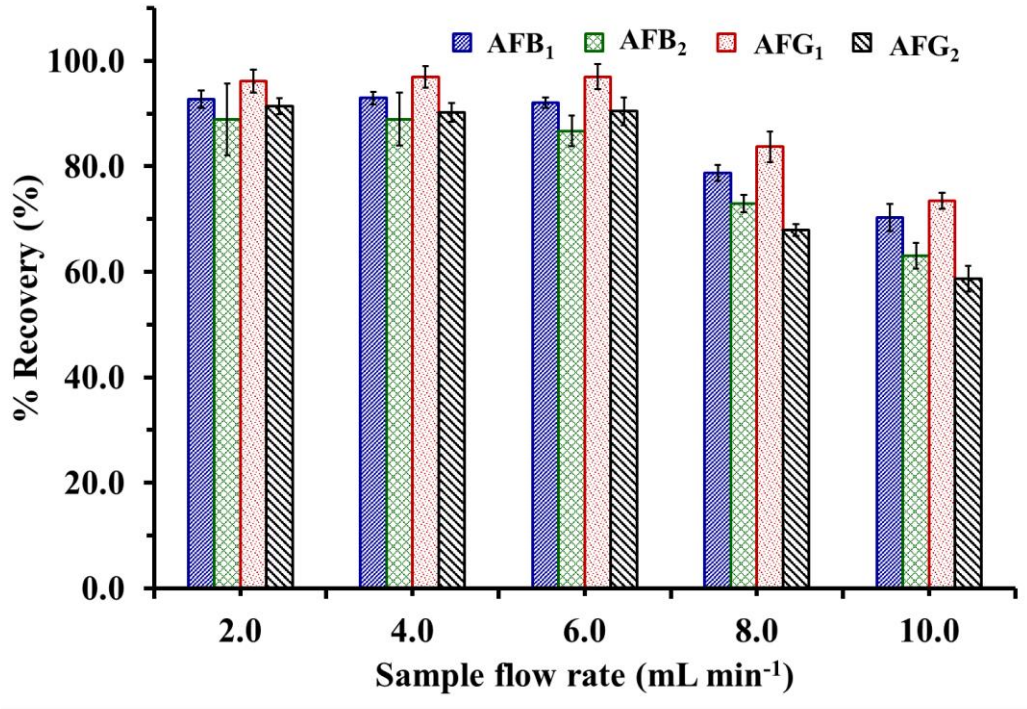

Fig. S6 Effect of sample flow rate on the efficiency of extraction of aflatoxins using the calix**[**4**]**arene**-**GO/PDA**-**CFs adsorbent.

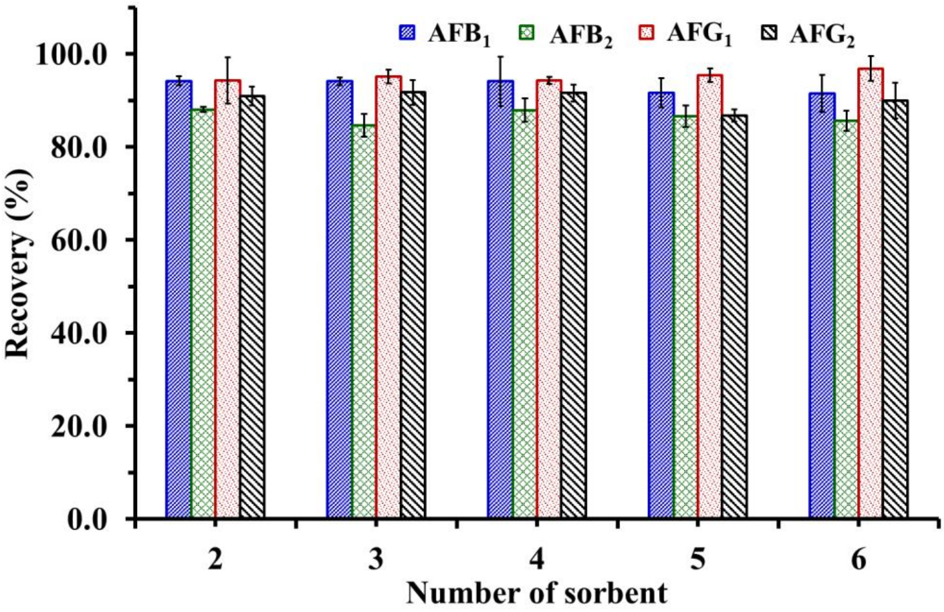

Fig. S7 Reproducibility of calix[4]arene-GO/PDA-CFs adsorbent for the extraction of aflatoxins.

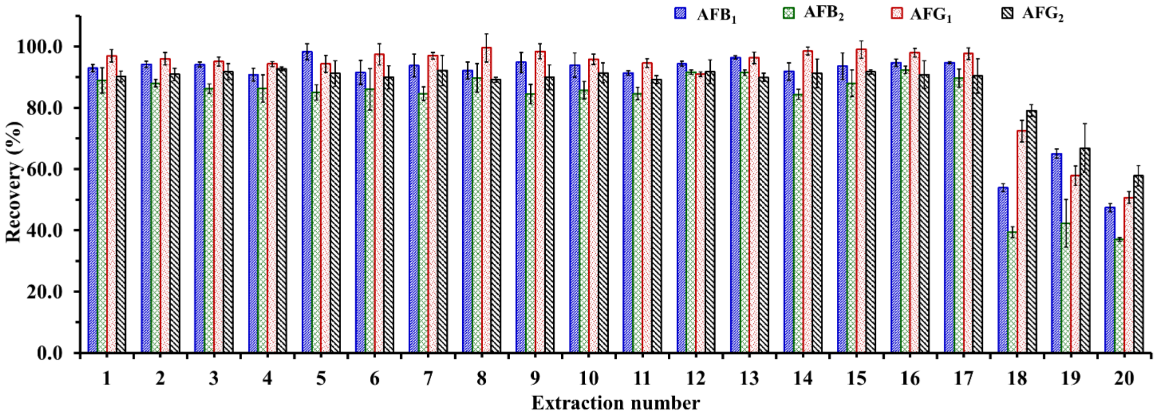

Fig. S8 Reusability of the calix[4]arene-GO/PDA-CFs adsorbent for the extraction of aflatoxins from corn samples (1.0 μg kg^{-1}).

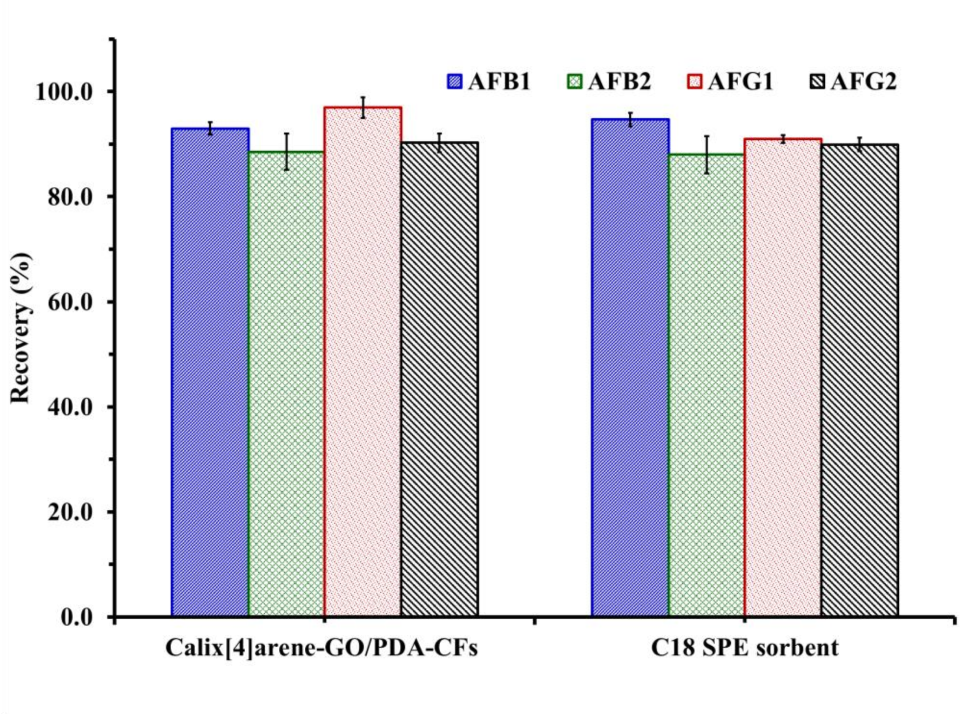

Fig. S9 Comparison of the extraction efficiency of calix[4]arene-GO/PDA-CFs and C18 SPE sorbent for the determination of aflatoxins.

Table S1 Analytical performances of the calix**[**4**]**arene**-**GO/PDA**-**CFs adsorbent coupled with HPLC-FLD for the determination of aflatoxins.

Aflatoxins	**Linear range (μg kg^{-1})**	**Regression linear equation**	**R^2**	**LOD (μg kg^{-1})**	**LOQ (μg kg^{-1})**
AFB_1	0.01 - 10.0	y = (7.63±0.42)x + (1.21±0.22)	0.9983	0.01	0.04
AFB_2	0.02 - 10.0	y = (9.29±0.37)x +(0.15±0.17)	0.9987	0.02	0.08
AFG_1	0.05 - 10.0	y = (5.17±0.19)x + (0.24±0.10)	0.9981	0.05	0.20
AFG_2	0.05 - 10.0	y = (4.14±0.10)x +(0.61±0.10)	0.9980	0.05	0.20

Table S2 Quantitative analysis of aflatoxins in corn samples

Corn samples	**Concentration (μg kg^{-1})**			
	AFB_1	**AFB_2**	**AFG_1**	**AFG_2**
Corn 1	0.127 ± 0.003	0.174 ± 0.057	<LOQ	<LOQ
Corn 2	0.082 ± 0.007	<LOQ	ND	<LOQ
Corn 3	<LOQ	ND	<LOQ	<LOQ
Corn 4	0.048 ± 0.002	<LOQ	ND	<LOQ
Corn 5	0.098 ± 0.007	ND	<LOQ	ND
Corn 6	ND	ND	0.305 ± 0.016	0.278 ± 0.014

ND = Not detectabl

Table S3 Recoveries of aflatoxins in spiked corn samples (n=5).

Corn samples	Added (μg kg^{-1})	Recovery (%)			
		AFB$_1$	AFB$_2$	AFG$_1$	AFG$_2$
Corn 1	0.1	94.1 ± 11.8	106.3 ± 11.7	98.4 ± 11.4	98.9 ± 14.7
	0.5	98.6 ± 1.4	103.2 ± 2.9	91.2 ± 3.4	104.8 ± 2.2
	2.0	98.3 ± 1.2	100.4 ± 2.8	95.2 ± 2.5	99.5 ± 0.9
Corn 2	0.1	91.5 ± 3.0	91.5 ± 1.5	97.9 ± 3.9	98.7 ± 1.4
	0.5	97.2 ± 2.3	97.2 ± 1.5	90.3 ± 2.1	98.4 ± 1.7
	2.0	98.8 ± 2.2	98.3 ± 1.7	92.3 ± 1.2	99.8 ± 1.3
Corn 3	0.1	99.3 ± 8.4	96.3 ± 6.9	84.9 ± 9.0	98.8 ± 11.8
	0.5	99.2 ± 3.9	97.6 ± 4.4	97.1 ± 3.5	95.81 ± 5.4
	2.0	100.5 ± 1.6	99.6 ± 1.9	94.7 ± 3.5	99.15 ± 1.5
Corn 4	0.1	106.7 ± 10.5	102.1 ± 7.8	93.4 ± 5.5	98.7 ± 8.8
	0.5	99.2 ± 3.1	102.1 ± 13.4	89.6 ± 7.5	98.5 ± 8.7
	2.0	100.9 ± 1.6	100.1 ± 4.8	94.4 ± 2.1	101.2 ± 0.2
Corn 5	0.1	83.0 ± 11.2	99.7 ± 4.3	91.4 ± 4.6	106.3 ± 3.0
	0.5	99.4 ± 4.3	100.6 ± 2.6	100.5 ± 8.8	102.6 ± 4.3
	2.0	100.1 ± 1.3	99.3 ± 3.2	95.8 ± 3.3	100.5 ± 2.6
Corn 6	0.1	94.0 ± 9.4	106.3 ± 12.6	98.4 ± 9.3	101.5 ± 2.4
	0.5	98.6 ± 1.6	103.2 ± 2.9	91.2 ± 8.5	103.6 ± 9.2
	2.0	98.3 ± 1.2	100.4 ± 1.7	95.2 ± 3.5	100.6 ± 0.8

Paper IV

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Polyaniline-coated magnetite nanoparticles incorporated in alginate beads for the extraction and enrichment of polycyclic aromatic hydrocarbons in water samples

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ABSTRACT

A magnetic solid-phase extraction sorbent consisting of polyaniline-coated magnetite nanoparticles entrapped in alginate beads (PANI/alginate/Fe_3O_4) was successfully synthesised and applied for the extraction and preconcentration of polycyclic aromatic hydrocarbons (PAHs) in water samples. The magnetite nanoparticles helped to provide an easy and rapid isolation of the sorbent from the sample solution using an external magnet. The alginate beads helped to increase the surface area for polyaniline coating. The polyaniline-coated alginate/magnetite composite helped to increase the extraction efficiency due to the π–π interactions between the polyaniline and the PAHs. Various parameters that affected the extraction efficiencies were optimised including the polymerisation time, the amount of sorbent, sample pH, extraction time, ionic strength, and desorption conditions. Under the optimal conditions, a linear response was achieved in the concentration range of 0.040–50.0 µg L^{-1}, and the limit of detection was 0.010 µg L^{-1}. This simple, convenient, cost-effective, and environmentally friendly method was successfully applied for the extraction and enrichment of PAHs in water samples. The recoveries ranged from 86.0% to 97.8% with a relative standard deviation <10 %.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are persistent pollutants in the environment that are composed of two or more fused aromatic rings [1]. They are produced from the incomplete combustion of organic materials and released into the environment via atmospheric fallout, urban run-off, municipal effluents, oil spillage, and industrial and vehicle emissions [2]. Due to their carcinogenic and mutagenic toxicity, the European Union (EU) and the United States Environmental Protection Agency (US EPA) have listed them as priority pollutants [3,4]. Moreover, some PAHs also cause endocrine disruption of important endocrine functions [5]. Therefore, the determination of PAHs in the environmental is important, however, they are usually present at trace levels in environmental samples at

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concentrations that are lower than the detection limit of analytical instruments. Therefore, a suitable sample preparation method is generally required prior to instrumental analysis to preconcentrate the target PAHs.

Various sample preparation methods have been reported for the extraction and preconcentration of PAHs such as solid-phase extraction (SPE) [6–8], solid-phase microextraction (SPME) [9,10], stir bar sorptive extraction (SBSE) [11], and dispersive liquid–liquid microextraction (DLLME) [2,12]. Among these methods, SPE is one of the most extensively used for the extraction and enrichment of PAHs due to its high extraction efficiency [7]. However, it still has some drawbacks, such as time-consuming and tedious operations. To overcome these problems, a new SPE mode called magnetic solid-phase extraction (MSPE) has attracted much attention [13–15]. In the MSPE procedure, the magnetic adsorbents used to adsorb the analytes can be easily and rapidly isolated from sample solutions using an external magnet [16,17]. Several types of magnetic materials were used as MSPE sorbents such as zero-valent iron (Fe) [18], maghemite (γ Fe_2O_3) [19], and magnetite (Fe_3O_4) [20]. However, bare magnetic nanoparticles have a low selectivity towards the target analytes and a low stability in acid aqueous media [21]. Therefore, modifications to the magnetic sorbents with high-affinity coating materials are usually required to improve their extraction efficiency and selectivity [16,22–24]. Polyaniline (PANI) is a good choice of such a high-affinity material for the extraction of PAHs due to its large benzene ring system that contributes to strong interactions with aromatic compounds via π–π interactions. Moreover, it also has a good chemical stability, large surface areas, a permeable porous structure, relatively low cost, and is easy to synthesis [25,26]. Polyaniline could be also polymerised in the presence of support media to produce an adsorbent with a defined shape [27,28].

In this work, a new MSPE sorbent of polyaniline-coated magnetite nanoparticles that were incorporated into alginate beads (PANI/alginate/Fe_3O_4) was developed. The alginate hydrogel was used to increase of the surface area that polyaniline can be coated [29]. PANI was therefore coated onto the surface of calcium alginate bead caged magnetite nanoparticles to improve the extraction efficiency of the sorbent. The developed sorbent was applied for the extraction and enrichment of PAHs in water. Benzo[a]anthracene, Benzo[a]pyrene, and Benzo[b]fluoranthene were selected as test compounds because of their toxicity, mutagenicity and they are grouped as probable human carcinogen. They are also included in the 2007 Priority List of Hazardous Substances.

2. Experimental

2.1. *Chemicals and reagents*

Aniline was purchased from Loba (Mumbai, India). Ammonium persulfate ($(NH_4)_2S_2O_8$), Iron (II) chloride tetrahydrate ($FeCl_2.4H_2O$), Iron (III) chloride hexahydrate ($FeCl_3.6H_2O$) were purchased from Sigma-Aldrich (Steinheim, Germany). Acetonitrile was of HPLC grade and was purchased from Merck (Darmstadt, Germany). Calcium chloride dehydrate ($CaCl_2.2H_2O$) was purchased from Ajax Finechem (NSW, Australia). Benzo[a]anthracene (BaA), Benzo[a]pyrene (BaP), Benzo[b]fluoranthene (BbF) standard solutions were purchased from Restek (Bellefonte, USA). Ultrapure water was prepared using a Maxima ultrapure water system (ELGA, Buckinghamshire, England). Working standard solutions were prepared by diluting the stock standard solution with acetonitrile.

2.2. *Instrumentation*

Chromatographic analysis was performed using a Hewlett-Packard 1100 series HPLC system (Agilent Technologies, Waldbronn, Germany). ChemStation software was used for data acquisition and evaluations. The separation was performed on a reverse-phase VertiSep^{TM} C_{18} column (5 µm particles size, 250 mm× 4.6 mm I.D.) (Restek Bellefonte, USA). The mobile phase was acetonitrile: water (95:5, %v/v) at a flow rate of 1.0 mL min^{-1}. The PAHs were detected with a fluorescence detector (FLD) with excitation (Ex) and emission (Em) wavelengths; BaA: Ex = 290, Em = 410; BbF: Ex = 266, Em = 450 and BaP: Ex = 270, Em = 410 nm. The injection volume and the column temperature were 20 µL and 30°C, respectively. The surface morphology of the developed sorbent was observed by scanning electron microscopy (SEM) JSM-5200 (JEOL, Tokyo, Japan). The Fourier transform infrared spectrometer (FT-IR) spectra were determined by FT-IR (Bruker, Germany). The N_2 adsorption and desorption isotherms were acquired using Quantachrome Autosorb 1 (Quantachome Instruments, USA).

2.3. *Preparation of polyaniline/alginate/Fe_3O_4 sorbent*

Figure 1(a) shows a schematic preparation of polyaniline/alginate/Fe_3O_4 sorbent. Fe_3O_4 nanoparticles were prepared by a chemical co-precipitation method [30]. Briefly, 5.0 g of $FeCl_3 \cdot 6H_2O$ and 2.0 g of $FeCl_2 \cdot 4H_2O$ were dissolved in 100 mL of deionised water and vigorously stirred in a nitrogen atmosphere. The mixed solution was heated and maintained at 80°C, then 10 mL of ammonium hydroxide was added dropwise, and the reaction was continuously refluxed for 1 h. The magnetite nanoparticles were separated from solution using a magnet, then thoroughly washed with 100 mL of distilled water three times, and finally the magnetite nanoparticles were dried at 60°C in an oven for 4 h.

For preparation of the alginate/Fe_3O_4 composite beads [31], sodium alginate (2.0% w/v) was dissolved in deionised water, 0.20 g of synthesised Fe_3O_4 was dispersed into 100 mL of the alginate solution by ultrasonication for 1 h to obtain homogenous colloidal suspension solution and this was added dropwise into a calcium chloride solution (5.0% w/v) while continuously stirring. The alginate/Fe_3O_4 composite beads that formed were kept in the calcium solution for 2 h for the complete bead formation and then separated from the solution by a magnet.

For polyaniline coating, 3.0 mL of the aniline monomer was added into 100 mL of 1.0 M HCl while stirring to obtain the aniline solution and the alginate/Fe_3O_4 composite beads were added into the aniline solution. Simultaneously, 1.80 g of $(NH_4)_2S_2O_8$ was added into 100 mL of 1.0 M HCl to obtain a $(NH_4)_2S_2O_8$ solution. The $(NH_4)_2S_2O_8$ solution was rapidly poured into the aniline solution. Polymerisation was allowed to occur at 30°C for 2 h. The product of the PANI-coated alginate/Fe_3O_4 sorbent was washed with ethanol and distilled water three times.

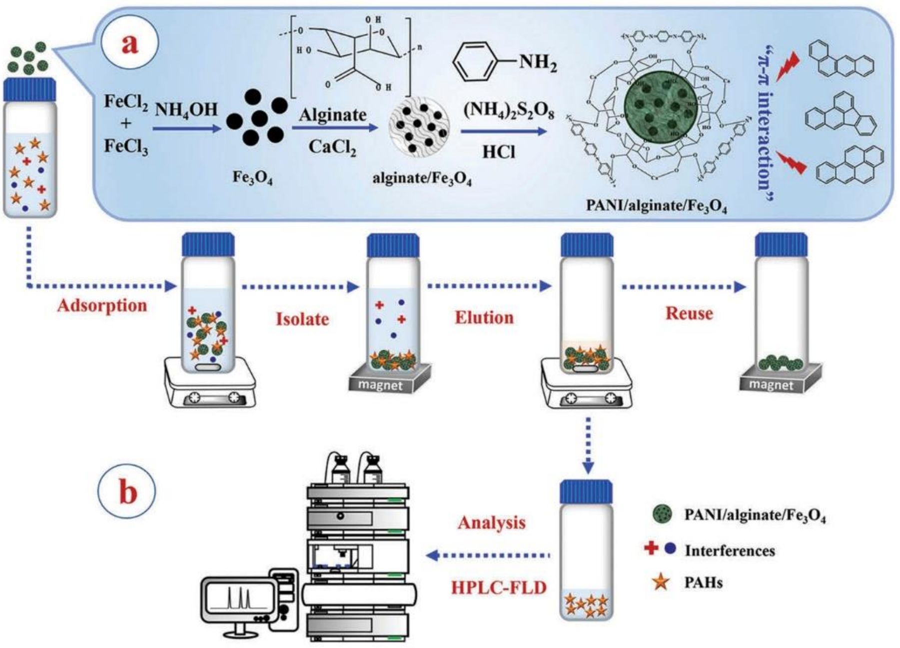

Figure 1. Schematic for the preparation of the (a) PANI/alginate/Fe_3O_4 sorbent and (b) the magnetic solid-phase extraction procedure using the PANI/alginate/Fe_3O_4 sorbent.

2.4. *Extraction procedure*

The extraction procedure was carried out as shown in Figure 1(b). Firstly, 0.40 g of the PANI/alginate/Fe_3O_4 sorbents was added into 10.0 mL of water sample and stirred at 1000 rpm for 20 min for the complete adsorption of the PAHs. Subsequently, the sorbents with the adsorbed PAHs was isolated from the sample solution using a magnet and the supernatant was decanted. Then, the extracted PAHs were desorbed from the sorbents with a desorption solvent while stirring at 1000 rpm for 30 min. The desorption solvent was then evaporated to dryness at 60°C, redissolved in 1.0 mL of acetonitrile and filtered through a PTFE filter (0.22 µm) before being injected into the HPLC system. The PANI/alginate/Fe_3O_4 sorbents were reused after washing with 2.0 mL acetonitrile and 5.0 mL of deionised water.

2.5. *Water samples*

To indicate the applicability of the developed method, the PANI/alginate/Fe_3O_4 sorbents were applied as the MSPE sorbent for the extraction and enrichment of PAHs in real water samples that is. reservoir water, river water, and wastewater samples. Reservoir water was collected from reservoir of Prince of Songkla University, river water samples were collected from three rivers in Hat Yai city, Songkhla, Thailand and two wastewater samples were collected from a household effluent from Hat Yai City, Songkhla, Thailand. All samples were filtered through the 0.45-µm filter to remove particulate matters and kept in brown bottles at 4°C.

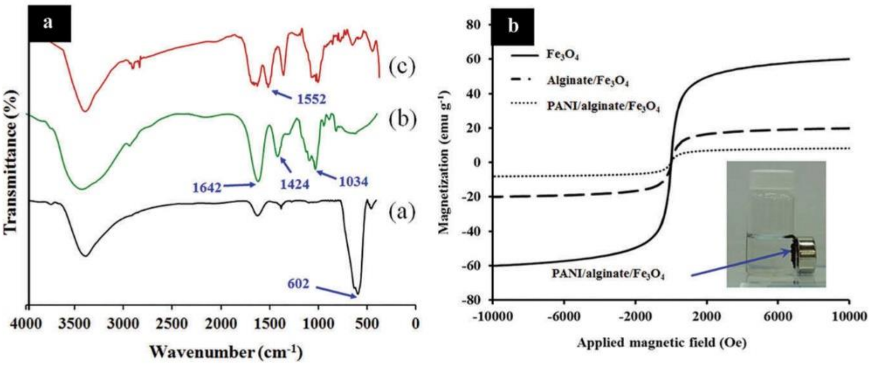

Figure 2. FT-IR spectra (A) of (a) Fe_3O_4, (b) Alginate and (c) PANI/alginate/Fe_3O_4 and (B) The hysteresis loops of Fe_3O_4, Alginate/Fe_3O_4 and PANI/alginate/Fe_3O_4. The inset represents the PANI/alginate/Fe_3O_4 beads separated by a magnet.

3. Result and discussion

3.1. *Characterisation of PANI/alginate/Fe_3O_4 sorbent*

The preparation of the PANI/Alginate/Fe_3O_4 sorbent was confirmed by FT-IR spectroscopy and SEM. Figure 2(a) exhibits the FT-IR spectra of the Fe_3O_4, alginate, PANI/alginate/Fe_3O_4 sorbent. The absorption peak at 602 cm^{-1} was attributed to the stretching of the Fe_3O_4 [32–34]. The absorption peaks at 1642, 1424, 1034 cm^{-1} were related to the stretching of the O=C–O (asymmetric), O=C–O (symmetric), and the C–O of alginate bead [28,35]. The characteristic peaks appeared at 1552 cm^{-1} (C=C stretching of the benzenoid ring) corresponded with the spectrum of PANI [36,37] and indicated that the polyaniline had been successfully synthesised and coated onto the alginate/Fe_3O_4 bead.

Vibrating sample magnetometry was also used to study the magnetic properties of the PANI/alginate/Fe_3O_4 sorbent. Figure 2 (b) shows the magnetic hysteresis loops of Fe_3O_4, alginate/Fe_3O_4, and PANI/alginate/Fe_3O_4. The saturation magnetisation value were 60.13, 19.90, and 8.03 emu g^{-1} for Fe_3O_4, alginate/Fe_3O_4, and PANI/alginate/Fe_3O_4, respectively. The magnetic strength of the developed sorbents was sufficient for magnetic separation, and it was rapidly isolated from the solution using an external magnet.

The surface morphology of dried alginate bead, Fe_3O_4/alginate, and PANI/alginate/Fe_3O_4 sorbent were investigated by SEM. The morphology of the alginate bead is shown in Figure 3(a, b). The surface of the alginate bead was rough and showed a high porosity. Figure 3(c, d) demonstrates the distribution of the Fe_3O_4 nanoparticles in the alginate bead. Figure 3(e, f) illustrates that the PANI was successfully coated onto the surface of the Fe_3O_4/alginate bead hence this attributed to the large surface area which could offer a high extraction efficiency for the PAHs, the extraction recovery >84%. The BET-specific surface area of PANI/alginate/Fe_3O_4 was determined by nitrogen adsorption and desorption isotherms as 27.87 m^2 g^{-1}.

3.2. *Optimisation of the magnetic solid-phase extraction*

In order to achieve the highest extraction efficiency with the shortest analysis time and a minimum use of solvent, several parameters such as the type of sorbent, polymerisation

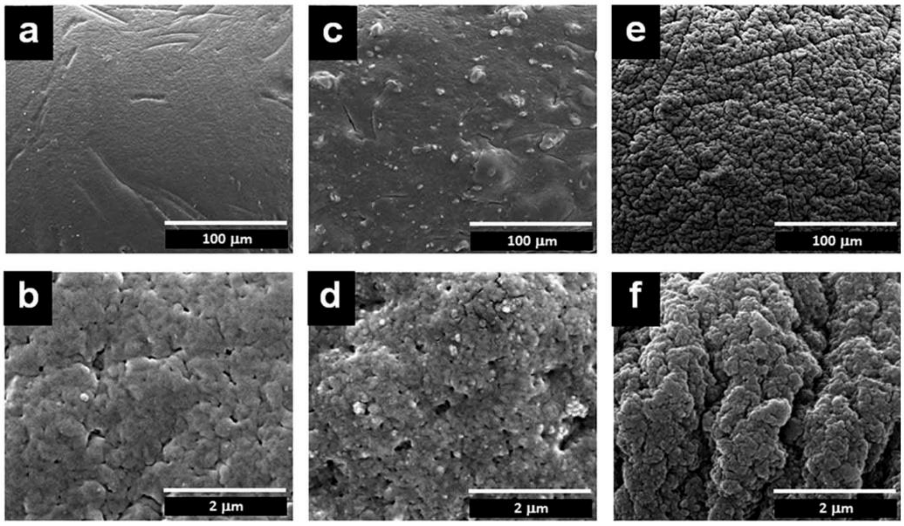

Figure 3. SEM image of alginate (a = 500x, b = 20,000x), Fe_3O_4/alginate (c = 500x, d = 20,000x) and PANI/alginate/Fe_3O_4 (e = 500x, f = 20,000x).

time, amount of sorbent, extraction time, desorption conditions, sample pH, and ionic strength were investigated and optimised. The optimisation of extraction conditions were conducted using a spiked deionised water containing 1.0 µg L^{-1} of each of the PAHs. The extraction efficiency was evaluated in terms of recovery.

3.2.1. *Type of sorbent*

The extraction abilities of Fe_3O_4, Fe_3O_4/alginate and PANI/alginate/Fe_3O_4 sorbent were first investigated. As shown in Figure 4, Fe_3O_4 and Fe_3O_4/alginate sorbents provided extraction efficiencies that were lower than 20%. While the PANI/alginate/Fe_3O_4 sorbent provided a high recovery of >84 %. These results confirmed that PANI helped to increase the adsorption capability of the target PAHs via π–π interactions. Hence, the PANI-coated alginate/Fe_3O_4 was applied as a MSPE sorbent for the extraction and enrichment of PAHs in water samples.

3.2.2. *Polymerisation time*

To obtain the highest extraction efficiency of the PANI/alginate/Fe_3O_4 sorbent, the effect of polymerisation time was studied over the range of 1.0–24.0 h. As shown in Figure S1, the extraction efficiency increased with the polymerisation time from 1.0 to 2.0 h and the extraction efficiency was decreased at any polymerisation time above 6 h. This was because polyaniline agglomerated and developed as a layer that was too thick and reduced the surface areas (Figure S2). Therefore, a polymerisation time of 2 h was selected.

3.2.3. *Amount of sorbent*

For the MSPE method, the amount of sorbent was one of the important parameters that influenced the extraction efficiency of the target analytes. To select the appropriate amount of PANI/alginate/Fe_3O_4 sorbent for the extraction of PAHs, different amounts of sorbent were investigated in the range of 0.20–0.80 g. The recoveries of PAHs increased

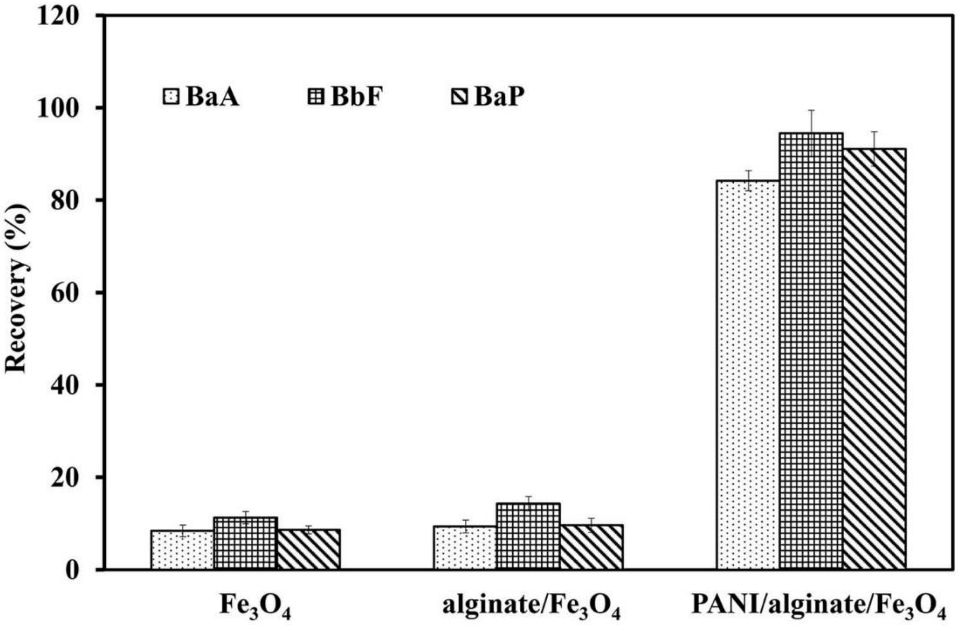

Figure 4. Effect of different sorbents on the recoveries of PAHs (1.0 µg L^{-1}) (n = 3); 20-min extraction time, 1000 rpm stirring of adsorption and desorption and 30-min desorption time.

with an increase of the amount of sorbent from 0.20 to 0.40 g (Figure 5(a)), and it remained almost constant with any further increase of sorbent. This indicated that 0.40 g of sorbent was sufficient for the extraction of PAHs in 10.0 mL of a spiked water sample. Therefore, 0.40 g was selected as the optimal sorbent amount and used for further experiments.

3.2.4. *Extraction time*

Extraction time is an important factor that influences the extraction efficiency. To obtain the highest extraction efficiency with the shortest analysis time. The extraction time was investigated in the range of 10–40 min. It can be seen from Figure 5(b), that the extraction efficiency of all target PAHs was increased with extraction times from 10 to 20 min, and then remained almost constant with any further increase of the extraction time up to 40 min. Therefore, to ensure complete adsorption, an extraction time of 20 min was selected as being the optimum.

3.2.5. *Desorption conditions*

After extraction was completed, the analytes were desorbed from the PANI/alginate/Fe_3O_4 sorbent. To ensure complete desorption of all target analytes, five organic solvents with different polarities were investigated including hexane, toluene, dichloromethane, methanol, and acetonitrile. Among these solvents, acetonitrile provided the highest recovery (Figure 5(c)), while a less polar solvent (hexane, toluene, and dichloromethane) provided a low desorption efficiency because the developed sorbent could not be dispersed well in these solvents leading to low desorption ability. Therefore,

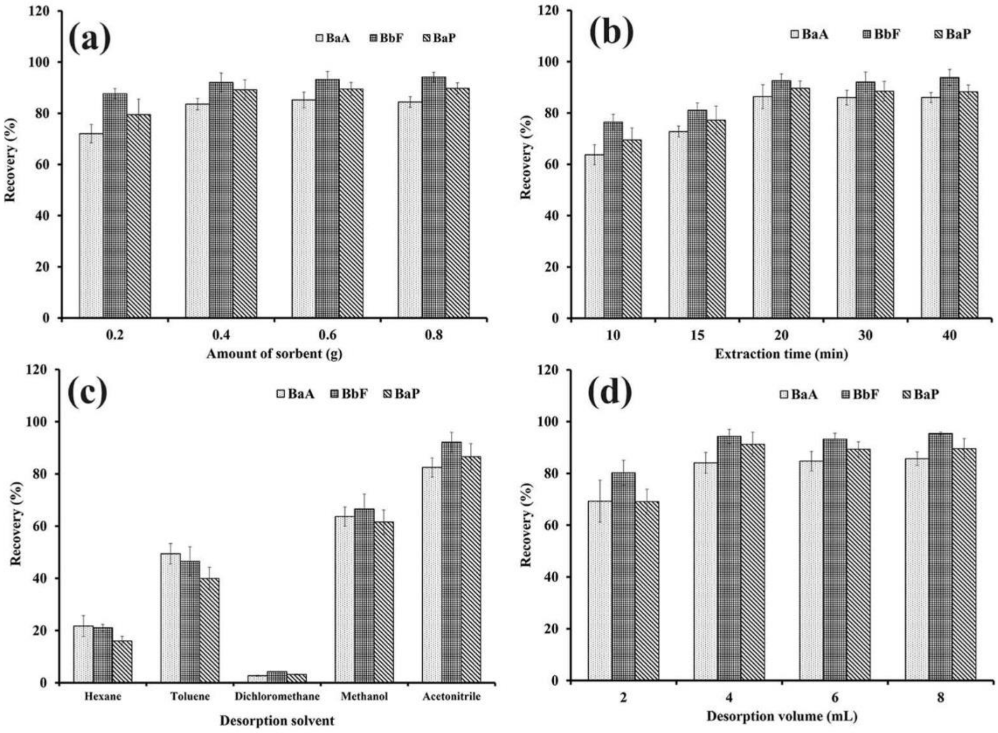

Figure 5. (a) Effect of the amount of sorbent, (b) extraction time, (c) desorption solvent and (d) desorption solvent volume on the recoveries of PAHs (1.0 µg L^{-1}) using the PANI/alginate/Fe_3O_4 sorbent (n = 3).

acetonitrile was further employed for desorption of PAHs from the PANI/alginate/Fe_3O_4 sorbent.

In order to obtain complete desorption of PAHs from the PANI/alginate/Fe_3O_4 sorbent with a minimal solvent volume and shortest desorption time, the effects of the volume of desorption solvent and the desorption time were investigated. All analytes were completely desorbed from the sorbent with 4.0 mL of acetonitrile (Figure 5(d)) and the desorption time of 30 min was sufficient to obtain the maximum desorption efficiency for all target analytes (Figure S3).

3.2.6. *Effect of sample pH and ionic strength and sample volume*

Since, the sample pH may affect the extraction efficiency and the stability of the sorbent. Therefore, the effect of sample pH on the extraction efficiency of the target PAHs was investigated by adjusting it with hydrochloric acid or sodium hydroxide solutions in the range of 2.0–9.0. As shown in Figure S4, the extraction efficiency showed no significant changes when the pH of the sample solution was changed, this is because the PAHs exist as neutral molecules. Therefore, for convenient analysis, there is no need to adjust the pH of the samples. The effect of ionic strength was also studies due to its ability to decrease the solubility of analytes in the sample solution and cause an increase in the extraction efficiency. In this work, the effect of ionic strength on the extraction efficiency of PAHs was investigated by adding NaCl to the sample solution over the concentration range of 0–15% w/v. As shown in Figure S5, the extraction efficiency was independent of the ionic strength. Hence, there is no need to add NaCl to the sample solution. These results indicated a good stability of the developed sorbent in various conditions.

The influence of sample volume on the extraction efficiency of PAHs was investigated in the range of 5.0–50.0 mL and the results as shown in Figure S6. The recovery was reduced when the sample volume was greater than 10.0 mL. Therefore, 10.0 mL was selected as an optimum sample volume for the further experiment.

3.2.7. *Effect of adsorption and desorption stirring rate*

The extraction efficiency of the PANI/alginate/Fe_3O_4 sorbent depended on the partition rate of analytes between sample solution and sorbent. The stirring rate was an effective way to increase the mass transfer of analytes from sample solution to the sorbent. Therefore, the effect of stirring rate were investigated from 500 to 1500 rpm. The results showed that the recovery increased with stirring rate and reached a maximum at 1000 rpm (Figure S7). Therefore, 1000 rpm was selected as an optimum stirring rate.

The effect of desorption stirring rate was also investigated in the range of 500–1500 rpm. It was observed that the recovery increased when the desorption stirring rate increased up to 1000 rpm and became constant at higher rate (Figure S8). Therefore, the desorption stirring rate of 1000 rpm was chosen for further experiment.

3.3. *Reproducibility, reusability, and adsorption capacity*

The preparation reproducibility of the PANI/alginate/Fe_3O_4 sorbent was evaluated in terms of lot-to-lot reproducibility. Six different lots of sorbent were prepared under the same conditions but with different times that were used to extract PAHs in spiked deionised water at 1.0 $\mu g\ L^{-1}$. The relative standard deviations (RSDs) were lower than 6% (Figure S9), and these were better than the acceptable values recommended by the AOAC (<16%). This indicated that the process for preparation of the PANI/alginate/Fe_3O_4 sorbent had a good reproducibility.

In order to investigate the reusability of the PANI/alginate/Fe_3O_4 sorbent, after the desorption of the analytes from the sorbent, to eliminate the memory effect, it was washed with 2.0 mL of acetonitrile and 5.0 of deionised water and no response of target analytes were observed which indicated that no carry-over was obtained. As shown in Figure S10, the recoveries were almost unchanged after six cycles. These results indicate that the PANI/alginate/Fe_3O_4 sorbent could be reused six times.

The adsorption capacity of PANI/alginate/Fe_3O_4 sorbent for BaA, BbF, and BaP was found to be 1.25, 1.19, and 1.15 $\mu g\ g^{-1}$, respectively.

3.4. *Comparative studies*

The extraction efficiency of PAHs using the PANI/alginate/Fe_3O_4 sorbent were compared with a commercial SPE sorbent (Sep-Pak C18 plus). As shown in Figure S11, the average recoveries were from 86.1% to 95.0% and 85.7% to 92.7% for the PANI/alginate/Fe_3O_4 sorbent and Sep-Pak C18 plus cartridge, respectively. The average recoveries of the developed sorbent and Sep-Pak C18 plus were compared by the statistical *t*-test [38] and there was no significant difference between the two sorbents ($P > 0.05$). However, the developed sorbent showed several advantages over the commercial SPE sorbent such as simpler to use and lower cost. Moreover, the PANI/alginate/Fe_3O_4 composite sorbent could be reused up to six times, whereas the commercial SPE sorbent cannot be reused. Therefore, the PANI/alginate/Fe_3O_4 sorbent can be used as an alternative sorbent for the extraction and enrichment of PAHs.

3.5. *Analytical performance*

Under the optimum extraction conditions, the analytical performance of the developed method was evaluated including its linear range, limit of detection (LOD) and limit of quantification (LOQ) and the result are summarised in Table S1. The developed method has a wide linearity over the range of 0.040–50.0 µg L^{-1} with a coefficient of determination (R^2) of greater than 0.999. The repeatability of the developed sorbent was investigated to evaluate the precision of the method and the RSDs was less than 10%, indicated that it had a good repeatability. The LOD and LOQ based on the signal-to-noise ratios of 3 and 10 were 0.01 and 0.04 µg L^{-1}, respectively. The LOD and LOQ values were much lower than the maximum contaminant level (MCL) in the surface water, that is. 0.2 µg L^{-1} for the BbF and BaP and 0.1 µg L^{-1} for BaA, respectively. Therefore, the developed method can effectively be used to determine BaA, BbF, and BaP in water samples.

3.6 *Application of the developed method for the determination of PAHs in water samples*

To demonstrate the applicability and reliability of the developed method, it was applied for the determination of PAHs in reservoir water, river water, and wastewater samples. The quantitative results are listed in Table 1. None of target PAHs was detected in the reservoir water, while the average concentration of PAHs in the river waters and waste waters in the range of not-detectable to 0.06 µg L^{-1}. The presence of PAHs may be due to incomplete combustion from the vehicle emissions deposited into the water samples. For waste water, PAHs are produced by cooking that are released into the effluents [2].

The accuracy of the developed method was validated by spiking standard PAHs into real water samples at three concentrations (i.e 0.10, 0.50, and 2.0 µg L^{-1}) and was then extracted and detected under optimum conditions. As listed in Table S2, the recoveries of BaA was lower than BbF and BaP due to its polar is more than BbF and BaP. However, the recoveries of the three PAHs were in the range of 86.0 ± 5.3% to 97.8 ± 8.3% which

Table 1. Concentration of PAHs in real water samples.

	Concentration (µg L^{-1})		
Water sample	BaA	BbF	BaP
Reservoir water	ND	ND	ND
River water 1	ND	<LOQ	<LOQ
River water 2	0.048 ± 0.007	0.046 ± 0.006	0.052 ± 0.009
River water 3	<LOQ	<LOQ	<LOQ
Waste water 1	<LOQ	<LOQ	<LOQ
Waste water 2	0.059 ± 0.008	0.040 ± 0.004	<LOQ

ND: not detectable.

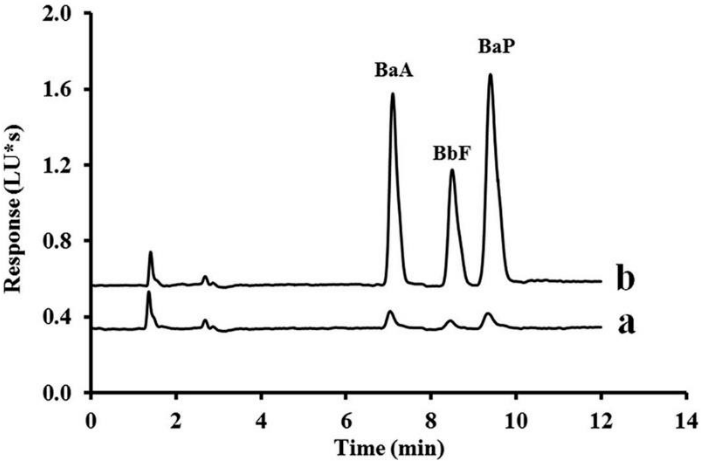

Figure 6. HPLC chromatograms of target PAHs in spiked wastewater samples (1.0 μg L^{-1}) (a) before and (b) after the extraction using the PANI/alginate/Fe_3O_4 sorbent.

are within the acceptable values (70–125%) of the AOAC guidelines. Satisfactory recoveries demonstrated no effect from the matrix compositions of the water samples. Figure 6 illustrates a typical chromatogram of PAHs in spiked wastewater samples at 1.0 μg L^{-1} before and after extraction using PANI/alginate/Fe_3O_4 sorbent. This result clearly demonstrated that the developed PANI/alginate/Fe_3O_4 sorbent could be applied for the extraction and determination of trace PAHs in water samples that contain different matrix interferences.

3.7. *Comparison of the developed method with other methods*

The analytical performance of this method for the extraction and determination of PAHs in water samples was compared with other existing methods. As shown in Table 2, the LOD of this method is lower than several methods [6,24,39–44]. Although, some methods provided a lower LOD, however, these methods required a larger sample volume [45] and longer extraction time [8]. The recoveries for this work were comparable [41,43] or better than others methods [6,8,24,39–41,44,45]. Hence, the analytical performance of the developed method was acceptable for trace analysis of PAHs.

4. Conclusion

In this work, polyaniline-coated magnetite nanoparticles incorporated into alginate beads was successfully synthesised and applied as a MSPE sorbent for the extraction and enrichment of PAHs in water samples. The coating of the composited alginate/Fe_3O_4 beads with polyaniline not only improved the adsorption ability of the PAHs but also provided a high extraction efficiency (86.0 ± 5.3 to 97.8 ± 8.3%) and a good stability and reproducibility. The low detection limit was 0.01 μg L^{-1} and that was below the MCL values required by the US EPA. The PANI/alginate/Fe_3O_4 sorbent exhibited a convenient and rapid collection of the sorbent from water samples without a column passing or

Table 2. Comparison of the developed method with other methods for the determination of PAHs.

Methods	Sorbents	PAHs	LOD (μg L^{-1})	Recovery (%)	Extraction time (min)	Sample volume (mL)	References
DLLME-HPLC-FLD	Organic solvent	BaA, BbF, BaP	0.05–0.08	86–95	-	4	[41]
SPE-HPLC-UV	Multiwalled carbon nanotubes	BaA, BbF	0.009–0.015	79–118	125	500	[8]
SPME-HPLC-DAD	Gold-functionalised stainless steel wire	BaP	0.10	85–120	15	15	[42]
SRSE-GC-MS	Poly(ethyleneglycol dimethacrylate/ graphene	BaA, BbF, BaP	0.019–0.056	63–99	120	50	[43]
MES-HPLC-FID	PANI/Zn-film/ stainless steel	BaP	0.05	82–110	30	1	[44]
MSPE-GC-MS	Magnetic N-doped carbon nanotubes	BaA	0.36	81–105	1	4	[39]
MSPE-HPLC-FLD	Ionic liquid-coated Fe_3O_4	BaA, BaP	0.0003–0.0017	76–105	10	300	[45]
MSPE-HPLC-UV	Graphitic carbon nitride/Fe_3O_4 composite	BaA	0.05	80–99	10	100	[6]
MSPE-HPLC-UV	Fe_3O_4/graphene oxide	BaA, BbF, BaP	0.09–0.13	77–103	10	50	[24]
MSPE-UPLC-DAD	Magnetic nanoparticles–nylon 6 composite	BbF	0.05	80–111	30	25	[40]
MSPE-HPLC-FLD	PANI/alginate/ Fe_3O_4 sorbent	BaA, BbF, BaP	0.01	86–98	20	10	This work

DLLME: dispersive liquid–liquid microextraction; SPE: solid-phase extraction;
SPME: solid-phase microextraction; SBSE: stir bar sorptive extraction; MES: microextractor stick; MSPE: magnetic solid-phase extraction.

filtration step that was time consuming. In addition, the developed novel sorbent was easily prepared, cost-effective and environmentally friendly. The developed method was successfully applied to determine BaA, BbF, and BaP in real water samples. It could be applied for the determination of PAHs in other samples.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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Supplemental Information

Polyaniline coated magnetite nanoparticles incorporated in alginate beads for the extraction and enrichment of polycyclic aromatic hydrocarbons in water samples

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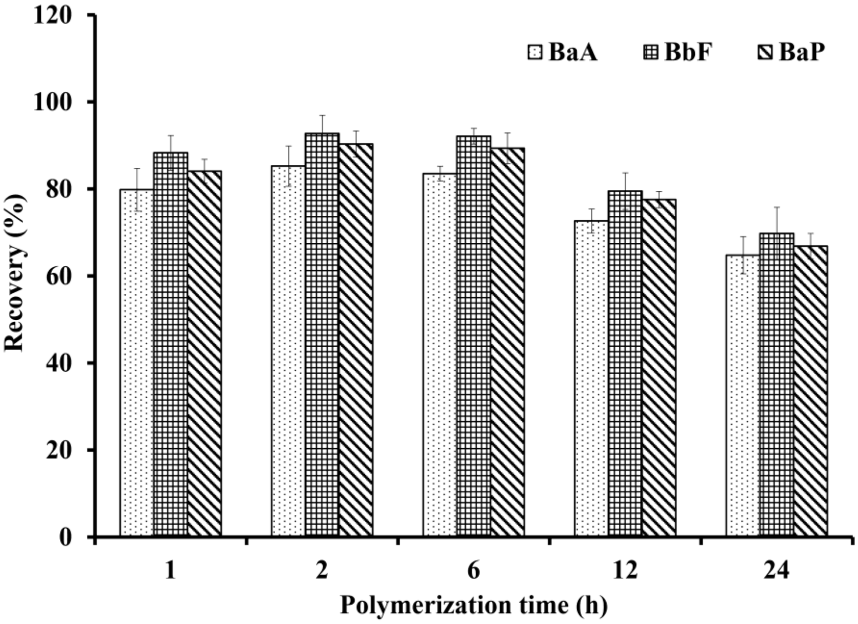

Figure S1. Effect of polymerization time of PANI/alginate/Fe_3O_4 sorbent on the recoveries of PAHs

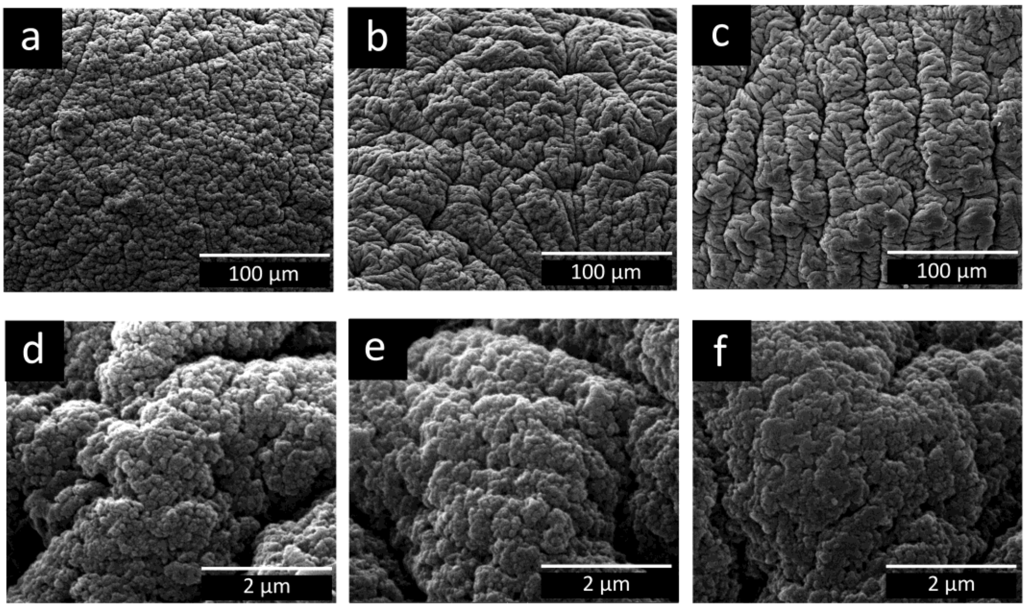

Figure S2. SEM images of the PANI/alginate/Fe_3O_4 sorbent at different polymerization times; 2 h (a=500x and d=20,000x), 6 h (b=500x and e=20,000) and 12 h (c=500x and f=20,000)

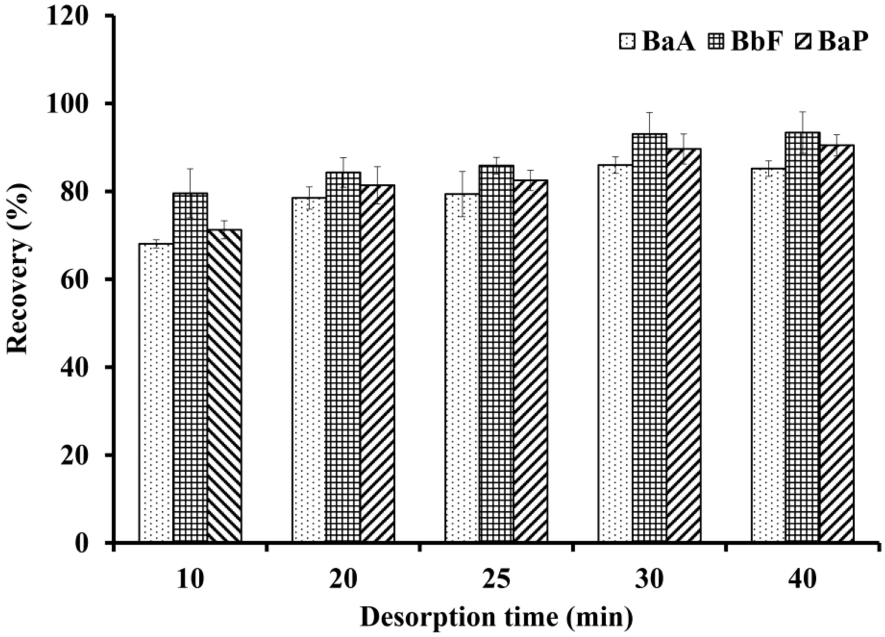

Figure S3. Effect of the desorption time on the recoveries of PAHs using the PANI/alginate/Fe_3O_4 sorbent

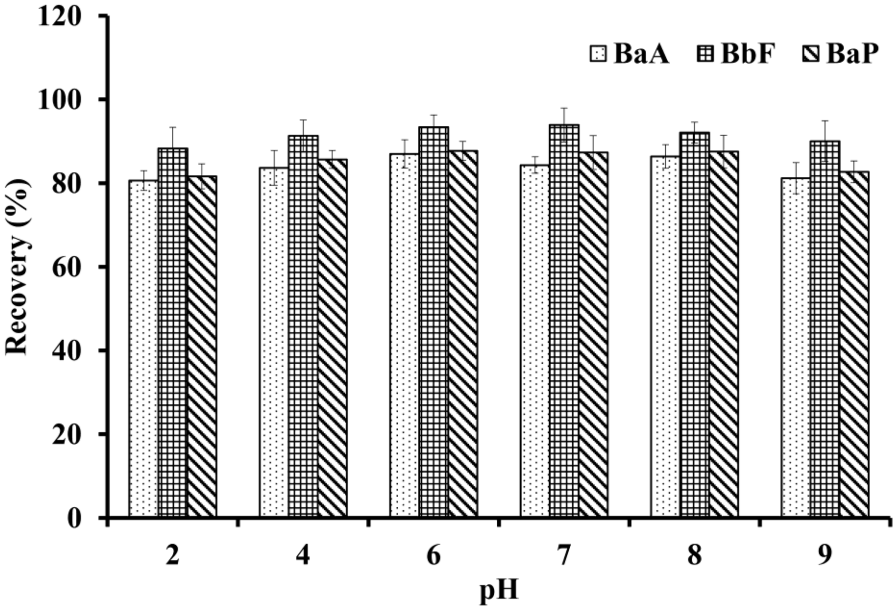

Figure S4. Effect of sample pH on the recoveries of PAHs in water samples using the PANI/alginate/Fe$_3$O$_4$ sorbent

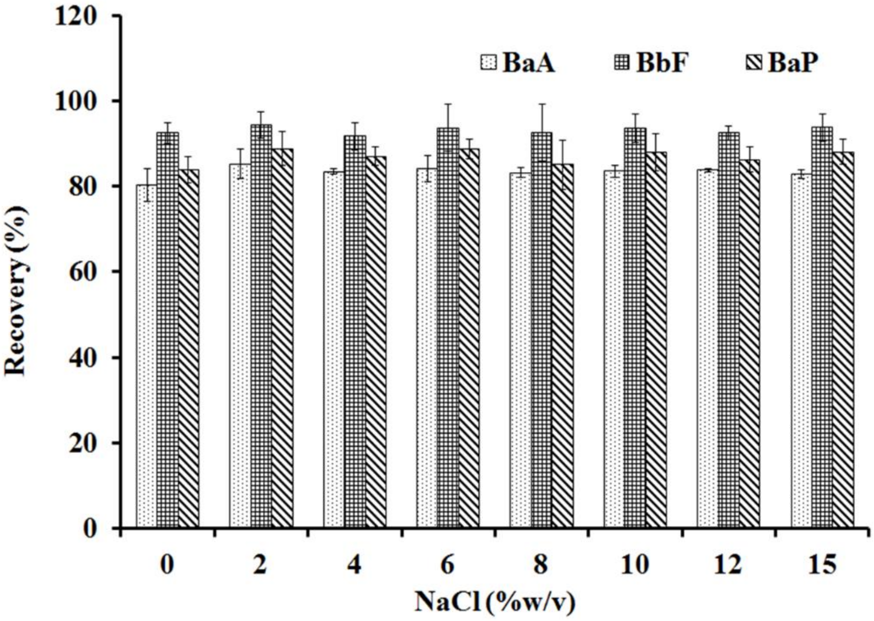

Figure S5. Effect of ionic strength on the recoveries of PAHs using the PANI/alginate/Fe$_3$O$_4$ sorbent

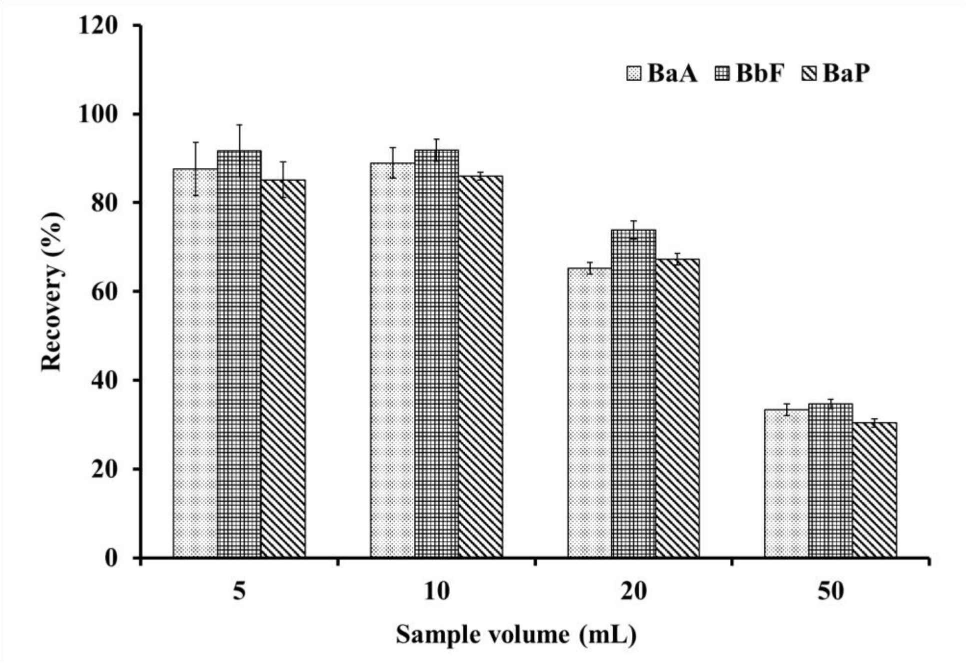

Figure S6. Effect of sample volume on the recoveries of PAHs using the PANI/alginate/Fe_3O_4 sorbent

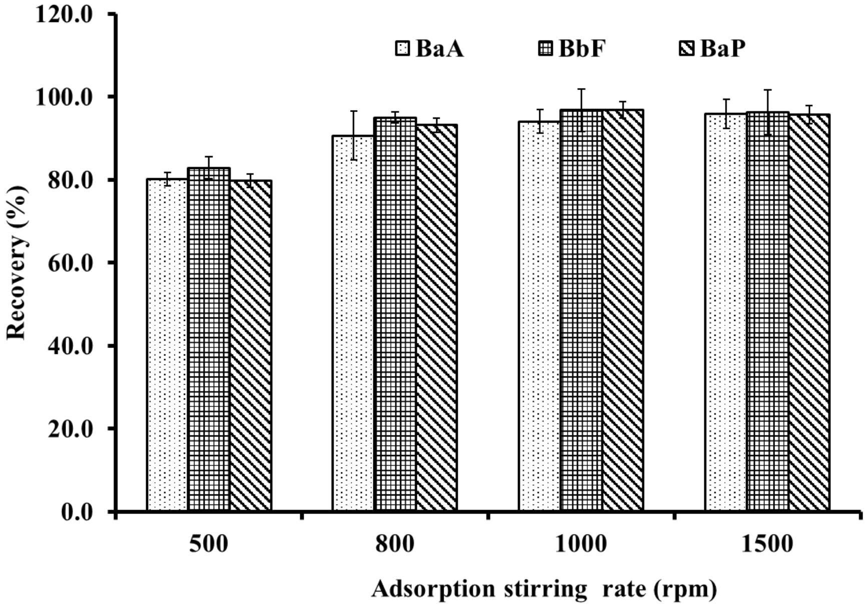

Figure S7 Effect of adsorption stirring rate on the recoveries of PAHs using the PANI/alginate/Fe_3O_4 sorbent

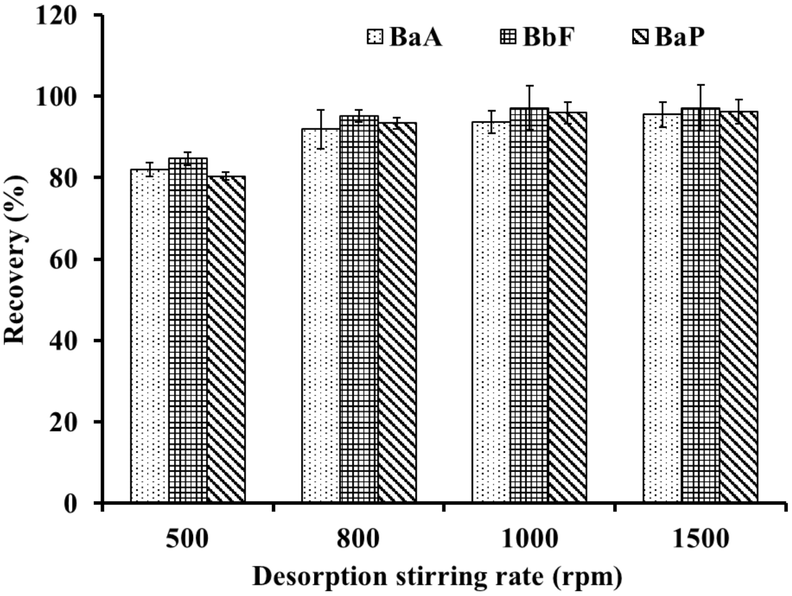

Figure S8. Effect of desorption stirring rate on the recoveries of PAHs using the PANI/alginate/Fe_3O_4 sorbent

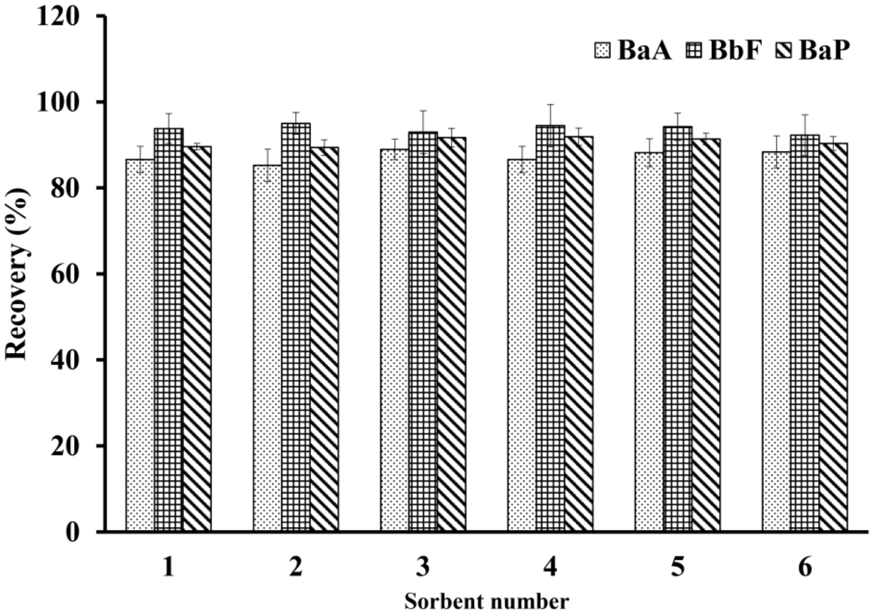

Figure S9. Reproducibility of the PANI/alginate/Fe_3O_4 sorbent for the extraction of PAHs at 1.0 μg L^{-1}

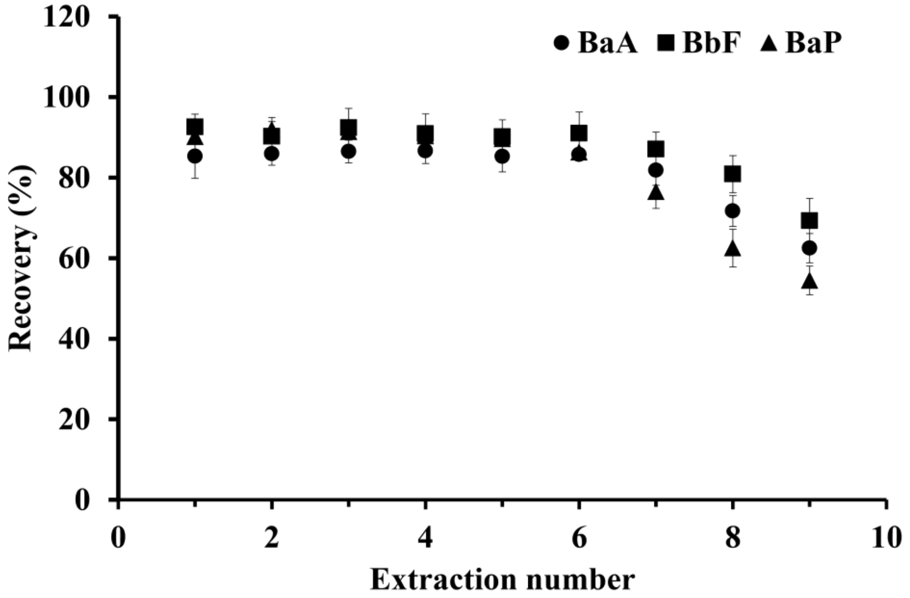

Figure S10. Reusability of the PANI/alginate/Fe_3O_4 sorbent for the extraction of PAHs from spiked deionized water at 1.0 μg L^{-1} (n=5)

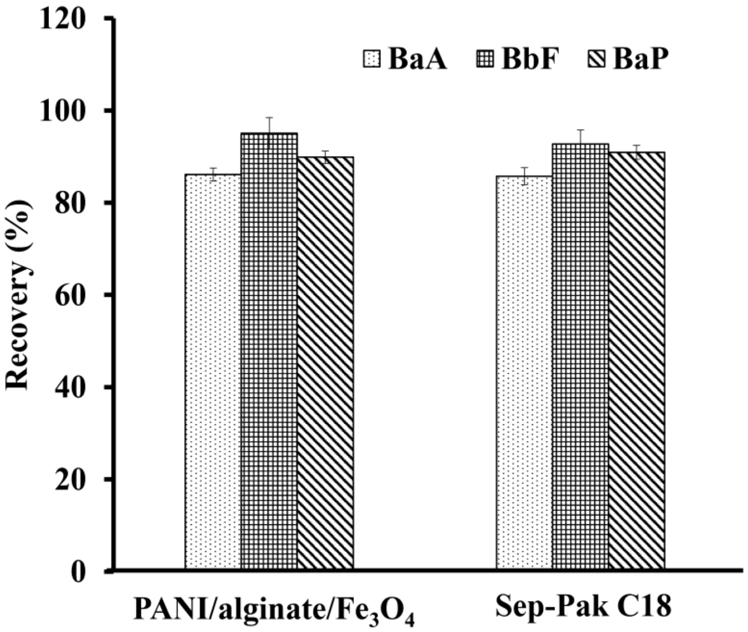

Figure S11. Extraction efficiency of PAHs in spiked deionized water; a comparison between the PANI/alginate/Fe_3O_4 sorbent and Sep-Pak C18 plus cartridge

Table S1 Analytical performance of the PANI/alginate/Fe_3O_4 sorbent for the extraction and determination of PAHs

Compounds	**Linear range (μg L^{-1})**	**Regression linear equation**	**R^2**	**LOD (μg L^{-1})**	**LOQ (μg L^{-1})**	**RSD (%)**
BaA	0.040 – 50.0	y = (8.558±0.049)x + (1.36±0.79)	0.9997	0.010	0.040	1.3-6.9
BbF	0.040 – 50.0	y = (6.748±0.045)x + (0.02±0.73)	0.9995	0.010	0.040	1.9-8.3
BaP	0.040 – 50.0	y = (6.278±0.067)x +(2.8±1.1)	0.9991	0.010	0.040	1.6-8.7

Table S2 Recoveries of PAHs in spiked water samples (n=5)

Water samples	**Added (μg L^{-1})**	**Recovery (%)**		
		BaA	**BbF**	**BaP**
Reservoir water	0.10	88.6 ± 4.7	96.9 ± 5.6	96.4 ± 3.7
	0.50	86.8 ± 4.8	97.7 ± 4.5	92.9 ± 3.1
	2.0	88.5 ± 5.5	97.5 ± 3.1	91.3 ± 4.2
River water	0.10	89.2 ± 7.2	95.5 ± 5.2	95.3 ± 5.9
	0.50	86.3 ± 3.5	96.4 ± 6.3	91.2 ± 3.9
	2.0	86.0 ± 5.3	97.8 ± 3.1	96.0 ± 3.6
Waste water	0.10	86.4 ± 5.2	96.3 ± 5.9	95.3 ± 6.9
	0.50	88.4 ± 5.1	97.8 ± 8.3	94.9 ± 6.2
	2.0	87.8 ± 5.3	96.7 ± 4.5	93.2 ± 3.7

Paper V

Bunkoed, O., **Nurerk, P.**, Wannapob, R., Kanatharana, P., Polypyrrole-coated alginate/magnetite nanoparticles composite sorbent for the extraction of endocrine-disrupting compounds. *Journal of Separation Science* 39 (2016) 3602-3609.

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Research Article

Polypyrrole-coated alginate/magnetite nanoparticles composite sorbent for the extraction of endocrine-disrupting compounds

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Magnetite nanoparticles incorporated into alginate beads and coated with a polypyrrole adsorbent were prepared (polypyrrole/Fe_3O_4/alginate bead) and used as an effective magnetic solid-phase extraction sorbent for the extraction and enrichment of endocrine-disrupting compounds (estriol, β-estradiol and bisphenol A) in water samples. The determination of the extracted endocrine-disrupting compounds was performed using high-performance liquid chromatography with a fluorescence detector. The effect of various parameters on the extraction efficiency of endocrine disrupting compounds were investigated and optimized including the type and amount of sorbent, sample pH, extraction time, stirring speed, and desorption conditions. Under optimum conditions, the calibration curves were linear in the concentration range of 0.5–100.0 μg/L, and the limit of detection was 0.5 μg/L. The developed method showed a high extraction efficiency, the recoveries were in the range of 90.5 ± 4.1 to 98.2 ± 5.5%. The developed sorbent was easy to prepare, was cost-effective, robust, and provided a good reproducibility (RSDs < 5%), and could be reused 16 times. The developed method was successfully applied for the determination of endocrine-disrupting compounds in water samples.

Keywords: Alginate / Endocrine disrupting compounds / Magnetite nanoparticles / Polypyrrole
DOI 10.1002/jssc.201600647

Additional supporting information may be found in the online version of this article at the publisher's web-site

1 Introduction

Endocrine-disrupting compounds (EDCs) are substances that interfere with the synthesis, transport, secretion, action, binding, or elimination of natural hormones in the body. As hormones are responsible for development, fertility, behavior, and the maintenance of homeostasis, consequently EDCs can cause adverse health effects for humans and other living organisms [1, 2]. EDCs are introduced into the aquatic environment by human activities, both domestic and industrial [3]. Most EDCs characteristics are persistence in the environment [4]. Thus, they can enter the food chain and adversely affect humans. Although the concentration of these compounds is relatively low in water, the continuous release and chronic exposure to these substances can result in adverse effects on aquatic life, and cause potential risks to human health [5].

Therefore, it is important to develop reliable, simple, rapid and highly sensitive methods for monitoring EDCs in environmental samples. Several chromatographic techniques have been reported for the determination of EDCs including HPLC [5–9], GC [10, 11], and CE [12, 13]. However, the use of the GC technique usually requires a tedious derivatization process, while the CE techniques lack stability and sensitivity for real samples. Among of them, HPLC has been extensively used for the determination of EDCs because of its good precision [5]. However, the amount of EDCs in water samples is relatively low and the matrices are often complex, thus, an effective sample preparation method involving pre-concentration is normally essential as the first step for instrumental analysis. Several sample preparation techniques have been reported for the extraction and pre-concentration of EDCs, such as dispersive liquid–liquid microextraction (DLLME) [14], hollow-fiber-based liquid-phase microextraction (HF-LPME) [7], stir bar sorptive extraction (SBSE) [15], SPME [5], and SPE [6]. Among these methods, SPE is one of the most extensively used due to its ability to provide a high extraction capability and efficiency. However, traditional SPE sorbent are expensive, the operation is complicate, involves several steps, and is time consuming. To overcome these problems, a magnetic solid-phase extraction

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Abbreviations: EDC, endocrine-disrupting compound

(MSPE) process has attracted much attention for its application of suitable sorbents that can be separated from sample solution by an external magnetic field so that separation is easier and faster [16–18].

The preparation of materials with a high affinity is obviously important for a sorbent based extraction. For the MSPE method, bare magnetite nanoparticles (Fe_3O_4) tend to aggregate to form large cluster, are prone to oxidation, lack selectivity in complex matrices and have a low dispersibility in water samples [19, 20]. Therefore, any suitable magnetic nanoparticles require specific modifications or are made suitable by being coated with higher affinity materials to make them selective and appropriate sorbents [21, 22]. In this work, we have developed a new sorbent consisting of polypyrrole-coated magnetite nanoparticles incorporated within alginate beads for the extraction and preconcentration of EDCs in water samples. Polypyrrole was used as a coating material because of its large surface area and also contains a conjugated π-structure that can adsorb EDCs through π–π and hydrophobic interactions [10]. In addition, polypyrrole can be easily synthesized under mild conditions and it also has good chemical stability [23, 24]. An alginate hydrogel was used to entrap the magnetite nanoparticle to help to prevent oxidation of the magnetite nanoparticles and to increase the surface area over which polypyrrole can be coated (in the pore and surface). The polypyrrole/Fe_3O_4/alginate sorbent was then used to extract EDCs in water samples. Because of their toxicity, estriol, β-estradiol and bisphenol A were selected in this study as test EDCs to investigate the performance of the developed polypyrrole/Fe_3O_4/alginate sorbent.

2 Materials and methods

2.1 Reagents

Methanol, acetonitrile, and 2-propanol were from Merck (Darmstadt, Germany). Ethanol and ammonium hydroxide were from JT Baker (Bangkok, Thailand). Calcium chloride dehydrate was from Ajax Finechem (NSW, Australia). Iron(II) chloride tetrahydrate ($FeCl_2.4H_2O$), iron(III) chloride hexahydrate ($FeCl_3.6H_2O$), alginic acid sodium salt, and pyrrole were from Sigma–Aldrich (Steinheim, Germany). Ultrapure water was obtained from a maxima ultrapure water system (ELGA, England). Stock standard solutions of the EDCs (1000 mg/L) were prepared in methanol and stored in a refrigerator (4°C). Working standard solutions were prepared by diluting the stock solution with acetonitrile.

2.2 Instrumental and analytical conditions

Chromatographic analysis was performed on an Agilent 1100 HPLC system (Agilent Technologies, Germany). The separations were performed on a reverse-phase VertiSep^{TM} C_{18} column (250 × 4.6 mm id, 5 μm particles size; Restek Bellefonte, USA). The mobile phase was a mixture of water (A) and acetonitrile (B). A gradient elution program was performed with the following sequence: 0 to 4.0 min = 40% B, 4.0 to 10.0 min = 60% B, 10.0 to 15.0 min = 40% B and this was continued to 20.0 min. The flow rate was kept at 1.0 mL/min. The three EDCs were analyzed by a fluorescence detector (FLD) with excitation at 280 nm and emission at 310 nm. The injection volume was 20 μL and the column temperature was fixed at 30°C.

The surface morphology of the developed sorbent was investigated by SEM JSM-5200 (JEOL, Tokyo, Japan). The FTIR spectra were recorded by FTIR spectrometer (Bruker, Germany).

2.3 Preparation of the polypyrrole/Fe_3O_4/alginate sorbent

The preparation procedures for the polypyrrole/Fe_3O_4/alginate sorbent were as follows: Fe_3O_4 nanoparticles were prepared according to a previous report with some modification [18]. Briefly, 4.50 g of $FeCl_3{\bullet}6H_2O$ and 1.50 g of $FeCl_2{\bullet}4H_2O$ were dissolved in 100 mL of deionized water. The resulting solution was stirred at 80°C and ammonium hydroxide was then added dropwise into the solution as it was being vigorously stirred for 1 h. The obtained magnetic nanoparticles of Fe_3O_4 were separated from the solution using a magnet and washed with 100 mL of water three times, then dried in an oven at 60°C for 6 h.

To prepare the Fe_3O_4/alginate composite sorbent, an alginate solution of 2.0% w/v was prepared by dissolving the alginic acid sodium salt in deionized water and 0.1 g of the synthesized Fe_3O_4 was then added into 100 mL of the alginate solution and sonicated for 30 min. The mixture was dropped into a calcium chloride solution (5.0% w/v) while being stirred at room temperature (25°C) using a 10.0 mL syringe through a needle. As soon as the mixture solution drops came into contact with the calcium chloride solution, the Ca–alginate gel beads cage for the Fe_3O_4 were formed. These beads were then left in calcium chloride solution for 2 h to obtain the complete formation of Fe_3O_4/alginate beads. The Fe_3O_4/alginate beads were then collected from the solution by a magnet and washed with distilled water twice.

The Fe_3O_4/alginate composited beads were washed with 10.0 mL of 2-propanol and incubated in 10.0 mL of the pyrrole monomer for 1 h. Then, the beads were separated from the monomer solution and added to a 0.2 M $FeCl_3$ solution. The polymerization was performed at 25°C for 6 h to obtain the polypyrrole/Fe_3O_4/alginate sorbent. Then, the polypyrrole/Fe_3O_4/alginate sorbent was washed with 10 mL of methanol and deionized water, respectively. This sorbent was applied as an MSPE sorbent for the extraction of EDCs from water samples.

2.4 Magnetic SPE procedure

The polypyrrole/Fe_3O_4/alginate sorbents were added into 10.0 mL of sample solution and mechanically stirred for 20 min to allow the analytes to be adsorbed onto the sorbent. After extraction, the sorbents were isolated from solution by

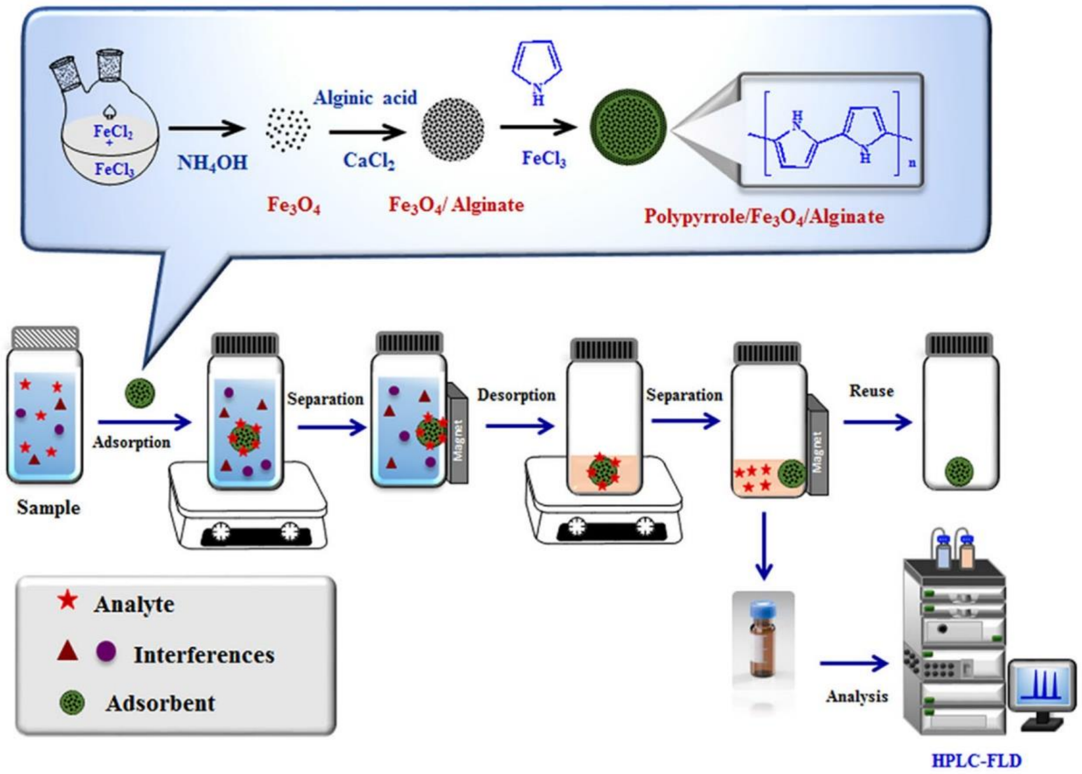

Figure 1. Schematic diagram of the synthesis and MSPE procedure using polypyrrole/Fe_3O_4/alginate sorbent follows by analysis with HPLC–FLD.

placing a magnet on the outer wall of the vial. The supernatant was decanted and the adsorbed analytes were eluted from the sorbents with the desorption solvent under stirring at room temperature. The desorption solvent were then collected and evaporated to dryness at 60°C, reconstituted with 0.5 mL of acetonitrile and filtered through a PTFE filter (0.45 μm). Finally, 20 μL of this solution was analyzed by HPLC–FLD. The polypyrrole/Fe_3O_4/alginate sorbent could be reused after washing with 2.0 mL of acetonitrile and water, respectively. The whole MSPE procedure is illustrated in Fig. 1.

3 Results and discussion

3.1 Characterization of polypyrrole/Fe_3O_4/alginate sorbent

The morphology of the alginate, Fe_3O_4/alginate and polypyrrole/Fe_3O_4/alginate surfaces were investigated using SEM. Figure 2A, D shows the morphology of the surface of the alginate beads after being dried, a porous structure was observed so the polypyrrole could be incorporated inside the bead which increased the active surface area. Figure 2B, E indicated that Fe_3O_4 nanoparticles were randomly distributed in the alginate bead, and the average size of the Fe_3O_4 nanoparticles was 80 ± 10 nm. Figure 2C, F shows that the surface of the polypyrrole/Fe_3O_4/alginate bead was rough and the polypyrrole was well incorporated and coated onto the surface of Fe_3O_4/alginate bead which increased the surface area for adsorption of the analytes.

FTIR spectroscopy was employed to characterize the composition of the synthesized alginate, Fe_3O_4 and polypyrrole/Fe_3O_4/alginate sorbent. As shown in Supporting Information Fig. S1A (a), the FTIR spectra of the alginate showed the characteristic band of C=O stretching, C–H bending and C–O–C stretching at 1633, 1431, and 1083 cm^{-1}, respectively. Supporting Information Figure. S1A (b) shows the absorption peak at 585 cm^{-1} that corresponded to the Fe–O vibration. The absorption peaks at 1480 and 1555 cm^{-1} were attributed to the absorption of the pyrrole ring (Supporting Information Fig. S1A (c)). This indicates that the polypyrrole is successfully coated onto the surface of Fe_3O_4/alginate sorbent.

Vibrating sample magnetometry (VSM) was used to study the magnetic properties of polypyrrole/Fe_3O_4/alginate sorbent. The saturation magnetization values obtained at

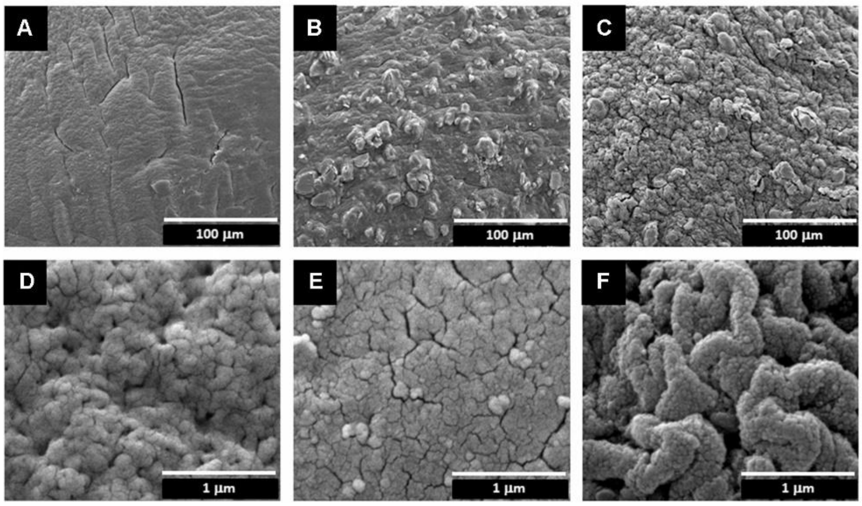

Figure 2. Scanning electron micrographs of the alginate bead surface (A = 500×; D = 30 000×), Fe_3O_4/alginate bead surface (B = 500×; E = 30 000×), and polypyrrole/Fe_3O_4/alginate surface (C = 500×; F = 30 000×).

room temperature was 19.90 emu/g (Supporting Information Fig. S1B). The magnetic strength of the polypyrrole/Fe_3O_4/alginate sorbents was enough for magnetic separation, and it was rapidly separated from the solution within 2 s using an external magnet. In addition, when the external magnet field was removed these sorbents redispersed rapidly in the sample solution.

3.2 Optimization of the magnetic SPE conditions

To obtain the highest extraction efficiency, short analysis time and less consumption of solvent, the effect of various parameters were optimized, i.e. type and amount of sorbent, sample pH, extraction time, stirring speed, and desorption conditions. When one parameter was changed, the other parameters were fixed at their optimal values. The optimization parameters were carried out using spiked deionized water containing of 10.0 μg/L of each of the EDCs. The recovery was used to evaluate the extraction efficiency and all the parameters were determined in triplicate.

3.2.1 The type of sorbent

The extraction capabilities of bare Fe_3O_4, Fe_3O_4/alginate and polypyrrole/Fe_3O_4/alginate sorbent were examined by extracting EDCs in spiked deionized water. As shown in Fig. 3, the recoveries of EDCs using bare Fe_3O_4 and Fe_3O_4/alginate sorbent were lower than 25% and the recoveries of the EDCs significantly increased in the presence of polypyrrole to demonstrate that the polypyrrole played an important role on the extraction efficiency of EDCs because it adsorbed the EDCs by hydrophobic and π–π interactions.

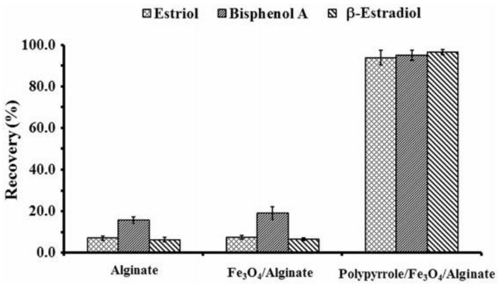

Figure 3. Comparison of the extraction efficiency of alginate, Fe_3O_4/alginate, and polypyrrole/Fe_3O_4/alginate sorbents for the determination of EDCs.

3.2.2 Effect of the amount of polypyrrole/Fe_3O_4/alginate sorbent

The amount of sorbent plays an important role in the extraction of analytes. To ensure that the target analytes were being completely adsorbed by sufficient sorbents, the amount of the polypyrrole/Fe_3O_4/alginate sorbent was investigated to obtain the highest extraction efficiency. As shown in Supporting Information Fig. S2, the results indicated that the sorbent amount had a significant effect on the extraction efficiency of EDCs, the recoveries increased when the amount of sorbent increased from 0.1 to 0.3 g and then it remained constant. This result indicated that 0.3 g of sorbent was sufficient to extract 10.0 μg/L EDCs from 10.0 mL water sample. Therefore, 0.3 g was chosen for the further experiments.

3.2.3 Sample pH

The sample pH is one of the important factors influencing the adsorption of analytes on the sorbent and also could affect the stability of the sorbent. The influence of the sample pH on the extraction efficiency of EDCs using polypyrrole/Fe_3O_4/alginate sorbent was investigated over the range of 3.0 to 9.0. As shown in Supporting Information Fig. S3, the sample pH had no obvious effect on the extraction efficiency of EDCs. It can be concluded therefore that the extraction of EDCs using the polypyrrole/Fe_3O_4/alginate sorbent was mainly based on π–π interactions. The independence of the extraction efficiency of the EDCs from the effects of different pH values indicated the good stability of the developed sorbents. Since, the pH values of the water samples are normally between 5.0 and 8.0. Therefore, the sample solutions were used directly without any pH adjustment.

3.2.4 Extraction time

EDCs should be completely extracted from the sample solution to the polypyrrole/Fe_3O_4/alginate sorbent within the shortest extraction time. In this work, the influence of the extraction time was investigated over the range of 5.0–30.0 min. As shown in Supporting Information Fig. S4, the extraction time had a significantly effect on the extraction efficiency. Maximum recovery was reached at 20.0 min and then remained almost constant with a further increase the time. Therefore, 20.0 min was selected as the optimal extraction time. In addition, after analytes were adsorbed, the sorbent was collected from the sample solution within 2 s.

3.2.5 Effect of stirring speed

The stirring speed of the sorbent also plays an important role in MSPE, as it can enhance the mass transfer rate of analytes from the sample solution to the sorbent which helps to reduce the extraction time. The effect of stirring speeds was investigated from 500 to 2000 rpm. As shown in Supporting Information Fig. S5, the results indicated that the recoveries of all analytes increased with stirring speed and reached a maximum at 1000 rpm. At lower stirring rates, the sorbent remained at the bottom of the vial since rotational forces were not strong enough and led to a low mass transfer rate of analytes to the sorbent. While, too high a stirring rate could cause damage to the developed sorbent, that would influence its reusability. Therefore, a stirring speed of 1000 rpm was selected.

3.2.6 Desorption conditions

The desorption solvent is an important factor that will affect the recovery. A suitable solvent can effectively desorb the analytes with a minimum volume while any interfering impurities are minimized. In this work, different polarities of solvent including methanol, acetonitrile, 2-propanol and acetone were investigated. As shown in Supporting Information Fig. S6, among the solvents tested, acetonitrile provided the highest recoveries and it was therefore selected as the desorption solvent for further experiments. The desorption solvent volume was also investigated in the range of 1.0 to 4.0 mL. As shown in Supporting Information Fig. S7, 2.0 mL was sufficient for complete desorption. In addition, the effect of the desorption time was also investigated over the range of 3 to 20 min. The results indicated that 5 min was sufficient for complete desorption (Supporting Information Fig. S8).

3.3 Reproducibility and reusability of the polypyrrole/Fe_3O_4/alginate sorbent

Six different batches of the sorbent were prepared and used to extract the test EDCs from spiked deionized water at 10.0 μg/L. The RSDs were lower than 5%, this indicated a good reproducibility of the sorbent preparation (Supporting Information Fig. S9).

The reusability of the developed sorbent was also investigated since this could reduce the overall cost and time. After desorption of the analytes from the sorbent, before the next use, the polypyrrole/Fe_3O_4/alginate sorbent was rinsed with 3.0 mL of acetonitrile and water, respectively, and no carryover of the analytes was detected on the sorbent. As shown in the Supporting Information Fig. S10, the results indicated that the polypyrrole/Fe_3O_4/alginate sorbent can be reused 16 times without significant loss of the extraction efficiency, the recoveries were higher than 80%, which indicated that the polypyrrole/Fe_3O_4/alginate sorbent had a good stability.

3.4 Analytical performances

Under the optimal conditions, the performances of the developed method were investigated including the linearity, LOD, and LOQ. To obtain the linearity of the method, the spiked deionized water in the concentration range from 0.5 to 200 μg/L were extracted using the polypyrrole/Fe_3O_4/alginate sorbent followed by HPLC analysis. The method showed a good linearity from 0.5 to 100 μg/L with the coefficient of determination (R^2) being higher than 0.99. The calibration curves for estriol, bisphenol A, and β-estradiol are shown in Supporting Information Table S1. The LOD and LOQ, based on $S/N = 3$ and 10, respectively, were 0.5 and 2.0 μg/L, respectively. Therefore, the developed method can be effectively used to determine the EDCs in water samples since it had a wide linear range and a low detection limit.

3.5 Comparative studies

The extraction efficiency of the polypyrrole/Fe_3O_4/alginate sorbent was compared to an Oasis HLB cartridge. Recoveries of the EDCs were 90.6–92.8 and 90.4–94.2% for the polypyrrole/Fe_3O_4/alginate and the Oasis HLB, respectively. The recoveries of the two sorbents were no significant

Table 1. Recoveries of EDCs in spiked water samples

Water sample	Added (μg/L)	Recovery (%)		
		Estriol	Bisphenol A	β-Estradiol
Tap water	2.0	93.3 ± 3.0	94.2 ± 4.4	97.8 ± 5.5
	5.0	92.5 ± 5.1	93.6 ± 7.2	96.8 ± 6.5
	20.0	91.3 ± 5.1	92.6 ± 7.2	95.3 ± 4.9
River water	2.0	94.3 ± 5.3	95.2 ± 4.6	97.1 ± 4.5
	5.0	91.3 ± 6.1	94.3 ± 5.2	95.9 ± 3.3
	20.0	91.5 ± 6.2	93.6 ± 4.7	94.8 ± 3.5
Wastewater	2.0	92.5 ± 6.1	96.3 ± 4.4	98.2 ± 5.5
	5.0	91.3 ± 4.5	92.8 ± 4.2	95.8 ± 3.5
	20.0	90.5 ± 4.1	92.6 ± 4.6	95.6 ± 3.1

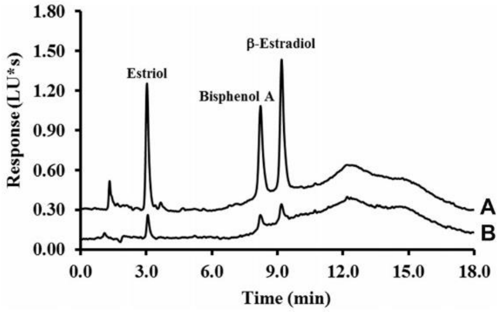

Figure 4. Chromatogram of the spiked water sample with (A) and without (B) extraction using the polypyrrole/Fe_3O_4/alginate sorbent.

differences, compared by the statistical *t*-test. Therefore, the polypyrrole/Fe_3O_4/alginate sorbent can be used as an alternative sorbent for the extraction of EDCs from water samples. The advantages of the developed MSPE sorbent over the conventional SPE cartridges are it was simpler to use and could be reused for up to 16 times, whereas the conventional SPE cartridges could not be reused.

3.6 Analysis of real water samples

The developed method was applied for the extraction and enrichment of EDCs in real water samples, i.e. tap, river, and wastewater samples. The levels found were from not-detectable to 1.60 ± 0.12 μg/L (Supporting Information Table S2). The recoveries of EDCs were studied by spiking the standard solutions into water samples at three concentration levels and the recoveries are listed in Table 1. The recoveries were in the range of 90.5 ± 4.1 to 98.2 ± 5.5%, with a RSD of less than 8%. Figure 4 shows the chromatogram of a spiked water sample with and without extraction using the polypyrrole/Fe_3O_4/alginate sorbent. The results demonstrated that the accuracy of the developed method was acceptable, so it can be used as an alternative method for the extraction and determination of EDCs in water samples.

3.7 Comparison of the developed method with other methods

To further demonstrate the advantages of the developed method, it was compared with previous work as shown in Table 2. Although some methods provided a lower detection limit, they used a highly sensitive MS detector [25, 26],

Table 2. Comparison of the developed method with other methods for the determination of EDCs

Extraction method	Detection	Sample	Extractants	LOD (μg/L)	Recovery (%)	Extraction time (min)	Sample volume (mL)	References
SPME	GC-MS	water	Bis(trimethylsilyl) trifluoroacctamide (derivatization)	0.002–0.378	–	60	3.0	[25]
SPE	GC-MS	water	Oasis HLB cartridges (derivatization)	0.0017–0.0053	63–116	130	500	[26]
MM-SPE-MP	LC-MS-MS	water	Fe_3O_4/poly (divinylbenzene-co-methacrylic acid)	0.001–0.036	56–110	15	500	[27]
MMIPs	HPLC-UV	Water and milk	MIPs	9.5	65–93	30	1.0	[28]
SPME	HPLC-DAD	water	Multiwall carbon nanotubes	0.1–0.3	85–102	10	250	[5]
DLLME	HPLC-DAD	food packaging	1-Octyl-3-methyl-imidazoliumhexa-fluorophosphate	0.5–1.5	98–103	3	10	[29]
MSPE	HPLC-FLD	Water	Polypyrrole/Fe_3O_4/ alginate bead	0.5	90–98	20	10	This work

DLLME, dispersive liquid–liquid microextraction; MMIPs, magnetic molecularly imprinted polymers; MSPE, magnetic solid phase extraction; MM-SPE-MP, magnetic-mediated solid-phase extraction micro-particle sorbent; SPME, solid phase microextraction which is expensive and requires complex instrumentation and some other methods used large sample volumes [5, 27]. In addition, GC–MS needed a derivatization step, which is tedious and time consuming. Some methods were complicated and required a long time for the synthesis of the molecularly imprinted polymer [28]. Compared to the dispersive liquid–liquid microextraction [29], the developed method is more simple and convenient, as a time duration of ~2 s was sufficient to collect the magnetic sorbent from the water sample using the external magnet. In the case of the extraction efficiency, the recoveries of the developed method was either comparable [5,29] or better than most other methods [26–28]. These observations indicated that the developed method can be used for the trace analysis of EDCs in real water samples.

4 Concluding remarks

A new polypyrrole/Fe_3O_4/alginate sorbent was successfully prepared and used for the extraction and preconcentration of EDCs in water samples. The polypyrole not only improved the adsorption ability of EDCs, but also improved the stability and dispersibility of the sorbent in an aqueous solution. The preparation procedure of the developed sorbent is relatively simple, rapid, cost-effective (~ 0.5 USD), and capable of mass production. The developed method provided a high extraction efficiency, a low detection limit, and had good reproducibility. The sorbent could be separated easily and rapidly from the sample solution using an external magnet without using a column and filtration step in comparison with a conventional SPE cartridge. In addition, the polypyrrole/Fe_3O_4/alginate sorbent can be reused up to 16 times, so that would help to reduce analysis costs. The developed method has the potential for use to extract other less polar organic compounds.

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The authors have declared no conflict of interest.

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Supporting Information

A polypyrrole coated alginate/magnetite nanoparticles composite sorbent for the extraction of endocrine disrupting compounds

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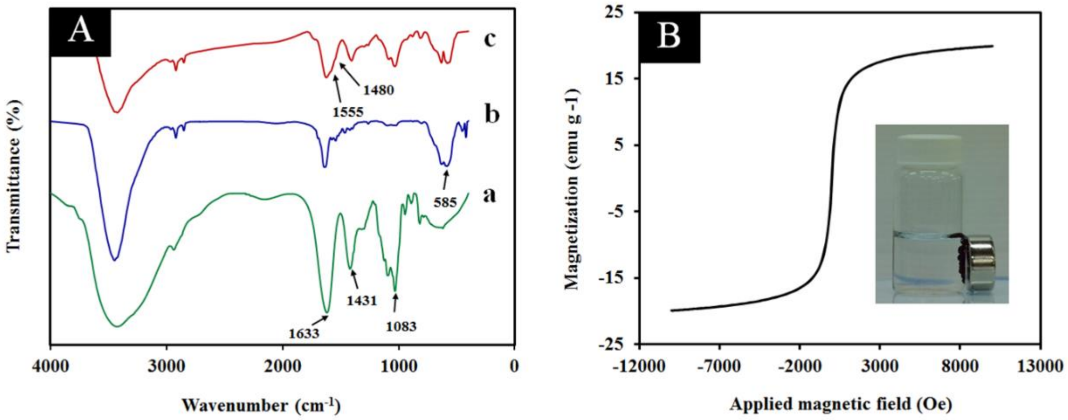

Fig. S1 (A) FT-IR spectra of (a) alginate, (b) Fe_3O_4 (c) polypyrrole/Fe_3O_4/alginate sorbent and (B) VSM curve, the inset represents the polypyrrole/Fe_3O_4/alginate beads separated by a magnet

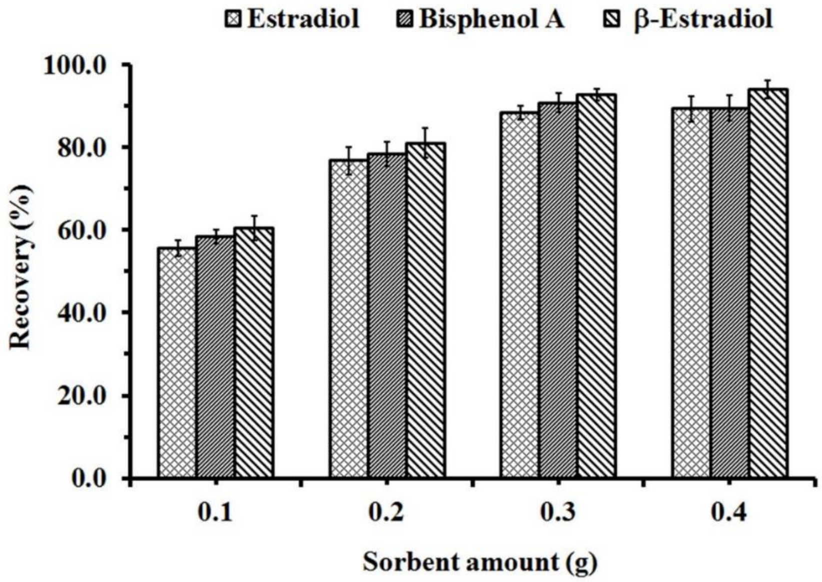

Fig. S2 Effect of the amount of sorbent on the extraction efficiency of EDCs using the polypyrrole/Fe_3O_4/alginate sorbent

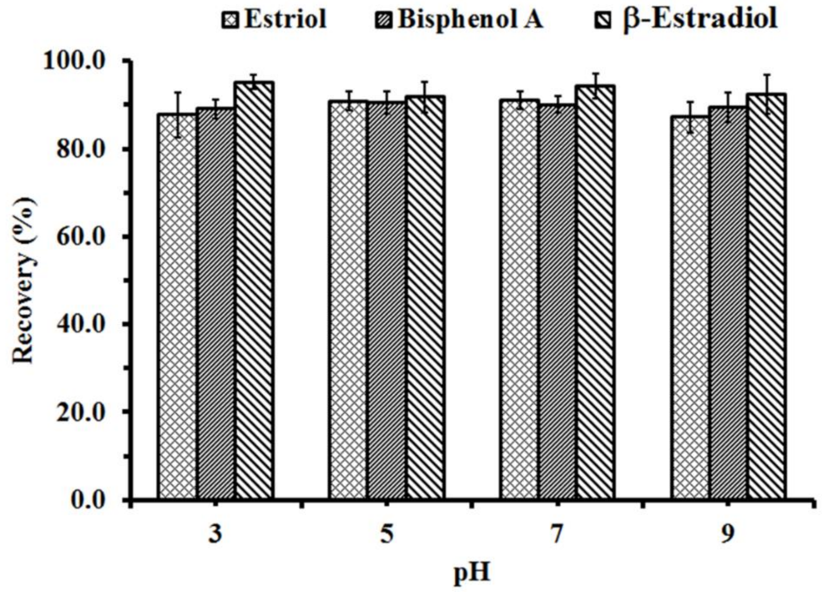

Fig. S3 Effect of sample pH on the extraction efficiency of EDCs using the polypyrrole/Fe_3O_4/alginate sorbent

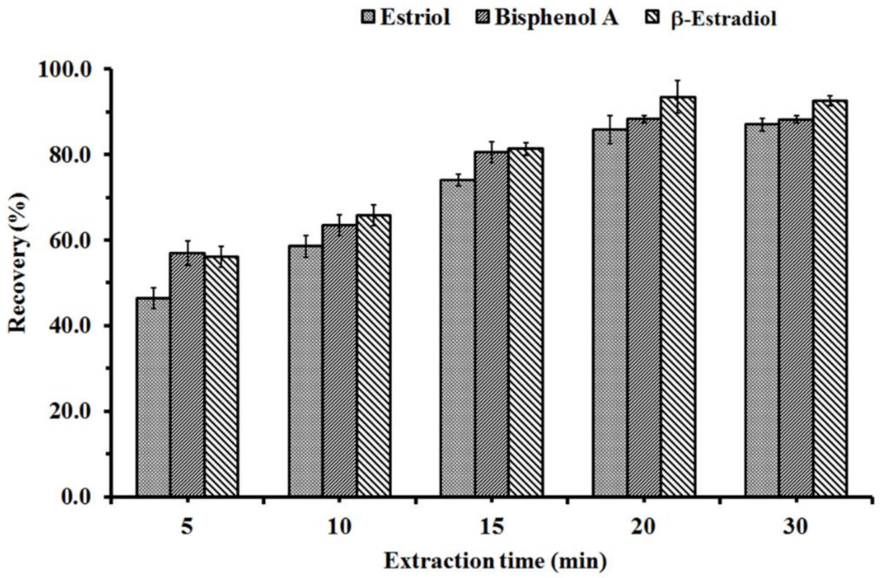

Fig. S4 Effect of extraction time on the extraction efficiency of EDCs using the polypyrrole/Fe_3O_4/alginate sorbent

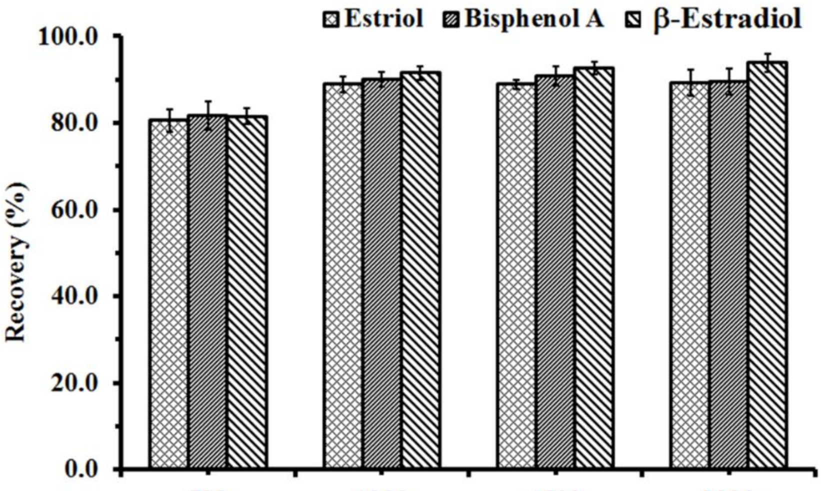

Fig. S5 Effect of stirring speed on the extraction efficiency of EDCs using the polypyrrole/Fe_3O_4/alginate sorbent

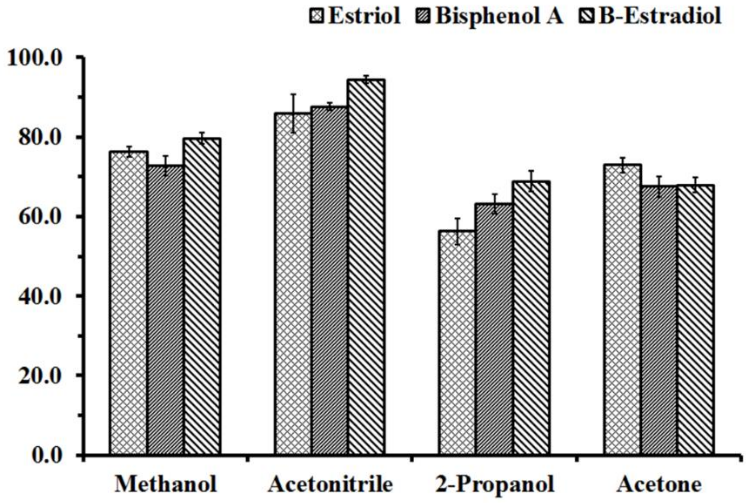

Fig. S6 Effect of desorption solvent on the recoveries of EDCs using the polypyrrole/Fe_3O_4/alginate sorbent

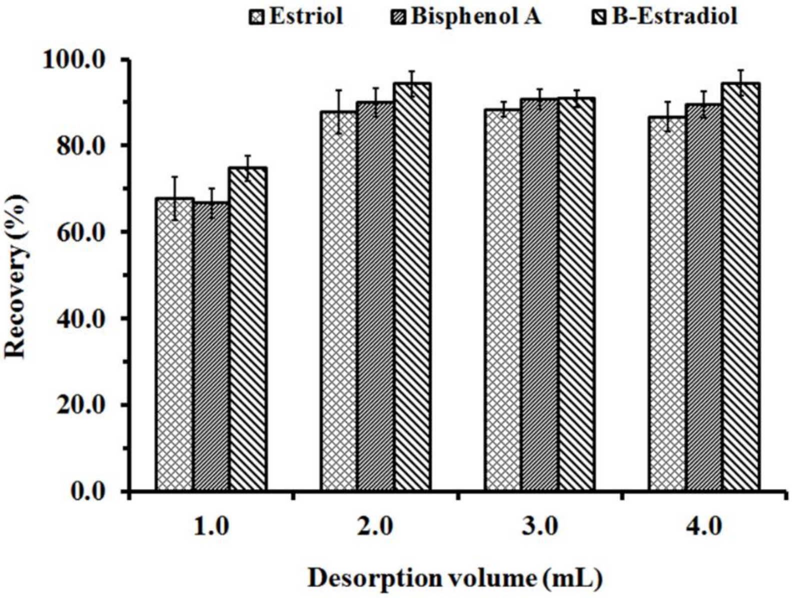

Fig. S7 Effect of desorption solvent volume on the recoveries of EDCs using the polypyrrole/Fe_3O_4/alginate sorbent

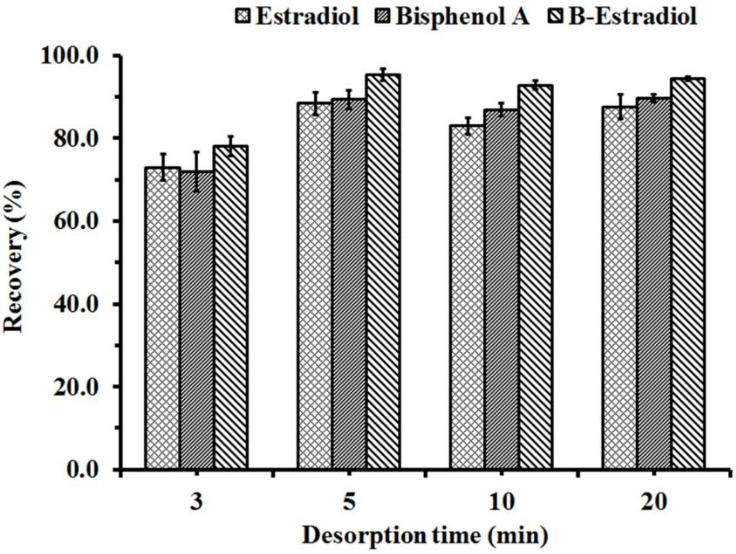

Fig. S8 Effect of desorption time on the recoveries of EDCs using the polypyrrole/Fe_3O_4/alginate sorbent

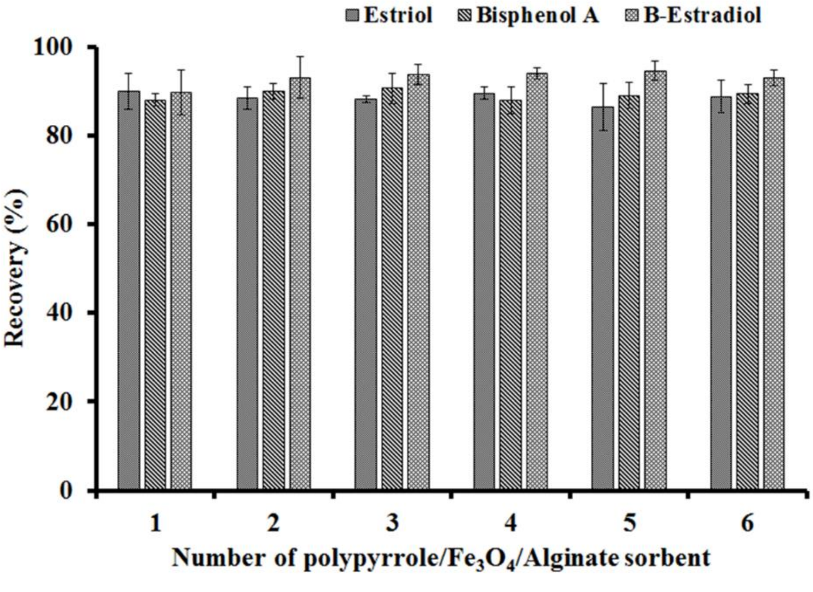

Fig. S9 The reproducibility of polypyrrole/Fe_3O_4/alginate sorbent that were prepared with the same conditions but at different times (n=6)

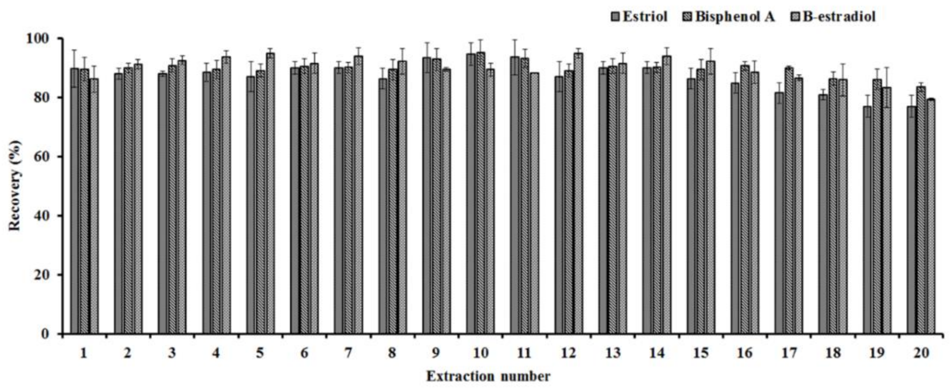

Fig. S10 Reusability of the polypyrrole/Fe_3O_4/alginate sorbent for extraction of EDCs from spiked deionized water (10.0 µg L^{-1})

Table S1. Analytical performance of the polypyrrole/Fe_3O_4/alginate sorbent for the extraction and determination of EDCs in water samples

Compounds	Linear range (µg L^{-1})	Regression line equation	R^2	LOD (µg L^{-1})	LOQ (µg L^{-1})
Estriol	0.5-100	$y = (450.8 \pm 13.9)x + (0.97 \pm 0.56)$	0.9943	0.5	2.0
Bisphenol A	0.5-100	$y = (459.3 \pm 5.6)x + (0.54 \pm 0.22)$	0.9991	0.5	2 .0
β-Estradiol	0.5-100	$y = (637.7 \pm 15.2)x + (0.82 \pm 0.61)$	0.9966	0.5	2.0

Table S2. Concentration of EDCs in water samples (n=5)

Water sample	Concentration (μg L^{-1})		
	Estriol	Bisphenol A	β-Estradiol
Tap water 1	ND	ND	ND
Tap water 2	ND	ND	ND
River water 1	ND	ND	ND
River water 2	ND	ND	ND
Wastewater 1	1.60 ± 0.12	< LOQ	ND
Wastewater 2	< LOQ	ND	ND

ND = not detectable

Paper VI

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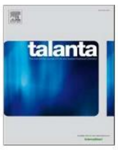

Environmentally friendly etching of stainless steel wire for plunger-in-needle liquid-phase microextraction of polycyclic aromatic hydrocarbons

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ABSTRACT

An environmentally friendly method of etching a stainless steel plunger wire, to replace the conventional hydrofluoric acid approach, was developed for plunger-in-needle liquid phase-microextraction (PIN-LPME). The one-step etching procedure was performed by immersing the plunger wire in a ferric chloride-hydrochloric acid ($FeCl_3$-HCl) solution. The etched wire was then used for LPME as the organic solvent holder. After solvent coating, the wire was directly exposed to a water sample for extraction of polycyclic aromatic hydrocarbons (PAHs), which were then subjected to thermal desorption in the injector of a gas chromatograph for gas chromatography-mass spectrometric (GC-MS) analysis. The parameters affecting PIN-LPME efficiencies (i.e., extraction solvent, solvent coating mode and time, stirring rate, extraction time and salting effect) were also investigated. Under the most favourable conditions, PIN-LPME-GC-MS exhibited high enrichment factors of between 70 and 349 for the 9 PAHs, low detection limits (between 0.006 and 0.058 ng mL^{-1}), and good precision (with relative standard deviations ranging from 4.4% to 9.7%). The developed method was successfully applied for the extraction and determination of PAHs in tap, river and drain water samples. Good relative recoveries of the PAHs over the range of 84.3–101.9% were obtained with spiked genuine water samples.

1. Introduction

In environmental analysis, the concentrations of target analytes in genuine samples are usually at trace (parts per billion or parts per trillion) levels; such sample matrices are normally also complex [1]. For these reasons, a sample preparation step is necessary in an analytical protocol to isolate and pre-concentrate the analytes prior to instrumental analysis [2]. One such widely used sample preparation method for generally hydrophobic analytes is liquid-liquid extraction (LLE). However, the procedure has major drawbacks such as tedious and time-consuming manipulation and the use of large amounts of undesirable organic solvents [3,4]. The impetus to overcome, or mitigate, these problems, has led to many studies focusing on the miniaturization of the sample preparation process.

Over the past 25 year, these efforts have resulted in putatively simple, fast and inexpensive methods being developed that are characterized by the minimization of time, labor and solvent and reagent consumption [5]. One such miniaturized sample preparation technique, the first to be developed, by Arthur and Pawliszyn in 1990 [6], is solid phase-microextraction (SPME). In SPME, a polymer-coated fiber is used to adsorb analytes from (primarily aqueous) samples. The fiber can be integrated into a syringe-like holder to allow solvent-less sampling, extraction and analyte introduction to an analytical instrument, using a single device [7,8]. Commercially available SPME fibers are still expensive, and while newer products have been introduced to address issues of fragility and coating instability under extreme thermal conditions, these remain demonstrable problems. SPME coatings also swell in organic solvents, thus restricting their applicability [9].

Partially to complement SPME, another miniaturized sample preparation technique developed a few years after the introduction of SPME, is liquid phase-microextraction (LPME). LPME uses microliters of solvent to concentrate analytes from primarily aqueous samples

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instead of hundreds of milliliters as used in LLE. In this way, high analyte enrichment (pre-concentration) may be obtained without a solvent evaporation (and reconstitution) step [10,11]. Various modes of LPME have since been developed. In single-drop microextraction (SDME), the organic solvent is suspended from the tip of a microsyringe and exposed to the sample or its headspace [12,13], in the same way that SPME is operated. This allows SDME to be easily conducted at low cost with minimal solvent usage. However, the solvent droplet can be unstable and easily detached from the needle tip, resulting in poor reproducibility across experiments [14]. Hollow fiber LPME (HF-LPME) was then developed to help to overcome droplet instability by holding the solvent within the lumen and the pores of the HF (usually made of, but not limited to, polypropylene) as a protective sheath [15]. As in solvent extraction, this technique is based on the partitioning of analytes between the aqueous sample, and solvent within the lumen or pores of the HF [16,17]. However, HF-LPME also has its own drawbacks, one of which is the formation of air bubbles on the surface of the HF, if the procedure is not handled sufficiently carefully. This can affect its repeatability [18].

As an alternative to commercial SPME, a home-made device was introduced that took advantage of the stainless steel plunger wire of a commercially available ultra-low volume plunger-in-needle microsyringe [19,20]. In the procedure known as plunger-in-needle (PIN)-SPME, the plunger wire was etched to form a microporous structure which was coated with a sorbent. The PIN microsyringe therefore mimicked almost exactly a commercial SPME fiber and holder, but was substantially less expensive. Following this, a new approach to LPME, termed PIN-LPME was developed in which solvent was loaded or "coated" on the etched wire surface for liquid-phase extraction [21]. For these studies, although the etched plunger wire provided high surface area and was shown to perform well for both SPME and LPME, the etching process used highly toxic and corrosive hydrofluoric acid [22] as the etchant. It is therefore desirable to have an alternative safer method to etch stainless steel wires for such sample preparation purposes.

The aim of this study was to introduce a more environmentally friendly and less toxic way of etching the stainless steel plunger wire for its use in PIN-LPME. The etching was performed using aqueous ferric chloride-hydrochloric acid solution ($FeCl_3$-HCl) [23] instead, replacing the commonly used toxic hydrofluoric acid etchant [9,24,25]. This $FeCl_3$-HCl-etched stainless steel plunger wire was evaluated for its application as the organic solvent holder and was directly exposed to water samples for extraction. The extract was subsequently subjected to thermal vaporization in a gas chromatograph injector port for gas chromatography-mass spectrometric (GC-MS) for analysis. To assess the performance of this $FeCl_3$-HCl etched stainless steel plunger wire, several polycyclic aromatic hydrocarbon (PAHs), a group of priority pollutants listed by the United States Environmental Protection Agency, were used as model analytes.

2. Experimental

2.1. Chemicals and reagents

Hydrochloric acid (HCl) (37%) was obtained from Merck (Darmstadt, Germany). Methanol (MeOH) and toluene of high performance liquid chromatography-grade were purchased from Fisher Scientific (Leicestershire, UK). Cyclohexane was supplied by VWR international (Radnor, PA, USA). 1-Octanol was purchased from Sigma-Aldrich (St. Louis, MO, USA). Dichloromethane was obtained from P.P. Chemical Sdn. Bhd. (Johor, Malaysia). 1-Octanol and ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) were purchased from Sigma-Aldrich. Sodium chloride (NaCl) was purchased from GCE Laboratory Chemicals (Darmstadt, Germany). The PAH standards, acenaphthylene (ACE), acenaphthene (ACN), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benz[*a*]anthracene (BEN) and chrysene (CHR), were purchased from Supelco (Bellefonte, PA, USA). Ultrapure water was obtained from an ELGA Purelab Option-Q (High Wycombe, UK) water purification system.

2.2. Apparatus and instrumentation

The PIN microsyringe (with a replaceable 26-gauge of 70 mm needle length, and 0.47 mm internal diameter (I.D.)) and a replacement needle (23-gauge, 50 mm needle length, 0.63 mm I.D.) were purchased from Scientific Glass Engineering/Trajan (Ringwood, VIC, Australia). The etched plunger wire tip (of ca. 1.0 cm length) was withdrawn into the latter shorter needle for protection during PIN-LPME procedures and GC-MS analysis. (The original 26-gauge needle was too long and its diameter too narrow for the present PIN-LPME application and was replaced.) An ultrasonic cleaner (Soniclean 160HT, Thebarton, S.A., Australia) was used for coating solvent onto the etched plunger wire under sonication. The surface morphology of the prepared plunger wire before and after etching were observed using scanning electron microscopy (SEM) (Model JSM-5200, JEOL, Tokyo, Japan) and confocal laser scanning microscopy system (Model LSM 800, Zeiss, Oberkochen, Germany). Analysis of PAHs was performed using a Shimadzu (Tokyo, Japan) GC-MS QP2010 system equipped with a DB-5MS fused silica capillary column (30 m × 0.250 mm I.D. × 0.25 µm film thickness) (Agilent Technologies, Palo Alto, CA, USA, http://www.agilent.com). Purified helium was used as the GC carrier gas at a flow rate of $1.00\ mL\ min^{-1}$. For analysis, the GC conditions were as follows: Initial oven temperature was at 60 °C and was held for 3 min, followed by an increase to 220 °C at a rate of $8\ °C\ min^{-1}$ and held for 1 min, and further increased to 295 °C at a rate of $15\ °C\ min^{-1}$ and held for 3 min. The injector temperature was set at 280 °C and injections were done in splitless mode. The GC-MS interface temperature was set as 280 °C and the solvent cut time was 5 min. Selected ion monitoring (SIM) mode was applied for identification and quantification of the PAHs. The selected ions are listed in Table S1 with the respective analyte retention times.

2.3. Sample preparation

Stock solutions of individual standards were prepared by dissolving each compound in MeOH at the concentration of $1000\ mg\ L^{-1}$. Working standard solutions were prepared by dilution with MeOH from the stock solutions, and stored at 4 °C. Water samples were freshly prepared by spiking ultrapure water with the analytes from the working solutions to obtain appropriate concentration levels (normally $10\ \mu g\ L^{-1}$).

Genuine water samples were collected from the Singapore River, a laboratory tap in the Department of Chemistry and a drain at the National University of Singapore. They were stored in glass bottles wrapped with aluminium foil, before being kept in the refrigerator at 4 °C until use.

2.4. Preparation of etched stainless steel plunger wire

The plunger wire was first cleaned with MeOH. The etching procedure was slightly modified from a previously published study [23] which reported an $FeCl_3$/HCl/nitric acid solution to etch microchannels for microfluidics work. In the present case, the plunger wire was immersed in a solution containing 0.50 g of $FeCl_3$ dissolved in 5.0 mL of HCl solution (20% w/v) for 15 min at 50 °C. After this, the etched part (ca. 1-cm long, measured from the tip) of the wire was washed with ultrapure water and then dried under room temperature for 30 min. The etched plunger wire was then reassembled into the PIN microsyringe, now serving as the PIN-LPME device, as shown in Fig. 1. The etched segment was then conditioned in the GC injector at 300 °C for 30 min before PIN-LPME.

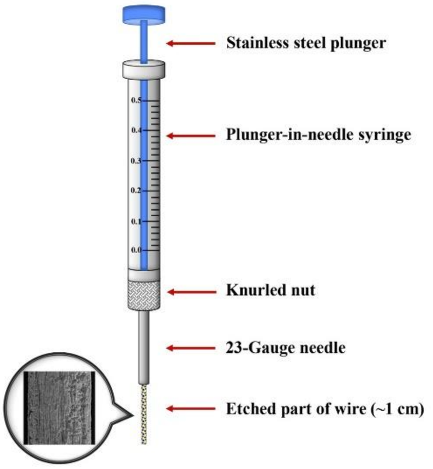

Fig. 1. Schematic of the PIN-LPME device. The insert shows a magnified SEM view of the etched surface (see also Fig. 2).

2.5. PIN-LPME

The PIN-LPME procedure was adopted from a previous report [21]. After etching the wire, there was an additional step of coating solvent onto the etched segment of the plunger wire. The latter was pushed out from the needle and immersed into an organic solvent for 5 min so as to allow coating. The solvent-loaded wire was then withdrawn back into the needle. For extraction, it was then re-exposed in a 10-mL sample solution, for the adsorption of the PAHs, with assistance of stirring, for 10 min. After extraction, the wire was withdrawn into the needle again for protection, and the device was removed from the sample. The needle was then inserted through the GC injection port septum. The wire was exposed in the injection port for thermal desorption (or volatilization) of the analytes at 280 °C for 7 min. The wire was cleaned by conditioning it in the injection port for another 7 min to remove any trace of the PAHs to eliminate analyte carryover. The wire was cooled down to ambient temperature, then loaded with solvent as described above, before the next experiment.

3. Results and discussions

3.1. Characterization of etched plunger wire

The morphologies of the plunger wire before and after etching by $FeCl_3$-HCl were investigated with SEM (Fig. 2). It can be seen that the originally smooth surface of the wire became roughened after etching, as expected. This etched surface allowed a thin film of organic solvent to be stably held for LPME as previously indicated [21]. The coated solvent on the wire was further investigated with a microscope and the images are shown in Fig. 3. The observations indicated that there was indeed a thin solvent (cyclohexane) film bounded on the etched surface of the wire after solvent immersion. The volume of cyclohexane coated on the wire was calculated to be ca. 2.51 nL using the method as described previously [21].

In addition, the preliminary extraction capabilities of non-etched and etched wires (and also without and with solvent coating) were investigated. As shown in Fig. 4, the non-etched wire could hardly extract any of the PAHs, indicating the lack of extraction (or adsorptive) capabilities of the non-etched wire. After etching, but without any solvent, several, but not all PAHs, were extracted. However, with the cyclohexane-coated etched wire all the PAHs considered were extracted successfully and had greater GC-MS intensities than those for the PAHs that were able to be extracted by the solvent-free etched wire. This demonstrated the much improved extraction capabilities of the wire after being etched and solvent-coated.

3.2. Optimization of PIN-LPME

3.2.1. Type of extraction solvent

Some factors should be considered when choosing a suitable organic solvent for enhancing PIN-LPME. Firstly, the solvent should have good affinity with the etched wire so that it could be held stably on the roughened surface. Secondly, the PAHs should have good solubilities in the solvent to ensure high extraction efficiency. Lastly, the solvent should be immiscible with water to avoid its dissolution during the extraction process [21,26]. On the basis of these considerations, 1-octanol, toluene and cyclohexane (with polarity indices of 3.4, 2.4 and 0.2, respectively) were investigated as extraction solvents. The results (Fig. S1) indicated that cyclohexane provided the highest extraction efficiency for most of the analytes. Based on the principle "like-dissolves-like", cyclohexane, which is the most non-polar of the three solvents, would have higher affinity for the PAHs. Therefore, cyclohexane was selected as the most suitable extraction solvent.

3.2.2. Solvent-coating mode and time

The coating of the cyclohexane onto the etched wire was investigated by examining two different modes (dynamic and static), and the influence of immersion (coating) duration in the cyclohexane. Sonication (set at maximum pulse swept power of 70 W) was applied in the dynamic mode of solvent coating, whereas in the static mode, no sonication was applied. By comparing the peak areas of fluoranthene, as a representative example of the PAHs, the results (Fig. S2) indicated that static coating achieved better extraction results than the dynamic mode. It is speculated that the high frequency ultrasonic vibration possibly resulted in the dislodgment of the cyclohexane from the etched plunger wire, thereby leading to lower peak areas obtained as compared to the static coating mode. (The peak area of fluoranthene obtained under 10 min of dynamic solvent coating was higher than the areas obtained for the cases of both 2 and 5 min of coating, but poorer repeatability was observed). For the static coating mode, the peak areas increased when the coating time was increased from 2 min to 5 min. The extraction mechanism possibly comprised both SPME and LPME [21] (see also Section 3.1 above), indicating that the solvent-coated etched wire was associated with a higher extraction efficiency for the PAHs. With a 5-min static coating time, the extraction solvent capacity was increased substantially (Fig. S2), compared to the case of a 2-min static coating time. However, the extraction efficiency was much reduced for the situation when the static coating time was increased to 10 min. This was an interesting result; it was possible that the SPME component might have been significantly inhibited due to the thickness of the solvent coating, resulting in lower overall extraction. Therefore, 5 min of static coating duration was considered most favourable.

3.2.3. Stirring speed

During LPME, the stirring of the sample facilitates the mass transfer of analytes into the organic solvent resulting in reduction of the time needed to attain equilibrium [27]. The effect of stirring speeds ranging from 200 to 500 rpm was investigated. As shown in Fig. S3, it was observed that the peak areas of the lower molecular weight PAHs (ACE, ACN, FLU and PHE) increased when the stirring speed was raised to 300 rpm, whereas the peak areas of the higher molecular weight PAHs (ANT, FLT, PYR, BEN and CHR) were enhanced when the stirring speed was increased to 400 rpm. All the peak areas decreased subsequently when the stirring speed was raised to 500 rpm. The latter observation might have been due to the loss of the organic solvent and analytes

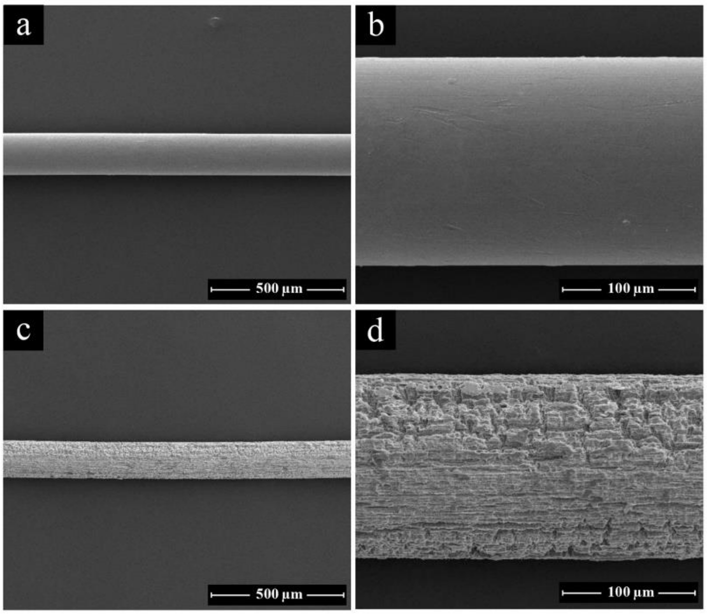

Fig. 2. Scanning electron micrographs of plunger wire before (a = 100 ×; b = 500 ×), and after etching (c = 100 ×; d = 500 ×).

from the wire at the higher stirring speed [14,28]. Therefore, 300 rpm was selected as the most favourable stirring rate for subsequent experiments. This stirring speed was chosen despite the lower peak areas obtained for the higher molecular weight PAHs as a compromise in regard of the stability of the solvent coating. Moreover, better repeatabilities were obtained at 300 rpm than at 400 rpm for the higher molecular weight PAHs.

3.2.4. Extraction time

LPME is an equilibrium-based technique that requires a specific extraction duration for the optimal partitioning of the analytes from the aqueous sample to the organic solvent [28]. In order to determine this effect, extraction times of between 5 and 20 min were examined. The results (Fig. S4) indicated that the peak areas of the PAHs increased when the extraction time was increased to 10 min, and decreased after extraction time was further increased to 20 min. These suggested that equilibrium was reached at ca. 10 min. The decrease in extraction efficiencies after 10 min might be attributed to the loss or dissolution of the cyclohexane at the longer extraction time [29]. Therefore, 10 min was selected as the most advantageous extraction time.

3.2.5. Salt addition

The salting-out effect was investigated this may reduce the solubilities of the analytes, shifting the equilibrium towards the organic

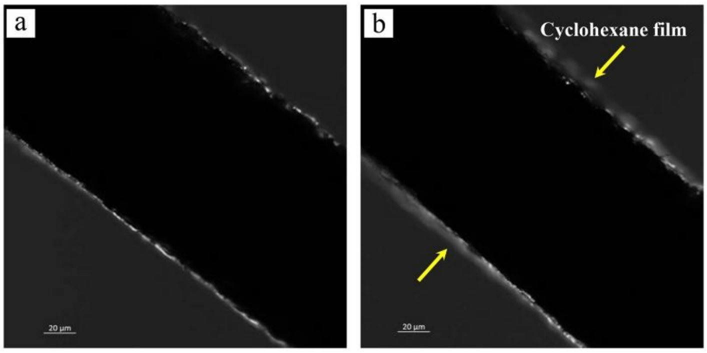

Fig. 3. Photographs of the etched wire, taken under an objective 10 × (a) before, and (b) after solvent immersion and coating. The arrows in (b) show the cyclohexane film.

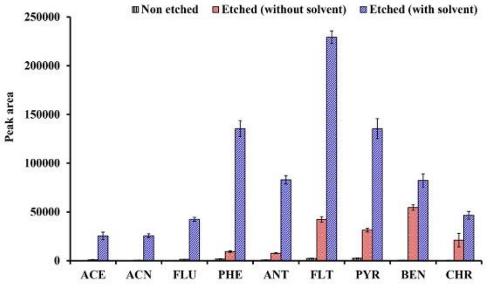

Fig. 4. The comparison of non-etched, etched wire, without and with solvent (cyclohexane) for PIN-LPME of PAHs.

solvent. However, addition of too much salt can increase the viscosity and density of the sample solution and negatively affect the kinetics of the extraction process and, accordingly, the extraction efficiency [16,30]. The influence of salt addition was investigated by the addition of NaCl from 0% to 10% (w/v). The results (Fig. S5) indicated that the peak areas increased slightly for four PAHs (ANT, FLT, PYR and BEN) when the salt concentration was increased to 2% (w/v). The peak areas of all PAHs decreased as more salt was added. Moreover, the repeatability of the analytical results at 2% (w/v) salt concentration was inferior to when no salt was added. This indicated that the addition of NaCl did not improve the extraction efficiency appreciably.

3.3. Analytical performance

Under the optimal conditions, the analytical performance of the developed method was evaluated for the extraction of PAHs. The linearity, limits of detection (LODs), and limits of quantification (LOQs), repeatability, reproducibility and enrichment factors (EFs) are summarized in Table S2. The developed method showed good linearity with the coefficients of determination (R^2) of ≥ 0.9915 for all of the PAHs studied. The LODs, calculated based on a signal-to-noise (S/N) ratio of 3, ranged from 0.006 to 0.058 $\mu g\,L^{-1}$. The LOQs, calculated based on a signal-to-noise (S/N) ratio of 10, ranged from 0.023 to 0.281 $\mu g\,L^{-1}$. The relative standard deviations (RSDs) ranged from 4.4% to 9.7% for five consecutive runs using a single wire, and the RSDs of wire-to-wire reproducibility of three different wires ranged from 4.2% to 12.7%, which were satisfactory in both cases as recommended by the Association of Official Analytical Chemists (AOAC) (less than 21% at a spiked concentration of 10 $\mu g\,L^{-1}$ [31]). The developed method achieved EFs ranging from 70 to 349.

To further demonstrate the advantages of the developed method, its analytical performance was compared with other reported works which considered the microextraction of PAHs in water samples, as summarized in Table 1. The EFs of the present method were higher than those determined by headspace solvent extraction (HSME)-GC [32] and headspace (HS)-SDME-HPLC [33]. The LODs of this work were lower than SPME-GC-MS methods [34,35] and comparable with HF-LPME-GC-MS [14] and agarose (AG)-LPME-GC-MS [27]. However, the HF-LPME and AG-LPME approaches required longer extraction times. Most importantly, the use of the present etching method did not compromise the results as compared to the application of hydrofluoric acid [21,24], which hitherto has been more widely used. This shows that the $FeCl_3$-HCl-etched plunger wire represented a good, viable relatively more environmentally benign alternative to that etched by hydrofluoric acid, for PIN-LPME applications.

3.4. Genuine sample analysis

The developed PIN-LPME-GC-MS method was applied for the determination of PAHs in tap water, river water and drain water samples. The results are shown in Table 2. PYR and BEN were detected in tap water at concentrations lower than their LOQs, and CHR was detected in river and drain water samples at the concentration of 0.47 ± 0.06 and 0.09 ± 0.04 $\mu g\,L^{-1}$, respectively. To evaluate the accuracy of the developed method, the water samples were spiked with PAH standards at two different concentrations (0.5 and 5.0 $\mu g\,L^{-1}$), and then processed with PIN-LPME. Satisfactory relative recoveries were obtained in the range of 85.8–98.3% for tap water, 88.1–93.1% for river water and 84.3–101.9% for drain water (the AOAC recommends recoveries of between 60% and 115% at the spiked concentration 10 $\mu g\,L^{-1}$ as satisfactory) [31], with %RSDs of < 9.5%. These values also indicated that the method can deal with the matrix effects presented by the respective genuine environmental samples. Fig. 5 shows a typical chromatogram obtained after the PIN-LPME-GC-MS analysis of a spiked (final concentration of 5.0 $\mu g\,L^{-1}$ of each PAH) river water sample. The results of the present work demonstrated that the developed method could be applied to the analysis of trace PAHs in various environmental water samples.

4. Conclusions

A stainless steel plunger wire was etched with aqueous $FeCl_3$-HCl solution. The etching procedure was a simple, fast and one-step

Table 1
Comparison of the developed method with other methods for the determination of PAHs.

Extraction method[a]	Analytical technique	Extractant	No. of PAHs[b]	Extraction time (min)	LOD ($\mu g\,L^{-1}$)	Relative recovery[c](%)	EF	Ref.
HSME	GC-FID	1-Butanol	6	12	4–41	–	9–56	[32]
HS-SDME	HPLC-FLD	β-Cyclodextrin	4	10	0.004–0.247	94–111	18–53	[33]
HF-LPME	GC-MS	Toluene	4	15	0.005–0.011	78–110	–	[14]
AG-LPME	GC-MS	Agarose gel	4	50	0.009–0.014	94–108	89–117	[27]
SPME	GC-MS	Polydimethylsiloxane	9	60	0.015–0.046	76–99	–	[34]
SPME	GC-MS	Ethoxylated nonylphenol-modified stainless steel wire	7	25	0.01–0.05	79–104	–	[35]
SPME	GC-FID	Hydrofluoric acid-etched stainless steel wire (no solvent)	5	30	0.26–0.63	85–103	2541–3981	[24]
PIN-LPME	GC-MS	Toluene	10	10	0.003–0.136	70–106	192–385	[21]
PIN-LPME	GC-MS	Cyclohexane	9	10	0.006–0.058	84–102	70–349	This work

[a] HSME, headspace solvent microextraction; HS-SDME, headspace single-drop microextraction; HF, hollow fiber; AG, agarose gel; SPME, solid-phase microextraction. FID, flame-ionization detection; HPLC, high-performance liquid chromatography; FLD, fluorescence detection.

[b] Number of PAHs considered in the respective studies.

[c] Relative recovery is defined as the ratio of the peak area of an analyte in an extract of spiked genuine sample to that of spiked ultrapure water.

Table 2
Results of PIN-LPME-GC-MS analysis of PAHs in genuine water samples.

Sample	Analyte	Non-spiked	0.5 µg L^{-1} spiking level		5.0 µg L^{-1} Spiking level	
		Concentration (µg L^{-1})	Relative recovery (%)	RSD (%) (n = 3)	Relative recovery (%)	RSD (%) (n = 3)
Tap water	ACE	n.d.[a]	85.8	5.4	91.6	5.5
	ACN	n.d.	89.9	4.3	86.3	1.9
	FLU	n.d.	98.3	6.5	98.2	6.3
	PHE	n.d.	89.5	3.2	90.0	6.0
	ANT	n.d.	87.8	3.2	89.7	1.0
	FLT	n.d.	86.1	2.4	93.6	5.6
	PYR	< LOQ	96.1	3.1	94.6	3.5
	BEN	< LOQ	87.6	9.0	90.8	6.5
	CHR	n.d.	90.9	6.3	97.5	1.9
River water	ACE	n.d.	89.3	2.6	92.5	4.8
	ACN	n.d.	89.5	7.6	93.1	5.8
	FLU	n.d.	89.9	8.9	91.9	4.3
	PHE	n.d.	86.9	2.5	91.8	6.1
	ANT	n.d.	91.6	6.2	92.6	2.2
	FLT	n.d.	92.6	6.1	91.1	8.7
	PYR	n.d.	91.8	3.9	90.1	2.5
	BEN	n.d.	92.6	5.8	92.7	2.9
	CHR	0.47 ± 0.06	88.1	9.3	91.1	6.3
Drain water	ACE	n.d.	88.6	5.4	84.3	4.2
	ACN	n.d.	87.3	7.4	88.0	3.5
	FLU	n.d.	86.6	7.0	93.2	7.3
	PHE	n.d.	89.6	3.9	93.2	5.0
	ANT	n.d.	89.5	9.5	89.8	1.2
	FLT	n.d.	92.4	6.7	101.9	1.5
	PYR	n.d.	92.7	6.8	97.0	1.2
	BEN	n.d.	88.0	6.5	92.4	6.2
	CHR	0.09 ± 0.04	89.6	1.5	95.6	4.9

[a] n.d. = not detected.

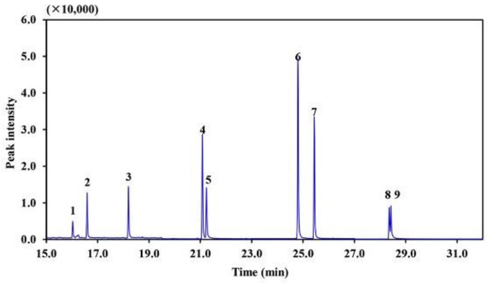

Fig. 5. Chromatogram of spiked river water sample (5.0 µg L^{-1} of each PAH) after PIN-LPME. Extraction conditions: NaCl, 0%; extraction time, 10 min; stirring speed, 300 rpm. Peaks: (1) ACE; (2) ACN; (3) FLU; (4) PHE; (5) ANT; (6) FLT; (7) PYR; (8) BEN; (9) CHR.

approach, similar to that of hydrofluoric acid etching. The conveniently etched plunger wires were successfully used as solvent holders in the plunger-in-needle-liquid-phase microextraction (PIN-LPME)-gas chromatography-mass spectrometric analysis of PAHs in environmental water samples. Good analytical performance was obtained, which includes good linearity (R^2 ≥0.9915), low limits of detection (between 0.006 and 0.058 µg L^{-1}), good repeatabilities (%RSD < 9.7%) and reproducibilities (%RSD < 12.7%). Satisfactory relative recoveries of between 84.3% and 101.9% were obtained when the developed method was applied to the analysis of PAHs in spiked tap water, river water and drain water. The method demonstrated good extraction capabilities of the $FeCl_3$-HCl-etched stainless steel plunger wire and its potential to be used in PIN-LPME, and other, applications. Use of $FeCl_3$-HCl solution as etchant serves as an environmentally friendlier approach than that of the more commonly employed but toxic hydrofluoric acid.

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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.2019.01.046.

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Supporting Information

Environmentally friendly etching of stainless steel wire for plunger-in-needle liquid-phase microextraction of polycyclic aromatic hydrocarbons

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Table S1. Information on MS analysis of PAHs.

PAHs	Molecular weight	Quantification ions (m/z)	Identification ions (m/z)	Retention time (min)
Acenaphthylene (ACE)	152	152	151, 153	16.1
Acenaphthene (ACN)	154	153	152, 154	16.7
Fluorene (FLU)	166	166	82, 165	18.2
Phenanthrene (PHE)	178	178	176, 179	21.1
Anthracene (ANT)	178	178	176, 179	21.3
Fluoranthene (FLT)	202	202	200, 203	24.8
Pyrene (PYR)	202	201	101, 202	25.4
Benz[*a*]anthracene (BEN)	228	228	226, 229	28.3
Chrysene (CHR)	228	228	226, 229	28.5

Table S2 Analytical performances of the developed PIN-LPME for the extraction of PAHs.

PAHs	**Linear range**	**R^2**	**LOD (μg L^{-1})**	**LOQ (μg L^{-1})**	**RSD[a] (wire) (%, n=5)**	**RSD[b] (wire to wire) (%, n=3)**	**EF[b]**
ACE	0.01-50	0.9946	0.006	0.023	6.4	11.8	70
ACN	0.01-50	0.9966	0.012	0.044	6.0	6.9	128
FLU	0.02-50	0.9915	0.034	0.143	9.0	12.7	168
PHE	0.01-50	0.9964	0.014	0.068	4.6	11.6	304
ANT	0.01-50	0.9970	0.030	0.139	9.7	9.4	315
FLT	0.01-50	0.9982	0.032	0.156	4.5	8.1	349
PYR	0.01-50	0.9987	0.020	0.097	6.5	8.1	301
BEN	0.01-50	0.9948	0.058	0.281	4.4	4.2	174
CHR	0.01-20	0.9921	0.021	0.071	6.6	8.0	97

[a] Calculated from a spiked sample at 10 µg L^{-1} of each PAH.

[b] EF is defined as the chromatographic peak area response of PAH obtained after extraction from a 10-mL spiked sample at 10 µg L^{-1} of each PAH to that with direct injection of 1 µL of standard solution containing 1.0 mg L^{-1} of each PAH.

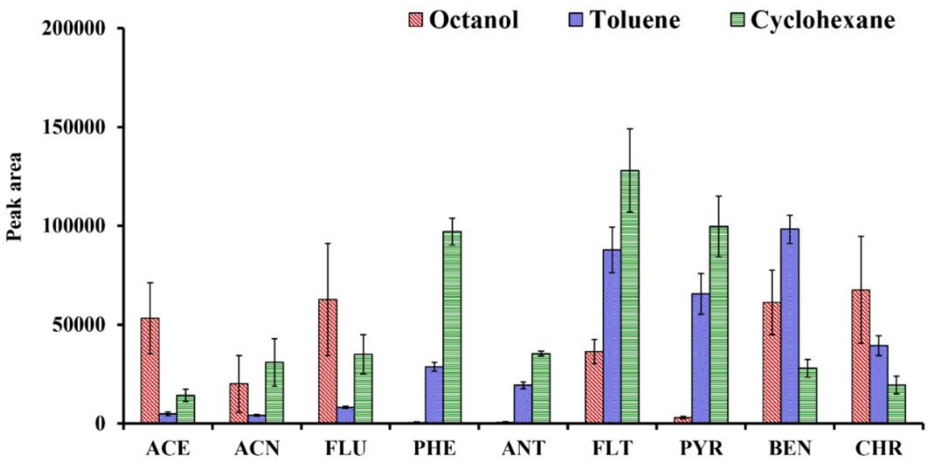

Fig. S1. Effect of different extraction solvents on PIN-LPME efficiency (sample spiked at 10 µg L^{-1} of each analyte). Extraction conditions: Sonication time during solvent coating, 2 min; NaCl, 0%; extraction time, 10 min.

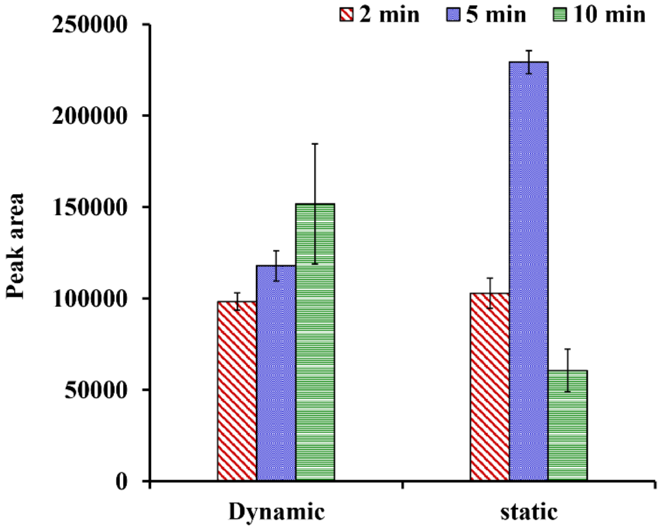

Fig. S2. Effect of solvent coating mode (at sonication pulse swept power of 70W) and coating time on PIN-LPME efficiency for fluoranthene (spiked at a final concentration of 10 µg L^{-1}) as representative analyte. Extraction conditions: NaCl, 0%; extraction time, 10 min; stirring speed, 300 rpm

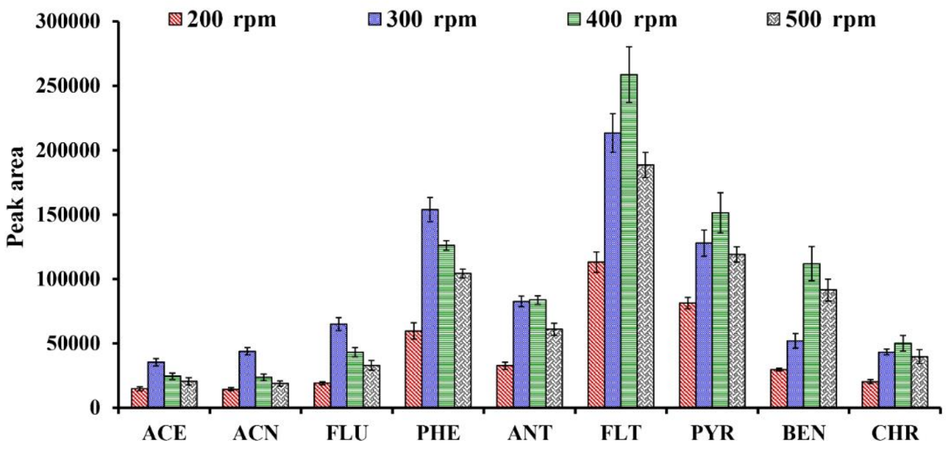

Fig. S3. Effect of stirring rate on PIN-LPME efficiency for PAHs (spiked at 10 µg L^{-1} of each analyte). Extraction conditions: NaCl, 0%; extraction time, 10 min.

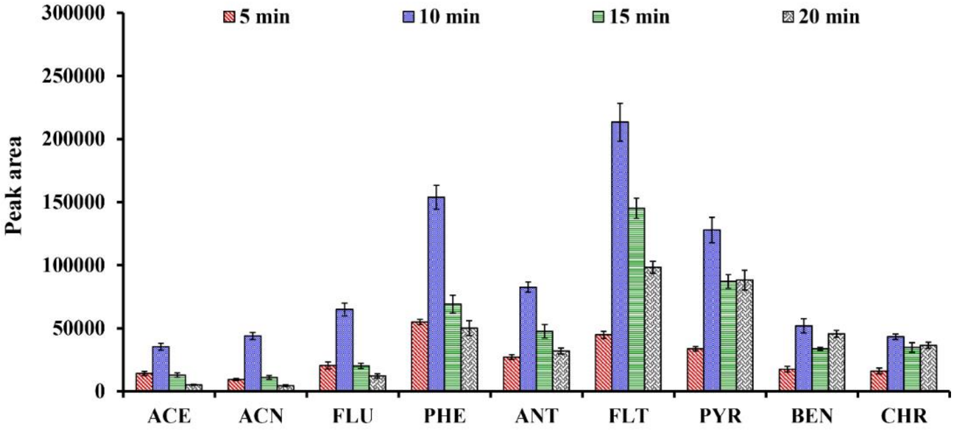

Fig. S4. Effect of extraction time on PIN-LPME efficiency for PAHs (spiked at 10 µg L^{-1} of each analyte). Extraction conditions: NaCl, 0%; stirring speed, 300 rpm.

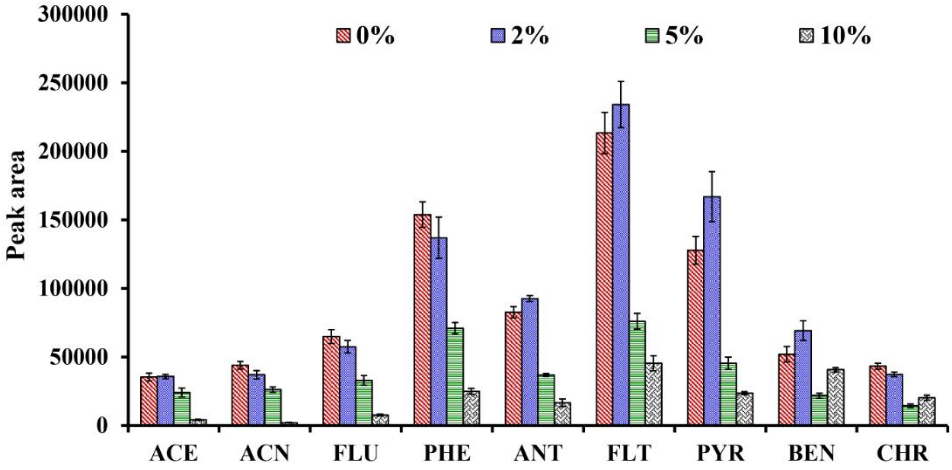

Fig. S5. Effect of salt addition effect on PIN-LPME efficiency (sample spiked at 10 µg L^{-1} of each analyte). Extraction conditions: Extraction time, 10 min; stirring speed, 300 rpm.

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List of Publication

Nurrokhimah, M., **Nurerk, P.**, Kanatharana, P., Bunkoed, O., A nanosorbent consisting of a magnetic molecularly imprinted polymer and graphene oxide for multi-residue analysis of cephalosporins *Microchimica Acta* (2019) 186: 822. https://doi.org/10.1007/s00604-019-3985-5

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Nurerk, P., Kanatharana, P., Bunkoed, O., A novel magnetic solid phase extraction sorbent for the determination of polycyclic aromatic hydrocarbons in water samples, Pure and Applied Chemistry International Conference 2016, 9-11 February 2016, Bangkok International Trade & Exhibition Centre, Bangkok, Thailand (Best Poster Presentation Award).

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