

# รายงานวิจัยฉบับสมบูรณ์

พัฒนาตัวดูดซับใหม่ Fe<sub>3</sub>O<sub>4</sub>/CNTs/Alginate สำหรับเพิ่มความเข้มข้น  
โพลีไซคลิกอะโรมาติกไฮโดรคาร์บอน

Development of a novel Fe<sub>3</sub>O<sub>4</sub>/CNTs/Alginate sorbent for the  
preconcentration of polycyclic aromatic hydrocarbons

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โครงการวิจัยนี้ได้รับทุนสนับสนุนจากเงินรายได้มหาวิทยาลัยสงขลานครินทร์  
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## กิตติกรรมประกาศ

โครงการวิจัยนี้ได้รับสนับสนุนจากทุนอุดหนุนจากคุณครูณาจารย์ มหาวิทยาลัยสงขลานครินทร์ สัญญาเลขที่ SCI560568SS ผู้วิจัยขอขอบคุณนักวิจัยที่ปรึกษา รองศาสตราจารย์ ดร. เจริญพิชญ์ คณาธารณา สถานวิจัย การวิเคราะห์สารปริมาณน้อยและไบโอเซนเซอร์ ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยสงขลานครินทร์ สำหรับสถานที่ทำวิจัยและเครื่องมือวิจัยที่เกี่ยวข้อง

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## บทคัดย่อ

พัฒนาตัวดูดซับคอมโพสิต Magnetic/multiwall carbon nanotube/alginate สำหรับสกัดและเพิ่มความเข้มข้นสารโพลีไซคลิกอะโรมาติกไฮโดรคาร์บอนในน้ำ ตัวดูดซับที่พัฒนาขึ้นเตรียมได้จากการกักอนุภาคแม่เหล็กขนาดนาโนร่วมกับท่อนาโนคาร์บอนผนังหลายชั้นในเม็ดแอลจิเนต (alginate bead) โดยท่อนาโนคาร์บอนผนังหลายชั้นสามารถดูดซับสารโพลีไซคลิกอะโรมาติกไฮโดรคาร์บอนได้ด้วยการเกิดอันตรกิริยาแบบ  $\pi$ - $\pi$  คุณสมบัติไฮโดรฟิลิกของแคลเซียมแอลจิเนตช่วยให้ตัวดูดซับกระจายในตัวอย่างน้ำได้ดีและคุณสมบัติของอนุภาคแม่เหล็กขนาดนาโนช่วยให้การแยกตัวดูดซับออกจากน้ำตัวอย่างทำได้ง่ายและรวดเร็ว เพื่อให้ได้ประสิทธิภาพของการสกัดสูงสุดได้มีการศึกษาปัจจัยต่างๆ ที่มีผลต่อการสกัด ภายใต้สภาวะที่เหมาะสมได้ช่วงความเป็นเส้นตรงของการตรวจวัด เบนโซ เอ แอนทราซีน (BaA) และ เบนโซ เอ ไพรีน (BaP) ในช่วงความเข้มข้น 5 นาโนกรัมต่อลิตรถึง 50 ไมโครกรัมต่อลิตรและสารเบนโซ บี ฟลูออเรนทีน (BbF) ให้ช่วงความเป็นเส้นตรง 10 นาโนกรัมต่อลิตรถึง 50 ไมโครกรัมต่อลิตร มีขีดจำกัดการตรวจวัด 5 นาโนกรัมต่อลิตรสำหรับสาร BaA และ BaP 10 นาโนกรัมต่อลิตรสำหรับสาร BbF มีร้อยละการได้กลับคืนอยู่ในช่วง 92 ถึง 98 เปอร์เซ็นต์ ได้มีการประยุกต์ใช้ตัวดูดซับที่พัฒนาขึ้นสำหรับตรวจวิเคราะห์สารโพลีไซคลิกอะโรมาติกไฮโดรคาร์บอนในน้ำจากแหล่งต่างๆ โดยตัวดูดซับที่พัฒนาขึ้นมีข้อดีคือ สามารถเตรียมได้ง่าย ใช้งานได้สะดวก มีราคาถูก และเป็นมิตรกับสิ่งแวดล้อม

## Abstract

A magnetic/multiwalled carbon nanotube/Alginate ( $\text{Fe}_3\text{O}_4/\text{MWCNTs}/\text{Alginate}$ ) composite sorbent was developed for the extraction, preconcentration and determination of trace polycyclic aromatic hydrocarbons in water samples. The developed composite sorbent was prepared by caging  $\text{Fe}_3\text{O}_4$  magnetic nanoparticle and MWCNTs into calcium alginate beads. The large surface area of the MWCNTs and their  $\pi$ - $\pi$  electrostatic interactions with the aromatic rings of PAHs facilitated strong adsorption. The hydrophilicity of the calcium alginate cage enhanced the dispersibility of the sorbent in the water sample and the  $\text{Fe}_3\text{O}_4$  facilitated a simple and fast separation of the sorbent from the water samples. Various parameters that could affect the extraction efficiency were optimized. Under optimal conditions, the linearity of the PAHs were in the range of  $5 \text{ ng L}^{-1}$  to  $50 \text{ } \mu\text{g L}^{-1}$  for benzo[a]anthracene [BaA] and benzo[a]pyrene [BaP] and  $10 \text{ ng L}^{-1}$  to  $50 \text{ } \mu\text{g L}^{-1}$  for benzo[b]fluoranthene [BbF]. The limit of detection was  $5 \text{ ng L}^{-1}$  for BaA, BaP and  $10 \text{ ng L}^{-1}$  for BbF. A satisfactory recovery from  $92.0 \pm 2.1$  to  $97.7 \pm 2.5$  % with a relative standard deviations of less than 5% was achieved. The developed  $\text{Fe}_3\text{O}_4/\text{MWCNTs}/\text{Alginate}$  composite sorbent was successfully applied for the extraction of PAHs in the water samples. The proposed method has several advantages such as its ease of preparation, a convenient and fast extraction procedure, is cost-effective, environmentally friendly and with high extraction efficiency.

## บทสรุปผู้บริหาร (Executive Summary)

### บทนำ

ปัจจุบันการปนเปื้อนของสารมลพิษในสิ่งแวดล้อมมีแนวโน้มเพิ่มมากขึ้น โดยเฉพาะสารโพลีไซคลิกอะโรมาติก ไฮโดรคาร์บอน (Polycyclic Aromatic Hydrocarbons; PAHs) ที่เกิดขึ้นจากการเผาไหม้ที่ไม่สมบูรณ์ของสารอินทรีย์รวมทั้งจากท่อไอเสียรถยนต์ ดังนั้นจึงทำให้มีการตกค้างอยู่ในสิ่งแวดล้อม ทั้งในน้ำ ดิน และอากาศ หากมนุษย์ได้รับสาร PAHs เข้าสู่ร่างกายจะทำให้เกิดความเป็นพิษต่อระบบต่างๆ ของร่างกายได้ เช่น ก่อให้เกิดมะเร็งในอวัยวะหลายชนิด

จากความเป็นพิษดังกล่าวและเพื่อความปลอดภัยของมนุษย์ องค์การพิทักษ์สิ่งแวดล้อมของสหรัฐอเมริกาได้จัดให้สารในกลุ่ม PAHs จำนวน 16 ชนิดอยู่ในกลุ่มของสารอันตรายและกำหนดค่าระดับการปนเปื้อนสูงสุด (Maximum contaminant levels; MCL) ของ PAHs ในน้ำไม่เกิน 200 นาโนกรัมต่อลิตร ดังนั้นการตรวจวัด PAHs ในสิ่งแวดล้อมจึงมีความจำเป็น โดยในการตรวจวิเคราะห์นั้นประกอบด้วย 2 ส่วนที่สำคัญ คือ ขั้นตอนการเตรียมตัวอย่างและขั้นตอนการวิเคราะห์ โดยมีขั้นตอนการเตรียมตัวอย่างก่อนการวิเคราะห์เพื่อเพิ่มความเข้มข้นซึ่งจะทำให้สามารถตรวจวัด PAHs ที่มีปริมาณน้อยได้และเป็นการกำจัดตัวรบกวนอื่นๆ ที่มีอยู่ในตัวอย่างซึ่งอาจจะส่งผลกระทบต่อผลการวิเคราะห์ได้ โดยเทคนิคการเตรียมตัวอย่างที่นิยมใช้สำหรับวิเคราะห์สาร PAHs คือการสกัดโดยใช้ตัวดูดซับของแข็งชนิด C18 ซึ่งบรรจุอยู่ในคาร์ทริดจ์ แต่ตัวดูดซับของแข็งดังกล่าวยังมีข้อด้อย คือ มีราคาแพงและเกิดการอุดตันได้ง่ายทำให้ไม่สามารถนำกลับมาใช้ซ้ำได้ ดังนั้นงานวิจัยนี้จึงสนใจพัฒนาตัวดูดซับชนิดใหม่ที่มีลักษณะเป็นเม็ดของแคลเซียมแอลจีเนตที่มีตัวดูดซับเป็นท่อคาร์บอนแบบผนังหลายชั้น (MCNTs) และอนุภาคนาโนแม่เหล็ก ( $Fe_3O_4$ ) อยู่ภายใน ซึ่งสามารถเตรียมได้ง่าย ใช้งานได้สะดวกและสามารถนำกลับมาใช้ซ้ำได้ โดยสารที่ต้องการวิเคราะห์คือ PAHs ซึ่งมีโครงสร้างประกอบด้วยวงแหวนอะโรมาติกที่สามารถดูดซับกับท่อคาร์บอนนาโนได้โดยเกิดอันตรกิริยาแบบ  $\pi$ - $\pi$  นอกจากนี้เนื่องจากท่อคาร์บอนนาโนมีลักษณะเป็นแผ่นแกรไฟต์ม้วนเป็นท่อซึ่งมีพื้นผิวสัมผัสมากทำให้มีประสิทธิภาพในการดูดซับ PAHs ได้ดี สามารถนำมาใช้เป็นตัวดูดซับในการสกัด PAHs ในน้ำแทนการใช้ตัวดูดซับทางการค้าที่มีราคาแพงได้

### วัตถุประสงค์

เพื่อพัฒนาตัวดูดซับชนิดใหม่ที่มีราคาถูก เตรียมได้ง่าย ใช้งานได้สะดวกสำหรับตรวจวัด PAHs ในน้ำ

## สรุป

งานวิจัยนี้เป็นการพัฒนาตัวดูดซับชนิดใหม่สำหรับสกัดและเพิ่มความเข้มข้นของสาร PAHs ในตัวอย่างน้ำร่วมกับการตรวจวิเคราะห์ด้วยเทคนิคโครมาโทกราฟีของเหลวสมรรถนะสูง (HPLC) โดยตัวดูดซับที่พัฒนาขึ้นคือ ตัวดูดซับคอมโพสิทระหว่าง ท่อนาโน คาร์บอนแบบผนังหลายชั้น อนุภาคนาโนแม่เหล็ก และ alginate bead (MWCNTs/Fe<sub>3</sub>O<sub>4</sub>/alginate) เพื่อให้ได้ประสิทธิภาพของการสกัดสูงสุด ใช้เวลาและตัวทำลายน้อย จึงได้หาสภาวะที่เหมาะสมของการสกัด โดยได้สภาวะที่เหมาะสมดังนี้ ความเข้มข้นของท่อนาโน คาร์บอนผนังหลายชั้น 0.05 % (W/V) ความเข้มข้นของแอลจินเนต 2 % (w/v) ปริมาณของตัวดูดซับ 0.2 กรัม เวลาที่ใช้ในการสกัด 10 นาที อัตราการคนของสารตัวอย่าง 1000 รอบต่อนาที เวลาที่ใช้ในการคายการดูดซับ 10 นาที ตัวทำละลายอินทรีย์ที่ใช้ในการคายการดูดซับคือ Acetonitrile : Toluene (1:1) และปริมาณตัวทำละลายที่ใช้ 2 มิลลิลิตร

ภายใต้สภาวะที่เหมาะสมของการสกัดพบว่าช่วงความเป็นเส้นตรงของ BaA และ BaP 0.005 ถึง 50 ไมโครกรัมต่อลิตรและช่วงความเป็นเส้นตรงของ BbF อยู่ในช่วง 0.010 ถึง 50 ไมโครกรัมต่อลิตร ขีดจำกัดการตรวจวัด (LOD) และ ขีดจำกัดการตรวจวัดเชิงปริมาณ (LOQ) ของ BaA และ BaP เท่ากับ 0.005 และ 0.020 ไมโครกรัมต่อลิตร ตามลำดับ และ BbF มีค่า LOD และ LOQ เท่ากับ 0.01 และ 0.04 ไมโครกรัมต่อลิตร

เมื่อเปรียบเทียบประสิทธิภาพในการสกัด PAHs ของตัวดูดซับที่พัฒนาขึ้นกับตัวดูดซับชนิด C18 ที่มีจำหน่ายทางการค้าและพบว่าตัวดูดซับทั้งสองชนิดให้ประสิทธิภาพในการสกัด PAHs ไม่แตกต่างกันอย่างมีนัยสำคัญแต่เมื่อเปรียบเทียบขั้นตอนการสกัดพบว่าวิธีการสกัดที่พัฒนาขึ้นสามารถทำได้ง่ายกว่า และใช้เวลาน้อยกว่า อีกครั้งตัวดูดซับที่พัฒนาขึ้นมีราคาถูก ตัวดูดซับที่พัฒนาขึ้นสามารถนำกลับมาใช้ซ้ำได้อย่างน้อย 10 ครั้ง ซึ่งทำให้สามารถลดค่าใช้จ่ายของการเตรียมตัวอย่างลง โดยได้ประยุกต์ใช้วิธีที่พัฒนาขึ้นตรวจวิเคราะห์การปนเปื้อนของสาร PAHs ในแหล่งน้ำต่างๆ ได้แก่ น้ำก๊อก น้ำจากแหล่งธรรมชาติ และน้ำเสีย โดยพบการปนเปื้อนของสาร PAHs ในน้ำจากแม่น้ำในช่วงความเข้มข้น 0.045 ถึง 0.088 ไมโครกรัมต่อลิตร และพบในน้ำเสียอยู่ในช่วง 0.018 ถึง 0.028 ไมโครกรัมต่อลิตร ความเข้มข้นที่ตรวจพบดังกล่าวต่ำกว่าค่าความเข้มข้นสูงสุดที่ยอมให้มีได้คือ 0.1 ไมโครกรัมต่อลิตร กำหนดโดยองค์กรพิทักษ์สิ่งแวดล้อมแห่งสหรัฐอเมริกา (US-EPA) และจากผลการศึกษาร้อยละการได้กลับคืนจากการเติมสารมาตรฐานในน้ำตัวอย่างที่ความเข้มข้นต่างๆ พบว่าให้ร้อยละการได้กลับคืนอยู่ในช่วง 92 ถึง 98 เปอร์เซ็นต์

## ภาคผนวก



# Extraction of polycyclic aromatic hydrocarbons with a magnetic sorbent composed of alginate, magnetite nanoparticles and multiwalled carbon nanotubes

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**Abstract** The article describes a magnetic composite sorbent for the extraction of traces of polycyclic aromatic hydrocarbons (PAHs) from water samples. The composite was prepared by caging Fe<sub>3</sub>O<sub>4</sub> nanoparticles (NPs) and MWCNTs into calcium alginate beads. The large surface area of the MWCNTs and their  $\pi$ -interactions with the aromatic rings of PAHs obviously facilitate strong adsorption. The hydrophilicity of the calcium alginate cage, in turn, enhances the dispersibility of the sorbent in the water sample. Finally, the use of magnetic NPs facilitates a simple and fast separation of the sorbent. The composite sorbent was successfully applied to the extraction of PAHs from (spiked) water samples. PAHs were quantified by HPLC with fluorescence detection. Under optimized experimental conditions, the calibration plot is linear in the range of 5 to 50  $\mu\text{g L}^{-1}$  for benzo[a]anthracene and benzo[a]pyrene, and 10 to 50  $\mu\text{g L}^{-1}$  for benzo[b]fluoranthene. Other figures of merit include a limit of detection of 5  $\text{ng L}^{-1}$  for benzo[a]anthracene and benzo(a)pyrene, and of 10  $\text{ng L}^{-1}$  for benzo[b]fluoranthene, recoveries ranging from 92.0 to 97.7 %, and relative standard deviations of <5 %. The method has several attractive features including an easily prepared and eco-friendly sorbent, a

convenient and fast extraction procedure, and a high extraction efficiency.

**Keywords** Magnetic nanoparticles · Multiwalled carbon nanotubes · Alginate bead · Polycyclic aromatic hydrocarbons · Benzo[a]anthracene · Benzo[a]pyrene · Benzo[b]fluoranthene

## Introduction

Polycyclic aromatic hydrocarbons are aromatic compounds with two or more fused benzene rings [1]. They are mainly produced by incomplete combustion of organic substances and can be easily spread into the environment via oil refinement, vehicle and industrial emissions and municipal discharges. PAHs have received much attention, due to their potential carcinogenicity and mutagenicity [2]. Thus, the World Health Organization have set maximum permissible concentrations for most of the PAHs in drinking water at 0.2  $\mu\text{g L}^{-1}$  [3]. However since, these compounds are hydrophobic compounds with low water solubility, they usually exist at very low concentrations in water sample. Therefore, an effective extraction and preconcentration method is normally required prior to instrumental analysis.

Various sample preparation methods have been used for the extraction and preconcentration of PAHs, such as solid phase extraction (SPE) [4–7], solid phase microextraction (SPME) [8, 9], stir bar sorptive extraction (SBSE) [10], stir rod sorptive extraction (SRSE) [11] and dispersive liquid-liquid microextraction [12]. Among these methods, SPE is the most widely used due to it providing a high extraction efficiency, for enrichment. However, traditional SPE methods have some drawbacks, such as they are time consuming, expensive and labor intensive. To overcome this problem, magnetic solid

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phase extraction (MSPE) methods have been developed and successfully applied for the extraction of various PAHs [13, 14]. In these methods magnetic adsorbents were dispersed into the sample solution, to provide a fast and efficient approach to adsorb and extract the target analytes. After the analytes were adsorbed, the adsorbent can be simply isolated from the sample solution using an external magnet and the analytes are then eluted from the adsorbent with a suitable organic solvent. To enhance the extraction efficiency, the surfaces of the magnetic particles were functionalized or combined with various materials [15]. For extraction and preconcentration of PAHs, multiwalled carbon nanotubes (MWCNTs) have attracted great attention due to their unique tubular structures and extremely large surface areas that allows them to have effective sorption properties for the benzenoid rings of aromatic molecules [16].

We report a  $\text{Fe}_3\text{O}_4$ /MWCNTs/alginate composite sorbent for the extraction of PAHs in water samples. This sorbent can be rapidly and easily prepared and incorporated into magnetic nanoparticles and MWCNTs into an alginate bead. Benzo[a]anthracene (BaA), benzo[b]fluoranthene (BbF) and benzo[a]pyrene (BaP) were selected as test compounds to investigate the performance of the developed composite sorbent because of their toxicity, mutagenic and carcinogenic potentials and they are also included in the 2007 Priority List of Hazardous Substances.

## Experimental

### Reagents

MWCNTs (purity  $\geq 95\%$ ) with an average diameter of 60–100 nm and a length of 2–5  $\mu\text{m}$  were purchased from Shenzhen Nano-Technologies Port Co., Ltd. (China, <http://www.nanotubes.com.cn>). Calcium chloride dehydrate ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ) was from Ajax Finechem (NSW, Australia, <http://www.ajaxfinechem.com>). Benzo[a]anthracene (BaA; 98 % purity), benzo[a]pyrene (BaP; 99 % purity) and benzo[b]fluoranthene (BbF; 99 % purity) standard solutions were from Restek (USA, <http://www.restek.com>). Acetonitrile was from Merck (Darmstadt, Germany, <http://www.merckgroup.com>).  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  were purchased from Sigma Aldrich (<http://www.sigmaaldrich.com>). Ultrapure water was obtained with a Maxima ultrapure water system to obtain a resistivity of 18.2  $\text{M}\Omega \cdot \text{cm}$ . (ELGA, Buckinghamshire, England). Working standard solutions were prepared by diluting the standard solutions with acetonitrile.

### Instrumentation

The HPLC analytical experiments were performed using a Hewlett–Packard 1100 series HPLC system (Agilent

Technologies, Germany, <http://www.agilent.com>). The analysis of PAHs was operated on a VertiSep<sup>TM</sup> USP C18 column (5  $\mu\text{m}$  particle size, 150  $\times$  4.6 mm I.D.) (Vertical Chromatography Co., Ltd., Thailand, <http://www.vertichrom.com>). The mobile phase was water: acetonitrile (5:95, %v/v) at a flow rate of 1.0  $\text{mL min}^{-1}$ , the column temperature was 30  $^\circ\text{C}$ . The PAHs were detected with a fluorescence detector (FLD) 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.

### Preparation of magnetite nanoparticles, multiwalled carbon nanotubes and alginate composite sorbent

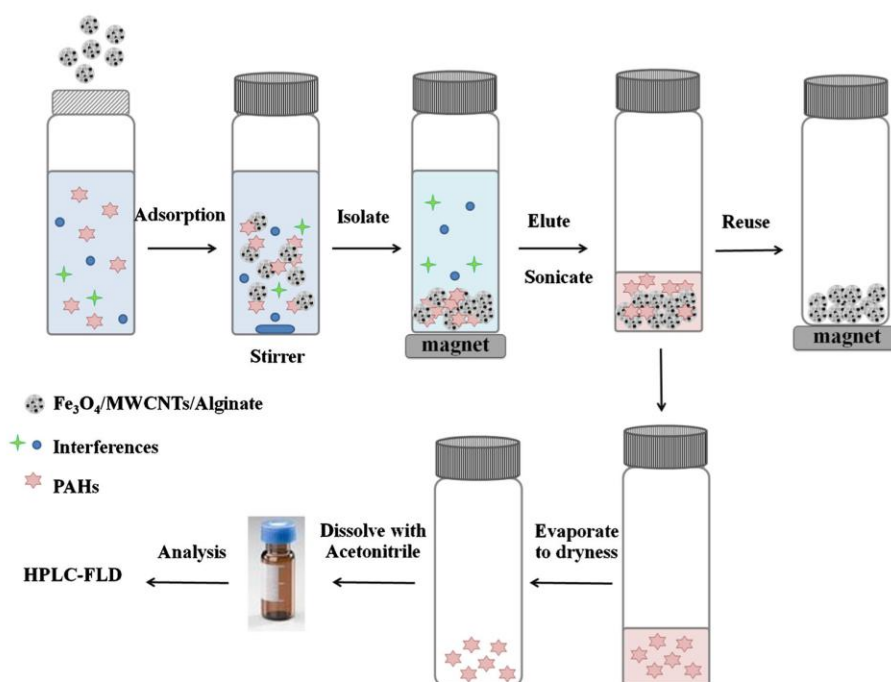
$\text{Fe}_3\text{O}_4$  nanoparticles were prepared following a previously reported procedure by the chemical co-precipitation method [17]. Briefly,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (4.70 g) and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (1.70 g) were dissolved into 80 mL of deionized water contained in a three necked flask and stirred under nitrogen. As the temperature was elevated to 80  $^\circ\text{C}$ , 10 mL of ammonium hydroxide was added dropwise, and the reaction was refluxed for 30 min. The obtained  $\text{Fe}_3\text{O}_4$  nanoparticles were separated from solution by an external magnet and washed with deionized water (200 mL, three times) to remove the unreacted chemicals, then the produced  $\text{Fe}_3\text{O}_4$  was dried in an oven at 40  $^\circ\text{C}$ .

To prepare the  $\text{Fe}_3\text{O}_4$ /MWCNTs/alginate composite sorbent, sodium alginate of 2.0 % w/v was prepared by dissolving it in deionized water, 0.1 g of synthesized  $\text{Fe}_3\text{O}_4$  and 0.05 g of MWCNTs was then dispersed into 100 mL of the alginate solution by ultrasonication for 1 h to obtain a homogeneous colloidal suspension. The mixture was dropped into a calcium chloride solution (5.0 % w/v) while being stirred using a 6.0 mL syringe through a needle. When the mixture solution drops came in contact with the  $\text{CaCl}_2$  solution, Ca-alginate gel beads were formed (diameter  $1.2 \pm 0.1$  mm). These gel beads were then aged in  $\text{CaCl}_2$  solution for 3 h to complete bead formation and were separated from the solution by an external magnet and rinsed with deionized water three times to remove free calcium chloride from the bead surfaces.

### Procedure for extracting PAHs from water samples

The whole procedure is shown in Fig. 1. Firstly, 0.20 g of the  $\text{Fe}_3\text{O}_4$ /MWCNTs/alginate composite sorbents were dispersed into 10.0 mL of spiked water. The mixture was stirred to allow the analytes to diffuse through the sorbent and to be adsorbed onto the MWCNTs over a suitable period of extraction time. Subsequently, an external magnet (4.0  $\times$  5.0  $\times$  1.0 cm) was deposited at the bottom of the vial and the sorbents were isolated from solution. The supernatant water was decanted and the adsorbed analytes were desorbed from the sorbents by ultrasonication with 4.0 mL of a mixture of acetonitrile:

**Fig. 1** Schematic diagram of the extraction procedure using Fe<sub>3</sub>O<sub>4</sub>/MWCNTs/alginate composite sorbents and analysis by HPLC with fluorescence detection



toluene (1:1 v/v). The eluents were then evaporated at 60 °C, reconstituted with 0.5 mL of acetonitrile and filtered through a PTFE filter (0.45 μm). Twenty microlitres of this solution was then injected into the HPLC system for analysis. The Fe<sub>3</sub>O<sub>4</sub>/MWCNTs/alginate sorbent could be reused after washing with the 2.0 mL acetonitrile and water, respectively.

### Water samples

To demonstrate the applicability of the developed method, Fe<sub>3</sub>O<sub>4</sub>/MWCNTs/alginate composite sorbent were applied for the extraction and preconcentration of PAHs in real water samples i.e. tap water, river water and wastewater. Tap water was collected from laboratory, river water was collected from two rivers in Hat Yai city, Songkhla, Thailand and wastewater samples were collected from a wastewater pond from Songklanagarind Hospital and a household effluent from Hat Yai City, Songkhla, Thailand. All water samples were filtered through 0.45 μm membrane to remove suspended particles and stored in brown glass bottles at 4 °C.

## Results and discussion

### System performance

The systems performance was determined under the optimal HPLC–FLD conditions. The method showed a wide linearity from 0.1 μg to 1.0 mg L<sup>-1</sup> for BaA and BaP,

0.2 μg to 2.0 mg L<sup>-1</sup> for BbF with a coefficient of determination ( $R^2$ ) greater than 0.999. The limits of detection were 0.1 μg L<sup>-1</sup> for BaA and BaP, and 0.2 μg L<sup>-1</sup> for BbF, respectively. A good peak separation of the three PAHs was obtained within 8 min.

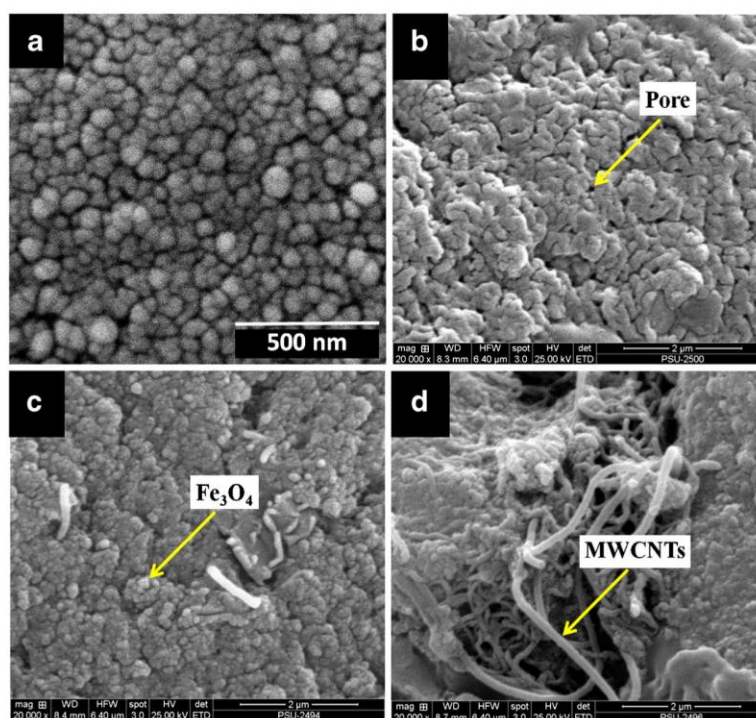
### Choice of materials

We describe the use of Fe<sub>3</sub>O<sub>4</sub>/MWCNTs/alginate composite sorbent for the extraction of PAHs in water samples and determined by HPLC with fluorescence detection. MWCNTs have a large surface area and their  $\pi$ -interaction with aromatic rings of PAHs which can enhance the extraction efficiency. The use of magnetic NPs facilitate a simple and fast separation of the sorbent from water samples, which help to reduce a total analysis time. These materials were then composited in calcium alginate cage which can enhance the dispersibility of the sorbent in water sample lead to enhanced extraction efficiency and also reduced extraction time.

### Preparation of magnetite nanoparticles, multiwalled carbon nanotubes and alginate composite sorbent

The characteristics of Fe<sub>3</sub>O<sub>4</sub> nanoparticles and Fe<sub>3</sub>O<sub>4</sub>/MWCNTs/alginate composite sorbent were investigated scanning electron microscopy (SEM) technique. Figure 2a shows a SEM image of Fe<sub>3</sub>O<sub>4</sub> nanoparticle, the size distribution was 72±12 nm ( $n=100$ ). Figure 2b shows the morphology of the surface of the dried alginate beads, a porous structure was

**Fig. 2** Scanning electron micrographs of  $\text{Fe}_3\text{O}_4$  nanoparticles (a), the alginate bead surface (b),  $\text{Fe}_3\text{O}_4$ /MWCNTs/alginate composite surface (c) and inside the  $\text{Fe}_3\text{O}_4$ /MWCNTs/alginate composite (d)



observed so the analyte could diffuse from the surface. Figure 2c shows that the surface of the  $\text{Fe}_3\text{O}_4$ /MWCNTs/alginate bead was rough and  $\text{Fe}_3\text{O}_4$  particles were well distributed throughout the bead Fig. 2d. Shows that MWCNTs were incorporated inside the beads and the analyte can adsorbed when diffuse through the pores of the alginate beads.

#### Optimization of extraction conditions

Parameters that affected the extraction efficiency of  $\text{Fe}_3\text{O}_4$ /MWCNTs/alginate composite sorbent were optimized to obtain the best extraction efficiency, the shortest analysis time and the use of the smallest amount of organic solvent i.e. the amount of MWCNTs, the optimum alginate concentration, amount of sorbent, extraction time, stirring speed, desorption solvent and its volume, and time required for desorption. The optimization experiments were conducted using a spiked water sample containing  $1.0 \mu\text{g L}^{-1}$  of each of the PAH analytes.

#### Effect of the amount of the multiwalled carbon nanotubes

The effect of the amount of MWCNTs on the extraction efficiency was investigated, different amounts of MWCNTs that ranged from 0.010 to 2.0 g were used. The result (Fig. S1, Electronic Supplementary Material, ESM) indicated that the amount of MWCNTs was a key parameter that affected the extraction efficiency. The recoveries of all tested PAHs increased with an increase of the amount of the MWCNTs and

reached a maximum when the amount of MWCNTs was 0.05 g, and decreased with any further increase of the amount of the MWCNTs. The large surface area afforded by the MWCNTs and their  $\pi$ - $\pi$  electrostatic interactions with the aromatic rings of PAHs facilitated strong adsorption between the two species. Masses greater than 0.05 g led to a decrease in the recovery due to the tested PAHs not being completely eluted from the sorbent. Hence, 0.05 g of MWCNTs was sufficient to extract PAHs.

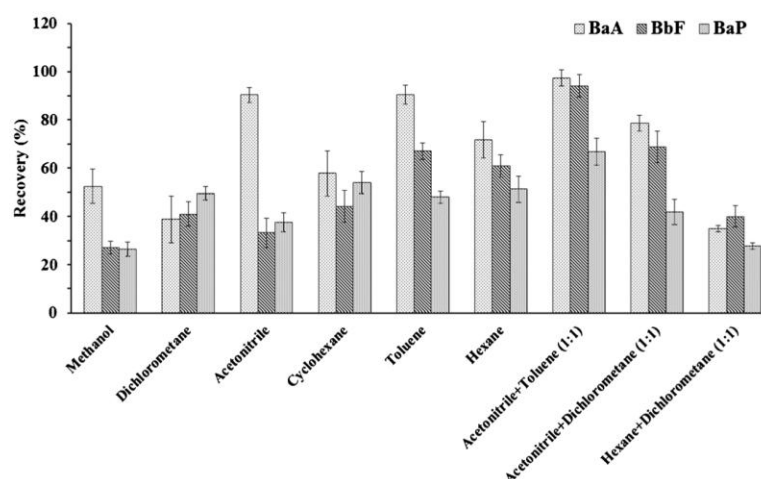
#### Effect of the concentration of the alginate

The concentration of alginate was investigated from 1.0 to 4.0 % w/v, (Fig. S2, ESM). Any increase of the alginate concentration to more than 2.0 % w/v led to a decrease of the recoveries, due to the high concentration of alginate providing a low porosity of the bead so the analyte had difficulty to diffuse and to be adsorbed by the MWCNTs. However, at lower concentrations of the alginate the beads were not stable and could not be reused. Therefore, a 2.0 % w/v of alginate was chosen as the optimal concentration.

#### Effect of the amount of sorbent

The amount of the sorbent was another key parameter that affected the extraction efficiency. To evaluate the effect of the amount of sorbent, 0.05, 0.10, 0.20, 0.30, 0.40 and 0.50 g of the  $\text{Fe}_3\text{O}_4$ /MWCNTs/alginate composite sorbent

**Fig. 3** Effect of the type of desorption solvent on the recovery of PAHs

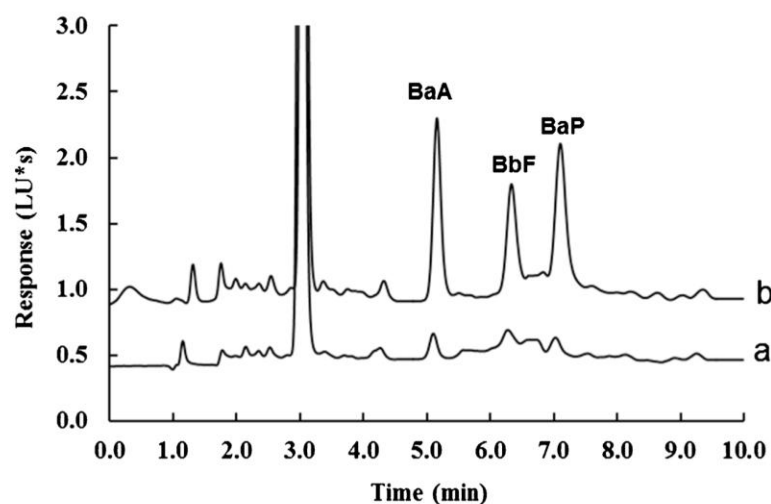


were investigated (Fig. S3, ESM). The recovery of the tested PAHs increased with the increase of the amount of sorbent until it reached a maximum at 0.20 g, and then remained almost constant when the amount of sorbent was greater than 0.20 g. Therefore, 0.20 g of sorbent was the amount selected for further experiments.

#### Extraction time

Generally, sufficient contact time is required to attain adsorption equilibrium for the analytes on the sorbent. The effect of the extraction time on the extraction efficiency of the PAHs was investigated (Fig. S4, ESM). The recoveries for the PAHs increased with any increase of extraction time from 5 to 10 min, and remained constant after 10 min. Hence, all further experiments were performed with a 10 min extraction time.

**Fig. 4** HPLC–FLD chromatogram of spiked water sample without extraction ( $0.05 \mu\text{g L}^{-1}$ ) (a) and spiked water sample after being extracted with the Fe<sub>3</sub>O<sub>4</sub>/MWCNTs/alginate composite adsorbent (b)



#### Effect of stirring speed

The extraction efficiency of the Fe<sub>3</sub>O<sub>4</sub>/MWCNTs/alginate sorbent depended on the partition rate of analytes between the sorbent and the sample solution. The stirring speed was an effective way to enhance the mass transfer of analyte from the solution to the sorbent as this helps to decrease the time required for extraction. Magnetic stirring speeds that ranged from 500 to 2000 rpm were investigated. It was observed that the recovery increased with stirring speed and reached a maximum at 1000 rpm (Fig. S5, ESM). Therefore, the stirring speed of 1000 rpm was chosen for further studies.

#### Effect of the desorption solvent

In order to obtain a satisfactory extraction efficiency, the selection of an appropriate organic desorption solvent was an important parameter, to ensure complete desorption of all

**Table 1** Concentration of PAHs in water samples ( $n=5$ )

Water sample	Concentration ( $\mu\text{g L}^{-1}$ )		
	BaA	BbF	BaP
Tab water 1	ND	ND	ND
Tab water 2	ND	ND	ND
River water 1	0.052±0.008	0.045±0.006	0.064±0.008
River water 2	0.061±0.010	0.052±0.006	0.088±0.011
Wastewater 1 <sup>a</sup>	ND	ND	ND
Wastewater 2 <sup>b</sup>	0.022±0.07	0.018±0.005	0.028±0.008

ND Not detected

<sup>a</sup> Wastewater sample collected from a wastewater pond from Hospital

<sup>b</sup> Wastewater sample collected from a household effluent

PAH analytes with the smallest volume. Methanol, dichloromethane, acetonitrile, cyclohexane, toluene, hexane, acetonitrile + toluene (1:1, %v/v), acetonitrile + dichloromethane (1:1, %v/v) and hexane + dichloromethane (1:1, %v/v) were investigated (Fig. 3). A mixture of acetonitrile and toluene (1:1 %v/v) provided the highest recovery for all the tested PAHs. Therefore, a mixture of acetonitrile and toluene (1:1 %v/v) was selected as the best PAHs desorption solvent. The optimum desorption time of 10 min (Fig. S6, ESM) and the volume of the desorption solvent of 4.0 mL were chosen for further experiments (Fig. S7, ESM).

### Reproducibility and reusability of the magnetite nanoparticles, multiwalled carbon nanotubes and alginate composite sorbent

The reproducibility of the  $\text{Fe}_3\text{O}_4/\text{MWCNTs}/\text{alginate}$  composite sorbent were investigated in terms of batch-to-batch reproducibility. Six different batches of the sorbent were used to extract PAHs from water sample spiked at  $1.0 \mu\text{g L}^{-1}$  under the same conditions. The relative standard deviations (RSD) were lower than 10 %, which was much better than the

acceptable values recommended by the AOAC (32 %). That is, the preparation procedures for the  $\text{Fe}_3\text{O}_4/\text{MWCNTs}/\text{alginate}$  composite sorbent provided for a good reproducibility.

The reusability of  $\text{Fe}_3\text{O}_4/\text{MWCNTs}/\text{alginate}$  composite sorbent was investigated by extracting consecutive samples of PAHs from water samples spiked at a concentration of  $1.0 \mu\text{g L}^{-1}$ . After each use of the sorbent, it was washed with 2.0 mL of acetonitrile and water, before reuse. After washing, the effect of carry-over of the analytes was also investigated, the same sorbent was further desorbed and analyzed under the same conditions. No analytes were carried-over after washing. The same sorbent was again used for extraction of PAHs. The results indicated that the  $\text{Fe}_3\text{O}_4/\text{MWCNTs}/\text{Alginate}$  composite sorbent could be used at least ten times without any significant loss of the adsorption capacity, the recoveries >83 % for all tested PAHs (Fig. S8, ESM).

### Comparative studies

The results obtained from the extraction using the  $\text{Fe}_3\text{O}_4/\text{MWCNTs}/\text{alginate}$  composite sorbent were compared to conventional C18 SPE cartridges (Fig. S9, ESM). Recoveries of the tested PAHs ranged from 90.3 to 96.6 and 89.7 to 94.7 % for the  $\text{Fe}_3\text{O}_4/\text{MWCNTs}/\text{alginate}$  composite sorbent and the C18 cartridge, respectively. The average recoveries of  $\text{Fe}_3\text{O}_4/\text{MWCNTs}/\text{alginate}$  composite sorbent and C18 cartridges were compared by the statistical *t*-test. There were no significant difference between the two sorbents ( $P < 0.005$ ). Therefore,  $\text{Fe}_3\text{O}_4/\text{MWCNTs}/\text{alginate}$  composite sorbent can be used as an alternative sorbent for extracting PAHs from water samples. Moreover, the  $\text{Fe}_3\text{O}_4/\text{MWCNTs}/\text{alginate}$  composite sorbent can be reused for a minimum of ten times, whereas a conventional C18 SPE cartridge cannot be reused.

### Analytical performance

In order to investigate the practicality of the developed method, validation parameters including the linearity, limit of

**Table 2** Comparison of analytical performance of the developed method with other methods for the extraction and determination of BaA in water sample

Extraction method	Extraction material	LOD ( $\text{ng L}^{-1}$ )	Recovery (%)	References
Micro-solid phase extraction	Multiwalled carbon nanotubes	25	81–84	[20]
Solid phase extraction	Sulfur microparticles	27	97–100	[21]
Solid phase microextraction	Polymeric ionic liquid	100	89–94	[8]
Solid phase extraction	Graphene	6.5	74–85	[22]
Solid phase microextraction	Ethoxylated nonylphenol	50	83–99	[4]
Stir rod sorptive extraction	Graphene-polymer composite	19	92–99	[11]
Magnetic solid phase extraction	$\text{Fe}_3\text{O}_4/\text{Graphene oxide}$	90	77–101	[23]
Magnetic solid phase extraction	$\text{Fe}_3\text{O}_4/\text{MWCNTs}/\text{alginate}$ composite	5	96–98	This work

detection and limit of quantification were investigated. To obtain the linearity of the method, the standard solutions used varied from 5 ng to 50  $\mu\text{g L}^{-1}$  and were extracted using Fe<sub>3</sub>O<sub>4</sub>/MWCNTs/alginate sorbent followed by HPLC-FLD. The method showed a wide linearity from 0.005 to 50  $\mu\text{g L}^{-1}$  for BaA and BaP, 0.01–50  $\mu\text{g L}^{-1}$  and for BbF the coefficient of determination ( $R^2$ ) was higher than 0.999. The calibration equations of BaA, BbF and BaP were  $y=(21.06\pm 0.03)x - (1.0\pm 0.5)$ ,  $y=(18.48\pm 0.04)x - (1.3\pm 0.7)$  and  $y=(28.41\pm 0.05)x - (1.3\pm 0.8)$ , respectively. The limits of detection (LOD) were 0.005  $\mu\text{g L}^{-1}$  for BaA and BaP, 0.01  $\mu\text{g L}^{-1}$  for BbF (signal-to-noise=3) and the limits of quantification (LOQ) were 0.02  $\mu\text{g L}^{-1}$  for BaA and BaP, 0.04  $\mu\text{g L}^{-1}$  for BbF (signal-to-noise=10), respectively. Therefore, the developed method had a wide linear range and low detection limit. It can be used to determine PAHs in water samples since its LOD value was lower than their maximum acceptable contaminant level (MCL) in surface water set by the US EPA, i.e. 0.2  $\mu\text{g L}^{-1}$  for BbF and BaP, and 0.1  $\mu\text{g L}^{-1}$  for BaA [18].

### Analysis of real water samples

Under the optimum conditions, the method was successfully applied to the determination of PAHs in real water samples i.e. tap water, river water and wastewater. The chromatograms of the spiked water samples before and after extraction are shown in Fig. 4. The quantitative results from the real water sample are shown in Table 1 and indicate that no residues of the PAHs were detected in tap water and wastewater collected from a wastewater pond from a hospital, but low concentrations were found in river water and wastewater collected from a household effluent. However, these were lower than the maximum contaminant level (MCL) allowed for surface water, 0.2  $\mu\text{g L}^{-1}$  for BbF and BaP, and 0.1  $\mu\text{g L}^{-1}$  for BaA, respectively [18]. The presence of BaA, BbF and BaP in river water may be due to incomplete combustion from the vehicle exhaust emissions deposited into the water. The contaminate of BaA, BbF and BaP in wastewater collected from household effluent may be due to the formation of PAHs during cooking procedures and discharged into the effluent [19]. The recoveries of PAHs at three spiked concentration were  $92.0\pm 2.1$  to  $97.7\pm 2.5$  % and were acceptable by the EPA method 8000C (70–130 %). Good precision were also obtained with an RSD lower than 5 % (Table S1, ESM). The results indicated that the developed sorbent was specific for the extraction of PAHs when applied to complex sample such as waste water.

### Comparison of the alginate, magnetite nanoparticles and multiwalled carbon nanotubes composite sorbent with other methods

A comparison between the performance of the developed method and some of the previously reported methods are

summarized in Table 2. The method showed a much lower detection limit with a similar range of recoveries. Compared to the traditional SPE sorbent, the extraction procedures of the method were simpler and faster due to the sorbent being easy to isolate from the sample solution using an external magnet. When compared to the SPME, the commercial SPME fibers were expensive and fragile. Therefore, the analytical performance of the developed method was acceptable for the extraction and determination of PAHs in water samples.

### Conclusion

A Fe<sub>3</sub>O<sub>4</sub>/MWCNTs/alginate composite sorbent with good dispersibility was prepared for the extraction of PAHs from water samples. PAHs could be efficiently adsorbed because of the  $\pi$ - $\pi$  interactions between the aromatic rings of PAHs and the MWCNTs. The developed method provided a good extraction efficiency and precision. The developed Fe<sub>3</sub>O<sub>4</sub>/MWCNTs/alginate composite sorbent is simple to prepare, cost-effective (~\$US 0.1 per sample), was a fast procedure and environmentally friendly. In addition, the sorbent could be reused for at least ten times, that would help to decrease the costs of analysis. This method has the potential for use to extract other non-polar molecule from water samples.

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## Electronic Supplementary Material

### Extraction of polycyclic aromatic hydrocarbons with a magnetic sorbent composed of alginate, magnetite nanoparticles and multiwalled carbon nanotubes

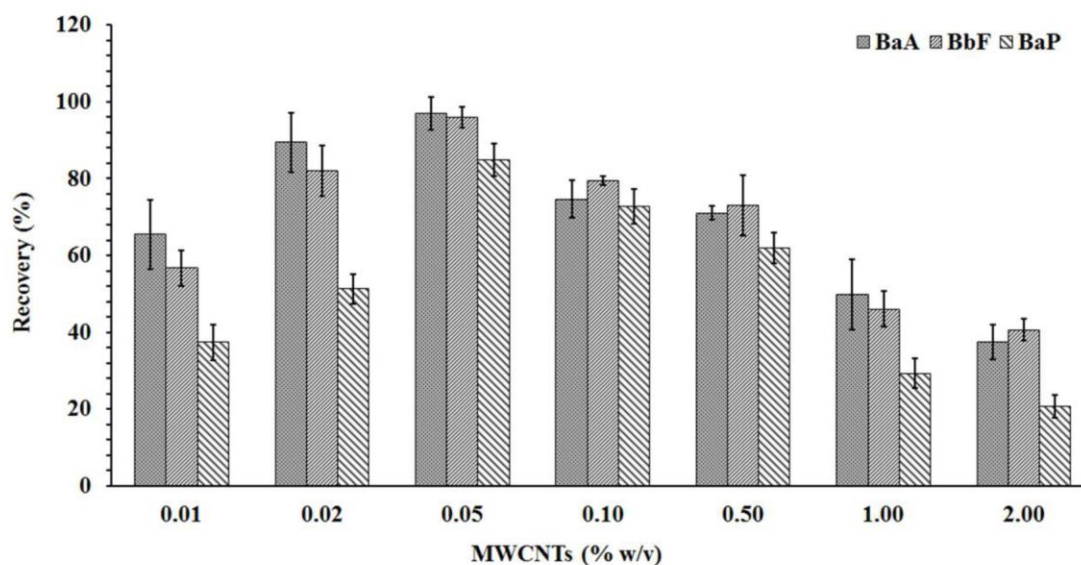
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<sup>1</sup>Trace Analysis and Biosensor Research Center, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand

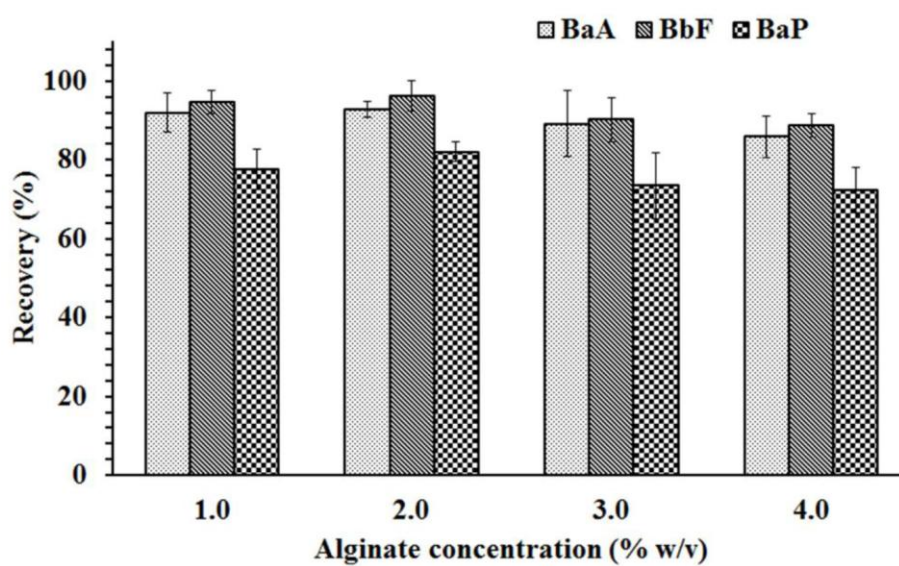
<sup>2</sup>Center of Excellence for Innovation in Chemistry, Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand

Corresponding author: Tel: +66 74288453; Fax: +66 74558841

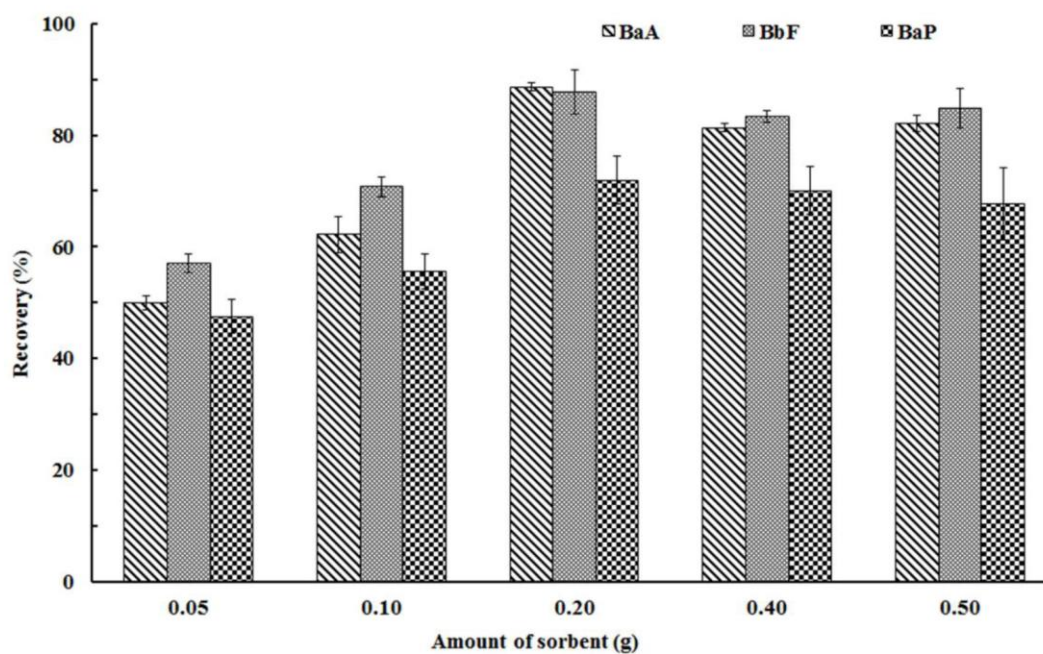
Email address: opas.b@psu.ac.th



**Fig. S1** Effects of the amount of MWCNTs on the recovery of PAHs



**Fig. S2** Effects of the alginate concentration on the recovery of PAHs



**Fig. S3** Effects of the amount of sorbent on the recovery of PAHs

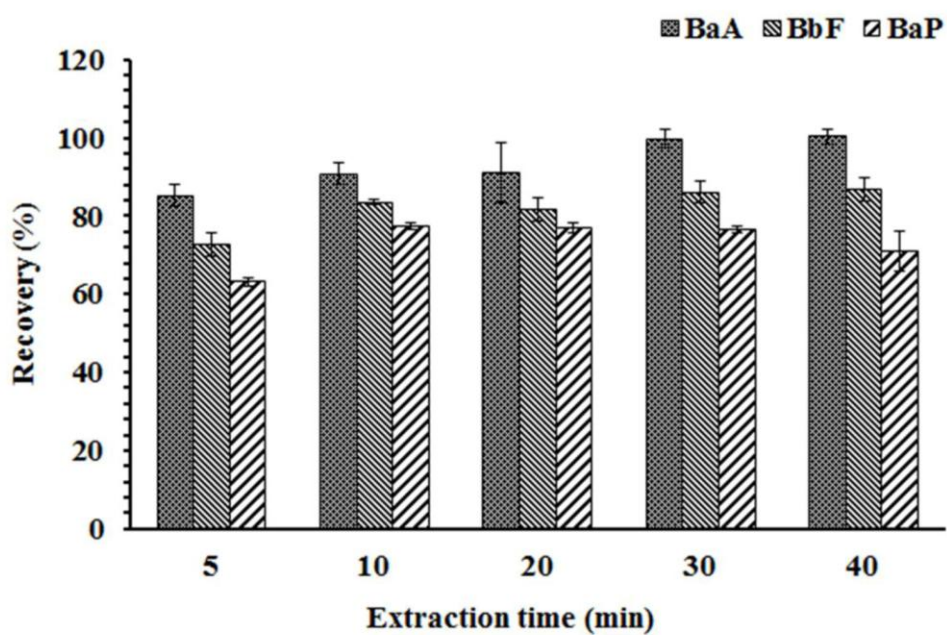


Fig. S4 Effect of the extraction time on the recovery of PAHs

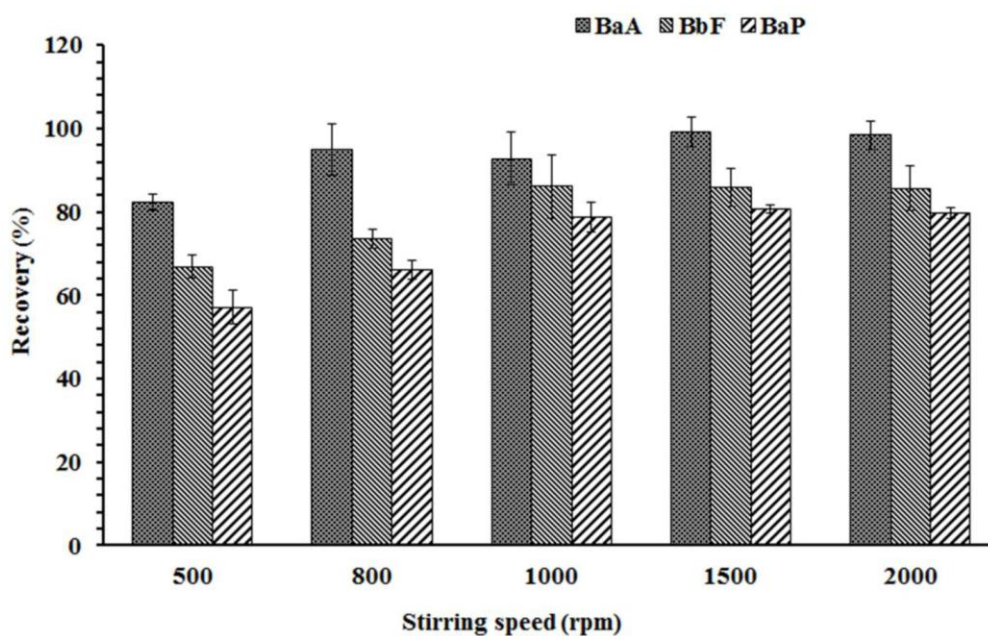
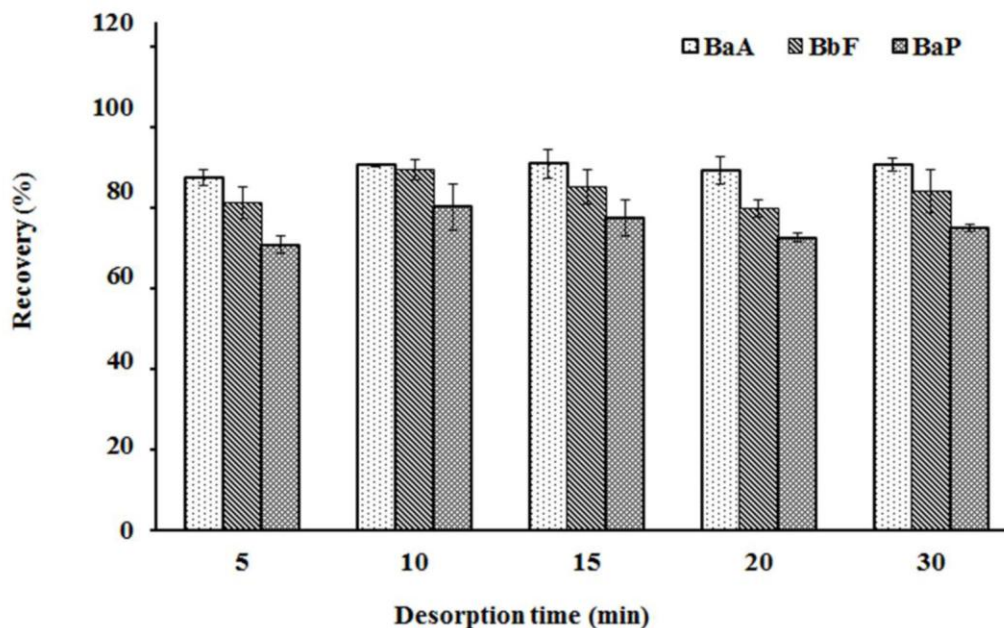


Fig. S5 Effect of the stirring speed on the recovery of PAHs

### Effect of the desorption time and desorption volume

Different desorption times (5, 10, 15, 20, 25 and 30 min) were investigated and 10 min was enough to obtain the maximum desorption efficiency for all the tested PAHs (**Fig. S6**). Hence, a desorption time of 10 min was chosen.

The influence of the volume of the desorption solvent on desorption efficiency of PAHs was also investigated the recoveries of the tested PAHs increased with an increase of the volume of the desorption solvent, reached a maximum at 4.0 mL and remained almost constant when the volume of the desorption solvent was further increased (**Fig. S7**). Therefore, to minimize the amount of organic solvent 4.0 mL was selected as a suitable volume of solvent for desorption.



**Fig. S6** Effect of the desorption time on the recovery of PAHs

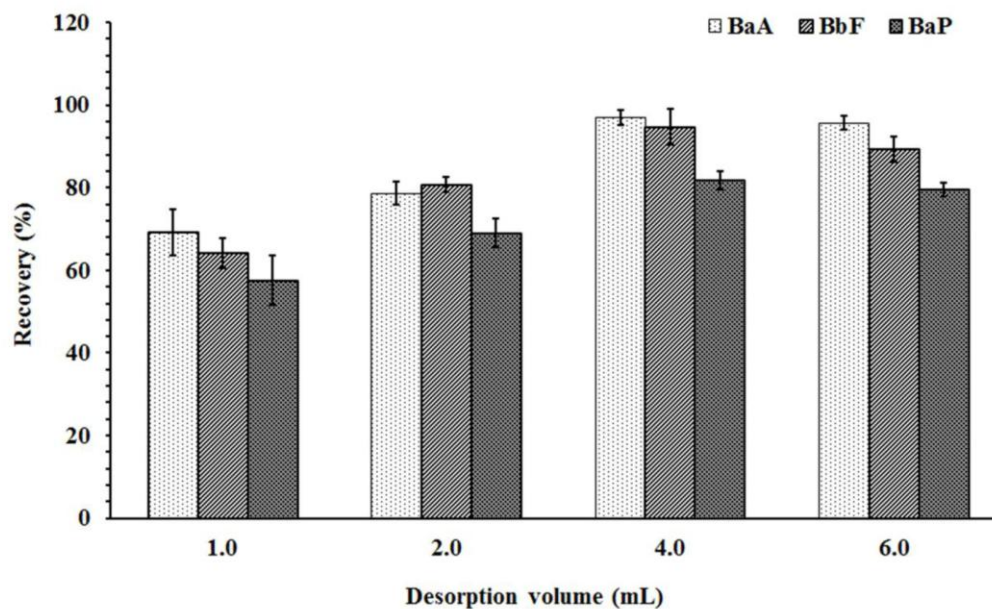


Fig. S7 Effect of the volume of desorption solvent on the recovery of PAHs

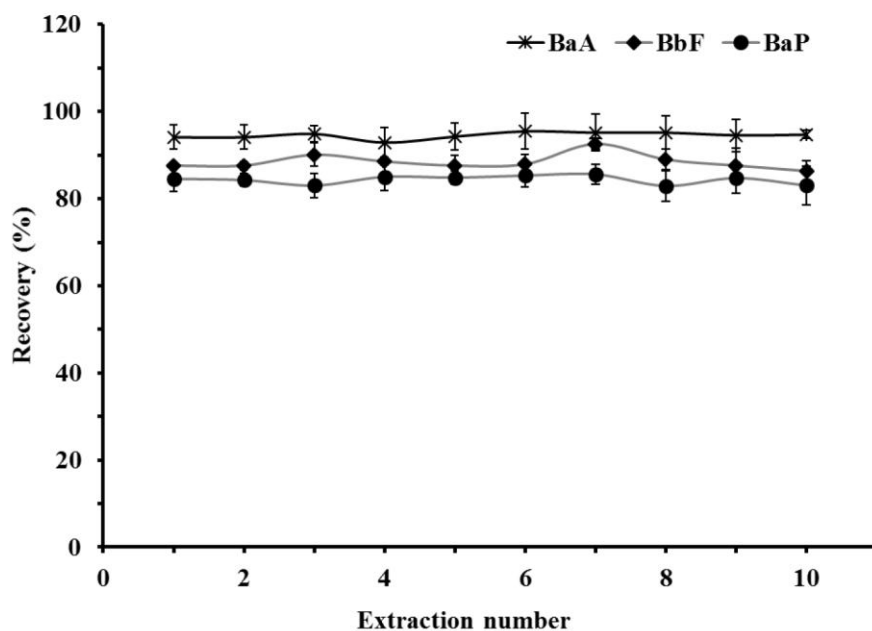
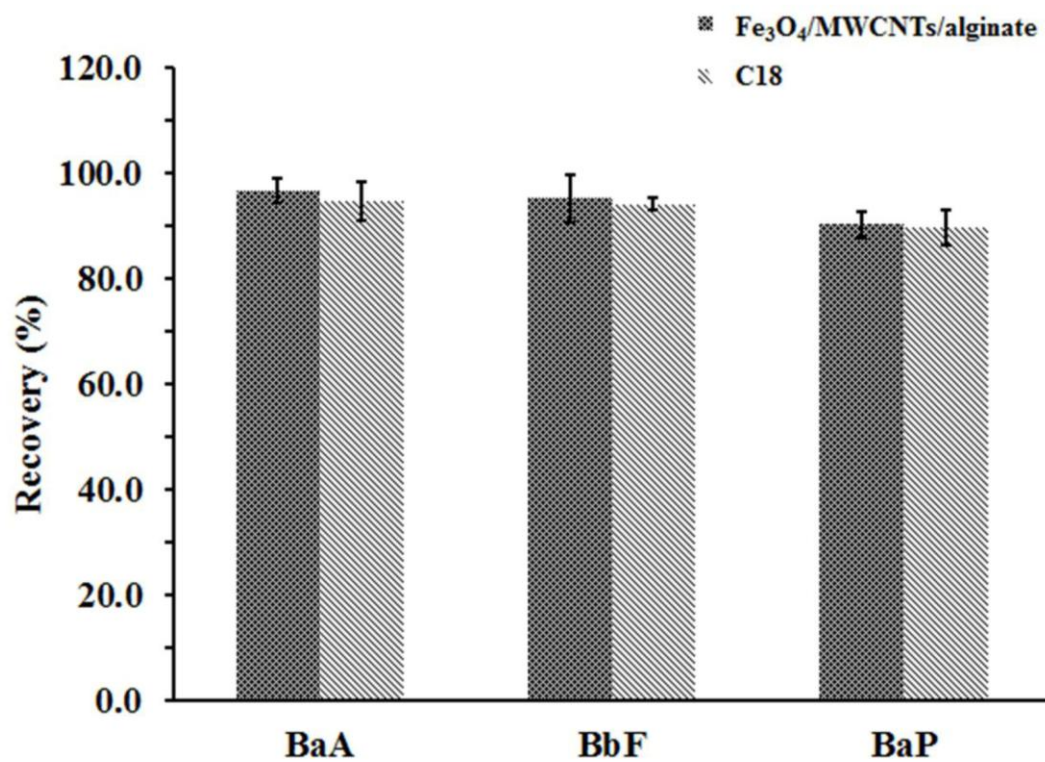


Fig. S8 Reusability of the Fe<sub>3</sub>O<sub>4</sub>/MWCNTs/alginate composite sorbent for extraction of 1.0  $\mu\text{g L}^{-1}$  of PAHs from water sample (n=3)



**Fig. S9** The extraction efficiency of PAHs in spiked deionized water, a comparison between the  $\text{Fe}_3\text{O}_4/\text{MWCNTs}/\text{alginate}$  composite sorbent and the conventional C18 SPE cartridge

**Table S1** Recoveries of BaA, BbF and BaP in spiked water samples

Water sample	Added ( $\mu\text{g L}^{-1}$ )	Recovery (%)		
		BaA	BbF	BaP
Tab water	0.1	$97.0 \pm 2.0$	$94.0 \pm 2.0$	$92.3 \pm 3.2$
	0.5	$97.7 \pm 2.5$	$95.3 \pm 2.1$	$94.0 \pm 2.0$
	2.0	$96.7 \pm 2.5$	$94.7 \pm 2.5$	$92.7 \pm 3.2$
River water	0.1	$95.3 \pm 3.2$	$95.1 \pm 2.2$	$94.6 \pm 1.6$
	0.5	$96.3 \pm 2.5$	$93.6 \pm 3.5$	$93.6 \pm 1.9$
	2.0	$97.7 \pm 1.5$	$93.8 \pm 1.9$	$93.0 \pm 2.0$
Wastewater	0.1	$96.7 \pm 2.1$	$95.7 \pm 2.5$	$93.3 \pm 3.0$
	0.5	$96.9 \pm 1.2$	$96.0 \pm 2.7$	$94.7 \pm 2.1$
	2.0	$96.1 \pm 1.8$	$96.7 \pm 2.8$	$92.0 \pm 2.1$