รายงานวิจัยฉบับสมบูรณ์

ตัวดูดซับของแข็งชนิดใหม่ครัยโอเจลคอมโพสิทกราฟีนออกไซด์เคลือบโพลีไพโรล สำหรับสกัดและเพิ่มความเข้มข้นสารซัลโฟนาไมด์

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โครงการวิจัยนี้ได้รับทุนสนับสนุนจากเงินรายได้มหาวิทยาลัยสงขลานครินทร์
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กิตติกรรมประกาศ

โครงการวิจัยนี้ได้รับสนับสนุนจากงบประมาณเงินรายได้มหาวิทยาสงขลานครินทร์ ประจำปี 2559 สัญญาเลขที่ SCI590697S ขอขอบคุณภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยสงขลานครินทร์สำหรับสถานที่ทำวิจัยและเครื่องมือวิจัยที่เกี่ยวข้อง

โอภาส บุญเกิด

พฤษภาคม 2561

บทคัดย่อ

ตัวดูดซับของแข็งชนิดใหม่ในลักษณะครัยโอเจลคอมโพสิทระหว่างโพลีไวนิลแอลกอฮอล์และกราฟีนออกไซด์เคลือบด้วยโพลีไพโรลได้ถูกพัฒนาขึ้นสำหรับตรวจวิเคราะห์สารซัลโฟนาไมด์ โพลีไพโรลและกราฟีนออกไซด์มีพื้นผิวสัมผัสมากทำให้ช่วยเพิ่มประสิทธิภาพการดูดซับซัลโฟนาไมด์โดยการเกิดพันธะไฮโดรเจนและอันตรกิริยาแบไฮโดรโฟบิก ในขณะที่คุณสมบัติมีรูพรุนสูงของโพลีไวนิลแอลกอฮอล์ครัยโอเจลช่วยลดปัญหาการอุดตันของตัวดูดซับซึ่งมีความดันกลับต่ำ ได้ศึกษาปัจจัยต่างๆ ที่มีผลต่อประสิทธิภาพของการสกัด ได้แก่ ชนิดของตัวดูดซับ เวลาในการเกิดพอลิเมอร์ สภาวะที่ใช้สำหรับคายการดูดซับ พีเอชของสารตัวอย่าง และความเข้มข้นของไอออนที่มีในตัวอย่าง ภายใต้สภาวะที่เหมาะสมวิธีที่พัฒนาขึ้นให้ช่วงความเป็นเส้นตรงตั้งแต่ 0.20 ถึง 100.0 ไมโครกรัมต่อลิตรสำหรับซัลฟาไดอะซีน ซัลฟาไทอะโซล และซัลฟาเมอราซีน และอยู่ในช่วง 0.10 ถึง 100.0 ไมโครกรัมต่อลิตร สำหรับสารซัลฟาเมทธาซีน ซัลฟาโมโนเมทอกซีน และซัลฟาไดเมทอกซีน โดยมีขีดจำกัดการตรวจวัดเท่ากับ 0.20 ไมโครกรัมต่อลิตรสำหรับสาร ซัลฟาไดอะซีน ซัลฟาไทอะโซล และซัลฟาเมอราซีน และ 0.10 ไมโครกรัมต่อลิตรสำหรับสารซัลฟาไดอะซีน ซัลฟาไทอะโซล และซัลฟาเมอราซีน ตัวดูดซับของแข็งครัยโอเจลคอมโพสิทระหว่างโพลีไวนิลแอลกอฮอล์และกราฟีนออกไซด์เคลือบด้วยโพลีไพโรลที่พัฒนาขึ้นให้ร้อยละการได้กลับคืนอยู่ในช่วง 85.5 ถึง 99.0 ร้อยละของค่าเบี่ยงเบนมาตรฐานน้อยกว่า 5 โดยตัวดูดซับที่พัฒนาขึ้นมีการทำซ้ำ และเสถียรภาพที่ดี สามารถใช้ซ้ำได้อย่างน้อย 10 ครั้ง ได้ประยุกต์ใช้ในการสกัดและเพิ่มความเข้มข้นสำหรับตรวจวัดสารซัลโฟนาไมด์ในตัวอย่างน้ำ

Abstract

A hybrid monolith sorbent of polypyrrole-coated graphene oxide embedded in polyvinyl alcohol cryogel was prepared and used as an effective solid phase extraction sorbent for the determination of trace sulfonamides. The large surface areas with many adsorption sites of polypyrrole and graphene oxide facilitated the high adsorption of sulfonamides via hydrogen bonding, π-π and hydrophobic interactions. The high porosity of the polyvinyl alcohol cryogel helped to reduce the back pressure that occurs in a conventional packed solid phase extraction cartridge. The effecting parameters on the extraction efficiency including the type of sorbent, the polymerization time, desorption conditions, the sample pH, the sample volume, the sample flow rate, and ionic strength were investigated and optimized. Under the optimum conditions, the developed method provided a wide linear range from 0.20 to 100.0 μg L^{-1} for sulfadiazine, sulfathiazole and sulfamerazine; and from 0.10 to 100 μgL^{-1} for sulfamethazine, sulfamonomethoxine and sulfadimethoxine. The limits of detection were 0.20 μg L^{-1} for sulfadiazine, sulfathiazole and sulfamerazine; and 0.10 μg L^{-1} for sulfamethazine, sulfamonomethoxine and sulfadimethoxine. The developed hybrid monolith polypyrrole-coated graphene oxide embedded in the polyvinyl alcohol cryogel sorbent provided good recoveries in the range of 85.5-99.0 % with RSDs of less than 5.0 %. The sorbent offered a good reproducibility, was robust and can be reused at least 10 times. It was successfully applied for the extraction and enrichment of sulfonamides from normal and supplemented water samples.

บทสรุปผู้บริหาร (Executive Summary)

บทนำ

ปัจจุบันการรักษาอาการติดเชื้อหรืออักเสบที่เกิดจากเชื้อแบคทีเรียนิยมใช้ยาปฏิชีวนะในการรักษา นอกจากนี้ยังมีการผสมยาปฏิชีวนะเหล่านี้ลงในอาหารสัตว์เพื่อป้องกันโรคที่เกิดจากการติดเชื้อจากแบคทีเรีย ซึ่งการใช้ที่มากเกินขนาด เกินความจำเป็นหรือผิดวิธี อาจทำให้เกิดปัญหาการตกค้างของยาเหล่านี้ในอาหาร และสิ่งแวดล้อม ซึ่งทำให้เกิดผลกระทบต่อผู้บริโภคและสิ่งแวดล้อมได้ โดยยาปฏิชีวนะชนิดหนึ่งที่นิยมใช้ในการรักษาการติดเชื้อที่เกิดจากแบคทีเรียคือ ยาในกลุ่มซัลโฟนาไมด์

ซัลโฟนาไมด์เป็นยาปฏิชีวนะที่นิยมใช้เนื่องจากสามารถรักษาอาการติดเชื้อที่เกิดจากแบคทีเรียแกมบวก แกมลบ และโพรโตซัวได้ และมีราคาถูก นอกจากนี้ยังมีการใช้เพื่อเร่งการเจริญเติบโตของสัตว์อีกด้วย แต่การผสมสารซัลโฟนาไมด์ลงในอาหารสัตว์อาจทำให้เกิดการตกค้างของซัลโฟนาไมด์ในเนื้อสัตว์และผลิตภัณฑ์ การตกค้างของซัลโฟนาไมด์แม้ปริมาณเล็กน้อยอาจก่อให้เกิดผลกระทบต่อสุขภาพของผู้บริโภค เช่น เกิดอาการแพ้ ก่อให้เกิดโรคมะเร็ง และหากได้รับต่อเนื่องเป็นเวลานานจะทำให้เกิดการดื้อยาได้ เพื่อความปลอดภัยของผู้บริโภค องค์กรอาหารและยาแห่งสหภาพยุโรป (EU FDA) ได้กำหนดปริมาณตกค้างสูงสุด (maximum residue limit, MRL) ของซัลโฟนาไมด์ในอาหารไม่เกิน 100 ไมโครกรัมต่อกิโลกรัม (EuropeanCommission 2010) ดังนั้นการตรวจวัดการตกค้างของซัลโฟนาไมด์จึงมีความจำเป็น

วิธีการโดยทั่วไปในการวิเคราะห์ซัลโฟนาไมด์ประกอบด้วย 2 ขั้นตอนสำคัญ คือ การวิเคราะห์ด้วยเครื่องมือและขั้นการเตรียมตัวอย่างก่อนการวิเคราะห์ ซึ่งเทคนิคที่ใช้ในการวิเคราะห์ซัลโฟนาไมด์ คือ โครมาโทรกราฟีของเหลวสมรรถนะสูง แต่เนื่องจากการตกค้างของสารซัลโฟนาไมด์มีปริมาณน้อยและมีตัวรบกวนมากดังนั้นจึงจำเป็นต้องมีขั้นตอนการเตรียมตัวอย่างที่เหมาะสมเพื่อกำจัดสารรบกวนและเพิ่มความเข้มข้นซึ่งจะทำให้สามารถตรวจวัดในปริมาณน้อยได้ เทคนิคการเตรียมตัวอย่างที่ได้มีการใช้สำหรับวิเคราะห์ซัลโฟนาไมด์ได้แก่ การสกัดโดยใช้ตัวทำลายอินทรีย์ (Liquid-liquid extraction; LLE) การสกัดด้วยตัวดูดซับของแข็งอนุภาคแม่เหล็ก (Magnetic solid phase extraction; MSPE) การสกัดด้วยตัวดูดซับของแข็งปริมาณน้อย (Solid phase microextraction; SPME) และการสกัดด้วยตัวดูดซับของแข็ง (Solid phase extraction; SPE) เทคนิคการเตรียมตัวอย่างที่น่าสนใจชนิดหนึ่งคือ การสกัดด้วยตัวดูดซับของแข็ง มีข้อดีคือสามารถเตรียมตัวดูดซับได้ง่าย ใช้ตัวทำละลายปริมาณน้อยและสามารถเพิ่มความเข้นข้นของสารตัวอย่างได้มาก โดยตัวดูดซับของแข็งแบบเดิมที่มีการใช้สกัดซัลโฟนาไมด์ได้แก่ C18 ซึ่งมีจำหน่ายเชิงพาณิชย์ แต่ตัวดูดซับดังกล่าวมีราคาแพง เกิดปัญหาการอุดตันได้ง่าย

ดังนั้นโครงการวิจัยนี้จึงได้สนใจพัฒนาตัวดูดซับของแข็งชนิดใหม่ ที่สามารถเตรียมได้ง่าย มีราคาถูก และไม่เกิดปัญหาการอุดตัน ในลักษณะของครัยโอเจลคอมโพสิทระหว่างโพลีไวนิลแอลกอฮอล์ กราฟีนออกไซด์ เคลือบด้วยโพลีไพโรล (Polypyrrole/Graphene oxide/PVA cryogel) สำหรับการวิเคราะห์หาปริมาณซัลโฟนาไมด์ เนื่องจากกราฟีนออกไซด์ ซึ่งเป็นวัสดุนาโนคาร์บอนที่มีลักษณะเป็นสองมิติของโครงข่ายคาร์บอนอะตอม (Karamani et al. 2013) ทำให้มีพื้นที่ผิวมาก สามารถเกิดอันตรกิริยาแบบ π-π กับสาร

ซัลโฟนาไมด์ได้ ครัยโอเจลเป็นวัสดุที่มีรูพรุนมากทำให้ไม่เกิดปัญหาการอุดตัน และโพลีไพโรลช่วยเพิ่มประสิทธิภาพการสกัดโดยการเกิดพันธะไฮโดรเจนกับสารซัลโฟนาไมด์ได้

ดังนั้นโครงการวิจัยนี้จึงสนใจพัฒนาตัวดูดซับของแข็งชนิดใหม่เพื่อสกัดและเพิ่มความเข้มข้นสำหรับวิเคราะห์การตกค้างปริมาณน้อยของสารซัลโฟนาไมด์ในสิ่งแวดล้อมและอาหาร โดยใช้ตัวดูดซับเป็นครัยโอเจลคอมโพสิทระหว่างโพลีไวนิลแอลกอฮอล์และกราฟีนออกไซด์ซึ่งสามารถเตรียมได้ง่าย โดยอาศัยการเกิดปฏิกิริยาพอลิเมอไรเซชันของโพลีไวนิลแอลกอฮอล์ จะได้ PVA cryogel ที่มีลักษณะรูพรุนมากและมีกราฟีนออกไซด์อยู่ภายในและเคลือบผิวของ PVA cryogel/graphene oxide ด้วยโพลีไพโรลทำให้มีคุณสมบัติเพิ่มการดูดซับของสารที่ต้องการวิเคราะห์มากขึ้นและสามารถเพิ่มขีดสามารถในการตรวจวัดได้

วัตถุประสงค์

เพื่อพัฒนาตัวดูดซับของแข็งชนิดใหม่ในลักษณะครัยโอเจลคอมโพสิทระหว่างโพลีไวนิลแอลกอฮอล์และกราฟีนออกไซด์เคลือบด้วยโพลีไพโรล ที่เตรียมได้ง่าย ใช้งานสะดวกและมีราคาถูก สำหรับวิเคราะห์หาปริมาณซัลโฟนาไมด์ที่ตกค้างปริมาณน้อย ด้วยเทคนิคโครมาโทกราฟีของเหลวสมรรถนะสูง

สรุป

โครงการวิจัยนี้ประสบความสำเร็จในการพัฒนาตัวดูดซับของแข็งชนิดใหม่ในลักษณะครัยโอเจลคอมโพสิทระหว่างโพลีไวนิลแอลกอฮอล์และกราฟีนออกไซด์เคลือบด้วยโพลีไพโรลสำหรับการสกัด เพิ่มความเข้มข้นและตรวจวิเคราะห์สารซัลโฟนาไมด์ในตัวอย่างน้ำ โดยโพลีไพโรลและกราฟีนออกไซด์มีพื้นผิวสัมผัสมากทำให้เพิ่มประสิทธิภาพการดูดซับซัลโฟนาไมด์ โดยการเกิดพันธะไฮโดรเจนและอันตรกิริยาแบไฮโดรโฟบิก ในขณะที่คุณสมบัติมีรูพรุนสูงของโพลีไวนิลแอลกอฮอล์ครัยโอเจลช่วยลดปัญหาการอุดตันของตัวดูดซับ ซึ่งมักจะเกิดขึ้นกับตัวดูดซับที่มีจำหน่ายทางการค้า โดยได้ศึกษาปัจจัยต่างๆ ที่มีผลต่อประสิทธิภาพของการสกัดและภายใต้สภาวะที่เหมาะสมวิธีที่พัฒนาขึ้นให้ช่วงความเป็นเส้นตรงตั้งแต่ 0.20 ถึง 100.0 ไมโครกรัมต่อลิตรสำหรับซัลฟาไดอะซีน ซัลฟาไทอะโซล และซัลฟาเมอราซีน และอยู่ในช่วง 0.10 ถึง 100.0 ไมโครกรัมต่อลิตรสำหรับสารซัลฟาเมทธาซีน ซัลฟาโมโนเมทอกซีน และซัลฟาไดเมทอกซีน โดยมีขีดจำกัดการตรวจวัดเท่ากับ 0.20 ไมโครกรัมต่อลิตรสำหรับสาร ซัลฟาไดอะซีน ซัลฟาไทอะโซล และซัลฟาเมอราซีน และ 0.10 ไมโครกรัมต่อลิตรสำหรับสารซัลฟาไดอะซีน ซัลฟาไทอะโซล และซัลฟาเมอราซีน ตัวดูดซับของแข็งครัยโอเจลคอมโพสิทระหว่างโพลีไวนิลแอลกอฮอล์และกราฟีนออกไซด์เคลือบด้วยโพลีไพโรลที่พัฒนาขึ้นให้ร้อยละการได้กลับคืนอยู่ในช่วง 85.5 ถึง 99.0 ร้อยละของค่าเบี่ยงเบนมาตรฐานน้อยกว่า 5 โดยตัวดูดซับที่พัฒนาขึ้นมีการทำซ้ำ และเสถียรภาพที่ดี สามารถใช้ซ้ำได้อย่างน้อย 10 ครั้ง ได้ประยุกต์ใช้ในการสกัดและเพิ่มความเข้มข้นสำหรับตรวจวัดสารซัลโฟนาไมด์ในตัวอย่างน้ำ

ภาคผนวก

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Hybrid monolith sorbent of polypyrrole-coated graphene oxide incorporated into a polyvinyl alcohol cryogel for extraction and enrichment of sulfonamides from water samples

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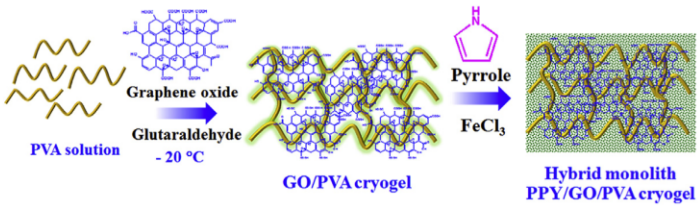
HIGHLIGHTS

- A hybrid monolith polypyrrole-coated graphene oxide incorporated into polyvinyl alcohol cryogel sorbent was developed.
- Its high surface area facilitated the high adsorption capability of the sulfonamides.
- The hybrid monolith PPY/GO/PVA cryogel showed a high extraction efficiency for sulfonamides (85.5–99.0%).

GRAPHICAL ABSTRACT



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ABSTRACT

A hybrid monolith sorbent of polypyrrole-coated graphene oxide embedded in polyvinyl alcohol cryogel was prepared and used as an effective solid phase extraction sorbent for the determination of trace sulfonamides. The large surface areas with many adsorption sites of polypyrrole and graphene oxide facilitated the high adsorption of sulfonamides via hydrogen bonding, π-π and hydrophobic interactions. The high porosity of the polyvinyl alcohol cryogel helped to reduce the back pressure that occurs in a conventional packed solid phase extraction cartridge. The effecting parameters on the extraction efficiency including the type of sorbent, the polymerization time, desorption conditions, the sample pH, the sample volume, the sample flow rate, and ionic strength were investigated and optimized. Under the optimum conditions, the developed method provided a wide linear range from 0.20 to 100.0 μg L^{-1} for sulfadiazine, sulfathiazole and sulfamerazine; and from 0.10 to 100 μg L^{-1} for sulfamethazine, sulfamonomethoxine and sulfadimethoxine. The limits of detection were 0.20 μg L^{-1} for sulfadiazine, sulfathiazole and sulfamerazine; and 0.10 μg L^{-1} for sulfamethazine, sulfamonomethoxine and sulfadimethoxine. The developed hybrid monolith polypyrrole-coated graphene oxide embedded in the polyvinyl alcohol cryogel sorbent provided good recoveries in the range of 85.5–99.0% with RSDs of less than 5.0%. The sorbent offered a good reproducibility, was robust and can be reused at least 10 times. It

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was successfully applied for the extraction and enrichment of sulfonamides from normal and supplemented water samples.

1. Introduction

Sulfonamides are synthetic antibiotics of low cost and high efficiency that are extensively used to treat diseases, prevent infections and promote growth [1]. However, they are poorly absorbed by the organism and their extensive use leads to their wide release into environmental water, mostly in excreted urine and feces [2,3]. Water-borne sulfonamides can enter the food chain and cause serious allergic reactions in humans. Therefore, it is important to develop a simple, sensitive and reliable analytical method for the determination of sulfonamides. High performance liquid chromatography (HPLC) is the most widely used method due to its high sensitivity, selectivity and good precision [4,5]. However, at trace levels in real samples, sulfonamides are usually present together with high matrix interferences, therefore, an instrumental analysis generally requires a suitable sample treatment to preconcentrate the target analytes and remove the matrix interferences [6].

Many sample preparation methods have been developed and applied for the extraction of sulfonamides such as matrix solid phase dispersion (MSPD) [5], magnetic solid phase extraction (MSPE) [7–9], liquid-liquid extraction (LLE) [10], liquid-liquid microextraction (LLME) [11,12], stir bar sorptive extraction (SBSE) [13], hollow fiber-based liquid phase microextraction (HF-LPME) [14], and solid phase extraction (SPE) [3,15,16]. Among these methods, SPE is one of the most widely used for the extraction and preconcentration of target analytes at trace level in aqueous solution due to its high preconcentration efficiency [17]. However, the main drawback of conventional packed SPE cartridges is the cartridge clogging that occurs when large sample volumes are loaded through the sorbent [18,19]. The cartridges are also expensive and cannot be reused [20]. This problem of cartridge clogging can be addressed using porous materials. Cryogel is a good choice of porous material for the preparation of solid phase extraction sorbent due to its extremely high porosity [21,22]. Poly(vinyl alcohol) (PVA) is now widely used to prepare cryogel material due to its non-toxicity, biodegradability and low cost [23,24]. However, PVA cryogels has a low surface area and low adsorption capacity for target analytes, therefore, the entrapment of adsorbent particles within the cryogels and high affinity coatings can increase their specific surface area and obtain a higher extraction efficiency and better selectivity. Recently, multiwall carbon nanotube, functionalized with sulfonate group (MWCNTs-SO_3^-) incorporated in PVA cryogel has been developed and used as an SPE sorbent to separate β-agonists from animal feeds [21] and molecularly imprinted polymer (MIP) composite cryogel was used to separate propranolol from complex sample [22]. These sorbents provided a high extraction efficiency and effectively reduce matrix interferences. Their elastic and highly porous interconnected structure provide a low back pressure [25].

Graphene oxide (GO) can help to enhance the adsorption of target analytes due to its large surface area [26]. It is a derivate of graphene and contains hydroxyl, epoxide and carboxyl groups on its surface that can adsorb sulfonamides via hydrogen bonding [9,27,28]. In addition, the existence of π-conjugated structure also endows GO with a strong affinity for benzenoid structures [29]. Another material that can improve the adsorption of sulfonamides from aqueous samples is a conducting polymer such as polypyrrole, which adsorbs benzenoid compounds via hydrogen bonding, π–π and hydrophobic interactions [30].

This work has focused on a synthesis of polypyrrole-coated GO that was incorporated into a PVA cryogel as a newly-designed hybrid monolith sorbent for the extraction and preconcentration of trace sulfonamides. Combining the high adsorption properties of the polypyrrole and graphene oxide, it not only improves the extraction efficiency and enrichment of sulfonamides but also reduces matrix interferences. This composite monolith porous materials facilitates to minimize any back pressure in a test cartridge. Due to their toxicity, sulfadiazine (SDZ), sulfathiazole (STZ), sulfamerazine (SME), sulfamethazine (SMT), sulfamonomethoxine (SMM), and sulfadimethoxine (SDM) were selected as test compounds to investigate the performance of the developed method.

2. Experimental

2.1. Chemicals and reagents

Poly (vinyl alcohol) (PVA) (MW 72,000 g mol^{-1}, ≥98% hydrolyzed) and acetic acid were from Merck (Darmstadt, Germany). Acetonitrile, methanol, pyrrole, glutaraldehyde, iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), graphene oxide powder, 15–20 sheets, 4–10% edge-oxidized, sulfadiazine (SDZ), sulfathiazole (STZ), sulfamerazine (SME), sulfamethazine (SMT), sulfamonomethoxine (SMM), sulfadimethoxine (SDM), were purchased from Sigma–Aldrich (Steinheim, Germany). Deionized water was from a Maxima ultrapure system (ELGA, Buckinghamshire, England). The GF/F Glass Microfiber filter was from Whatman International Ltd (Maidstone, English). The HLB cartridge was from Waters (Milford, USA).

2.2. Instrumentals

Chromatographic separation and determination of the sulfonamides was performed on the 1100 series (Agilent Technologies Inc., Germany) and the data were acquired using ChemStation software. The separation was conducted on a VertiSep^{TM}pHendure C18 analytical column, 5 μm, 150 mm × 4.6 mm i.d. (Vertical chromatography Co., Ltd., Bangkok, Thailand). The mobile phase consisted of (A) water and (B) acetonitrile. A gradient elution was conducted by changing the composition of the mobile phase as follows; 0–3 min, 16% B; 3–6 min, 16–35% B; 6–8 min, 35–40% B; 8–10 min, 40–45% B; 10–12 min, 45% B and 12–15 min, 45-16% B. The flow rate of the mobile phase was 1.0 mL min^{-1}. The injection volume and column temperature were 20 μL and 30 °C, respectively. All the target sulfonamides were detected at 270 nm. The FTIR spectra were determined by FTIR spectroscopy (PerkinElmer, Waltham, MA, USA). The morphology of the developed sorbent was studied by scanning electron microscopy (JSM-5200, JEOL, Tokyo, Japan). The surface area of the developed sorbent were determined from nitrogen adsorption and desorption isotherms using Quantachrome Autosorb 1 system (Quantachome Instruments, USA).

2.3. Preparation of hybrid monolith PPY/GO/PVA cryogel sorbent

The preparation method for the polypyrrole-coated graphene oxide entrapped in polyvinyl alcohol cryogel sorbent (PPY/GO/PVA cryogel) is shown in Fig. 1. PVA solution (3.0% w/v) was prepared by dissolving PVA powder in deionized water at 90 °C and stirring for 10 min to obtain a homogeneous solution. Then, the PVA solution was cooled at room temperature (27 ± 2 °C) and the pH was adjusted to 1.0 with 5.0 M HCl [31,32]. Subsequently, the graphene oxide powder was added into the PVA solution (0.050% w/v) and dispersed by ultrasonication for 10 min and 1.0 mL of the mixed solution was then poured into a polypropylene tube, 20.0 μL of glutaraldehyde (crosslinking agent) was added and the solution vortexed for 10 s to obtain a homogeneous solution. The mixed solution was then kept in the freezer at −20 °C for 12 h. The frozen composited GO/PVA cryogel was removed from the tube and thawed at room temperature (27 ± 2 °C). Then it was washed with deionized water until neutral pH was obtained.

For the polypyrrole coating on the composite GO/PVA cryogel was produced by placing the GO/PVA cryogel into 2-propanol and stirring at 500 rpm for 10 min. Then the residual 2-propanol was removed. The GO/PVA cryogel was transferred to the pyrrole solution, incubated for 30 min to saturate the cryogel with pyrrole monomer and then the residual pyrrole solution was removed. The polymerization of the polypyrrole was adopted from previous report [33], 0.60 g of $FeCl_3 \cdot 6H_2O$ was dissolved in 2-propanol (20 mL) and added to a rotator tube containing the pyrrole saturated GO/PVA cryogel. The polymerization was performed on a rotator mixer at room temperature (27 ± 2 °C) for 2.0 h. The resulting hybrid monolith polypyrrole-coated GO/PVA cryogel sorbent was washed first with 10.0 mL of 2-propanol, then with methanol and finally with deionized water. Subsequently, the sorbent was packed in polypropylene cartridges (5.0 mL) and used as a solid phase extraction sorbent for the extraction of sulfonamides from solutions.

2.4. Solid phase extraction procedure

The developed hybrid monolith PPY/GO/PVA cryogel sorbent was packed into a 5.0 mL polypropylene tube between two membrane filters. The membrane filter was used to protect the sorbent from some matrix interferences in real samples and then the cartridge was connected with an SPE vacuum manifold. Before sample loading, the sorbent was conditioned with 2.0 mL of methanol and then with deionized water. The certain volumes of the samples were loaded through the sorbent at certain flow rates and then washed with 2.0 mL of deionized water. The retained sulfonamides were eluted from the PPY/GO/PVA cryogel sorbent with a known volume of methanol (eluent) at a flow rate of 1.0 mL min^{-1}. The collected eluent was then evaporated to dryness at 60 °C and the dry residue was redissolved with 1.0 mL of mobile phase. Finally, the resulting solution was filtered through a 0.22 μm disposable PTFE syringe filter and 20.0 μL was injected into the HPLC system for analysis.

2.5. Water samples

Tap water samples were collected from the laboratory, river water samples were collected from two rivers in Songkhla province, two samples of livestock wastewater were collected from Songkhla province and lake water samples were collected from Songkhla Lake, Songkhla province, Thailand. All samples were filtered through 0.45 μm nylon membrane filters and stored at 4 °C until analysis.

3. Results and discussions

3.1. Characterization of hybrid monolith PPY/GO/PVA cryogel sorbent

The morphologies of the PVA cryogel, composite GO/PVA cryogel and hybrid monolith PPY/GO/PVA cryogel were investigated

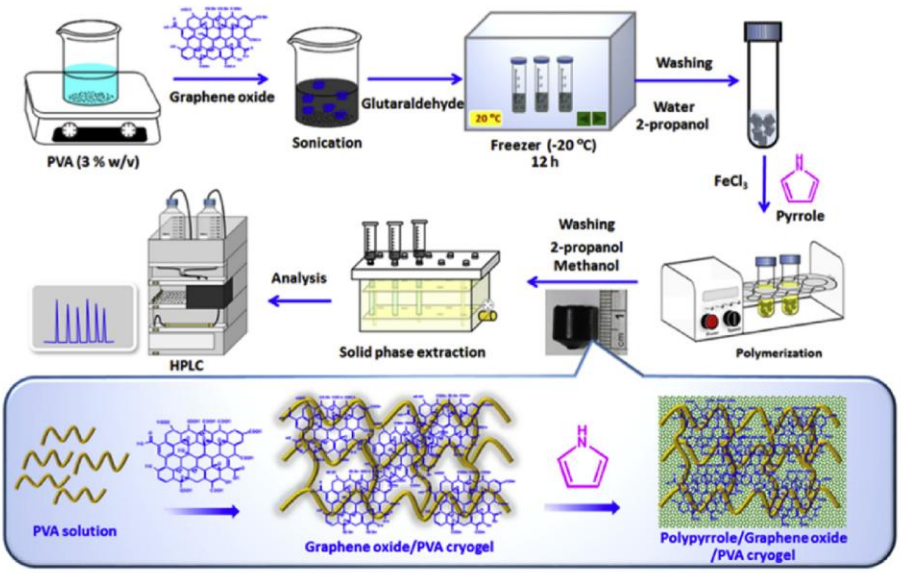

Fig. 1. Schematic diagram of the preparation of hybrid monolith PPY/GO/PVA cryogel sorbent.

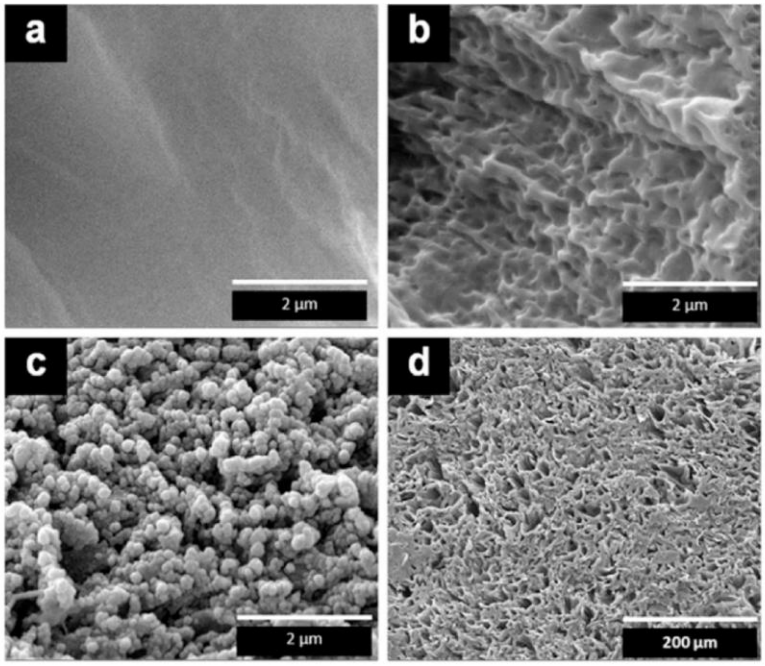

Fig. 2. SEM images of the PVA cryogel (a), composite GO/PVA cryogel (b), hybrid monolith PPY/GO/PVA cryogel (c) and cross section of hybrid monolith PPY/GO/PVA cryogel sorbent (d).

by SEM technique and are illustrated in Fig. 2. The SEM images show that the cryogel sorbent had a smooth surface (Fig. 2a). The SEM image of the composite GO/PVA cryogel (Fig. 2b) showed a rough surface which indicates that the GO was well distributed and entrapped in the PVA cryogel. Fig. 2c shows the SEM image of a hybrid monolith PPY/GO/PVA cryogel displaying the polypyrrole layer's typical "cauliflower" morphology on the surface of the GO/PVA cryogel. The nanostructure of the polypyrrole helped to increase the surface area for adsorption of the target analytes. The cross-sectional SEM image (Fig. 2d) shows that the hybrid monolith PPY/GO/PVA cryogel sorbent had the high porosity. The pore structure benefitted from its increasing mass transfer and also by decreasing the back pressure during sample loading.

FTIR spectra of the GO, PVA cryogel, GO/PVA cryogel and monolith hybrid PPY/GO/PVA cryogel are shown in Fig. S1. Graphene oxide showed a characteristic peak at 1624 cm^{-1} and 1401 cm^{-1} were corresponded to the C=O stretching and deformation vibration from carboxyl. The absorption band at 3420 cm^{-1} and 1262 cm^{-1} were attributed to the O–H stretching and C–O stretching vibrations from-COOH group. The FTIR spectrum of PVA exhibited the absorption band at 3322 cm^{-1} and 2946 cm^{-1} corresponding to the hydroxyl groups and the $-CH_2-$ asymmetric stretching. The absorption band at 1432 cm^{-1} were attributed to the O–H and C–H bending. The peak at 1096 cm^{-1} was attributed to C–O group. The absorption peak at 1633 and 1570 cm^{-1} were attributed to the absorption peaks of pyrrole ring. The peak at 923 cm^{-1} was attributed to C–H wagging. It indicates that polypyrrole was successfully coated onto the surface of composited GO/PVA cryogel sorbent.

The BET specific surface area of different sorbents were also determined by N_2 adsorption-desorption isotherms. The surface area of the PVA cryogel, GO/PVA cryogel, PPY/PVA cryogel and hybrid monolith PPY/GO/PVA cyogel equal to 16.57, 18.51, 24.34 and 34.52 m^2g^{-1}, respectively. This results indicated that polypyrrole coated graphene oxide incorporated into PVA cryogel can improve the surface area and extraction efficiency of the target analytes.

3.2. Optimization of solid phase extraction

The highest extraction efficiency, the lowest solvent consumption and the shortest sample preparation time were then carefully investigated. The parameters that may affect the extraction efficiency of the sulfonamides using the hybrid monolith PPY/GO/PVA cryogel sorbents included the type of sorbent, the polymerization time, concentration of graphene oxide, the desorption conditions, the sample pH, the sample flow rate, and the sample volume and ionic strength were optimized. The recovery was used to evaluate the extraction efficiency of the developed method. All optimization experiments were performed in triplicate.

3.2.1. Effect of the type of sorbent

The extraction efficiency of sulfonamides using the PVA cryogel, composite GO/PVA cryogel, composite PPY/PVA cryogel and hybrid monolith PPY/GO/PVA cryogel sorbent were first investigated. The results indicated that the extraction efficiency of the hybrid monolith PPY/GO/PVA cryogel sorbent was higher than those obtained using the PVA, GO/PVA and PPY/PVA sorbent (Fig. 3). The adsorption capacity of the PVA cryogel, composite GO/PVA cryogel, composite PPY/PVA cryogel and hybrid monolith PPY/GO/PVA cryogel sorbent for sulfadiazine equal to 0.42, 1.11, 3.72 and 6.36 mg g^{-1}, respectively. The improvement of the extraction efficiency and adsorption capacity of the hybrid monolith PPY/GO/PVA cryogel sorbent for the extraction of sulfonamide were due to the combination of GO and PPY which increase the surface area and multiply the adsorption sites. Sulfonamides can be adsorbed via hydrogen bonding, hydrophobic and π-π interaction. Therefore, hybrid monolith PPY/GO/PVA cryogel was chosen as SPE sorbent for the extraction and enrichment of sulfonamides.

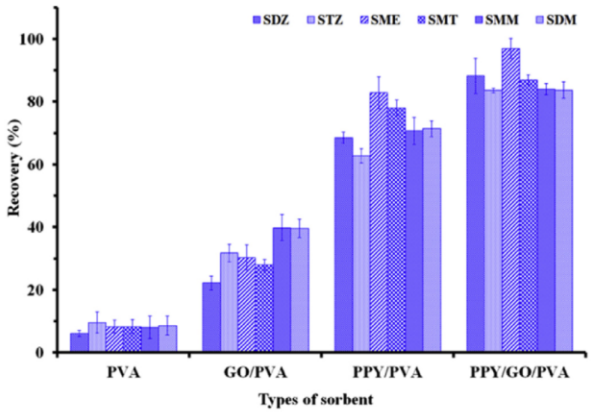

Fig. 3. Comparison of the recovery of the PVA, GO/PVA, PPY/PVA and PPY/GO/PVA sorbent for extraction of sulfonamides.

3.2.2. Effect of polymerization time and concentration of graphene oxide

The polymerization time is one of the important parameters that affects the thickness of the polypyrrole layer and further affects the extraction capacity of the sorbent. Therefore, the effect of the polymerization time was investigated and the results are shown in Fig. S2, the extraction efficiency increased when the polymerization time increase from 1.0 to 2.0 h probably due to the increasing amount of the polypyrrole particles. However, the extraction efficiency decreased when the polymerization time was longer than 2.0 h. The reason may be that the polypyrrole layer was too dense (Fig. S3), resulting in a reduced surface area and adsorption sites. The surface area of hybrid monolith PPY/GO/PVA cryogel sorbent at the polymerization time of 1.0, 2.0, 4.0 and 6.0 h were 30.50, 34.52, 30.40 and 23.48 m^2g^{-1} respectively. Thus, the polymerization time of 2.0 h was enough to achieve a satisfactory recovery and was selected for subsequent experiments.

The concentration of graphene oxide was investigated in the concentration range of 0.010–0.10% w/v. The extraction efficiencies of sulfonamides increased as the concentration of graphene oxide increased from 0.010 to 0.050 %w/w, and it remained almost constant with any further increase of graphene oxide concentration (Fig. S4). Thus, the optimal concentration of graphene oxide of hybrid monolith PPY/GO/PVA cryogel sorbent was 0.050 %w/v.

3.2.3. Desorption condition

After the extraction was completed, the adsorbed sulfonamides were eluted from the sorbent. To obtain the highest eluting efficiency, several solvents with different polarities were investigated *i.e.* acetonitrile, methanol, ethyl acetate and dichloromethane with the polarity index of 5.8, 5.1, 4.3 and 3.1, respectively. Since sulfonamides are polar compounds, their elution with slightly more polar solvents is better than with less polar solvents (Fig. 4a). In this work, methanol gave the highest recovery, therefore, it was selected as the desorption solvent in subsequent experiments. The effect of the desorption solvent volume was also investigated. The result indicated that 2.0 mL of methanol was sufficient for the desorption of all target sulfonamides (Fig. 4b).

3.2.4. Effect of sample pH

The sample pH is an important factor affecting chemical species of target analytes and also the effective surface charge of the sorbent, which can affect the extraction efficiency of target analytes. Sulfonamides are amphoteric compounds that can have cationic, neutral or anionic forms. Therefore, the pH of the sample solution needs to be investigated and optimized. In this work, the sample pH was adjusted with HCl or NaOH in the range of 3.0–11.0. As shown in Fig. 4c, there was no significant difference in the recovery of sulfonamides between pH 3.0 and pH 9.0, in which range sulfonamides are in a neutral form, and the recovery decreased at a pH higher than 9.0 due to their having an anionic form in that pH range [34,35]; carboxyl acid group of graphene oxide could also be deprotonated under the same condition [36]. Therefore, the presence of repulsive interaction between the sulfonamides and the sorbent resulted in decreasing extraction efficiency. These results indicated that the sulfonamides adsorbed on the surface polypyrrole and graphene oxide through hydrogen bonding, π-π and hydrophobic interaction. Considering that the pH of the real samples was lower than 9.0, therefore no need to adjust the sample pH.

3.2.5. Effect of sample volume

Although high enrichment factors were obtained with increasing sample volume, the enrichment was limited by the number of available adsorption sites of the sorbent. In this work, influence of sample volume on the extraction efficiency of sulfonamides was investigated in the range of 5.0–40.0 mL. As shown in Fig. 4d, the recovery was reduced when the sample volume was greater than 20.0 mL. Considering the enrichment factor and extraction efficiency, 20.0 mL was chosen as an optimum sample volume for the next experiment.

3.2.6. Effect of sample flow rate

For the SPE procedure, a fast sample flow rate would not allow the analytes to be adsorbed completely onto the SPE sorbents, while a slow sample flow rate would make the extraction time too long. Therefore, the sample flow rate needs to be optimized to obtain the fastest flow rate that provides the highest extraction efficiency. The influence of the sample flow rate on the recovery of sulfonamides was investigated in the range of 0.5–5.0 mL min^{-1}. As shown in Fig. S5, the extraction efficiency decreased when the sample flow rate was faster than 2.0 mL min^{-1}. Therefore, the 2.0 mL min^{-1} was selected as the optimum sample flow rate.

3.2.7. Effect of salt concentration

The content of salt may affect the partitioning of the analytes between sorbent and sample solution, which can enhance or decrease the extraction efficiency. Therefore, the influence of salt addition on the extraction efficiency of sulfonamides was investigated by the addition of NaCl in spiked deionized water in the range of 0.0–15.0% w/v. The results are shown in Fig. S6. The salt content of up to 2.0% w/v did not have a significant effect on the extraction efficiency of sulfonamides and the recovery decreased when the concentration of salt was higher than 2.0% w/v. This may due to the increased viscosity of the sample solution and the consequent reduction in the mass transfer of analytes to the sorbent and diminished adsorption ability of the developed sorbent. Therefore, further experiments were performed without salt addition.

3.3. Analytical performance

To evaluate the analytical performance of the developed method for the extraction and determination of sulfonamides. Under the optimum conditions, the linearity, limit of detection (LOD) and limit of quantification (LOQ) were investigated and the results are summarized in Table 1. Good linearity was obtained in the range of 0.20–100.0 μg L^{-1} for SDZ, STZ, and SME; and in the range of 0.10–100.0 μg L^{-1} for SMT, SMM and SDM with a coefficients of determination (R^2) greater than 0.99 and the relative standard deviations (RSD) less than 8.0%. The LOD and LOQ based on the

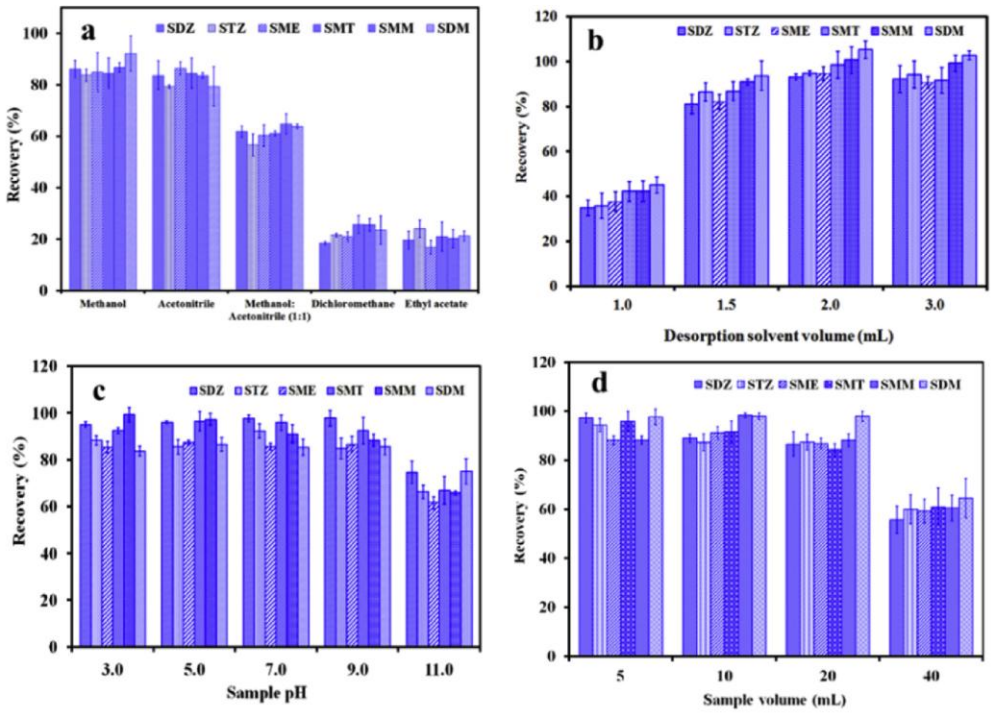

Fig. 4. Effect of desorption solvent (a), desorption solvent volume (b), sample pH (c) and sample volume (d) on the recovery of sulfonamides using the hybrid monolith PPY/GO/PVA cryogel sorbent.

signal-to-noise ratios of 3 and 10 were 0.20 and 0.80 μg L^{-1} for the SDZ, STZ, and SME; and 0.10 and 0.40 μg L^{-1} for the SMT, SMM and SDM. It can be concluded that the developed method can be used for the determination of trace sulfonamides in real samples.

3.4. Real samples analysis

The developed hybrid monolith PPY/GO/PVA cryogel sorbent was applied for the extraction of sulfonamides from different water samples including tap water, river water, livestock wastewater and lake water. The results are shown in Table S1. SMM was detected in livestock wastewater at a concentration of lower than the LOQ and SMT was also detected in livestock wastewater in the concentration range of lower than LOQ to 0.77 ± 0.03 μg L^{-1}. To evaluate the accuracy of the developed method, the water samples were spiked with sulfonamides at three concentrations (1.00, 5.00 and 20.00 μg L^{-1}) and then extracted and analyzed under the optimum conditions. The results are shown in Table S2. The recoveries of all target sulfonamides were in the range of 85.5–99.0% with relative standard deviations less than 5%. The satisfactory recoveries were within the acceptable range as recommended by the AOAC (70–120%) [37]. The chromatograms of spiked wastewater samples

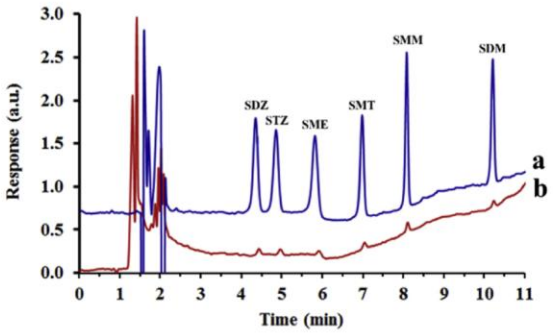

Fig. 5. Typical chromatograms of spiked wastewater sample (1.0 μg L^{-1}) with (a) and without (b) extraction using the hybrid monolith PPY/GO/PVA cryogel sorbent.

Table 1
Analytical performance for the determination of sulfonamides using the hybrid monolith PPY/GO/PVA cryogel sorbent.

Sulfonamides	Linear range (μg L^{-1})	Regression line equation	R^2	LOD[a] (μg L^{-1})	LOQ[b] (μg L^{-1})	RSD (%)
SDZ	0.20–100	y = (0.082 ± 0.003)x + (3.10 ± 2.29)	0.9926	0.20	0.80	0.7–6.1
STZ	0.20–100	y = (0.081 ± 0.003)x + (2.77 ± 2.15)	0.9932	0.20	0.80	0.8–5.5
SME	0.20–100	y = (0.084 ± 0.003)x + (3.32 ± 2.51)	0.9938	0.20	0.80	1.2–7.1
SMT	0.10–100	y = (0.073 ± 0.003)x + (2.06 ± 2.12)	0.9921	0.10	0.40	1.6–5.6
SMM	0.10–100	y = (0.080 ± 0.003)x + (2.79 ± 2.39)	0.9917	0.10	0.40	2.0–6.3
SDM	0.10–100	y = (0.074 ± 0.003)x - (2.37 ± 2.15)	0.9920	0.10	0.40	2.0–5.7

[a] LOD is the lowest concentration of an analyte that can be detected, but not necessarily quantified.
[b] LOQ is the lowest concentration of an analyte that can be determined with acceptable precision and accuracy.

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

Method	Adsorbent	Sample	LOD (μg L^{-1})	Recovery (%)	Reference
HPLC-UV	$CoFe_2O_4$–graphene	Milk	1.59	62–104	[6]
HPLC-DAD	Magnetite–embedded with silica functionalized with phenyl chains	Milk	7.0–14.0	81.9–115.0	[8]
HPLC-UV	Microwave–assisted liquid–liquid microextraction	Water	0.33–0.85	75.1–115.8	[11]
HPLC-DAD	Molecularly imprinted polymers	Water	0.2–3.0	70–120	[34]
HPLC-DAD	Micro–solid phase extraction (μ-SPE) using TiO_2 nanotube arrays	Water	0.27–0.60	82.8–101.7	[38]
HPLC-UV	Polypropylene membrane protected micro–solid phase extraction (MP–μ–SPE)	Milk	0.38–0.62	71.3–83.8	[39]
HPLC-UV	Magnetic molecularly imprinted polymers (MMIPs)	Water	0.76–1.2	61.2–94.1	[40]
HPLC-DAD	Hybrid monolith PPY/GO/PVA cryogel	Water	0.1–0.2	85.5–99.0	This work

with and without extraction using hybrid monolith PPY/GO/PVA cryogel sorbent are shown in Fig. 5. The results indicated that extraction using the developed method can improve the method detection limit and can be used to detect trace sulfonamides.

3.5. Reproducibility and reusability

The reproducibility of the hybrid monolith PPY/GO/PVA cryogel sorbent was investigated in terms of lot-to-lot reproducibility by the preparation of six different lots under the same conditions. These sorbents were then applied to extract sulfonamides under the optimum conditions. The relative standard deviations of the average recovery from the six different lots were lower than 10% (Fig. S7). This result indicated a good reproducibility of the sorbent preparation.

The reusability of the hybrid monolith PPY/GO/PVA cryogel sorbent was also investigated by spiking sulfonamides in wastewater samples. After the first use, the sorbent was washed with 2.0 mL of methanol and then the carryover effects were investigated. No target analytes peaks were detected, which indicated that the developed sorbent could be reused. As shown in Fig. S8, the hybrid monolith PPY/GO/PVA cryogel sorbent could be reused at least 10 times without loss of the extraction efficiency (>80%). These results also indicated that the coating of polypyrrole on the surface of the graphene oxide incorporated in the PVA cryogel has a good stability. After 10 cycles, the recovery of sulfonamides was decreased may be due to the losing of polypyrrole particles from the sorbent (Fig. S9). On the other hand, traditional particle-packed SPE sorbent cartridges cannot be reused due to the difficulty of completely removing adsorbed interferences.

3.6. Comparison between the hybrid monolith PPY/GO/PVA cryogel sorbent and a traditional packed SPE cartridge

The extraction efficiency of the hybrid monolith PPY/GO/PVA cryogel sorbent was compared to a traditional packed SPE cartridge, HLB sorbent. The recoveries for the hybrid monolith PPY/GO/PVA cryogel sorbent of SDZ, STZ, SME, SMT, SMM and SDM were 88.1 ± 5.0, 86.6 ± 3.8, 96 ± 3.2, 87.0 ± 1.5, 85.6 ± 3.5, 87.6 ± 2.6%, respectively. For the traditionally packed SPE cartridge, the recoveries were 72.6 ± 4.0, 72.0 ± 4.9, 80.3 ± 3.3, 76.0 ± 5.6, 79.7 ± 6.0, and 71.0 ± 4.4%, respectively. The better recoveries were obtained using the hybrid monolith PPY/GO/PVA cryogel sorbent due to its larger surface area and high adsorption sites.

3.7. Comparison with other extraction methods

The analytical performance of the developed method for the determination of sulfonamides based on the hybrid monolith PPY/GO/PVA cryogel sorbent was compared with other reported methods (Table 2). The LODs of the developed method were lower than those of the previous methods [6,8,11,34,38–40]. The extraction efficiency of the developed method provided results better than [6,11,34,39,40] or comparable with the other methods [8,38]. These results have demonstrated that the developed method is highly sensitive and accurate for the determination of trace sulfonamides in water samples. In addition, the hybrid monolith PPY/GO/PVA cryogel sorbent can be reused at least 10 times which also helps to reduce the analysis costs.

4. Conclusions

In this work, a hybrid monoliths of polypyrrole-coated graphene oxide incorporated into a PVA cryogel were successfully prepared and applied for the extraction and enrichment of six sulfonamides from different water samples. The combination of polypyrrole and graphene oxide helped to improve the extraction efficiency of the sulfonamides due to their high specific surface area and the greater adsorption by the sites for the target analytes. The high porosity of the PVA cryogel helped to prevent the high back pressure that normally occurs with conventional packed SPE cartridges. The results showed that the developed method offers good sensitivity, accuracy and precision. The satisfactory recoveries from different water samples indicated that the developed method can be used as an efficient extraction and preconcentration method for the determination of trace sulfonamides in water samples.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.aca.2017.01.052.

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Supporting Information

Hybrid monolith sorbent of polypyrrole-coated graphene oxide incorporated into a polyvinyl alcohol cryogel for extraction and enrichment of sulfonamides from water samples

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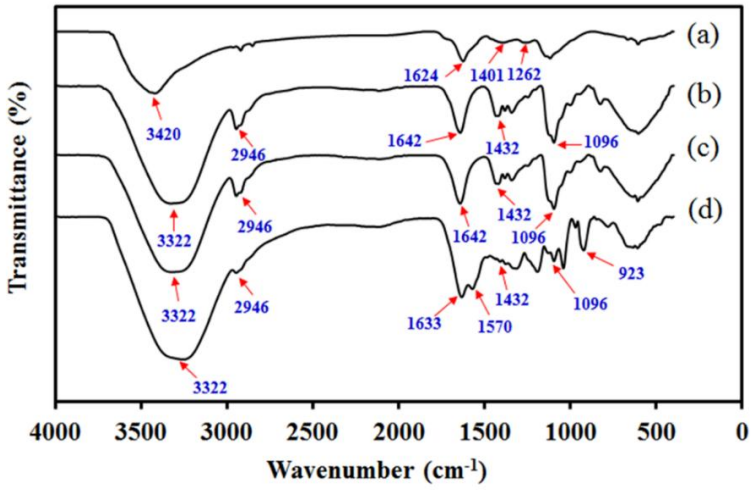

Fig. S1 FTIR spectra of the GO (a), PVA cryogel (b), GO/PVA cryogel (c) and hybrid monolith PPY/GO/PVA cryogel sorbent (d)

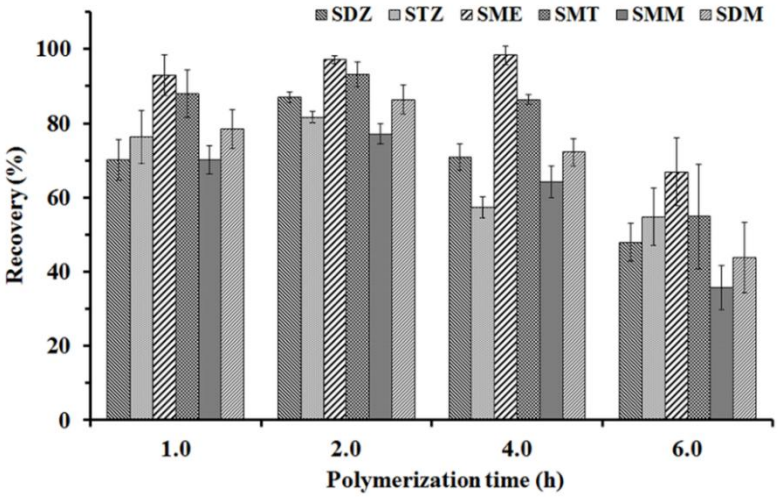

Fig. S2 Effect of polymerization time on the recovery of the sulfonamides using the hybrid monolith PPY/GO/PVA cryogel sorbent

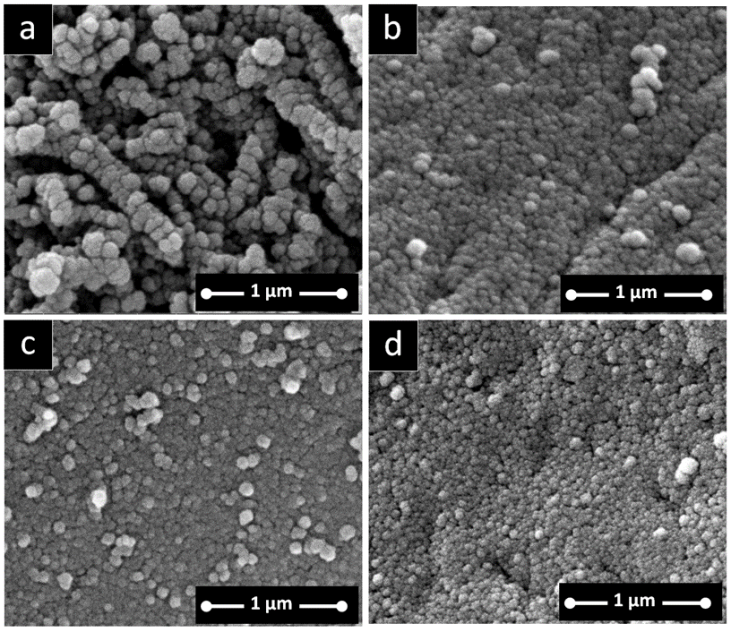

Fig. S3 SEM images of the hybrid monolith PPY/GO/PVA cryogel sorbent at different polymerization times; 1 h (a), 2 h (b), 4 h (c) and 6 h (d)

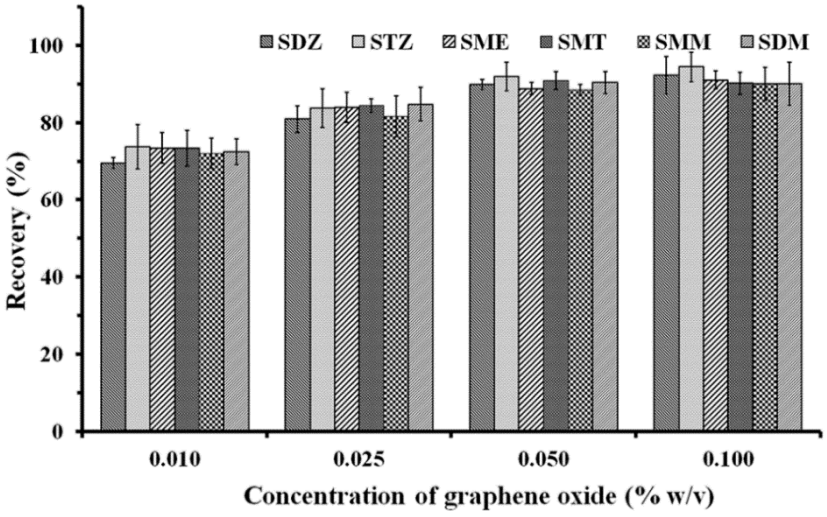

Fig. S4 Effect of concentration of graphene oxide on the recovery of sulfonamides using the hybrid monolith PPY/GO/PVA cryogel sorbent

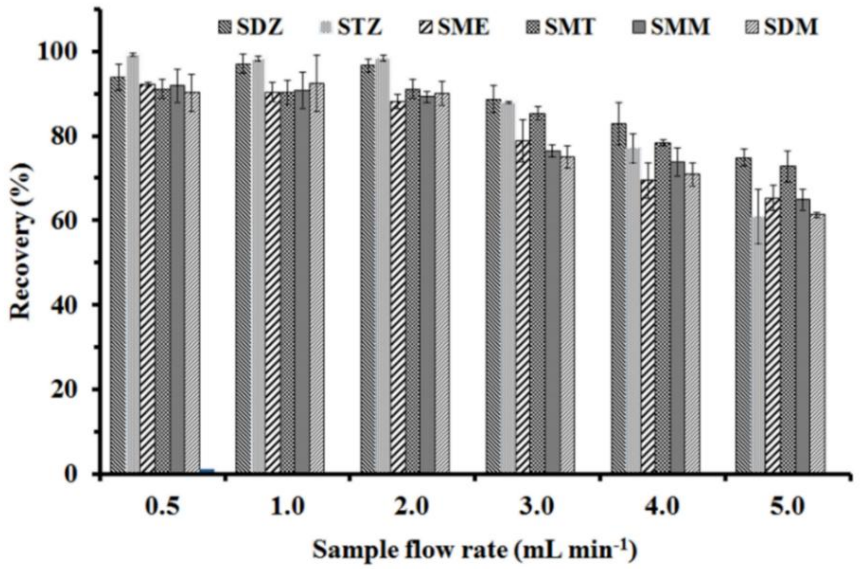

Fig. S5 Effect of sample rate on the recovery of sulfonamides using the hybrid monolith PPY/GO/ PVA cryogel sorbent

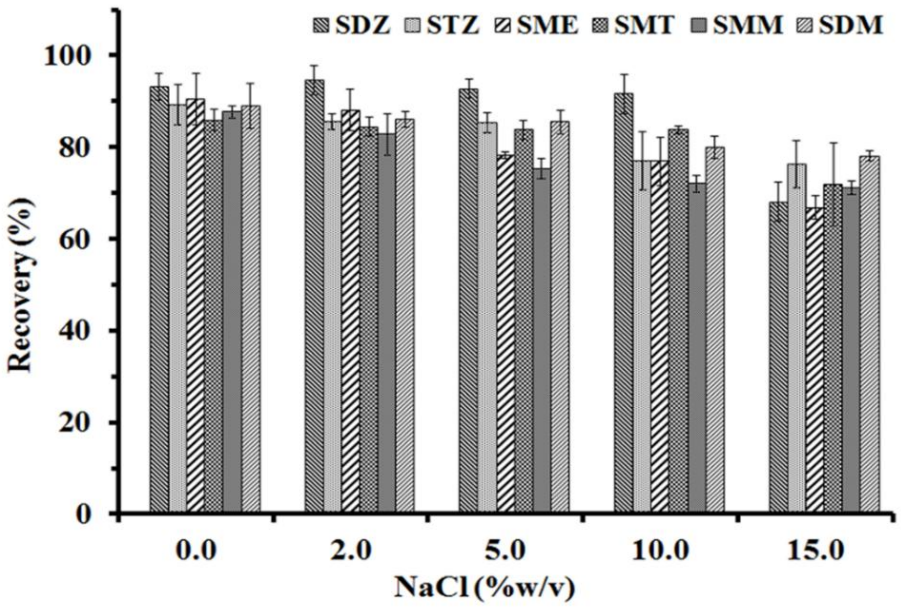

Fig. S6 Effect of salt concentration on the recovery of sulfonamides using the hybrid monolith PPY/GO/PVA cryogel sorbent

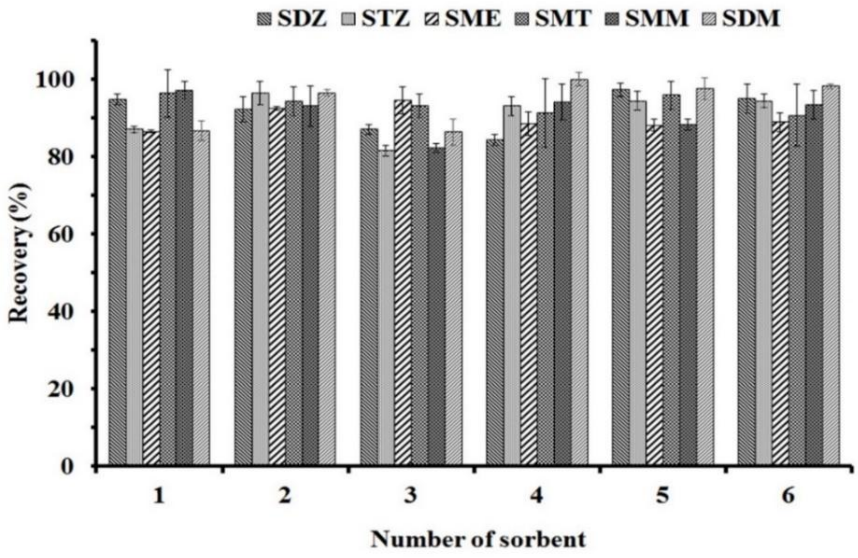

Fig. S7 The reproducibility of the hybrid monolith PPY/GO/PVA cryogel sorbent

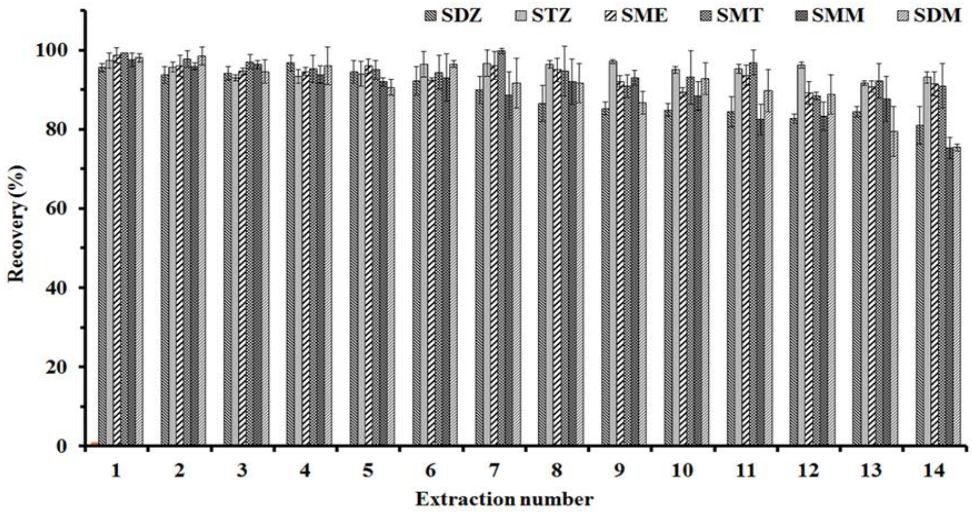

Fig. S8 The reusability of the hybrid monolith PPY/GO/PVA cryogel sorbent for the extraction of sulfonamides in spiked wastewater sample

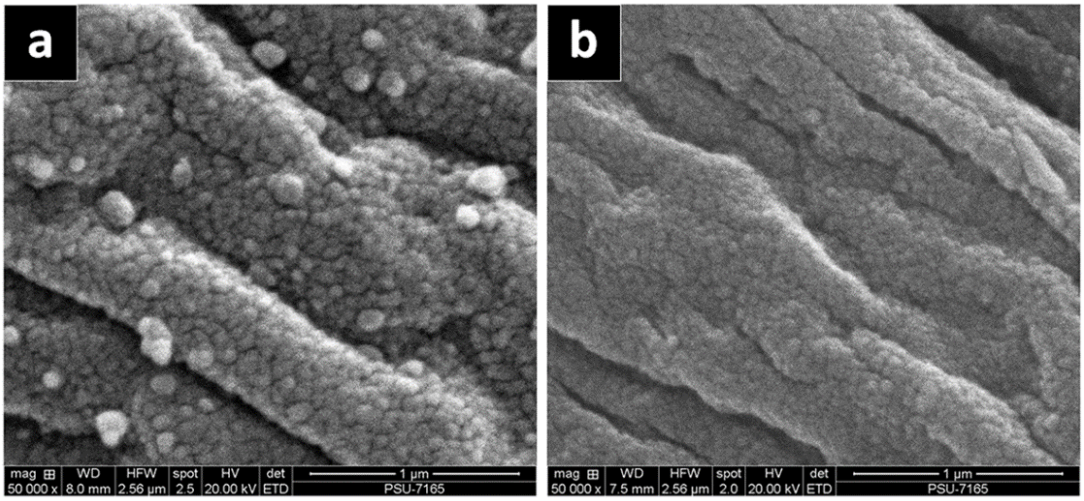

Fig. S9 SEM images of hybrid monolith PPY/GO/PVA cryogel before (a) and after reused 10 times (b)

Table S1 Concentration of sulfonamides in real water samples

Samples	Concentration (µg L-1)					
	SDZ	STZ	SME	SMT	SMM	SDM
Tap water 1	ND	ND	ND	ND	ND	ND
Tap water 2	ND	ND	ND	ND	ND	ND
River water 1	ND	ND	ND	ND	ND	ND
River water 2	ND	ND	ND	ND	ND	ND
Wastewater 1	ND	ND	ND	< LOQ	< LOQ	ND
Wastewater 2	ND	ND	ND	0.77 ± 0.03	< LOQ	ND
Lake water 1	ND	ND	ND	ND	ND	ND
Lake water 2	ND	ND	ND	ND	ND	ND

Table S2 The recoveries of sulfonamides in spiked water samples

Samples	Spiked concentration ($\mu g\ L^{-1}$)	Recovery ± RSD (%)					
		SDZ	STZ	SME	SMT	SMM	SDM
Tap water	1.0	90.9 ± 2.2	96.0 ± 2.0	89.7 ± 3.8	93.5 ± 3.9	89.9 ± 0.3	89.5 ± 2.5
	5.0	89.1 ± 2.6	88.3 ± 1.7	92.8 ± 1.2	89.7 ± 2.7	90.3 ± 2.3	91.0 ± 4.9
	20.0	93.1 ± 0.9	91.9 ± 3.0	98.2 ± 0.8	95.8 ± 3.3	88.3 ± 1.8	91.6 ± 2.8
River water	1.0	85.7 ± 0.3	93.3 ± 2.0	92.3 ± 2.6	91.9 ± 0.3	89.8 ± 1.1	96.8 ± 1.7
	5.0	86.3 ± 1.7	88.5 ± 1.3	91.6 ± 0.7	90.8 ± 0.6	85.5 ± 0.4	88.0 ± 1.6
	20.0	85.7 ±3.6	85.5 ± 0.7	85.5 ± 0.4	89.7 ± 4.1	87.1 ± 0.5	90.6 ± 1.7
Waste water	1.0	91.3 ± 1.9	87.1 ± 0.6	88.1 ± 4.4	95.9 ± 0.9	91.4 ± 1.5	88.9 ± 2.7
	5.0	85.6 ±2.3	86.7 ± 1.0	86.1 ± 0.8	93.2 ± 4.0	87.2 ± 1.7	88.2 ± 1.1
	20.0	85.8 ± 0.6	85.8 ± 0.7	85.7 ±1.1	96.9 ± 1.9	89.4 ± 1.3	85.9 ±3.2
Lake water	1.0	86.0 ± 0.8	88.9 ± 3.8	86.6 ± 0.5	99.0 ± 1.5	87.3 ± 2.0	90.5 ± 3.3
	5.0	87.1 ± 1.1	92.1 ± 3.3	88.5 ± 1.3	89.4 ±4.5	86.4 ± 0.3	92.7 ±3.9
	20.0	85.5 ± 0.6	96.1 ± 3.2	85.7 ± 0.8	89.2 ±3.9	85.9 ± 0.9	87.7 ± 0.8