Sorbent-based microextraction for preconcentration of sulfonamide residues prior to their analysis by liquid chromatography

Wannipha Khiaophong

A Thesis Submitted in Partial Fulfillment of Requirements for
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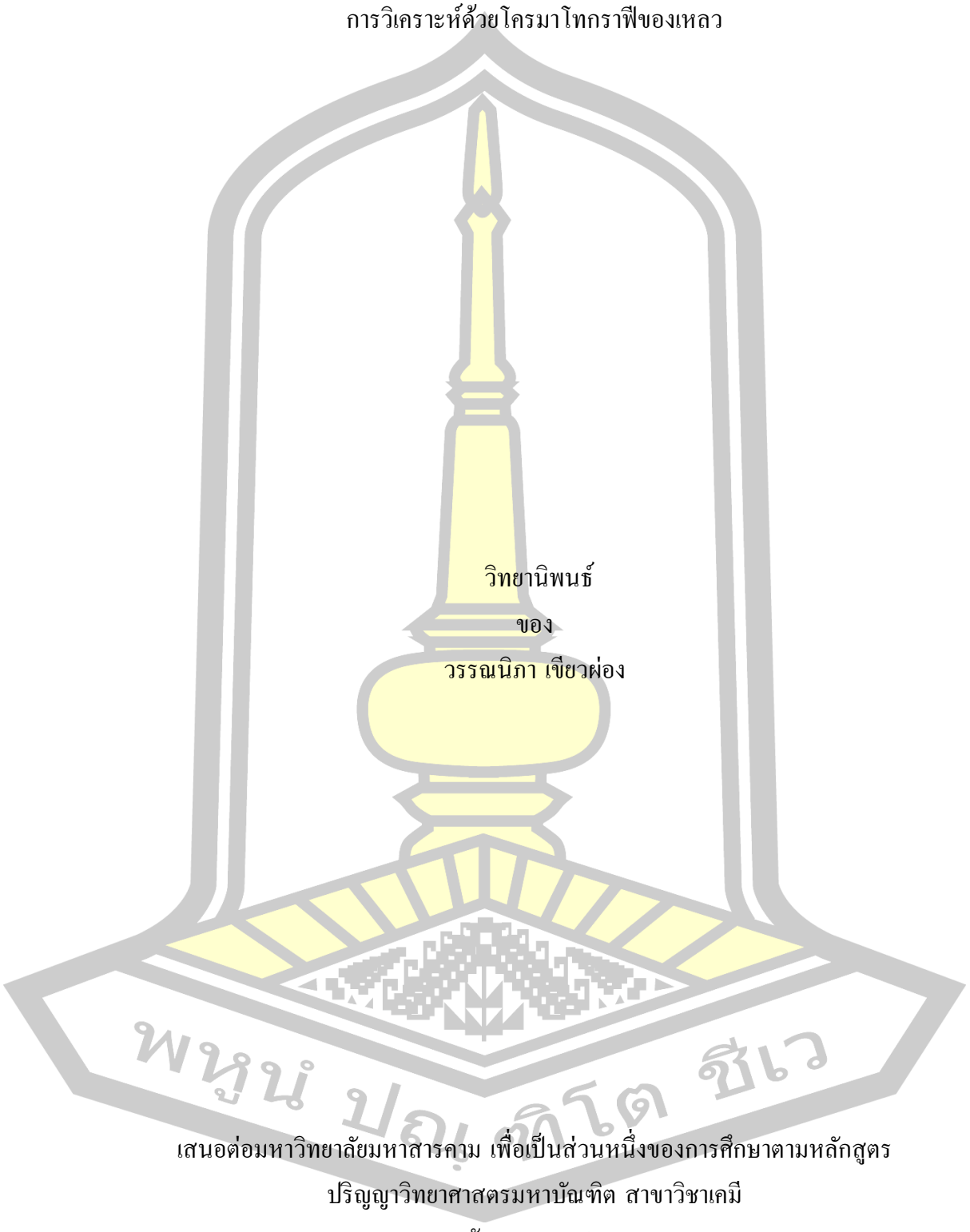

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The examining committee has unanimously approved this Thesis, submitted by Miss Wannipha Khiaophong , as a partial fulfillment of the requirements for the Master of Science Chemistry at Mahasarakham University

Examining Committee

.....Chairman
(Assoc. Prof. Yanawath Santaladchaiyakit , Ph.D.)

.....Advisor
(Assoc. Prof. Jitlada Vichapong , Ph.D.)

.....Committee
(Asst. Prof. Orrasa Prasitnok , Ph.D.)

.....Committee
(Asst. Prof. Kraingkrai Ponhong , Ph.D.)

Mahasarakham University has granted approval to accept this Thesis as a partial fulfillment of the requirements for the Master of Science Chemistry

.....	.....
(Prof. Pairot Pramual , Ph.D.)	(Assoc. Prof. Krit Chaimoon , Ph.D.)
Dean of The Faculty of Science	Dean of Graduate School

พหุน ปณฺ ฑิโต ชีเว

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AUTHOR Wannipha Khiaophong

ADVISORS Associate Professor Jitlada Vichapong , Ph.D.

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ABSTRACT

In this study, demonstrates the development of sorbent-based microextraction and chromatographic methodologies for monitoring of sulfonamide residues. The sample preparation procedure was based on a miniaturization of two sorbents using surfactant coated silica and sodium alginate- melamine sponge. The as prepared sorbents were physicochemically and morphologically characterized. Parameters influencing extraction efficiency were investigated and optimized. Two alternative methods are simple and also environmentally friendly which assessed using Analytical Eco-scale and Analytical GREEnness metric (AGREE).

Micro-solid phase extraction (μ-SPE) using surfactant coated silica for extraction and preconcentration of sulfonamide residues at trace levels in environmental water and honey samples prior their analysis by high performance liquid chromatography coupled with photodiode array detector (HPLC-PDA) was successfully developed. The sample solutions were dispersed in a small amounts of solid sorbent by vacuum manifold for sample preparation, and extraction occurred by adsorption in a short time. Finally, the analytes were subsequently desorbed using an

appropriate. The optimum conditions of the proposed extraction method, were mixed standard/sample solution (10 mL), 0.4 g silica, 0.03 M CTAB (150 µL), and 500 µL methanol (as elution solvent). The proposed method, under optimal conditions, showed excellent linearity in different ranges (9–300 µg L^{-1}), the coefficient of determination (R^2) of greater than 0.99, good repeatability (RSD < 6.72 %), good sensitivity (LODs in the range of 1 to 3 µg L^{-1}), and high enrichment factor (5.63–13.33). The developed µ-SPE method was applied to analyze sulfonamide residues in water and honey samples with relative recoveries of 60.9–119.4 % were obtained.

Sodium alginate-melamine sponge (alginate-MS) modified with surfactant as an adsorbent in µ-SPE for trace determine of sulfonamide residues in honey samples prior to ultra performance liquid chromatography-photodiode array detector (UPLC-PDA) analysis was investigated. The optimum conditions of the proposed method, were mixed standard/sample solution (100 mL), alginate-MS (1x1x1 cm^3), 0.1 M CTAB (1000 µL), and 500 µL acetonitrile (as elution solvent). Under optimal conditions, excellent linearity in different ranges (3–70 µg L^{-1}), the coefficient of determination (R^2) of greater than 0.99, good repeatability (RSD < 12.83 %), good sensitivity (LODs in the range of 0.3 to 0.9 µg L^{-1}) and high enrichment factor (40.4–76.1). The proposed method was successfully applied to honey sample with the relative recoveries in the range of 58.7–144.3 %

Keyword : surfactant coated silica sorbent, alginate-MS

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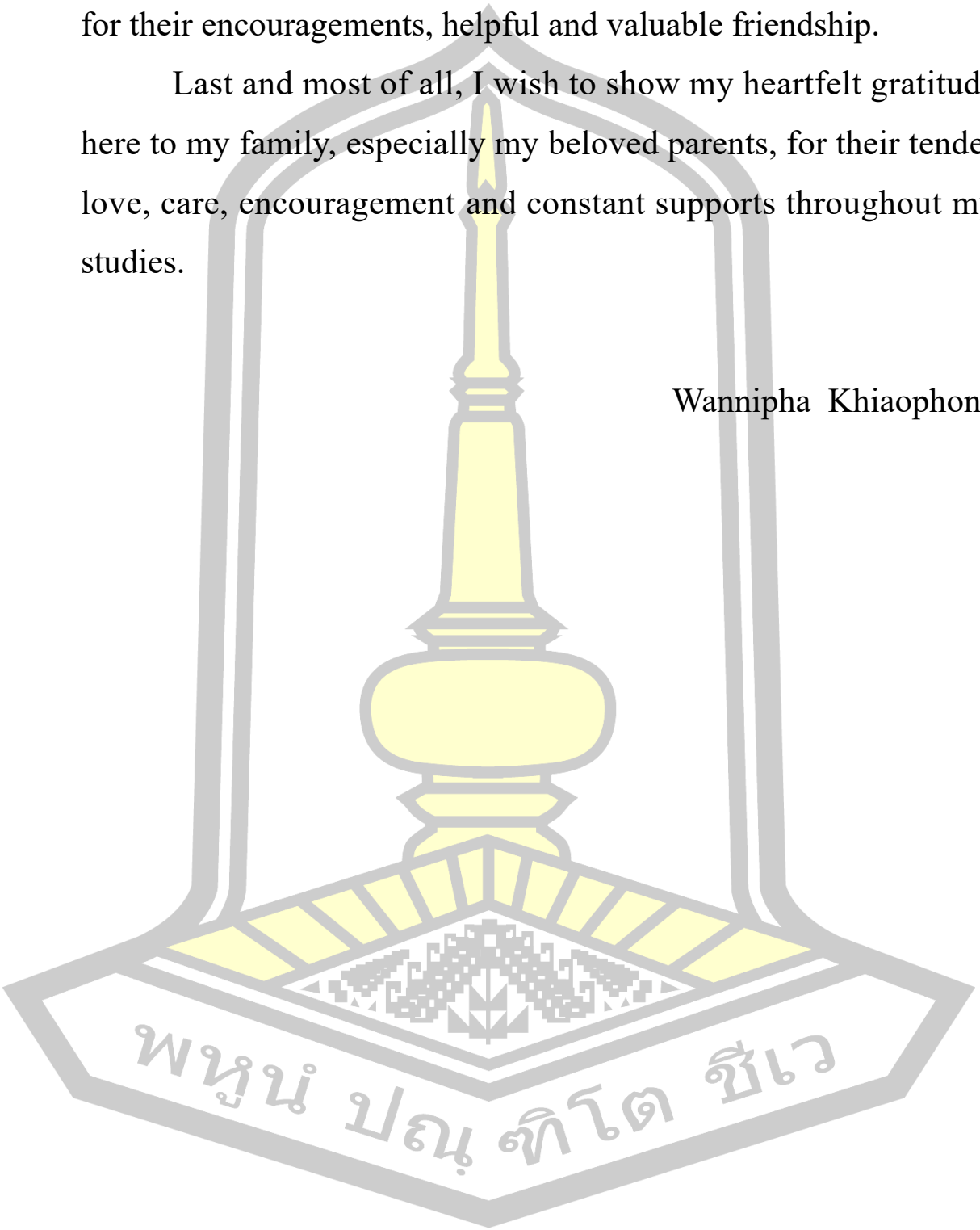
Wannipha Khiaophong



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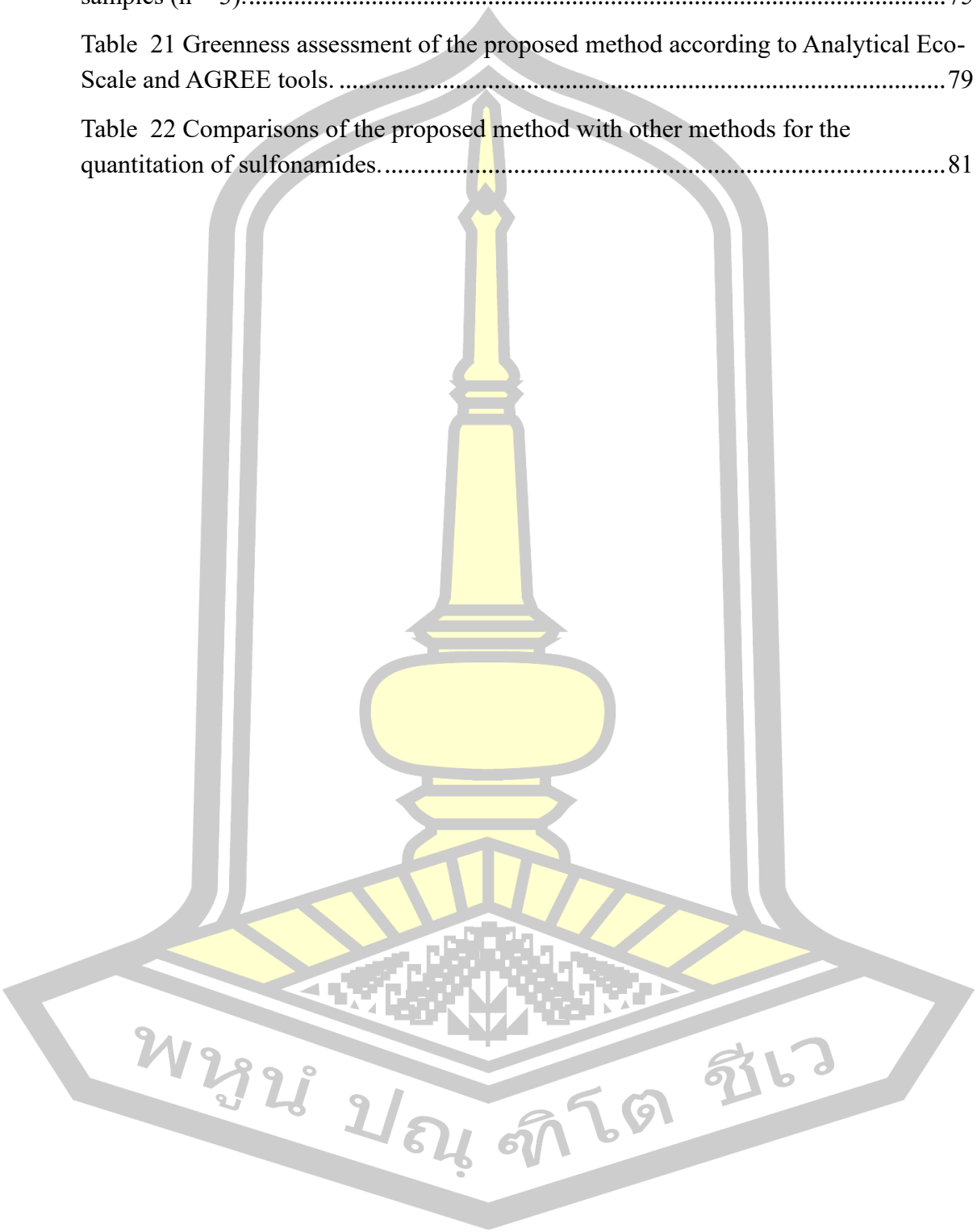

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CHAPTER 1
INTRODUCTION

1.1 Background and rational

Sulfonamides are N-substituted derivatives of sulfanilamide [1], were the first antimicrobial group of drugs used in the therapy. These compounds are still used today in the medicine and they are used in the veterinary medicine for both therapeutic and pro- phylactic purposes [2]. However, the residues of sulfonamides in food could cause allergic reactions, urination and hematopoietic disorder. Long-term accumulation may deal great harm to human health because it may cause damage to kidney function, drug resistance, carcinogenicity, etc. [3]. The Minimum Required Performance Limit (MRPL) for analytical methods for the detection of sulfonamides in European Union (EU) was set at 10 ng g^{-1} of honey [4]. Hence, several laboratories had developed analytical methods for sulfonamides residues monitoring programs. Improved methods of sulfonamides analysis are a constant challenge for the researchers. Several methods have been developed for this purpose applying many kinds of analytical techniques, such as high performance liquid chromatography, gas chromatography (GC) [5], thin layer chromatography [6] and enzyme-linked immunosorbent assay (ELISA) [7]. Although various GC and gas chromatography-mass spectrometry (GC-MS) methods have been used, they require the polar sulfonamides to be chemically derivatized due to their low volatility, and, to overcome matrix interference, exhaustive cleanup is required [8]. Due to their polarity, therefore liquid chromatography including high performance liquid chromatography (HPLC) [9] and ultra performance liquid chromatography (UPLC) are preferred methods for determining sulfonamides [10]. However, these techniques not always provide the desired sensitivity, sample clean-up and enrichment methods are recommended prior to instrumental analysis to enhance the sensitivity and obtain accurate results.

Solid phase extraction (SPE) is one of the methods widely used as a sample preparation tool in separation of analytes from different matrices. While effective, SPE is labour and time intensive, and large sample volumes are required to achieve regulatory LODs [11]. Nowadays, SPE-based miniaturized technigue such as micro-

SPE (μ-SPE) has been proposed as an improved technique. Micro-SPE was performed under a high pressure allows the use of smaller sorbent particle sizes (<5 μm), increasing extraction efficiency and thus reducing the required sample volumes [12]. This method is based on the adsorption of analytes to the surface of the adsorbent, followed by their selective elution using a suitable elution solvent [13]. Various types of sorbents have been used including Oasis HLB cartridge [14], Isolute ENV+ [15], Strata X [16] and MCX [17] activated carbon, silica gel and clay are among the others. Additionally, there are eco-friendly adsorbents derived from natural polymers such chitosan and sodium alginate (SA) [18]. Appropriate sorbents are critical to the accuracy, sensitivity, and excellent anti-interference capacity of the target detection in the preconcentration step [19]. Consequently, the development and design of alternative functional materials are the foundation of innovation in analytical chemistry.

Surfactants are amphiphilic compounds, which contain a nonpolar hydrocarbon- chain bonded to a polar group (anionic, cationic, neutral or zwitterionic) [20]. They are used in extraction method including, liquid-liquid extraction and solid-phase extraction. In solid-phase extraction procedure, surfactants are used to increase the dispersion of sorbent particles in the bulk solution or to enhance sorption ability the surface of the solid material to increase the extraction properties of the sorbent. Overall, surfactants in extraction processes significantly improve the efficiency and selectivity of the procedures, as well as the solubility of the compounds, resulting in higher extraction recovery of the analytes and cost-effective sample preparation. Recently, the use of surfactants meet the requirements of Green Analytical Chemistry (GAC) because these compounds are non-toxic, non-volatile, and non-flammable, which minimizes the risk to humans and the environment [21].

The goal of this study was to develop and validate of a method for the separation and determination of sulfonamide residues in environmental water and honey samples. Two sorbents using surfactant coated silica and sodium alginate-melamine sponge were studied. The dispersed sample was transferred into the prefabricated SPE cartridge, which integrated extraction and cleanup into one single-step. The sorbent was then characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FTIR)

and N_2 sorption analyses. The extraction conditions were optimized by one parameter at a time while the other remaining factors were kept constant. Finally, this method was applied to assay of sulfonamides in environmental water and honey samples prior to HPLC and UPLC analysis. This alternative method is simple and is also environmentally friendly which assessed using Analytical Eco-scale and Analytical GREEnness metric (AGREE) method.

1.2 Purposes of the research

1. To develop a sample preparation method using silica gel and alginate-melamine sponge (MS) for determination of sulfonamides.
2. To improve recovery and preconcentration extraction efficiency.
3. To apply the developed methods to the analysis of real samples.

1.3 Scopes of research

1. Preconcentration method was validated by the following parameters: calibration curves, limits of detection (LODs), limits of quantitation (LOQs), and reproducibility.

2. Developed method was applied to analysis of sulfonamide residues (sulfathiazole, sulfamethazine, sulfamethoxazole, sulfadimethoxine) in water and food samples.

1.4 Benefits of research

1. The developed sample preparation method enables accurate, precise and rapid extraction of sulfonamides.
2. The developed sample preparation techniques can be applied to the determination of sulfonamides in real samples.

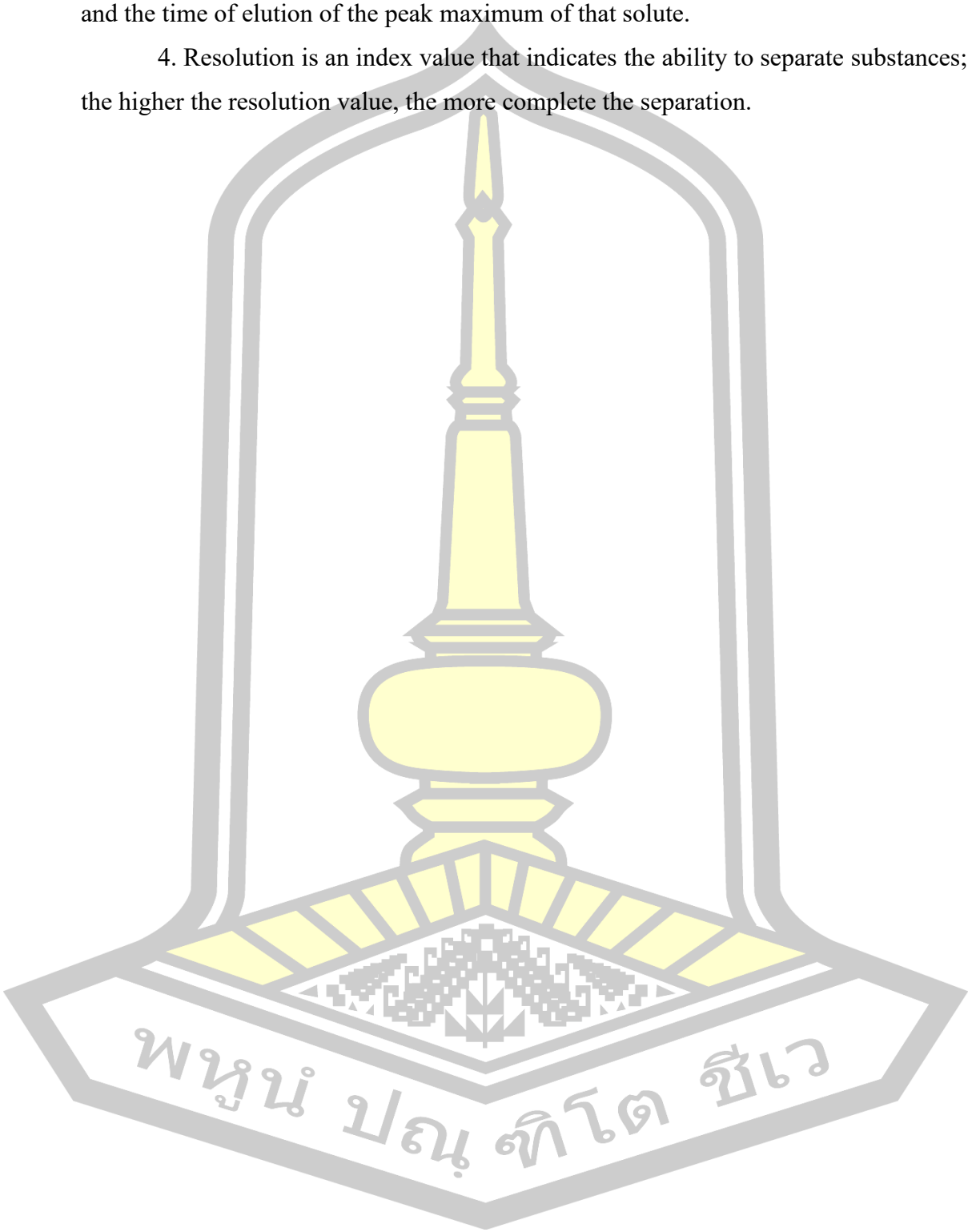
1.5 Definition of terms

1. The preconcentration process tries to boost a sample's concentration before examination or detection.

2. The limit of detection (LOD) is the lowest quantity of analyte that can be dominated to absence of analyte within a stated confidence limit.

3. The retention time is the run time between the time of injection of a solute and the time of elution of the peak maximum of that solute.

4. Resolution is an index value that indicates the ability to separate substances; the higher the resolution value, the more complete the separation.



CHAPTER 2
LITERATURES REVIEW

2.1 Sulfonamide antibiotics

Sulfonamides are antibiotics that are used in both human and animal medicine to treat and prevent infectious illnesses [9]. The 1935 publication of "A Contribution to Chemotherapy of Bacterial Infections" marked the achievement of the discovery of Sulfonamides' antibacterial action [22], [23]. They can cure a variety of bacterial illnesses and are quite effective [9]. Additionally, sulfonamides (SAs) operate as competitive inhibitors of p-aminobenzoic acid in the cycle of folic acid metabolism, which prevents bacteria from multiplying [24]. Sulfonamide antimicrobials have a SO_2NH_2 group, an aromatic amine group at the N4 position and a 5- or 6-member aromatic heterocyclic ring with one or more nitrogen at the sulfonamide-N1 position. An example, the sulfonamide structure is presented in Figure 1 [25].

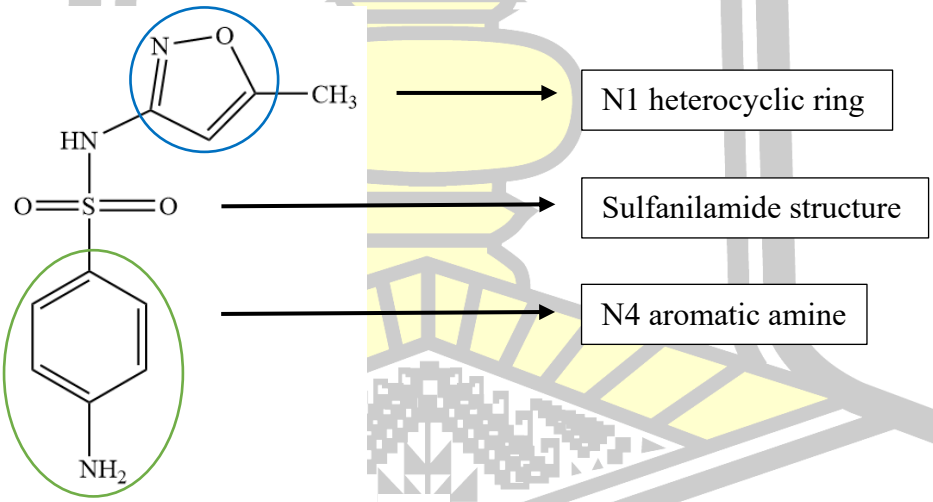


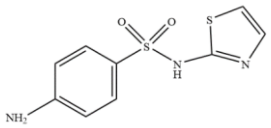
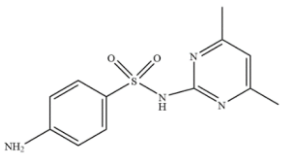
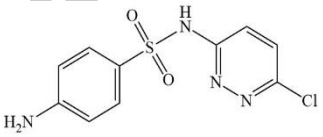
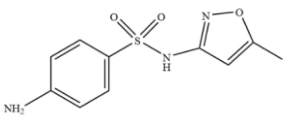
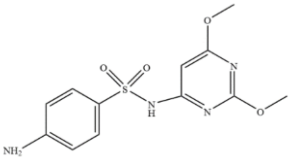
Figure 1 Structure of sulfonamide.

Sulfonamides are frequently used in animal husbandry to cure, prevent, or encourage the growth and inhibit the development of bacteria in animals, especially chickens, pigs, cattle, and fish [24]. Sulfonamides are widely used, and as a result, these antibiotics may either be discharged into the environment or persist in animal products like meat, milk, and eggs. cause soil and water sources to be contaminated [26], resulting in medication allergies and antibiotic resistance, harming consumer

health [27]. To guarantee consumer safety The maximum residue limits (MRLs) for all sulfonamides in consumable animal products have been established at 100 μg kg^{-1} by the European Union (EU) [28].

The physical and chemical properties of sulfonamides are shown in Table 1, which molecular weights range from 214 to 310 g mol^{-1}.

Table 1 Properties of the studied sulfonamides antibiotics from other chemical classes.

Sulfonamide antibiotic	Water Solubility (mg L^{-1}) at 25 °C	Log K_{ow}	pKa	Structure
Sulfathiazole (STZ)	373	0.05	7.2	
Sulfamethazine (SMZ)	1500	0.14	7.59	
Sulfachloropyridazine (SCP)	8235	0.31	6.1	
Sulfamethoxazole (SMX)	3942	0.89	5.6	
Sulfadimethoxine (SDM)	433.1	1.63	5.94	

2.2 Surfactant

Long-chain hydrophobic alkyl groups and hydrophilic quaternary ammonium groups make up surfactants. As such, they exhibit properties of both water-soluble and water-insoluble (also known as oil-soluble) constituents [29], [30]. A surfactant's molecular structure aids in lowering the surface tension of a liquid (such as water and air) as well as the interfacial tension that exists between two liquids (such as water and oil) or between a liquid and a solid (such as in the case of wetting phenomena, which is the process by which a liquid can make surface contact with a solid due to intermolecular interactions) system [31]. Surfactants start to form aggregates in aqueous solutions that are in dynamic equilibrium with the monomers in the bulk aqueous solution at critical micelle concentrations (CMC). There are significant differences in surfactants in terms of micelle size, shape, and number of monomer surfactants in the aggregate form (referred to as the aggregation number). The amphiphilic molecules can form different kinds of assemblies depending on the surfactant structure and the circumstances of the fluid [32]. The four varieties of surfactants are anionic, cationic, non-ionic, and zwitterionic, depending on the charge on the head groups [33] (Structures of surfactants used in this work are shown in Table 2). Numerous investigations have failed to pinpoint the exact mechanism of interaction between the target and adsorbent. Surfactant modification has become a popular strategy to boost adsorbent efficiency because of its many benefits, which include convenience of application, low cost, and the capacity to significantly increase adsorbent efficiency through adsorption. To modify the extraction media, surfactants are employed in a range of extraction methods, including ion-pair extraction, cloud point extraction, hemicelle/admicelle extraction, and solid phase microextraction [32]. The pertinent studies on the use of surfactants to increase extraction efficiency are shown in Table 3.

Table 2 Structures of surfactant.

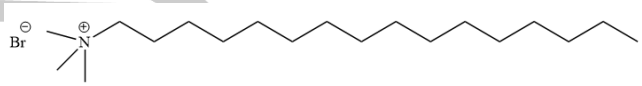
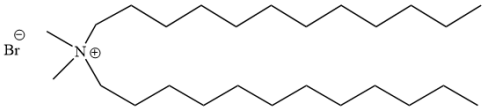
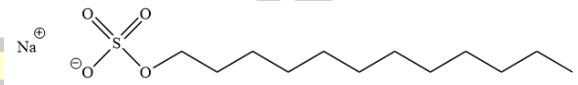
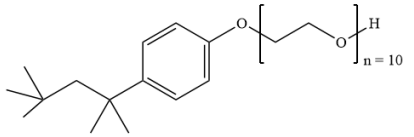
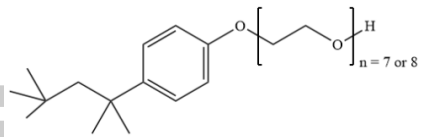
Surfactant	Type	CMC (mM)	Hydrophilic-lipophilic balance (HLB)	Structures
Cetyltrimethylammonium bromide; CTAB	Cationic (+)	1.0	7.3	
Didodecyldimethylammonium bromide; DDAB	Cationic (+)	0.085	18.1	
Sodium dodecyl sulfate; SDS	Anionic (-)	8.0	40.0	
Triton X-100	Non-ionic	0.22	12.4	
Triton X-114	Non-ionic	0.2	12.4	

Table 3 Surfactant modified adsorbent.

Author (year)	Analytes/ Samples	Adsorbent	Surfactant	Detection	Ref.
Kazemi et al. (2016)	Sulfadiazine/ milk, honey, urine and environmental water sample	Graphene oxide-silica	Cetyltrimethylammonium bromide (CTAB)	PDA Spectrophotometer	[34]
Liu et al. (2018)	Sulfamethazine, sulfamethoxazole/aqueous environments	Activated carbon	Cetyltrimethylammonium bromide (CTAB)	HPLC	[35]
Mateos et al. (2019)	Polycyclic aromatic hydrocarbons/ wastewater samples.	Graphene/ sepiolite	Cetyltrimethylammonium bromide (CTAB)/ Cetrimonium Chloride (CTAC)	HPLC	[36]
AlMasoud et al. (2020)	Rhodamine B/ industrial wastewater samples	Clay	Cetyltrimethylammonium bromide (CTAB)	UPLC-ESI-MS/MS	[37]

2.3 Sodium alginate adsorbent (SA)

Recently, there has been a lot of interest in sodium alginate (SA), an acidic, renewable, and biodegradable biopolymer generated from brown algae. This linear polymer is made up of different amounts of alpha-1,4-l-glucuronic acid (G units) and poly-β-1,4-d-mannuronic acid (M units) connected by 1-4 links [38]. Furthermore, there are a lot of hydroxyl (-OH) and carboxyl (-COOH) groups in the molecular structure of SA. When SA is crosslinked with calcium (Ca) ions, ion exchange occurs and calcium alginate hydrogels are created (as shown in Figure 2) [39]. Because of its adaptable qualities such as porosity, swelling behavior, surface chemistry, biodegradability, hydrophilicity, and high natural abundance sodium alginate is currently of greater interest to scientists than other materials [40]. Alginate is widely employed in many commercial applications, including water treatment [41], food, cosmetics, and pharmaceuticals [38]. The adsorption of SA has been the subject of numerous investigations; nevertheless, the notable enhancements that these investigations have pointed out are primarily associated with SA's poor stability [42] . Sodium alginate (SA) has been combined with chitosan, humic acid, polyaniline, cellulose, carbon nanotubes, and sponge scaffolds in order to increase its mechanical strength and adsorption capacity [43]. Relevant research on the application of sodium alginate as an adsorbent to enhance the adsorption capacity for the elimination of residues from aqueous solutions, including heavy metals, dyes, and antibiotics, is shown in Table 4.

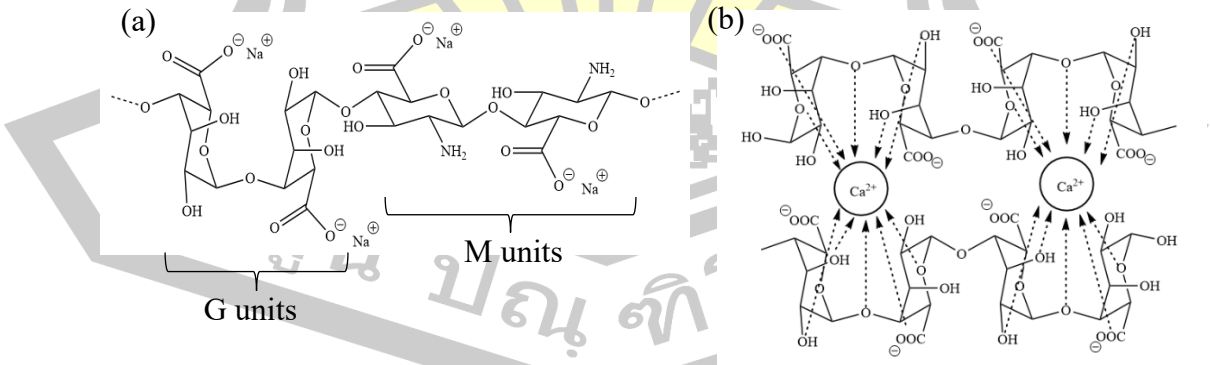


Figure 2 Structures of (a) sodium alginate pure and (b) alginate hydrogels.

Table 4 Sodium alginate adsorbent.

Author (year)	Analytes/ Samples	Adsorbent	Detection	Ref.
Feng et al. (2017)	Ca^{2+} / water sample	Alginate-MS	AAS	[18]
Wu et al. (2023)	Shlortetracycline, tetracycline, oxytetracycline	Sodium alginate/chitosan composite-modified semi-carbonized fiber (SA/CS-SF)	HPLC	[44]
Roy et al. (2024)	Sulfamethoxazole / wastewater samples.	EPS-alginate	LC-MS	[45]
Hidayat et al. (2024)	Congo Red / aqueous samples	Hydrogel beads (SA-CTAB)	UV-Vis spectrophotometer	[46]
Yan et al. (2017)	Cr(VI) / water sample	Core-shell/bead-like alginate@PEI	UV-Vis spectrophotometer	[47]

2.4 Micro solid phase extraction (μ-SPE)

Effective sample preparation techniques are often necessary before instrumental analysis because of the sample's complex matrix and low amounts of antibiotic residues [48]. In 1951, Braus et al.'s groundbreaking work introduced solid phase extraction (SPE) as a solution to these issues [49]. SPE is now regarded as a dependable sample handling method by most people and is becoming more and more popular [50]. SPE has drawbacks despite its widespread use, including poor recovery, complicated and many stages, copious amounts of solvents, adsorbents, and eluents, and issues with repeatability brought on by sample residues [51]. The majority of these problems are resolved by miniaturization, which makes it possible to analyze small amounts using a minimal amount of sample and solvent. Because the extraction process is partial and does not require numerous steps, these approaches offer great recovery and reproducibility at a cheap cost while enabling the collection and extraction of small quantities of analytes from small volumes of samples almost entirely without the need for solvent. Micro-solid phase extraction (μ-SPE) is a viable small-scale extraction method that has gained popularity because of its many benefits, including ease of use, low solvent consumption, low sorbent requirements, great extraction efficiency, and extremely cheap cost [52]. Antibiotic residues have now been recovered from water and food samples using a range of adsorbents, such as molecularly imprinted polymers, carbon nanoparticles, graphene, functionalized silica, and metal–organic frameworks (MOFs). Additionally, biopolymers include cellulose, chitosan, agarose, or alginate are the most extensively employed natural adsorbents [53]. The study related to the μ-SPE method is shown in Table 5.

Table 5 Micro solid phase extraction method.

Author (year)	Analytes/ Samples	Sorbent/ Extraction method	Detection	Analytical performance	Ref.
Álvarez et al. (2014)	Sulfadimethoxine, sulfadiazine, sulfapyridine, sulfamerazine, sulfamethazine, sulfamonomethoxine, sulfachloropyridazine, sulfamethoxazole/ river and reservoir waters	MIP/ SLM-protected-MI-MSPE	HPLC-DAD	Recovery (%): 70-120 LOD: 200-3000 ng L^{-1}	[54]
Teo et al. (2016)	Carbamazepine/ surface waters	C_{18}/ µ-SPE-IDMS	LC-MS/ MS	Recovery (%): 96.7-103.5 LOD: 0.5- 1.5 ng L^{-1}	[55]
Zang et al. (2017)	Chlorophenols - 2,3-DCP - 2,4-DCP - 3-CP - 2,4,6-TCP / cosmetic	Fe_3O_4@rGO-g-C_3N_4/ M-µSPE	HPLC-UV	Recovery (%): 80.5-104.0 LOD: 0.2-0.3 ng g^{-1} RSD (%): 5.6-9.6	[56]
Mirikaram et al. (2016)	OCPs/ soil	MWCNTs/ µ-SPE-DLLME	GC-ECD	LOD: 0.11-1.07 ng g^{-1} RSD (%): <14	*[57]*

Manaf et al. (2018)	Steroids/ urine	β-cyclodextrin/ µ-SPE	LC-MS/MS	LOD: 250-500 ng L^{-1} RSD (%): 2.1-4.9	[58]
Basheer et al. (2018)	Heterocyclic aromatic amines - 1-methyl-9H-pyrido[3,4-b] indole - 9H-pyrido[3,4-b] indole - 3-amino-1-methyl-5H-pyrido[4,3-b] indole - 2-amino-1-methyl-6-phenylimidazo[4,5-b] pyridine - 3-amino-1,4-methyl-5H-pyrido[4,3-b] indole - 2-amino-9H-pyrido-[2,3-b] indole / seawater	Activated alumina/ µ-SPE	HPLC-FLD	Recovery (%): 79.9-95.2 LOD: 4-26 ng L^{-1} RSD (%): 1.3-7.5	[59]

González et al. (2018)	Cannabinoids/ urine	JWH-015 MIP/ MIP-µ-SPE	LC-MS/MS	LOD: 32-750 ng L^{-1} RSD (%): 1-8	[60]
Álvarez et al. (2018)	Thiabendazole, carbendazim, imazalil	Thiabendazole MIP/ MI-MSPE	HPLC-DAD	LOD: 4-9 ng g^{-1} RSD (%): <4	[61]

2.5 Sample preparation and chromatographic determination of sulfonamides

Current analytical techniques for determining sulfonamides in sample typically involve a first liquid-solid extraction (LSE) step, followed by a solid phase extraction (SPE) clean-up. Methanol and acetonitrile are among the most often utilized solvents for the extraction of sulfonamides from solid materials [62]. These kinds of organic solvents are typically employed extensively to extract organic molecules from dietary, biological, and environmental materials. Despite the advancement of numerous (micro)extraction methods, including dispersive liquid-liquid extraction, hollow fiber liquidphase microextraction, QuEChERS (rapid, easy, cheap, effective, robust & safe) extraction, etc., After extraction, one of the following methods may be used to make the final determination: liquid chromatography-tandem mass spectrometry (LC-MS/MS) [63], high-performance liquid chromatography (HPLC) [64], ultra-high-performance liquid chromatography-mass spectrometry (UPLC-MS/MS) [65], capillary electrophoresis [66] or spectrophotometry [67]. Related research on the analysis of sulfonamides is shown in Table 6.

Table 6 Literatures on sample preparation and chromatographic determination of sulfonamides.

Author (year)	Analytes / Samples	Chromatographic condition/ Preconcentration technique	Ref.
Shishov et al. (2020)	Sulfamethoxazole, sulfamethazine / chicken meat	HPLC-UV: Column: C18(2) (250 mm × 4.6 mm, 5 μm) Mobile phase: methanol/phosphate buffer (0.05 mol L^{-1}, pH 8.0) at a ratio of 60:40 (v/v) Flow rate: 0.6 mL min^{-1} Injection volume: 20 μL Detector: UV Wavelength: 220 nm DES: Sample: 1.0 g DES: 2 g Agitation: ultrasound bath (325 W, 35 kHz, 50 °C, 30 min), centrifuged at 5000 rpm	[28]

Oyedeji et al. (2021)	Enrofloxacin, sulfadimethoxine, sulfamerazine, sulfamethoxazole, sulfamoxole, tylosin / refrigerated meat, gizzard tissues , chicken, turkey, live chickens, including muscle	HPLC: Column: XTerra MS C18, 125Å (4.6×100 mm, 3.5 μm) Mobile phase: (A) water + 1 mL formic acid (B) ACN + 1 mL formic acid Flow rate: 1.2 mL min^{-1} gradient mode Injection volume: 10 μL Detector: Diode array detector (DAD) Wavelength: 275, 270, 257 and 245 nm SPE Sample: 2 g Agitation: vortex for 20 s ,centrifuging for 5 min at 3500 rpm SPE cartridge: 3 mL mixture of water and methanol (4:1, v/v) Eluent: 2 mL of 10% ammonium hydroxide:methanol (1:19, v/v)	*[68]*

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Jullakan et al. (2021)	Sulfathiazole, sulfamerazine , sulfamonomethoxine ,sulfadimethoxine / milk	HPLC: Column: C18 column (5.0 μm, 4.6 × 150 mm) Mobile phase: A 0.20% acetic acid B acetonitrile Flow rate: 1 mL min^{-1} gradient mode Injection volume: 20 μL Detector: Diode array detector (DAD) Wavelength: 270 nm d-MSPE: Sample: 10 g SPE cartridge: 3.0 mL of ethyl acetate Agitation: stirred at 1000 rpm for 30 min	[9]

Wu et al. (2021)	Sulfapyridine , sulfadiazine , sulfathiazole, sulfamerazine , sulfisoxazole , sulfamethizol, sulfabenzamide , sulfamethazine, sulfamethoxypyridazine, sulfachloropyridazine / Water, honey	HPLC: Column: Phenomenex KinetexC18 LC column (100 mm × 3.0 mm, 2.6 mm) Mobile phase: (A) acetonitrile (B) water Flow rate: 0.25 mL min^{-1} gradient mode Injection volume: 10 μL Detector: MS/MS PMA/MMF-SPME: Sample: 2 g Add: 20 mL ultrapure water, 5.0% NaCl (w/v)	[69]

CHAPTER 3
METHODOLOGY

3.1 Reagents and Standards

All of the chemicals were analytical-grade or better. They were acquired from several vendors, as listed in Table 7. Deionized water (18.2 MΩ.cm) was supplied by a RiOs Type I simplicity 185 water purification system (Millipore, USA).

Table 7 Chemicals and reagents used in this work.

No	Chemicals	Formula	Company	Country
1.	Sulfathiazole; STZ	$C_9H_9N_3O_2S_2$	Sigma-aldrich	China
2.	Sulfamethazine; SMZ	$C_{12}H_{14}N_4O_2S$	Sigma-aldrich	Israel
3.	Sulfachloropyridazine; SCP	$C_{10}H_9ClN_4O_2S$	Sigma-aldrich	China
4.	Sulfamethoxazole; SMX	$C_{10}H_{11}N_3O_3S$	Sigma-aldrich	Switzerland
5.	Sulfadimethoxine; SDM	$C_{12}H_{14}N_4O_4S$	Sigma-aldrich	China
6.	Methanol	CH_3OH	Merck	Germany
7.	Acetonitrile	CH_3CN	Merck	Germany
8.	Silica gel	SiO_2	Merck	Germany
9.	Cetyltrimethylammonium bromide; CTAB	$C_{19}H_{42}BrN$	Sigma-aldrich	Germany
10.	Sodium dodecyl sulfate; SDS	$CH_3(CH_2)_{11}SO_4^-$ Na^+	Merck	Germany
11.	Triton X-114	$C_{16}H_{26}O_2$	Merck	Germany
12.	Sodium alginate; SA	$C_6H_9O_7Na$	Sigma-aldrich	Germany
13.	Calcium chloride	$CaCl_2$	Kemaus	Australia

Melamine sponge; MS (cosmetic grade) were purchased from an online vendor.

3.2 Instrumentation

The HPLC system consists of a Waters 1525 Binary HPLC pump (USA), and a Waters 2489 UV-Visible detector operated at 270 nm. A Luna® C18(2) 100 A° column (150 mm × 4.6 mm, 5.0 µm) (Phenomenex, USA) was used as an analytical column carried out at room temperature. The injection volume was 20 µL. Empowers 3 software was used for data processing. Chromatographic analysis using isocratic elution with 25% acetonitrile in water as the mobile phase at a flow rate of 1.0 mL min^{-1}.

The UPLC system consists of a Waters acquity H class pump (USA), and a Waters acquity™ ultra performance LC PDA detector operated at 270 nm. A Xselect™ Hss C18 XP column (3.0 mm × 75 mm, 2.5 µm) (Waters, Ireland) was used as an analytical column carried out at room temperature. The injection volume was 3 µL. Empowers 3 software was used for data processing chromatographic analysis. Using isocratic elution with a mobile phase of 25% acetonitrile in water and a flow rate of 0.6 mL min^{-1}.

The morphology of modified biosorbent material were characterized by transmission electron microscope (TEM; Model FEI, Technai G^2 F20, USA) and environmental scanning electron microscope (E-SEM; Model : Quattro-S, Thermo Fisher Scientific, USA). N_2 sorption were measured by Brunner-Emmett-Teller (BET) (Micromeritics® TriStar II Plus (Georgia, USA)). PerkinElmer FT-IR spectometer (Model; spectrum two serial No. 117106, USA) was used to record FTIR spectra. Solid phase extraction manifold (LiChrolut® Vacuum Manifold, Merck, Germany) was used for extraction procedure. A vortex mixer (Fisher Scientific, USA) was also used.

3.3 Real samples

Surface water samples were obtained from the different areas located near agricultural in Maha Sarakham, Thailand.

Honey samples were purchased from a supermarket in Maha Sarakham, Thailand.

3.4 Experimental

3.4.1 Preparation of standard sulfonamides for surfactant-modified silica adsorbents extraction

The mixture of standard sulfonamide solutions such as STZ, SMZ, SMX, and SDM was prepared in methanol and working solution was diluted in deionization water before injected into HPLC with the optimum conditions. A calibration curve for each analyte was constructed by plotting between the peak areas versus the concentration of mixed standard sulfonamides solution at seven different concentrations. The linearity range was evaluated by the calibration curve ($y = mx+ c$) and the correlation coefficient (R^2) value.

The sensitivity of the method was evaluated by limit of detection (LOD) calculated as three times the signal-to-noise ratio 3:1, and limit of quantitation (LOQ) calculated as ten times the signal-to-noise ratio 10:1. Precision of the method was determined by analyzing mixed standard sulfonamides solution at a concentration of 9 and 50 µg L^{-1} in a same day and in three difference days, and the repeatability was evaluated in terms of %RSD.

3.4.2 Preparation of standard sulfonamides for alginate-MS adsorbents extraction

The mixture of standard sulfonamide solutions such as STZ, SCP, SMX, and SDM was prepared in methanol and working solution was diluted in deionization water before injected into UPLC with the optimum conditions. A calibration curve for each analyte was constructed by plotting between the peak areas versus the concentration of mixed standard sulfonamides solution at seven different concentrations. The linearity range was evaluated by the calibration curve ($y = mx+ c$) and the correlation coefficient (R^2) value.

The sensitivity of the method was evaluated by limit of detection (LOD) calculated as three times the signal-to-noise ratio 3:1, and limit of quantitation (LOQ) calculated as ten times the signal-to-noise ratio 10:1. Precision of the method was determined by analyzing mixed standard sulfonamides solution at a concentration of 3 and 10 µg L^{-1} in a same day and in three difference days, and the repeatability was evaluated in terms of %RSD.

3.5 Silica based adsorbent for micro-solid phase extraction (µ-SPE) procedure for surfactant-modified silica adsorbents

Figure 3 schematically illustrates the procedure of µ-SPE. Briefly, a 5.00 mL empty cartridge prop up by cotton fabric was used to prepare the SPE extraction cartridge by adding 0.4 g silica into the cartridge on cotton fabric. Then, 10 mL of mixed standard/sample solution with 0.03 M CTAB (150 µL) was passed through the SPE cartridge by vacuum manifold for sample preparation coupled with Millipore Sigma^{TM} pump. In this step, sulfonamide-CTAB was adsorbed in silica sorbent. After that, the cartridge was eluted with 500 µL of methanol. For further analysis, 20 µL of eluate was injected into HPLC-PDA system.

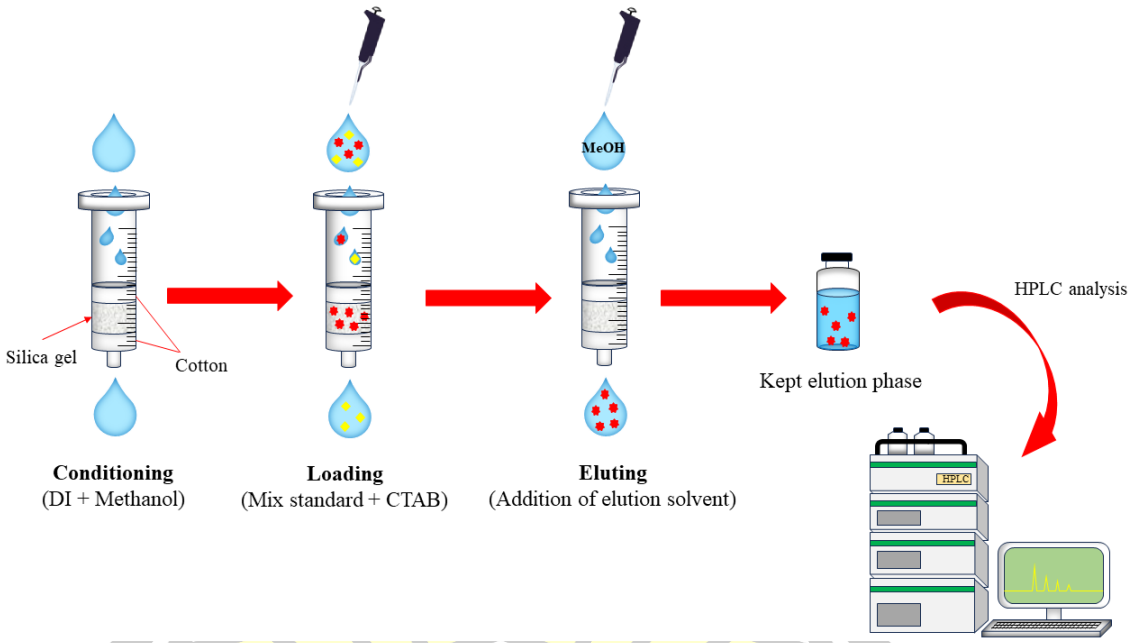


Figure 3 Schematic diagram of the proposed µ-SPE procedure for sulfonamides.

3.5.1 Optimization of sorbent amount

The amount of adsorbent is very important in the extraction of the target substance. In this work, sorbent amount were studied in the range of 0.09, 0.2, 0.4 and 0.6 g.

3.5.2 Optimization of type of surfactant

Each type of surfactant has a substantial impact on extraction because of its varying degree of compatibility with the target molecule. Three different types of surfactants were examined: Triton X-114, SDS, CTAB and without surfactants.

3.5.3 Optimization of concentration and volume of surfactant

The resulting concentrations of CTAB surfactant that were investigated were 0.07, 0.05, 0.03, and 0.01 M. The surfactant volumes that were examined were 50, 100, 150, and 200 µL.

3.5.4 Optimization of desorption solvent

One of the most important extraction process parameters for eluting analyte on the adsorbent surface is the desorption solvent. Three different kinds of desorption solvents such as DI water, MeOH, and ACN were employed in this investigation.

3.5.5 Optimization of desorption solvent volume

It is commonly recognized that the dilution impact in the elution step is influenced by the volume of the desorption solvent. The target compounds were eluted using volumes of 300, 500, 700, and 900 µL.

3.6 Preparation of alginate adsorbent

Preparation of alginate adsorbent was shown in Figure 4. Briefly, Melamine sponge (MS) cubes were sized and formed uniformly at $1\times1\times1 cm^3$, and they were immersed in a 0.5 wt% sodium alginate solution for 12 hours in order to allow the alginate gel to completely penetrate the MS's inner pores. After that, it was frozen to harden and then submerged for 6 hours in a solution containing 3 wt% $CaCl_2$ to enable the alginate solution to gellate onto the MS surface. Before being used, the alginate-MS was washed with deionized water to remove impurities and dried in an oven.

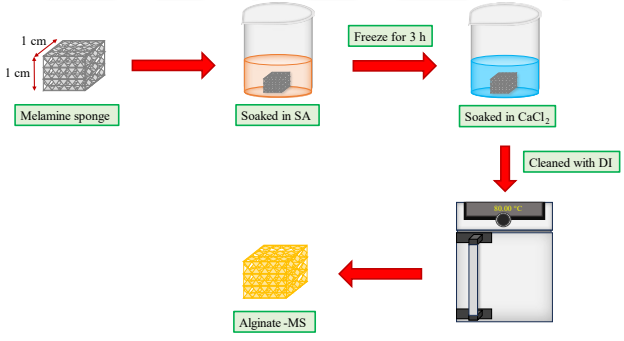


Figure 4 Preparation of alginate adsorbent.

3.6.1 Optimization of size of sponge

As the size of the sponge influences extraction efficiency, it also has a substantial effect on surface area and preconcentration. Therefore, the adsorbent sizes of 0.5×0.5×0.5, 1×1×1, and 2×2×2 cm^3 were investigated.

3.6.2 Optimization of concentration of sodium alginate and calcium chloride

The concentration of sodium alginate used in the production of adsorbents were examined at weight percentages of 0, 0.5, 1, 2, 3, and 4 wt%. The following concentrations of $CaCl_2$ were investigated because they aid in the adsorbent's ability to gelate: 2, 3, 4, 5, and 6 wt%.

3.7 Alginate-MS adsorbents for micro-solid phase extraction (µ-SPE) procedure

Using an empty 5.00 mL cartridge supported by cotton, the extraction procedure was carried out. The SPE extraction cartridge was prepared a vacuum manifold to prepare the sample in conjunction with a Millipore Sigma™ pump, by inserting the alginate-MS sorbent into the cartridge on the cotton fabric. Then, 100 mL of a mixed standard/sample solution containing 1000 µL of 0.1 M CTAB was run through the SPE cartridge. By using sulfonamide-CTAB was adsorbed in alginate-MS sorbent in this step. Subsequently, 500 µL of acetonitrile was used to elute the cartridge. Then, the eluate was filter through 0.2 µm membrame filter prior injected into UPLC-PDA system for analysis. The extraction method is shown in Figure 5.

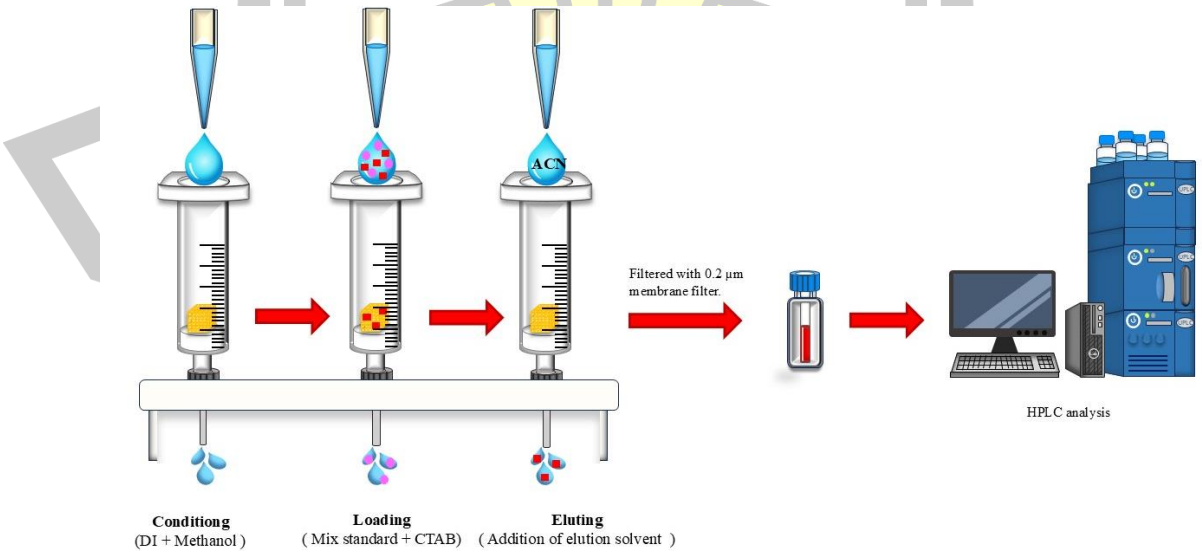


Figure 5 Micro-solid phase extraction (µ-SPE) procedure for alginate-MS adsorbents.

3.7.1 Optimization of type of surfactant

The differing degrees of compatibility between each type of surfactant and the target molecule have a significant effect on extraction. The four types of surfactants including CTAB, DDAB, SDS, Triton X-1114 and without surfactants were investigated.

3.7.2 Optimization of concentration and volume of surfactant

The resulting concentrations of CTAB surfactant that were investigated at 0.05, 0.07, 0.1, 0.2 and 0.3 M. The surfactant volumes were examined at 500, 700, 1000, 1300 and 1500 µL.

3.7.3 Optimization of desorption solvent

One of the most important extraction process parameters for eluting analyte on the adsorbent surface is the desorption solvent. Three different kinds of desorption solvent such as MeOH, ACN, EtOH and DI water were employed in this investigation.

3.7.4 Optimization of desorption solvent volume

It is commonly recognized that the dilution impact in the elution step is influenced by the volume of the desorption solvent. The target compounds were eluted using volumes of 300, 500, 700, and 1000 µL.

3.8 Reusability

3.8.1 Reusability for surfactant-modified silica adsorbents extraction

Reusability is the capacity of the sorbent to be used again following the extraction procedure outlined in Section 3.5.The sorbent was subjected to two methanol rinses before a subsequent µ-SPE cycle was applied. Rinse and extract again until the peak area was significantly reduced or the sorbent was denatured.

3.8.2 Reusability for alginate-MS adsorbents extraction

Reusability is the capacity of the sorbent to be used again following the extraction procedure outlined in Section 3.7.The sorbent was subjected to two acetonitrile rinses before a subsequent µ-SPE cycle was applied. Rinse and extract again until the peak area was significantly reduced or the sorbent was denatured.

3.9 Real sample preparation

Surface water samples were obtained from the different areas located near agricultural in Maha Sarakham, Thailand. It was prepared following our previously work [70]. These samples were filtered through a Whatman (No.1) filter paper and passed through 0.45 µm nylon membrane filter before extraction using the proposed method.

Honey samples were purchased from a supermarket in Maha Sarakham, Thailand. It was prepared following our previously reported method [71]. Five grams of honey sample was weighed into 50 mL volumetric flask and diluted to the marker with water. The sample was filtered through a Whatman (No.1) filter paper to remove the particulate matter and then passed through 0.45 µm nylon membrane filter before extraction using the proposed method.

3.10 Statistical analysis

Data results are given as the mean ± standard deviation (SD) of three measurements (n = 3).

The average result (mean) was calculated by summing the individual result and dividing by the number (n) of individual values. It is calculated Eqs. (1) as follows:

$$\bar{x} = \frac{X_1 + X_2 + X_3 + \cdots}{n} \quad (1)$$

The standard deviation was a measure of how precise the average is, that is, how well the individual number agree with each other. It is a measure of a type of error called random error. It is calculated Eqs. (2) as follows:

$$SD = \sqrt{\frac{(X_1 - \bar{x})^2 + (X_2 - \bar{x})^2 + (X_3 - \bar{x})^2 + \cdots}{n - 1}} \quad (2)$$

The percentage relative standard deviations (%RSD) are calculated from the standard deviation and mean using Eqs. (3) as follows:

$$\%RSD = \frac{SD}{\bar{x}} \times 100 \quad (3)$$

In all graphs, a linear regression analysis was conducted using Microsoft Excel 2013 software. The extraction efficiency is evaluated in term of enrichment factor (EF) which is calculated using Eqs. (4) as follows [72]:

$$EF = \frac{C_{sed}}{C_0} \quad (4)$$

where C_{sed} and C_0 are the analyte concentration in the extraction phase and the initial analyte concentration in the aqueous samples, respectively.

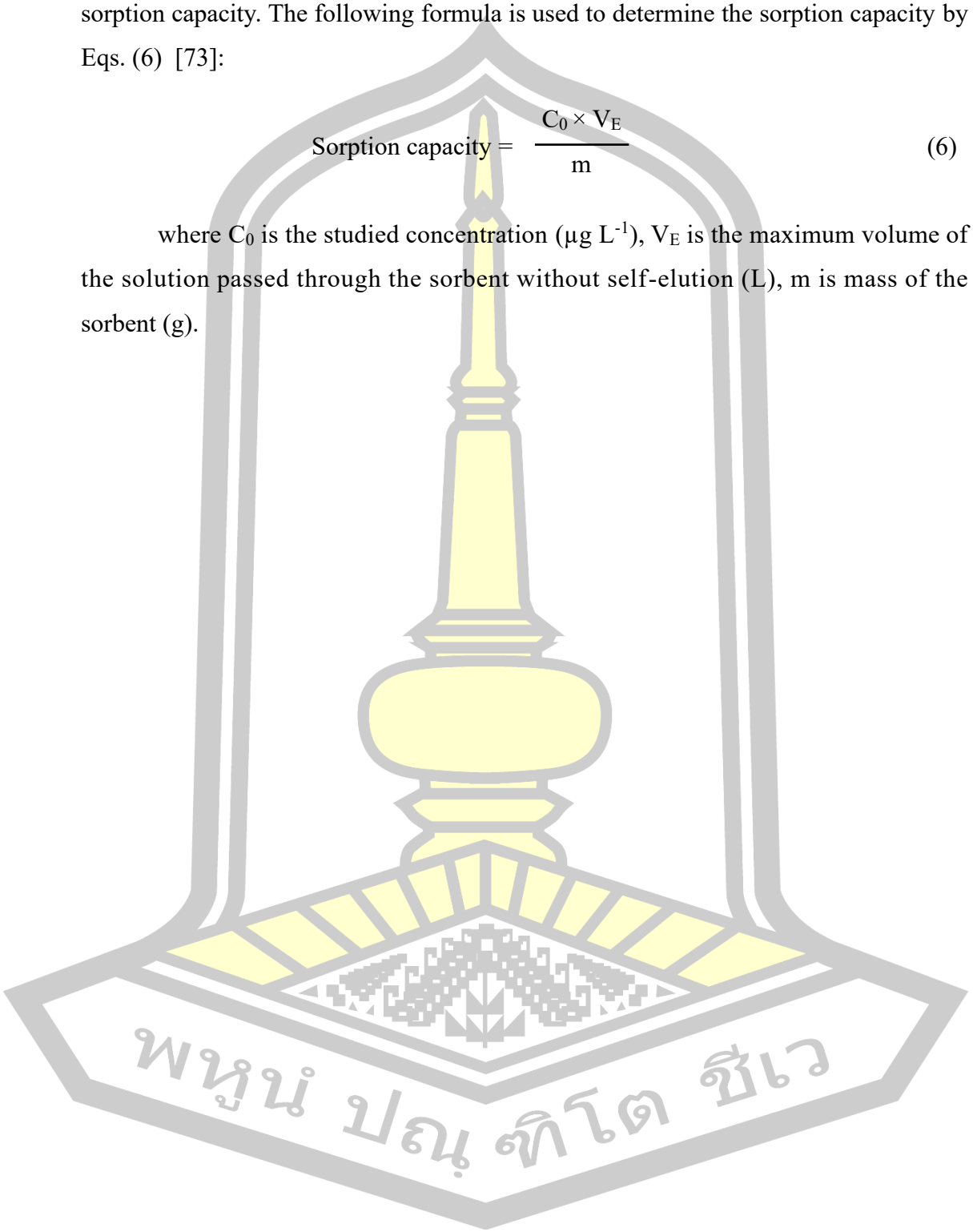
The matrix effect can be quantitatively evaluated by contrasting the response of the analyte in standard solution with that of a post extract spiked with the analyte at the same concentration. The matrix effect can be calculated using the Eqs. (5) below:

$$ME(\%) = \frac{\text{Slope of spiked real sample}}{\text{Slope of standard solution}} \times 100 \quad (5)$$

The amount of material adsorbed per unit of adsorbent is used to calculate the sorption capacity. The following formula is used to determine the sorption capacity by Eqs. (6) [73]:

$$\text{Sorption capacity} = \frac{C_0 \times V_E}{m} \quad (6)$$

where C_0 is the studied concentration (μg L^{-1}), V_E is the maximum volume of the solution passed through the sorbent without self-elution (L), m is mass of the sorbent (g).



CHAPTER 4
RESULTS AND DISCUSSION

4.1 High-performance liquid chromatography for sulfonamides analysis.

The HPLC separation of the studied sulfonamides was performed on a reversed-phase system (see Section 3.2). Under the mention condition, the studied sulfonamides of interest were separated within 13 min with the order of elution, retention time and resolutions as summarized in Table 8. A chromatogram of mixture standards is shown in Figure 6.

Table 8 The retention time and resolutions of sulfonamides.

No.	Sulfonamide	Retention time (t_R, min)	Resolutions (Rs)
1	Sulfathiazole; STZ	2.7	-
2	Sulfamethazine; SMZ	4.6	4.2
3	Sulfamethoxazole; SMX	8.0	5.8
4	Sulfadimethoxine; SDM	13.5	9.4

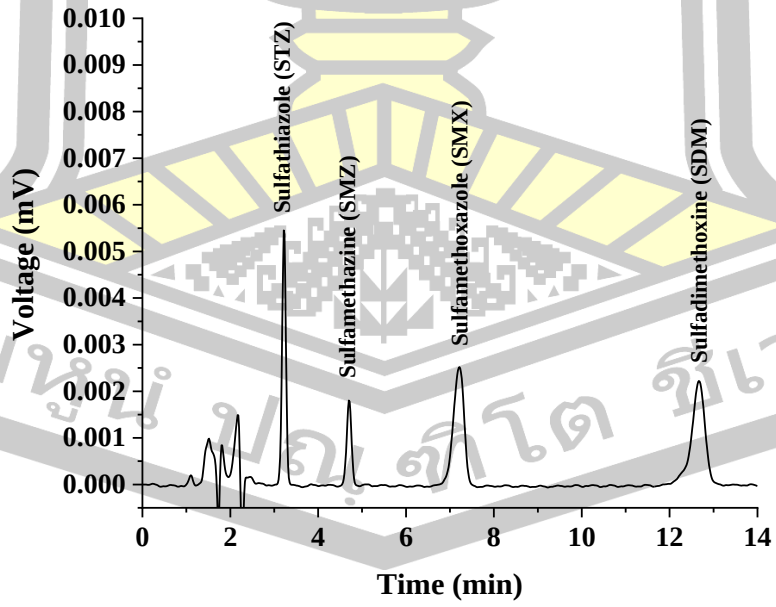


Figure 6 Chromatogram of 100 µg L^{-1} sulfonamide residues obtained by HPLC.

4.1.1 Analytical performance of the HPLC system direct injection

Under the selected HPLC conditions, the analytical performance were evaluated by examining linear range, precision, LOD and LOQ. Calibration curves were constructed by triplicate injections of standard sulfonamides solutions. Peak area of each analyte was plotted against it concentration. LOD and LOQ are defined by the concentration giving the signal-to-noise ratios (S/N) of 3 and 10, respectively. The precision of the method was performed by five replicate injections of the standard mixture of 100 µg L^{-1} sulfonamides. The results are summarized in Table 9. It was found that, the calibration curve were linear in the range of 90-3000 µg L^{-1}. The LODs and LOQs were in the range of 3-30 and 9-90 µg L^{-1}, respectively. The results showed good precision with the RSDs of lower than 4.66% for retention time, while the RSDs of peak area were lower than 3.99%.

Table 9 Analytical performance of the HPLC system for sulfonamides determination

Analyte	Linear range (µg L^{-1})	Linear equation	R^2	LOD (µg L^{-1})	LOQ (µg L^{-1})	Intra-day[a] precision (n=5), RSD (%)		Inter-day precision (n=3 × 5), RSD (%)	
						t_R	Peak area	t_R	Peak area
Sulfathiazole	90 - 3000	y = 114090x + 2188	0.9995	3.0	9.0	0.37	2.50	0.35	2.35
Sulfamethazine	90 - 3000	y = 132593x + 1712.3	0.9996	3.0	9.0	0.21	1.59	0.21	2.61
Sulfamethoxazole	90 - 3000	y = 108579x + 259.84	0.9999	10.0	30.0	0.68	4.66	1.15	3.77
Sulfadimethoxine	90 - 3000	y = 120897x - 1581.8	0.9999	30.0	90.0	0.57	3.81	0.91	3.99

[a)] Precision were investigated at the concentration of 90 µg L^{-1}

4.1.2 Optimization of μ-SPE procedure for surfactant-modified silica adsorbents

Parameters affecting the extraction efficiency of the μ-SPE procedure, including sorbent amount, kind and concentration of surfactant, kind and volume desorption solvent, were optimized using a univariate method, and the peak area of the four sulfonamides was used as the experimental response. All the experiments were performed in triplicate and the mean of the results were used for optimization. Error bars represent the standard error (n=3).

4.1.2.1 Optimization of sorbent amount

It is a primary consideration to investigate an appropriate amount of solid sorbent on the extraction efficiency of the μ-SPE procedure; therefore, different amounts of silica sorbent in the range of 0.09 to 0.6 g were studied. As illustrated in Figure 7, the peak area of most studied sulfonamides increased with increasing the amounts of silica sorbent from 0.09 to 0.4 g and decrease afterwards. The large and compact amount of adsorbent at 0.6 g causes a residue of the target substance on the adsorbent during the desorption step, which lowers the extraction efficiency. Finally, the amount of silica sorbent 0.4 g was chosen in following experiments.

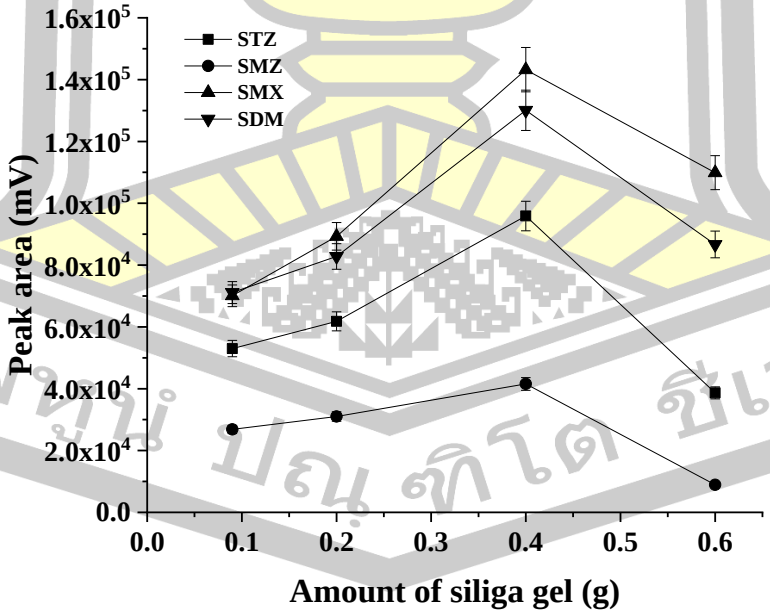


Figure 7 Effect of amount of silica gel.

4.1.2.2 Optimization of kind of surfactant

The addition of the surfactant also greatly influenced the extraction efficiency of the proposed microextraction method because it favors mass transfer of analytes from the aqueous to the organic phase [74]. Nonionic and ionic surfactants with different hydrophilic-lipophilic balance (HLB) values, which measure the degree of their hydrophilicity or lipophilicity, were used [75]. Estimation of HLB values based on chemical groups of molecules in accordance with Davies' method [76] was performed. Surfactants with lower HLB values are more hydrophobic. Three different surfactants were studied including cationic surfactants (cetyltrimethyl-ammonium bromide (CTAB), HLB = 7.3), anionic surfactants (sodium dodecyl sulfate (SDS), HLB = 40.0), non-ionic surfactants: Triton X-100, HLB = 12.4) and without surfactants [75]. The results was shown in Figure 8. It was found that CTAB provided high extraction efficiency in term of peak area. Because of among studied surfactants CTAB (HLB = 7.3) characterized by a low HLB value provided high hydrophobic interactions between hydrophobic tail of surfactant and hydrophobic sites of analytes and was chosen for further studied.

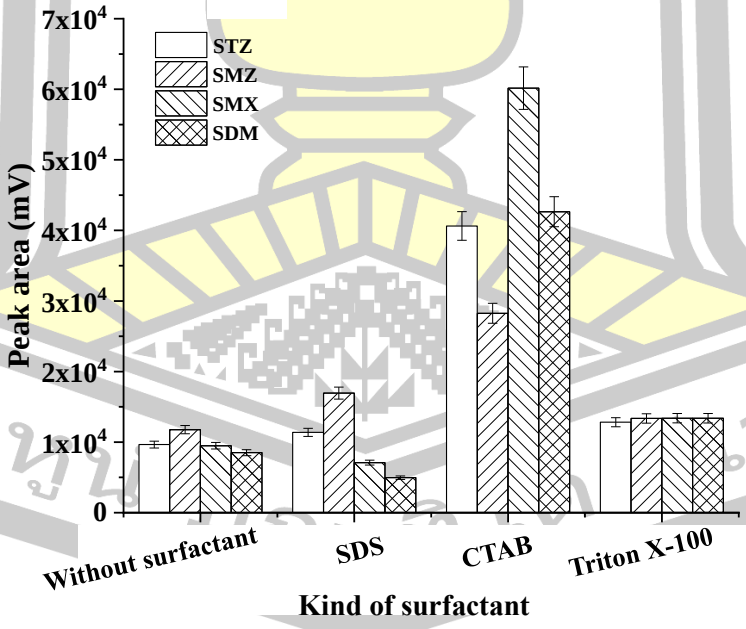


Figure 8 Effect of kind of surfactant.

4.1.2.3 Optimization of concentration and volume of surfactant

The effect of concentration of CTAB was investigated in the range of 0.01-0.07 M. It was observed that the addition of CTAB 0.03 M provided higher extraction efficiency (as shown in Figure 9). This may be due to, in surfactant solution, molecular deposition on the surface of the solvent makes water-soluble hydrocarbons or parts of water dissolved in hydrocarbon compounds. The surfactant surrounds the target and binds to the pores of the sorbent, which allows the sorbent to adsorb better. When the concentration of surfactant increased, the peak area decreased due to the high concentration the more viscosity resulting in the detection decreased of target substances. Consequently, the addition of CTAB 0.03 M was used in this studied. A surfactant volume was varied between 50 and 200 µL using CTAB 0.03 M (as shown in Figure 10), and the other conditions were kept constant. The peak area of sulfonamides increased with increasing the surfactant volume to 150 µL and then decreased afterward. Therefore, CTAB 0.03 M of 150 µL was chosen for further experiments.

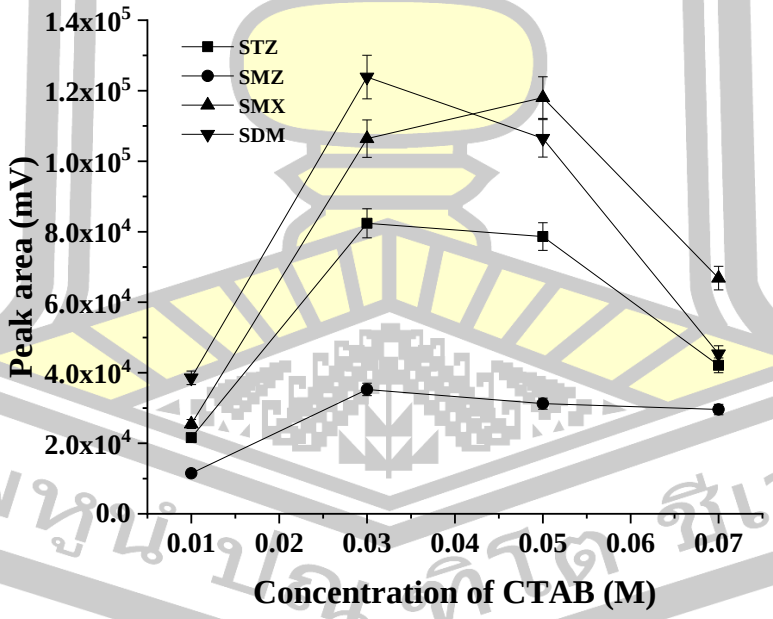


Figure 9 Effect of concentration of CTAB.

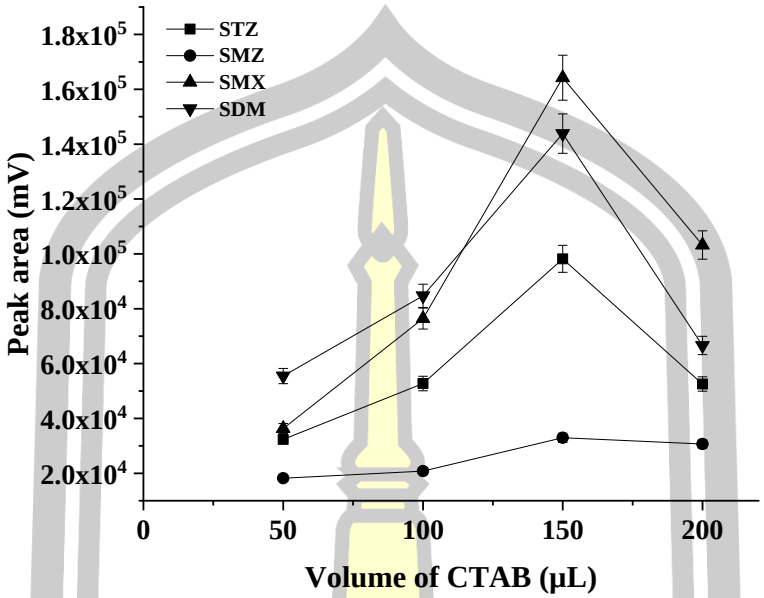


Figure 10 Effect of volume of CTAB.

4.1.2.4 Optimization of desorption solvent

Suitable organic solvents are known to disrupt mixed hemimicelles and they were also used to elute analytes from the sorbent. In this work, different solvents, including water (DI), methanol (MeOH) and acetonitrile (ACN), were investigated. The findings in Figure 11 demonstrate that MeOH had the maximum elution efficiency for the majority of sulfonamides because it was insufficiently vigorous to stop the hydrophobic and adsorption processes of STZ and SMZ, preventing their full elution. Therefore, MeOH was used as desorption solvent in μ-SPE procedure.

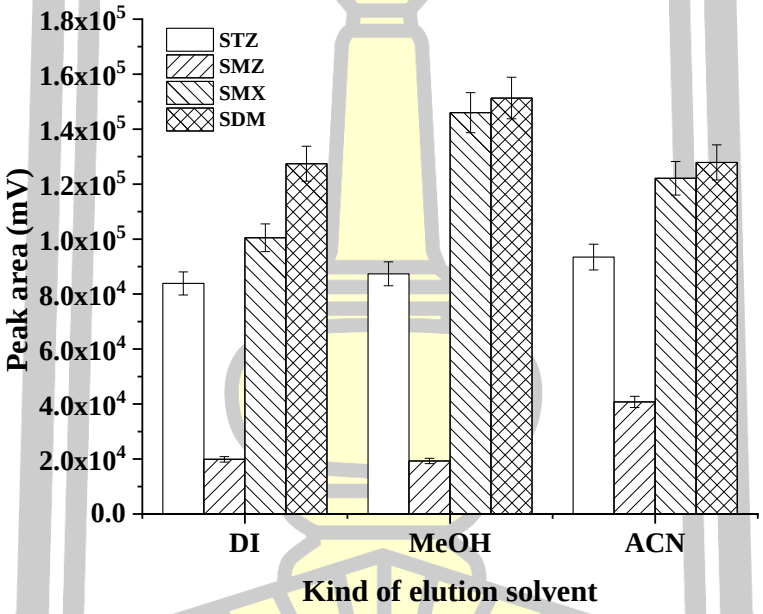


Figure 11 Effect of kind of desorption solvent.

4.1.2.5 Optimization of desorption solvent volume

In the desorption process, the bonds between the sorbent and the analyte are broken by means of an eluent or solvent. For the compounds bound to the sorbent to be extracted, the elution solvent needs to be sufficiently potent and compatible with the target molecules. The desorption solvent volume in this work was investigated in the 300-900 µL range (as shown in Figure 12). It was discovered that when the volume of dispersion solvent was raised to 500 µL, the extraction efficiency slightly enhanced. The extraction efficiency of SMX and SDM dramatically declined with increasing volumes, but STZ and SMZ saw a minor rise. This is because the four target compounds have varying polarities; SMX and SDM have lower polarity than STZ and SMZ. Since this work used an elution solvent with neutral polarity, SMX and SDM could be fully eluted from the sorbent beginning with a 500 µL volume. The extraction efficiency significantly decreased as the volume of the desorption solvent grew due to the dilution effect. The 500 µL volume was insufficient to fully elute the material from the sorbent since STZ and SMZ had high polarity. As a result, more substances can be eluted when the desorption solvent volume is increased. But in this work, a 500 µL desorption solvent volume was selected since SMX and SDM considerably dropped while STZ and SMZ somewhat rose with a larger desorption solvent volume.

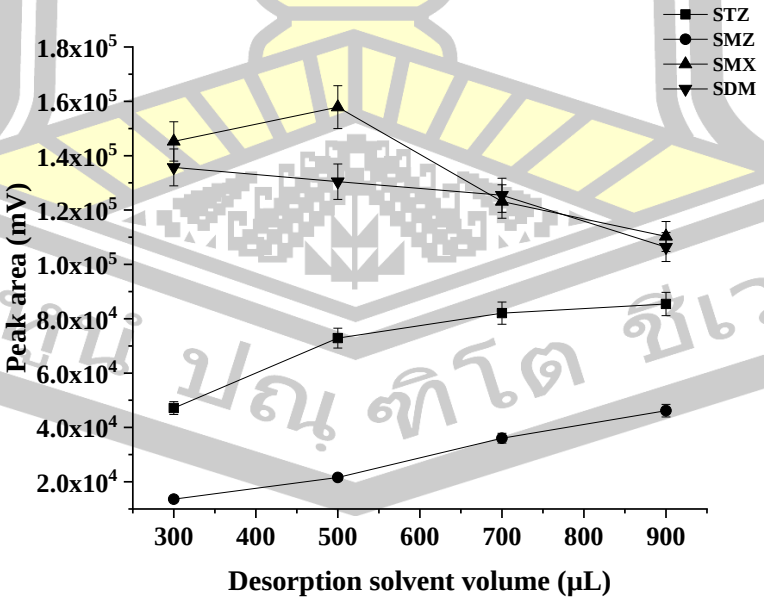


Figure 12 Effect of desorption solvent volume.

4.1.3 Reusability

Utilization is a significant consideration in monitoring the efficiency and sustainability of sorbent materials. Before applying a subsequent µ-SPE cycle, the sorbent was rinsed two times with methanol. The regeneration and reusability of the produced sorbent were examined under optimum parameters. It was found that the peak area of studied sulfonamides had significant decrease after three extraction cycles (data not shown). Because of some interaction cavities were destroyed or blocked after further use, which slightly decreased the enrichment factor of some analytes.

4.1.4 Sorption capacity

The adsorption capability of the silica sorbent was investigated using a mixed solution containing 100 µg L^{-1} of each sulfonamide antibiotic. As a consequence, the sorbent's adsorption capacity for the sulfonamide in the four antibiotic mixture was 2.5 µg g^{-1}.

4.1.5 Characterization of modified sorbent

4.1.5.1 Transmission electron microscope; TEM

TEM micrographs of the silica sorbents were illustrated in Figure 13. In Figure 13(a) show TEM micrographs of silica pure, 13(b) silica after adsorption and 13(c) silica after desorption. TEM provides the 'true diameter' (from a statistically small sample) [77]. It was found that the addition of surfactant could affect the formation of coating layer suggesting enhancement of surface area and surface interacting sites toward surfactant. Therefore, these results also supported the successful coating of surfactant-coupled silica (as shown in Figure 13(b)).

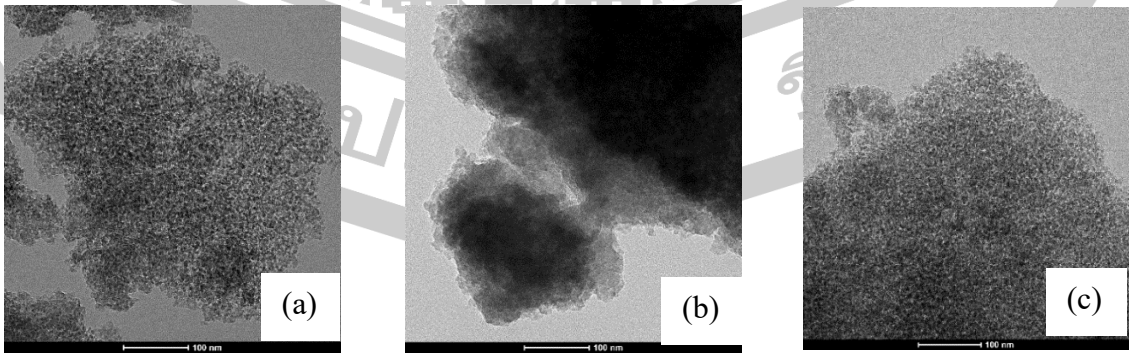


Figure 13 TEM of (a) silica pure (b) silica adsorption and (c) silica desorption.

4.1.5.2 Brunner-Emmett-Teller; BET

Surface area and porosity are two important physical properties which used to determine the capacity of the materials. The specific surface area and pore volume of each of these adsorbents were assessed using the nitrogen physical adsorption desorption measurement in order to further assess the porous characteristics of silica. As shown in Figure 14. It exhibits Type-IV adsorption isotherms, which indicate the presence of mesoporous. The specific surface areas and porosity parameters of silica were listed in Table 10. The surface area of silica pure was up to 533.60 m^2 g^{-1}, higher than the surface area of silica adsorption, This means that the target chemical is coated on the adsorbent surface, lowering the silica adsorption surface area measurement.

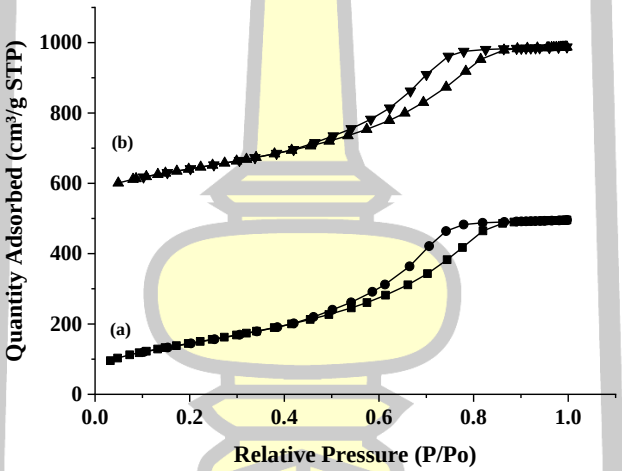


Figure 14 BET adsorption/desorption isotherms of silica (a) silica pure (b) silica adsorption.

Table 10 BET surface area, pore size and pore volume of silica.

Sample	BET surface area (m^2 g^{-1})	Pore diameter (Å)	Pore volume (cm^3 g^{-1})
Silica pure	533.60	59.38	0.24
Silica adsorption	515.61	60.42	0.23

4.1.6 Analytical performance of the proposed method

Using the optimized conditions, the analytical performance of the proposed method for analysis of sulfonamides were validated by obtaining linearity, sensitivity in terms of limits of detection (LODs) and limits of quantification (LOQs), precision and accuracy. Table 11 summarizes the validation data of the developed method. The calibration graphs showed satisfactory linearity in the range of 9-300 µg L^{-1} with R^2 values greather than 0.99. The LOD and LOQ values were carefully studied based on signal-to-noise (S/N) ratios of 3 and 10, respectively, and were obtained in the ranges of 1-3 µg L^{-1} and 3-9 µg L^{-1}, respectively. The EFs were found be in the range 5.63-13.33 folds when computed as the ratio of the concentration ratio of the analytes in the extraction phase (C_{sed}) later the sedimented phase and in the aqueous sample (C_o). The RSDs of peak areas obtained from the intraday (n = 5) and interday (n = 3 × 5) experiments were used to study the reproducibility of the proposed methodology. All targets had satisfactory intraday and interday precision, with RSD values below 4.95% and 5.00%, respectively. Figure 15 the proposed µ-SPE-HPLC methodology.

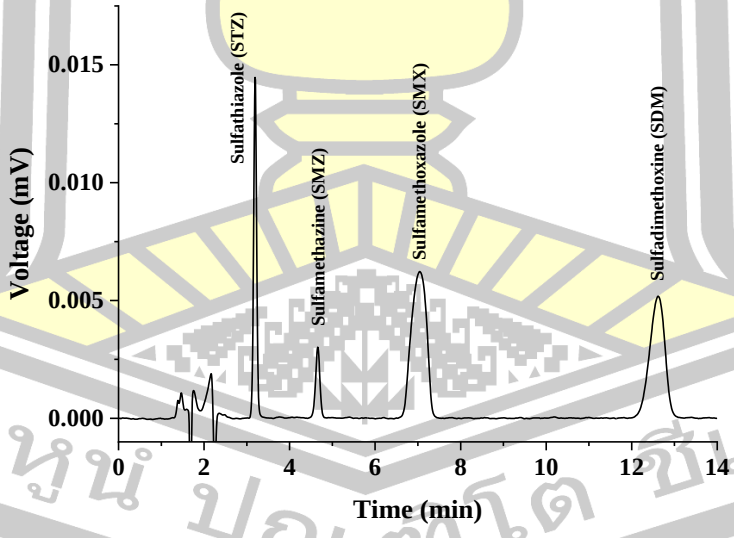


Figure 15 Chromatogram of 100 µg L^{-1} sulfonamide residues after preconcentration by the proposed microextraction method.

Table 11 Analytical performance of the proposed method for determination of sulfonamide residues.

Analyte	Linear range (µg L^{-1})	Linear equation	R^2	LOD (µg L^{-1})	LOQ (µg L^{-1})	Intra-day[a] precision (n=5), RSD (%)		Inter-day precision (n=3 × 5), RSD (%)		EF (C_{sed}/C_0)
						t_R	Peak area	t_R	Peak area	
Sulfathiazole	9 - 300	$y = (1\times10^6x)+258.29$	0.9965	1.0	3.0	0.37	1.26	0.54	4.29	11.29
Sulfamethazine	9 - 300	y = 451571x–1049.2	0.9971	3.0	9.0	0.21	3.00	0.37	4.00	5.63
Sulfamethoxazole	9 - 300	$y = (1\times10^6x)+1676.2$	0.9989	1.0	3.0	1.90	4.95	1.60	5.00	13.33
Sulfadimethoxine	9 - 300	$y = (1\times10^6x)+ 18038$	0.9975	1.0	3.0	0.90	3.77	0.89	4.77	11.40

[a)] Precision were investigated at the concentration of 9 µg L^{-1}

4.1.7 Application to real samples

To study the feasibility and applicability, the developed μ-SPE procedure was applied for the anlysis of sulfonamide residues in real samples. For complex sample analyses, the matrix effect (ME, %) should be calculated based on the ratio of the calibration slopes obtained in the sample and solvent [78]. The matrix effect level can be indicated by the ME (%) as follows: 80-120 (no effect); 50≤ME(%) < 80, and 120 < ME(%)≤150 (minor effect); and ME(%) < 50, and ME(%) > 150 (major effect) [78], [79]. For all studied samples had a relatively low matrix effect (ME: 51-125% (as shown in Table 12)). No sulfonamide residue was detected in the studied sample. Spiked samples were also analyzed, and the acceptable relative recoveries were obtained from 60.9 to 119.4% with the RSDs better than 8.7% (as shown in Table 13). The results demonstrated that the precision and accuracy of procedure were acceptable. The overlaid chromatograms of blank and spiked surface water samples are shown in Figure 16-18), honey samples (Figure 19-20).

Table 12 The matrix effect.

Sample	**Matrix effect (ME, %)**			
	STZ	**SMZ**	**SMX**	**SDM**
Water I	68.6	98.7	100	100
Water II	74.1	109	100	100
Water III	98.3	125.8	100	100
Honey I	61.8	93.9	98.7	100
Honey II	51.2	72.6	84.9	80.2

Table 13 Recovery obtained from the determination of sulfonamides in the studied samples (n = 3).

Sample	Spiked (µg L^{-1} for water, µg kg^{-1} for honey)	STZ		SMZ		SMX		SDM	
		RR (%)	RSD (%)	RR (%)	RSD (%)	RR (%)	RSD (%)	RR (%)	RSD (%)
Water I	0	ND	ND	ND	ND	ND	ND	ND	ND
	9	64.6	1.5	110.4	3.3	113.8	2.5	113.3	1.8
	30	61.8	0.0	87.9	1.8	113.3	1.7	108.3	0.2
	50	67.9	2.9	100.9	0.9	114.3	2.2	119.1	1.6
Water II	0	ND	ND	ND	ND	ND	ND	ND	ND
	9	94.8	0.1	92.6	2.1	119.4	0.8	114.9	1.0
	30	97.3	4.9	119.8	1.3	105.6	1.9	119.4	3.1
	50	77.7	1.4	105.9	3.3	103.4	1.0	117.9	0.7
Water III	0	ND	ND	ND	ND	ND	ND	ND	ND
	9	80.7	4.8	74.9	1.4	102.1	4.1	115.5	0.4
	30	87.5	2.0	87.4	1.1	117.6	0.3	108.3	3.5
	50	95.2	1.7	116.9	0.5	114.8	0.8	113.9	0.3
Honey I	0	ND	ND	ND	ND	ND	ND	ND	ND
	9	68.1	8.7	93.3	0.5	113.1	2.2	116.7	6.4
	30	67.7	0.6	75.6	0.5	103.9	5.1	101.1	0.4
	50	62.9	4.2	93.9	1.3	103.1	0.1	107.1	1.4
Honey II	0	ND	ND	ND	ND	ND	ND	ND	ND
	9	65.9	2.4	94.1	5.6	106.6	1.0	113.2	3.9
	30	60.9	2.8	81.0	3.8	95.9	3.8	106.7	0.2
	50	62.0	4.8	76.4	4.8	88.8	0.1	87.8	2.2

RR: Relative recovery , RSD: Relative standard deviation , ND: Not detected

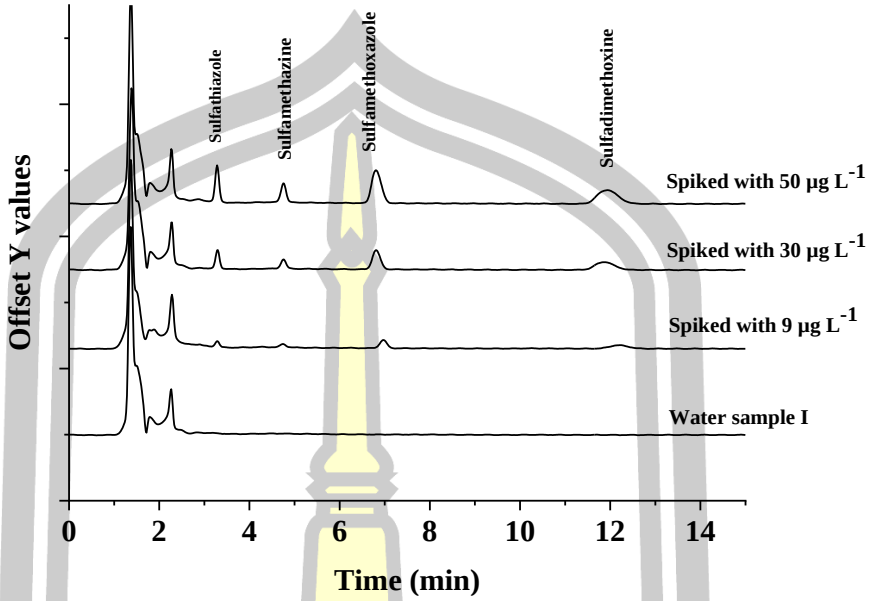


Figure 16 The overlaid chromatograms of blank and spiked surface water sample I.

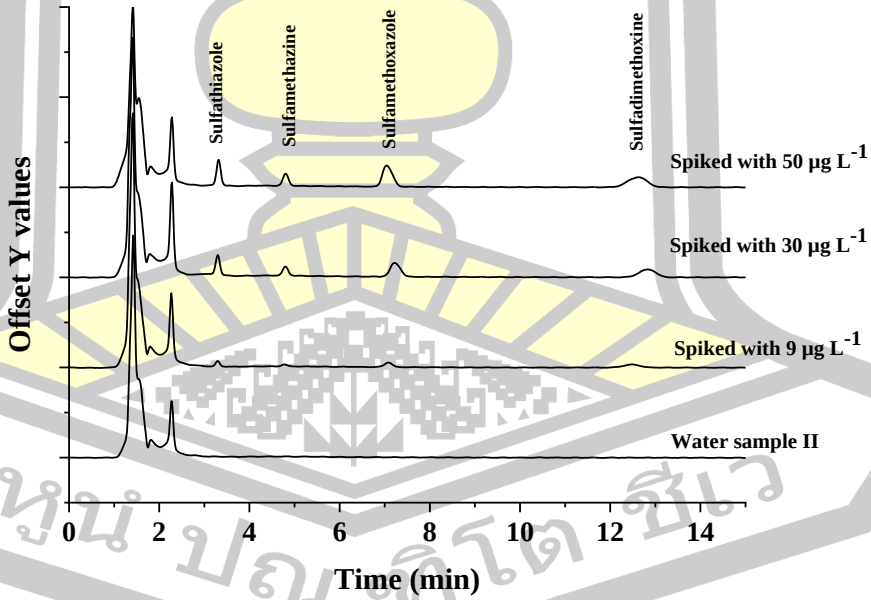


Figure 17 The overlaid chromatograms of blank and spiked surface water sample II.

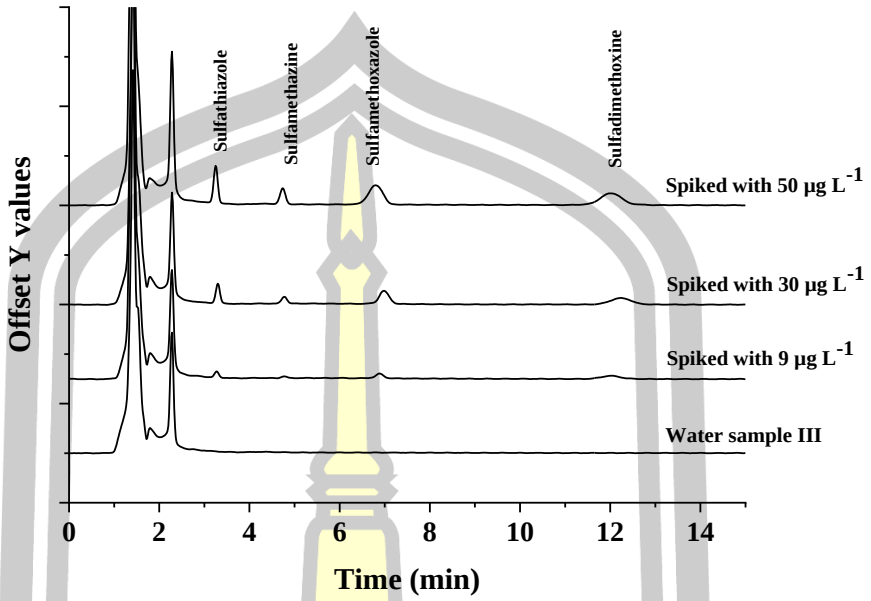


Figure 18 The overlaid chromatograms of blank and spiked surface water sample III.

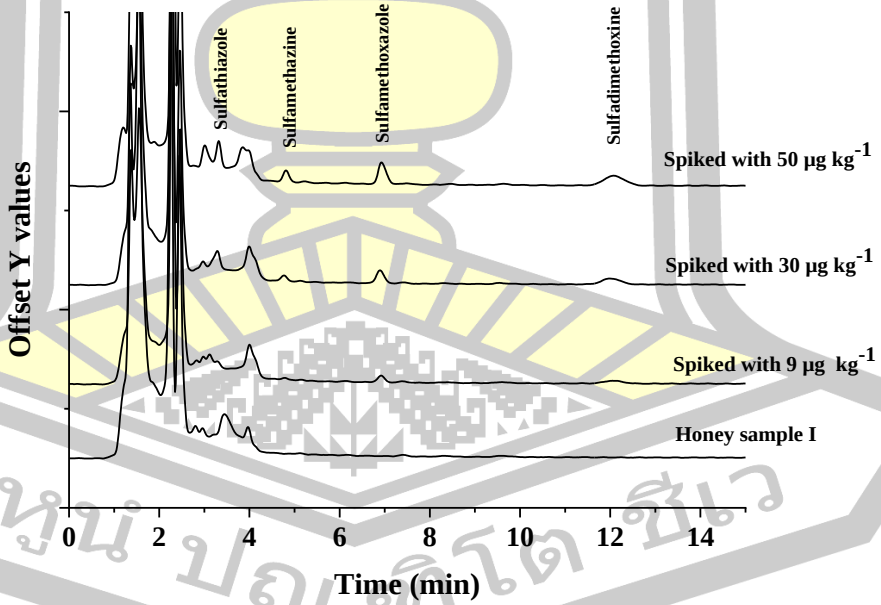


Figure 19 The overlaid chromatograms of blank and spiked honey sample I.

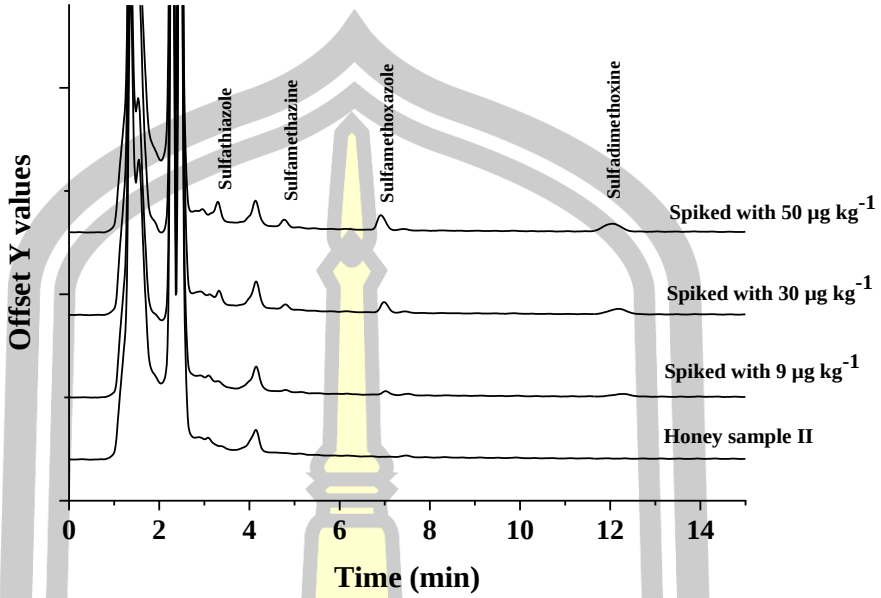


Figure 20 The overlaid chromatograms of blank and spiked honey sample II.

4.1.8 Assessment of method greenness

Analytical Eco-Scale evaluation tool [80] and Analytical GREEnness metric (AGREE) [81] were employed to evaluate the green profile of the proposed microextraction method. Briefly, the Analytical Eco-scale approach provides quantitative information regarding the greenness of the analytical method in terms of the type and amount of reagents and solvents, instrument energy, occupational hazards, and waste generation. To determine the final eco-scale score, penalty points are allocated to each parameter, and the total penalty points are subtracted from 100. A set of penalty points (PPs) are used to assign the departure from ideal greenness. The PPs for hazardous chemicals can be determined by multiplying the sub-total PPs for a given quantity and the hazard. The ultimate AEC value can be calculated from "AEC = 100 - total PPs". The scores higher than >75 illustrate an ideal green, the scores between 50 and 75 are acceptable green, and the scores <50 are insufficient green method [82]. The developed microextraction method demonstrated a final score of 82 (as shown in Table 14), indicating that this method is acceptable as a green method for sulfonamide analyses. The eco-scale tool indicates that the new method is more environmentally friendly based on these scores.

The ultimate score in AGREE metrics is mapped as a fraction of unity from 0 to 1 using AGREE software, which automatically generates a subsequent pictogram divided into twelve sections [81]. Each section of the pictogram is assigned specific colour coding indicated by a green-yellow-red colour scale, which corresponds to the performance of each GAC principle [83]. The ultimate AGREE score is shown at the center of the pictogram, in which case a method is considered green such as the reduction or elimination of hazardous chemicals, minimizing waste generation, optimizing energy consumption, and improving health and safety aspects if it scores over 0.6 [84]. Furthermore, the AGREE evaluation resulted in a final score of 0.55, indicating the greenness attributes of the established method, as depicted in Table 14. A number greater than 0.6 indicates a high level of adherence to green analytical chemistry principles, such as reducing or eliminating hazardous compounds, reducing waste creation, optimizing energy use, and increasing health and safety. It displays a strong commitment to environmental stewardship and sustainability [84], [85]. A plan is regarded environmentally friendly if it has a score of more than 0.6,

and the somewhat weaker green hue in the center zone supports this concept. Sectors 3 and 12 were identified as the lowest performing subsectors in the colored pictogram. The agreement noticed between Analytical Eco-Scale and AGREE pictograms for the compared methods indicated that they are the most reliable greenness assessment tools that could provide integrated information on the whole procedures including all analytical steps for the studied methods.

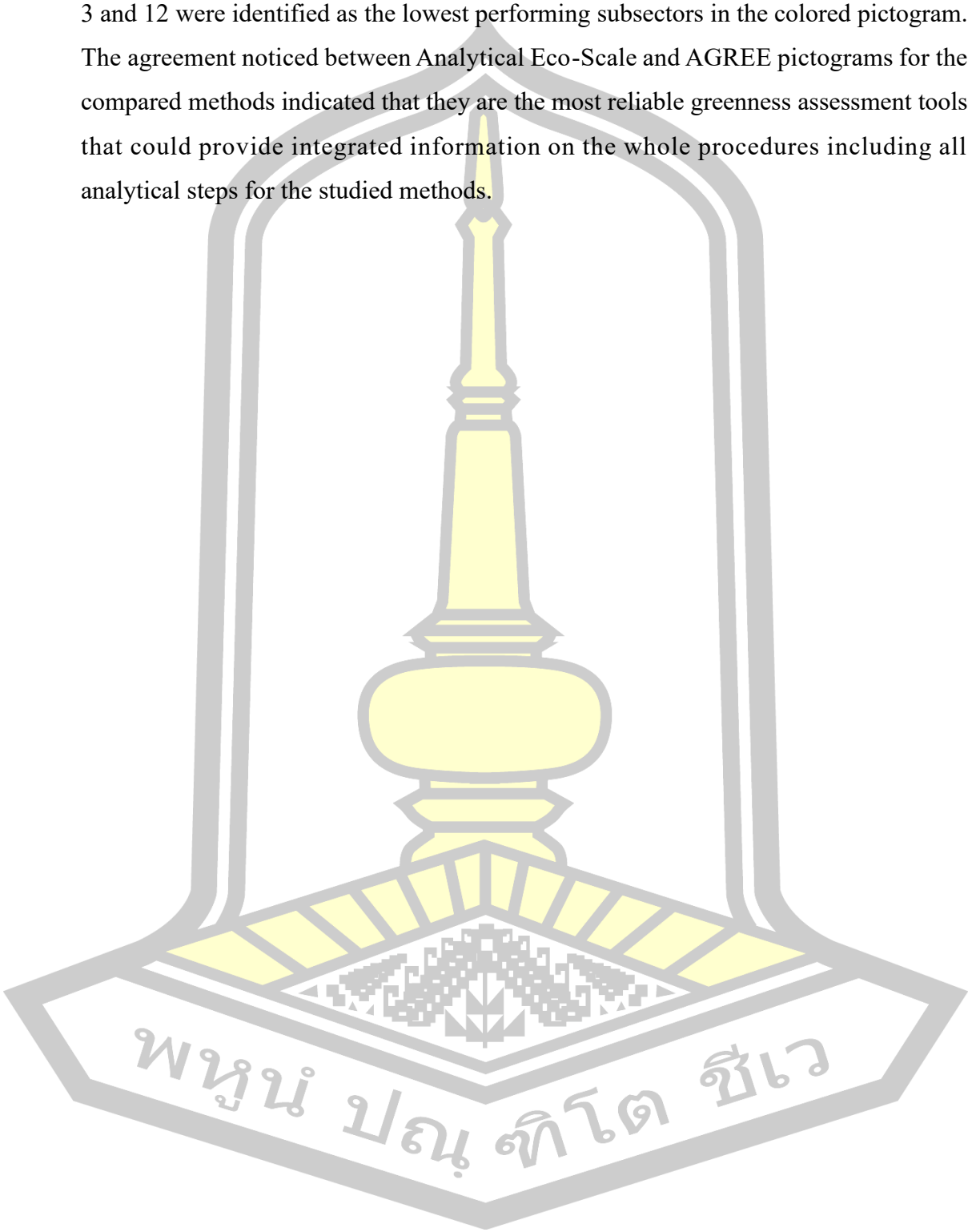
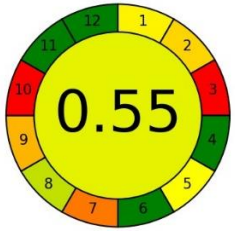


Table 14 Greenness assessment of the proposed method according to Analytical Eco-Scale and AGREE tools.

Analytical Eco-Scale						**AGREE Assessment**
Reagent	**Penalty points (PPs)**					
	Amount PP	**Hazard PP**	**Total PPs (Amount PP × Hazard PP)**	**Instrument**	**PPs**	
ACN (<10 mL)	1	4	4	HPLC-UV	1	
MeOH (<10 mL)	1	6	6	Occupational hazard	0	
CTAB (<10 mL)	1	2	2	Waste	5	
Subtotal PP			12		6	
Total PPs			18			
Analytical Eco-sale score (AEC)			82			



4.1.9 Comparison with other reported methods

To illustrate the advantages of the proposed method for the determination of sulfonamides, a comparison with previously reported sorbent-based techniques is detailed in Table 15. The advantages of the present method are simplicity, short time analysis, environmentally friendly, and cost-effective method. The sensitivity of the proposed method in terms of limit of detection is almost comparable to that obtained from another microextraction method. Owing to the large specific surface area and selective adsorption of surfactant-coated silica, the developed adsorbent was useful for the extraction of sulfonamides. The significant advantages of the proposed μ-SPE are low consumption of sample volume and no need for any expensive or specialist reagents for this reaction. In addition, the developed sorbent used in this work could be simply prepared when compared with previously reported sorbents.

Table 15 Comparisons of the proposed method with other methods for the quantitation of sulfonamides.

Sample Preparation Method	Analytes	Samples	Linear range	LODs	Ref.
Water-compatible poly (hydroxyethyl methacrylate) polymer sorbent for miniaturized syringe assisted extraction	Sulfadiazine, sulfamonomethoxine	Milk	7.0-700 ng g^{-1}	0.19-0.26 ng g^{-1}	[86]
Carboxylated graphene oxide/polyvinyl chloride as solid-phase extraction	Sulfacetamide, sulfamerazine, sulfamonomethoxine, sulfadoxine, sulfadimethoxine, sulfaphenazolum, sulfanitran	Anti-acne cosmetics	0.05-10.0 mg L^{-1}	3.4-7.1 mg L^{-1}	[87]
Thiol-functionalized magnetic carbon nanotubes for magnetic micro-solid phase extraction	Sulfadiazine, sulfamethazine, sulfamonomethoxine, sulfamethoxazole	Milks and chicken meat	0.1-500 µg L^{-1}	0.02-1.5 µg L^{-1}	[88]
Nanostructured polyaniline based pipette tip solid phase Extraction	Sulfadiazine, sulfapyridine, sulfametoxazole	Honey and milk	50-50000 ng mL^{-1}	9.5-16.5 ng mL^{-1}	[89]
Poly(ethylene glycol) diacrylate-based solid-phase extraction	Sulfadiazine, sulfathiazole, sulfapyridine, sulfamethazine, sulfamonomethoxine, sulfamethoxazole, sulfisoxazole	Bacon, liver from pork and chicken meat	0.1-100 µg mL^{-1}	7.5-16.2 µg kg^{-1}	[90]

Nanocomposite adsorbent of metallic copper, polypyrrole, halloysite nanotubes and magnetite nanoparticles	Sulfathiazole, sulfamerazine, sulfamonomethoxine, sulfadimethoxine	Milk	5.0-150.0 µg kg^{-1} 2.5-100.0 µg kg^{-1}	2.5- 5.0 µg kg^{-1}	[91]
3D printed device coated with solid-phase extraction resin for the on-site extraction	Sulfanilamide, sulfadiazine, sulfamerazine, sulfamethazine, sulfamethoxypyridazine, sulfamethoxazole, sulfadimethoxine	environmental water	20-1000 µg L^{-1}	0.6-6 µg L^{-1}	[92]
Silica/CTAB-SPE	Sulfathiazole, sulfamethazine, sulfamethoxazole, sulfadimethoxine	Environmental water and honey	9-300 µg L^{-1}	1-3 µg L^{-1}	This work

4.2 Analysis of sulfonamides by ultra performance liquid chromatography

The UPLC separation of the studied sulfonamides was performed on a reversed-phase system (see Section 3.2). The investigated sulfonamides of interest were separated under the aforementioned conditions in 4 minutes, according to the sequence of elution, retention time, and resolutions shown in Table 16. A chromatogram of mixture standards is shown in Figure 21.

Table 16 The retention time and resolutions of sulfonamides.

No.	Sulfonamide	Retention time (t_R, min)	Resolutions (RS)
1	Sulfathiazole; STZ	0.9	-
2	Sulfachloropyridazine; SCP	1.5	5.5
3	Sulfamethoxazole; SMX	2.0	3.7
4	Sulfadimethoxine; SDM	3.3	8.7

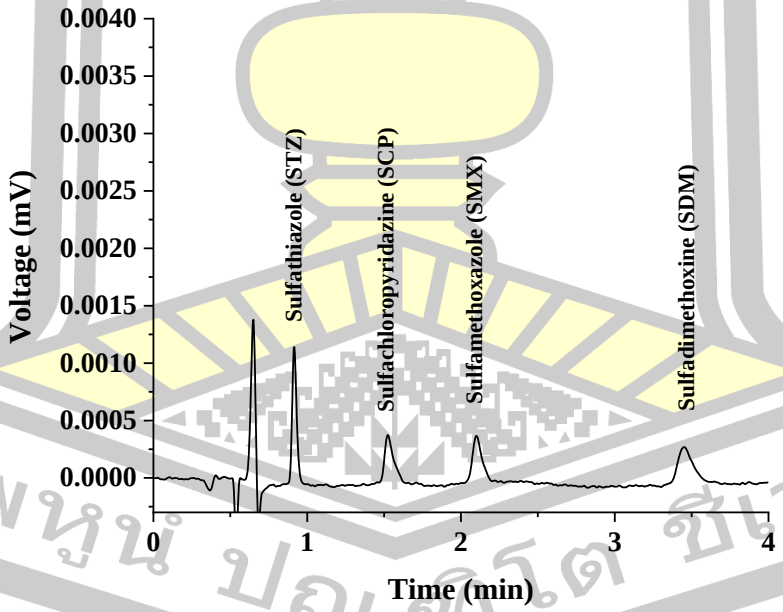


Figure 21 Chromatogram of sulfonamide residues 100 µg L^{-1} determined with UPLC.

4.2.1 Analytical performance of the UPLC system direct injection

Under the selected UPLC conditions, the analytical performance were evaluated by examining linear range, precision, LOD and LOQ. Calibration curves were constructed by triplicate injections of standard sulfonamides solutions. Peak area of each analyte was plotted against it concentration. LOD and LOQ are defined by the concentration giving the signal-to-noise ratios (S/N) of 3 and 10, respectively. The precision of the method was performed by five replicate injections of the standard mixture of 100 µg L^{-1} sulfonamides. The results are summarized in Table 17. It was found that, the calibration curve were linear in the range of 90-3000 µg L^{-1}. The LODs and LOQs were in the range of 10-30 and 30-90 µg L^{-1}, respectively. The results showed good precision with the RSDs of lower than 2.77% for retention time, while the RSDs of peak area were lower than 3.02%.

Table 17 Analytical performance of the UPLC system for sulfonamides determination

Analyte	Linear range (µg L^{-1})	Linear equation	R^2	LOD (µg L^{-1})	LOQ (µg L^{-1})	Intra-day[a] precision (n=5), RSD (%)		Inter-day precision (n=3 × 5), RSD (%)	
						t_R	Peak area	t_R	Peak area
Sulfathiazole	90 - 3000	y = 19297x + 437.67	0.9987	10.0	30.0	0.47	2.77	0.61	2.38
Sulfamethazine	90 - 3000	y = 21174x - 924.58	0.9981	30.0	90.0	0.41	2.20	0.42	2.95
Sulfamethoxazole	90 - 3000	y = 21359x - 259.54	0.9979	30.0	90.0	1.64	1.98	1.33	1.81
Sulfadimethoxine	90 - 3000	y = 20426x + 241.33	0.9989	30.0	90.0	1.03	2.43	0.84	3.02

[a)] Precision were investigated at the concentration of 300 µg L^{-1}

4.2.2 Optimization of preparation of alginate-MS as adsorbent

The performance of the alginate-MS absorbent was shown to be affected by the concentration of sodium alginate and calcium chloride, which were optimized using the univariate method. The peak regions of the four sulfonamides were used to calculate the experimental responses. Each experiment was conducted in triplicate, with the average result serving as the basis for optimization. The error bars show the standard errors (n = 3).

4.2.2.1 Optimization of size of sponge

The size of the sponge has a major impact on the sorbent's effectiveness. Because a sorbent of the right size can absorb the target substance to the greatest extent and will improve the likelihood of coming into touch with the analyte. According to the size of the sponge used to make the sorbent, a sponge measuring 1×1×1 cm^3 produced the highest extraction efficiency (as shown in Figure 22). At the size of 0.5×0.5×0.5cm^3, the sorbent was small and had a small adsorption surface area, resulting in low extraction efficiency. Additionally, at 2×2×2 cm^3, the sorbent was too large to fit in a 5 ml syringe. Therefore, in this work, the size of 1×1×1 cm^3 was selected as the sorbent in this work.

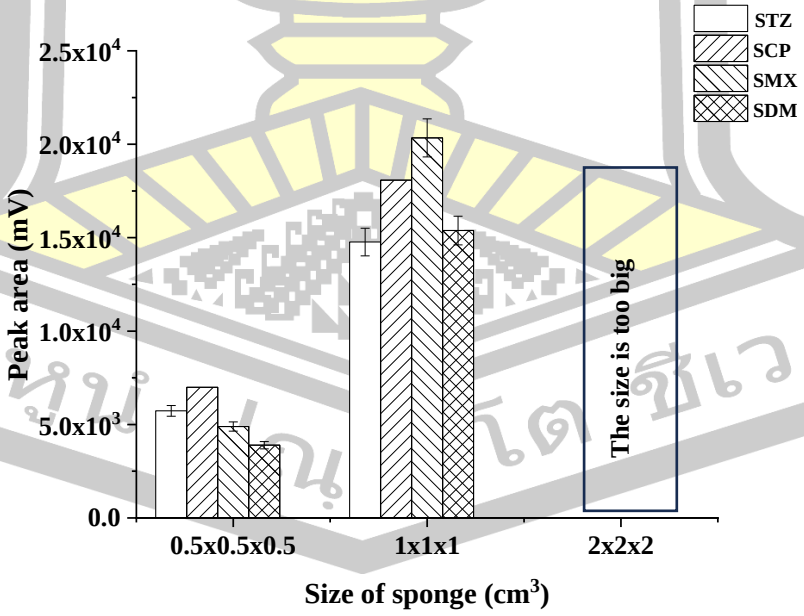


Figure 22 Effect of size of sponge.

4.2.2.2 Optimization of concentration of sodium alginate and calcium chloride

The optimal concentration of calcium chloride and sodium alginate is one of the key elements affecting the very stable crosslinking. Maintaining structural integrity is made easier by this constant crosslinking. In this work, sodium alginate concentrations ranging from 0 to 4 weight percent were examined (as shown in Figure 23). The concentration of 0.5 wt% was found to yield the optimum extraction efficacy, while concentrations of 1-4 wt% caused the adsorbent to shrink in size and surface area. The calcium chloride concentration range of 2-5 wt% demonstrated the stability of the adsorbent structure. As the result shown in Figure 24, the concentration of 3 wt% produced the largest peak area, so it was chosen to be used in the adsorbent synthesis.

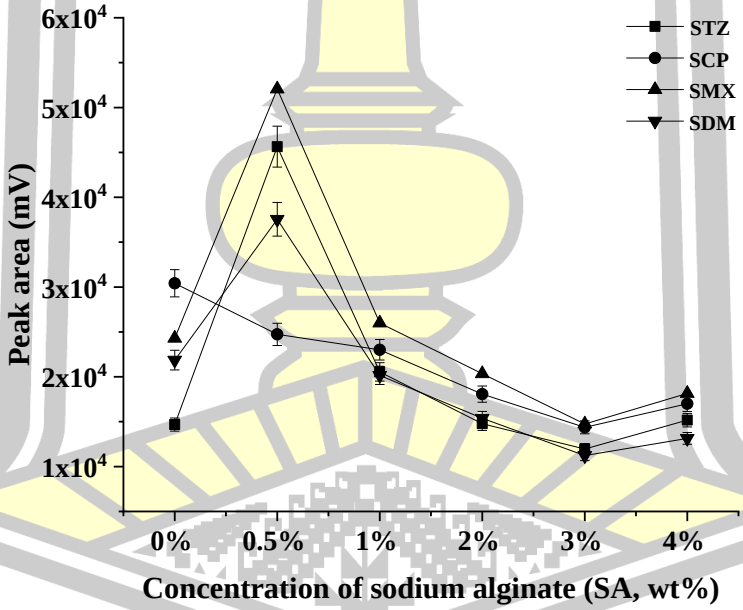


Figure 23 Effect of concentration of sodium alginate.

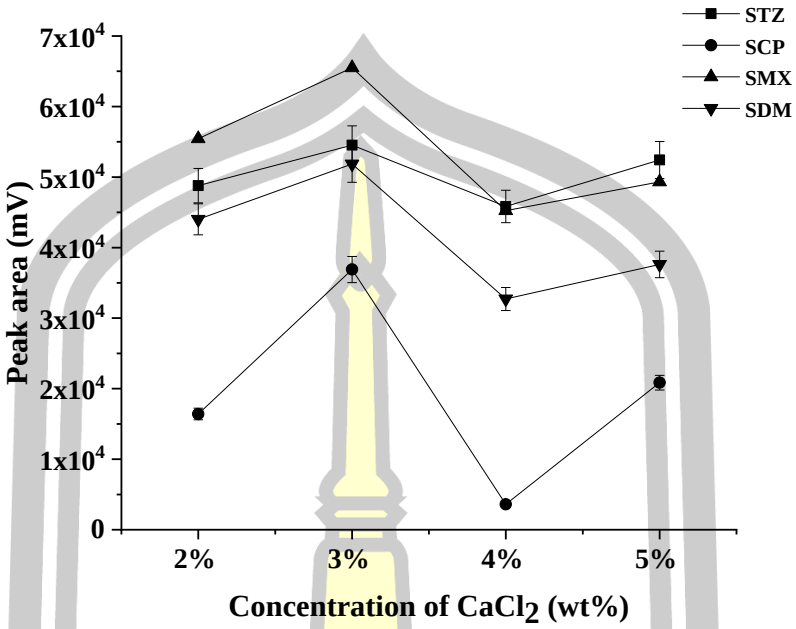


Figure 24 Effect of concentration of calcium chloride ($CaCl_2$).

4.2.3 Optimization of μ-SPE procedure using alginate-MS as adsorbents

The μ-SPE extraction performance was affected by the kind, concentration, and volume of surfactant as well as the type and volume of sorption solvent, all of which were optimized using the unimodal approach. The peak regions of the four sulfonamides matched the experimental findings. All the experiments were studied in triplicate, and the average of those runs served as the basis for optimization. Standard errors are displayed via error bars (n=3).

4.2.3.1 Optimization of kind of surfactant

Surfactants are known to change energy interactions at interfaces, usually by influencing surface or interfacial tension. Consequently, surfactants are frequently utilized to enhance adsorbents. The target chemical is surrounded by surfactants, which raise its affinity for surface contacts. This study examined a number of surfactants, including didodecyldimethylammonium bromide (DDAB), cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), Triton X-114 and without surfactant. As shown in Figure 25, CTAB had the highest extraction efficiency due to its positive charge, which enables the sulfonamide to attach to the adsorbent efficiently by electrostatic attraction. Consequently, CTAB was chosen for this project.

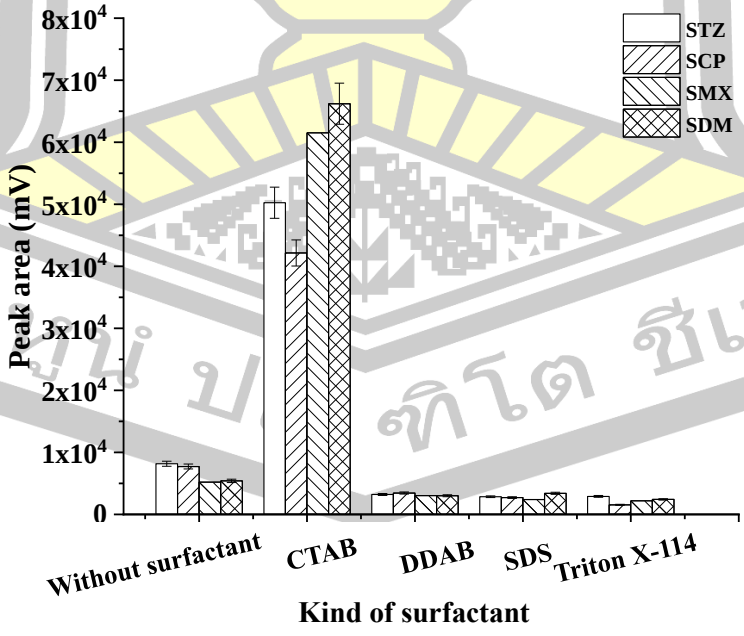


Figure 25 Effect of kind of surfactant.

4.2.2.2 Optimization of concentration and volume of surfactant

To examine the effects of CTAB concentration, a range of 0.05-0.3 M was employed. Figure 26 shows that a greater extraction efficiency was obtained with the addition of 0.1 M CTAB. This may occur because soluble hydrocarbons are created in the surfactant solution as a result of molecule accumulation on the solvent's surface, or it may be because a portion of the water is dissolved in the hydrocarbon compound. With the surfactant sticking to its surface and enveloping the target, the adsorbent will be able to absorb more efficiently. Since higher concentration of surfactant increases viscosity, which in turn affects target detection, the peak area decreases as surfactant concentration rises. Because of this, the trial included 0.1 M CTAB. The other parameters were maintained constant while the volume of surfactant was adjusted between 500 and 1500 µL using 0.1 M CTAB (as shown in Figure 27). The peak area of sulfonamides increased as the volume of surfactant increased to 1000 µL and then decreased later, so 0.1 M CTAB of 1000 µL was chosen for additional experiments.

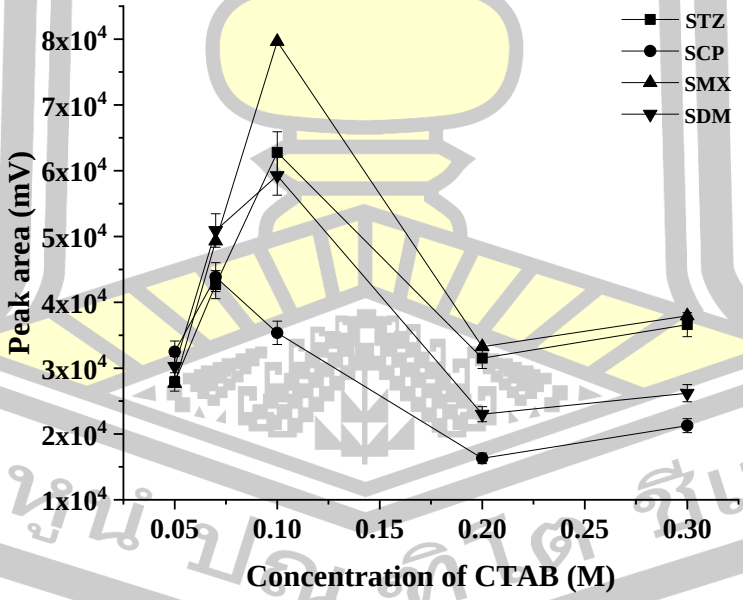


Figure 26 Effect of concentration of CTAB.

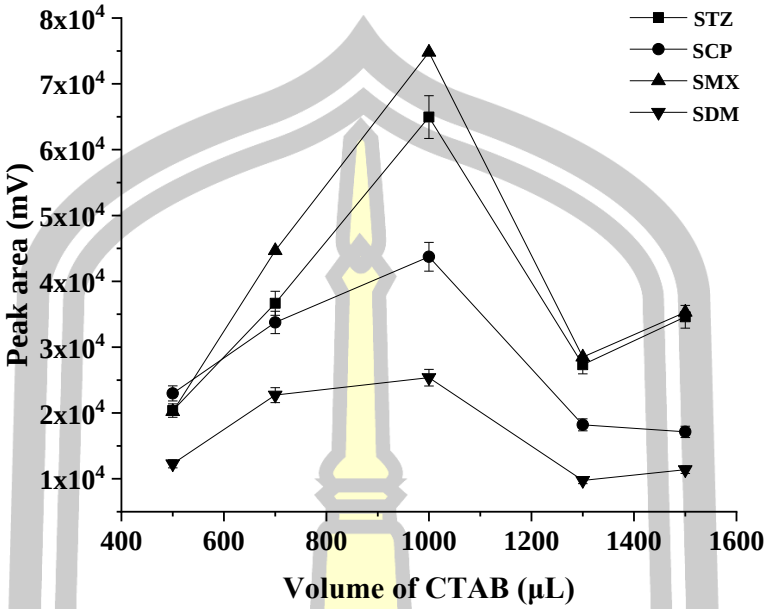


Figure 27 Effect of volume of CTAB.

4.2.3.3 Optimization of desorption solvent

It is widely recognized that appropriate organic solvents have the ability to both dissolve mixed hemimicrycles and remove analytes from adsorbents. This study examined a number of solvents, including methanol (MeOH), ethanol (EtOH), DI water, and acetonitrile (ACN). The result in Figure 28 illustrates that whereas ACN and EtOH have comparable elution efficiency for the majority of sulfonamides. However ACN produces superior of chromatographic signals (As shown in Figure 29,30). As a result, ACN was selected as desorption solvent.

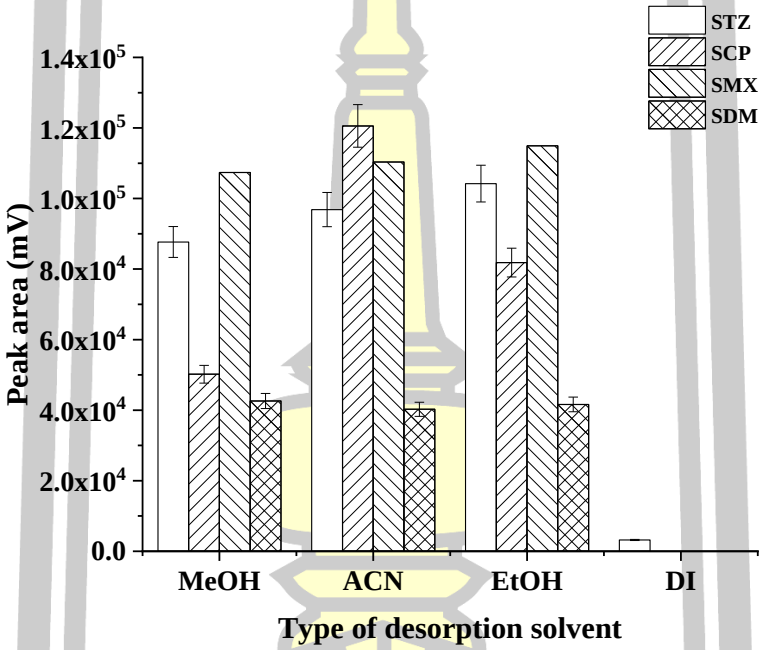


Figure 28 Effect of desorption solvent type.

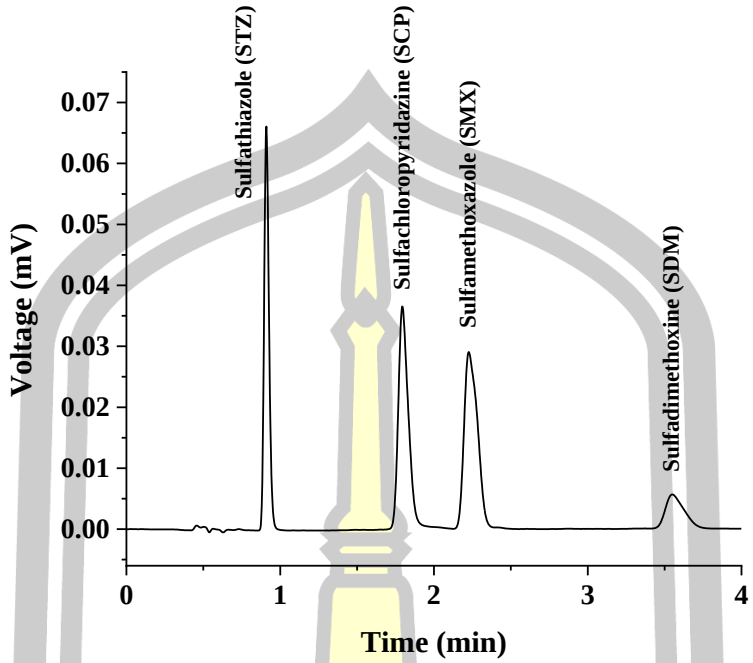


Figure 29 Chromatogram of desorption solvent (ACN).

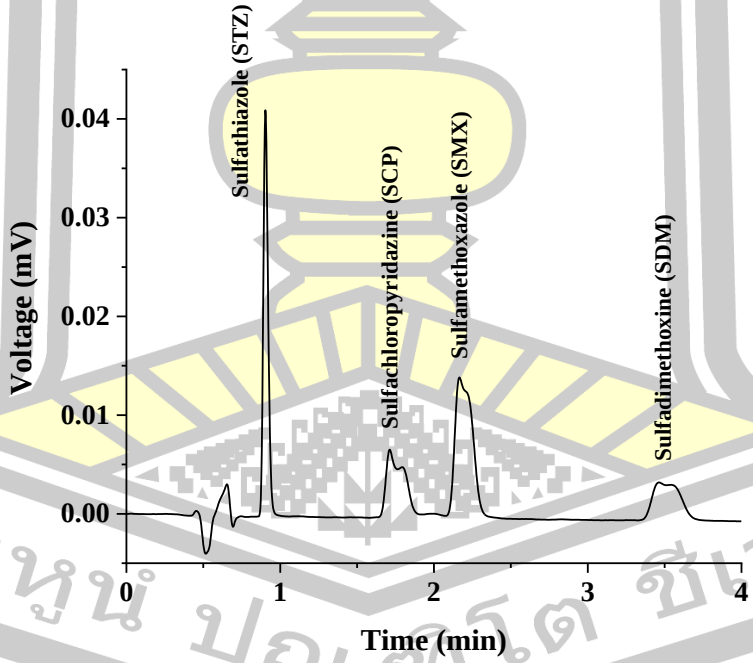


Figure 30 Chromatogram of desorption solvent (MeOH).

4.2.3.4 Optimization of desorption solvent volume

The volume of the desorption solvent (ACN) was investigated in the range of 300-1000 µL. As shown in Figure 31, it was discovered that the solvent volume of 300 µL was insufficient to elute the solvent phase from the adsorbent, which in turn prevented the target molecules from being extracted from the adsorbent. However, increasing the volume of the desorption solvent to 500 µL resulted in an improvement in extraction efficiency. However, if more adsorption solvent was employed, the analyte in the sample solution would become more soluble, which would lower the extraction efficiency. Therefore, the desorption solvent used was 500 µL of ACN.

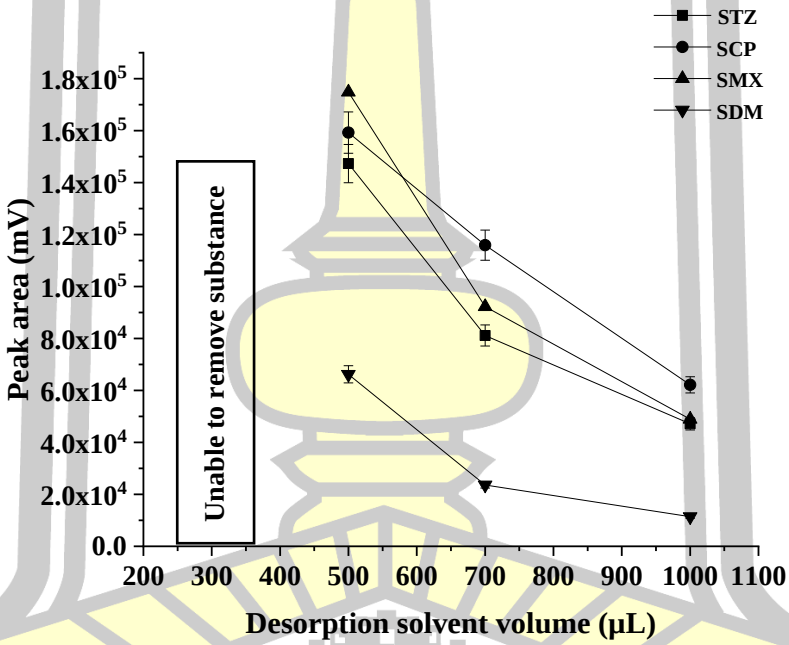


Figure 31 Effect of desorption solvent volume.

4.2.4 Reusability

The results of a study on the reusability of alginate-MS are shown in Figure 32. In this study, the adsorbent was cleaned two times using acetonitrile before to the μ-SPE cycle. The regeneration and reusability of the produced adsorbents were investigated under ideal circumstances. After three extraction cycles, the peak areas of the sulfonamides under investigation significantly increased because of the adhesion of the additives from the prior extraction procedure, which made it possible for more sorbent surface areas to bind to the target substance. In the fourth cycle, the white membrane separated from the sorbent, indicating that the sorbent was denatured. Consequently, this experiment's adsorbents might be utilized three times.

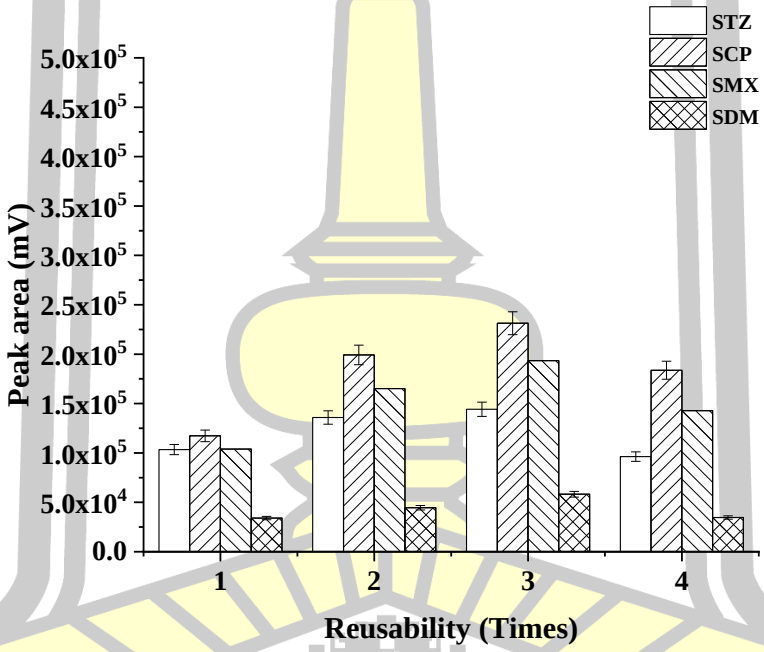


Figure 32 The reusability of alginate-MS for adsorbing sulfonamides.

4.2.5 Selectivity

Target molecules other than sulfonamides, such as benzoylurea, benzimidazoles, carbamates, and pyrethroids, were investigated for the selectivity of alginate-MS sorbent under suitable extraction conditions. Alginate-MS sorbent was shown to be selective for sulfonamides in the investigation since it was unable to adsorb any other target chemicals.

4.2.6 Sorption capacity

To investigate the impact of sample volume, mixtures containing 100 µg L^{-1} of each sulfonamide antibiotic were utilized. Sulfonamide solutions ranged in volume from 30 to 170 mL. The peak areas of the majority of sulfonamide increased quickly when the sample volume went from 100 to 130 mL, as shown in Figure 33. Following that, some of the peak areas shrank as a result of the excess solution self-leaching. Consequently, the greatest sample volume that could be used with the developed technique was 130 mL. Furthermore assessed was the adsorption capacity, which is the quantity of sulfonamide antibiotic absorbed per unit of adsorbent. The mixture of four sulfonamides had an adsorption capability of 162.5 µg g^{-1} for each sulfonamide, according to the results.

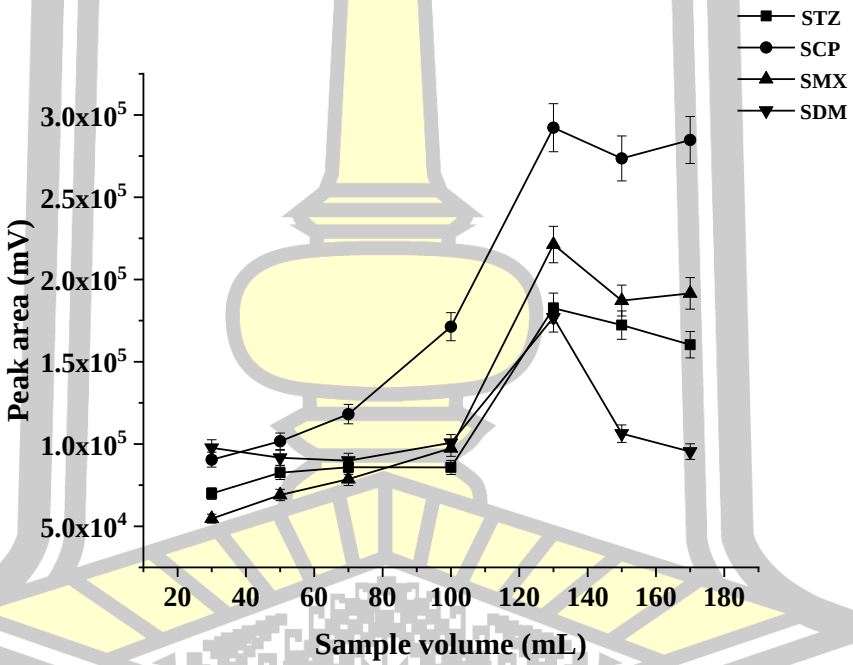


Figure 33 Sorption capacity of sample volume.

4.2.7 Characterization of modified sorbent

4.2.7.1 Scanning electron microscope; SEM

Based on the analysis of the scanning electron microscopy images, displays the melamine sponge SEM micrographs (as shown in Figure 34(a)), as well as alginate-MS (as shown in Figure 34(b)), alginate-MS after adsorption (as shown in Figure 34(c)), and alginate-MS after desorption (as shown in Figure 34(d)). The alginate layer is inside the sponge's pores, as seen in Figure 34b. Furthermore, the surface area of the adsorbent was seen to thicken throughout the adsorption process (as shown in Figure 34(c)). This is because the surfactant addition can have an impact on how the coating layer forms, meaning that the surfactant's surface and interaction site would both grow. These findings thus confirm that the adsorbent and surfactant have an effective connection. Furthermore, the adsorbent was discovered to be slightly denatured during desorption (as shown in Figure 34(d)), which is compatible with the adsorbent's reusability despite only being utilized three times.

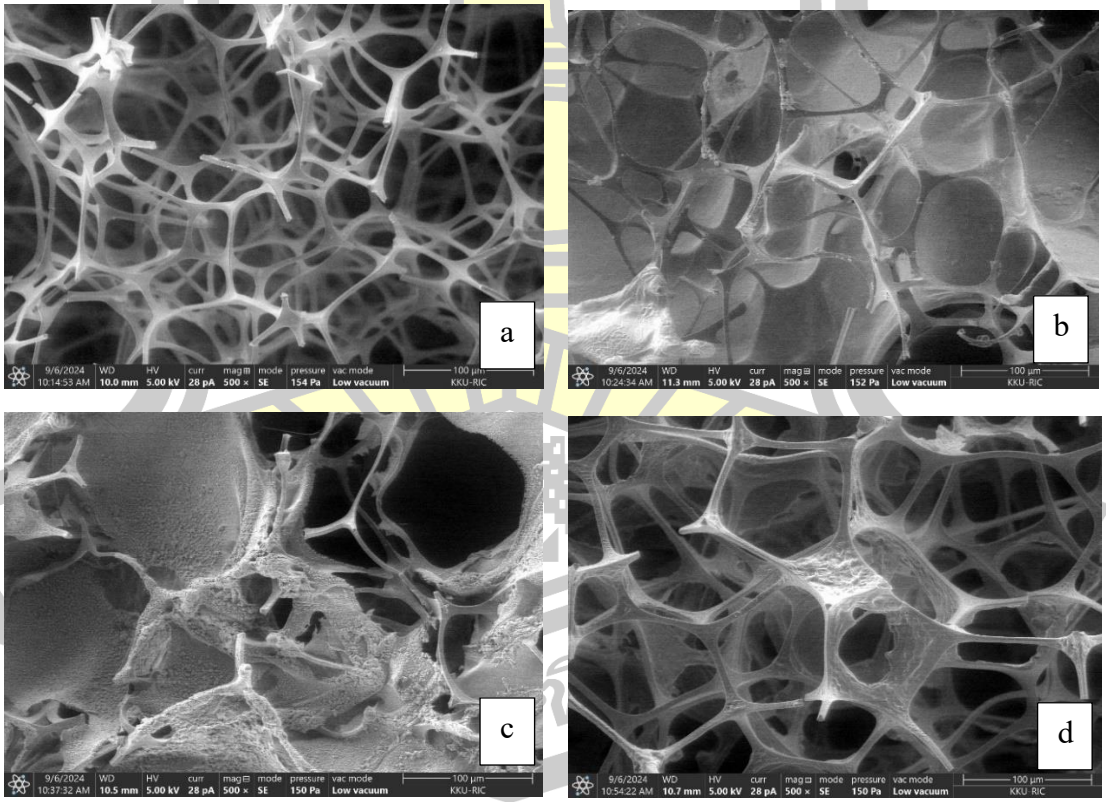


Figure 34 SEM of (a) melamine sponge, (b) alginate-MS, (c) alginate-MS adsorption and (d) alginate-MS desorption.

4.2.7.2 Fourier transform infrared spectroscopy; FTIR

Figure 35 displays the FTIR spectra of the MS samples. According to the spectra, the stretching vibration of the secondary amine (N-H) and O-H on the MS surface are responsible for the absorption peak at 3351.14 cm^{-1}. The observed C=N stretching was 1543.94 cm^{-1}. The C-H bending vibration of methylene was consistent with the peaks at 1459.25 and 1326.29 cm^{-1}. The stretching vibration of the C-O groups, which are the distinctive functional groups of sodium alginate, at 1029.38 cm^{-1}, the symmetric stretching vibration of the COO groups at 1423.48 cm^{-1}, and the asymmetric stretching vibration of the COO groups at 1598.92 cm^{-1} all indicated the presence of sodium alginate on the sponge in the alginate-MS spectra. Additionally, significant absorptions at 2920.05 and 2850.83 cm^{-1} in the alginate-MS adsorption spectra were attributed to the C-H stretching vibrations of the methyl and methylene groups of the CTAB. These findings suggest that during the extraction process, CTAB is present on the adsorbent's surface. It is evident that the CTAB signal is significantly diminished during the desorption process since it is nearly entirely eluted.

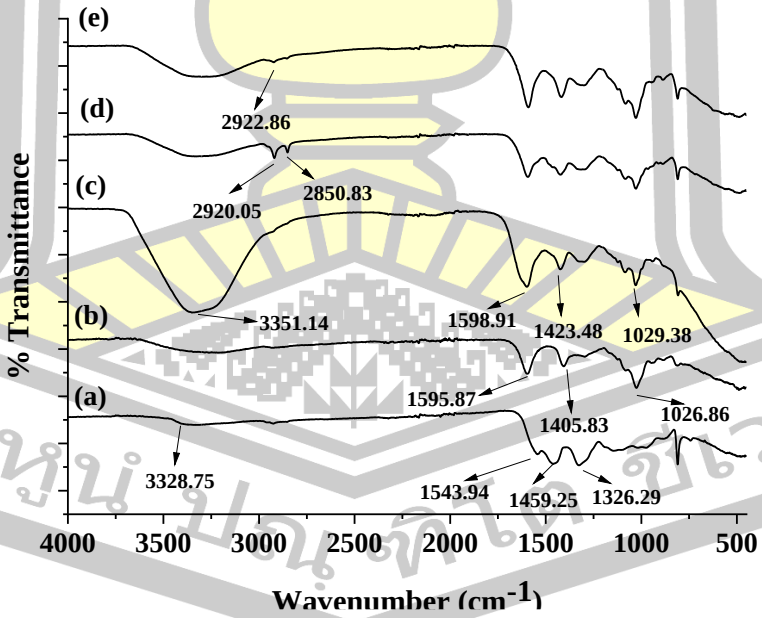


Figure 35 FTIR of (a) melamine sponge (b) sodium alginate (c) alginate-MS (d) alginate-MS adsorption and (e) alginate-MS desorption.

4.2.8 Analytical performance of the proposed method

The analytical performance of the suggested technique for the measurement of sulfonamides was verified under the optimal circumstances by measuring linearity, precision, accuracy, and sensitivity in terms of limits of quantification (LOQs) and limits of detection (LODs). The developed method's validation data is compiled in Table 18. The calibration graphs, with R^2 values more than 0.99, demonstrated acceptable linearity in the range of 3-70 µg L^{-1}. Based on signal-to-noise (S/N) ratios of 3 and 10, respectively, the LOD and LOQ values were thoroughly examined and were found to be in the ranges of 0.3-0.9 µg L^{-1} and 0.9-3 µg L^{-1}, respectively. When the EFs were calculated as the ratio of the analyte concentration ratio in the settled phase (C_{sed}), the sedimented phase later, and the aqueous sample (C_0), they were found to be in the range of 40.4-76.1 folds. To investigate the reproducibility of the suggested methodology, the RSDs of peak areas from the intraday (n = 5) and interday (n = 3 × 5) tests were utilized. The intraday and interday precision of all goals was found to be satisfactory, with RSD values falling below 4.95% and 12.83%, respectively. Figure 36 shows the chromatogram of sulfonamide after extraction by the proposed method.

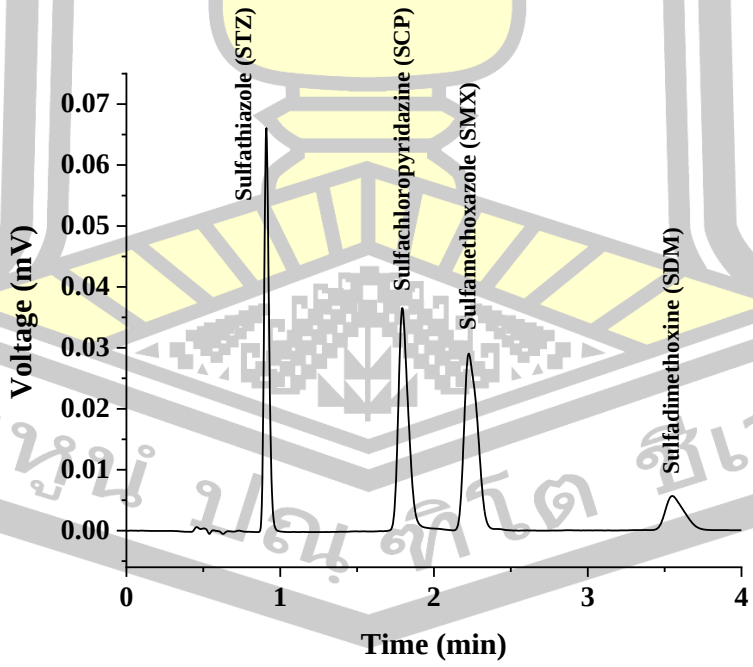


Figure 36 Chromatogram of 100 µg L^{-1} sulfonamide residues after preconcentration by alginate-MS adsorbent.

Table 18 Analytical performance of the proposed method for determination of sulfonamide residues.

Analyte	Linear range (µg L^{-1})	Linear equation	R^2	LOD (µg L^{-1})	LOQ (µg L^{-1})	Intra-day precision[a] (n=5), RSD (%)		Inter-day precision (n=3 × 5), RSD (%)		EF (C_{sed}/C_0)
						t_R	Peak area	t_R	Peak area	
Sulfathiazole	3 - 70	y = (1×106x) + 389.31	0.9923	0.3	0.9	0.64	1.26	0.53	12.83	76.1
Sulfachloropyridazine	3 - 70	y = (1×106x) - 695.42	0.9982	0.9	3.0	1.42	3.00	1.01	9.21	58.2
Sulfamethoxazole	3 - 70	y = 969697x + 703.86	0.9980	0.9	3.0	0.59	4.95	0.49	7.08	68.3
Sulfadimethoxine	3 - 70	y = 600070x + 720.1	0.9915	0.9	3.0	0.46	3.77	0.65	11.01	40.4

[a)] Precision were investigated at the concentration of 10 µg L^{-1}

4.2.9 Application to real samples

The developed μ-SPE approach was used to the analysis of sulfonamide residues in real samples in order to assess its application and feasibility. The matrix yield (ME%) for complicated sample analysis should be computed using the sample-to-solvent ratio of the calibration in matrix slopes. STZ had a high matrix yield (ME: 13-37.5%) for all samples (Table 19). Among these samples were SMX in samples 1 and 3 (ME: 36.1, 31.1%, respectively), and SDM in sample 3. SCP revealed a comparatively low matrix yield (ME: 52.9-120.2%) for all samples. The examined samples had no sulfonamide residues. Furthermore, satisfactory recoveries of 58.7 to 144.3% were obtained with RSD better than 9.9% from the analysis of spiked samples (Table 20). The results demonstrated that the precision and accuracy of procedure were acceptable. The overlaid chromatograms of blank and spiked honey samples are shown in Figure 37-39).

Table 19 The matrix effect.

Sample	Analytes	Calibration in matrix	R^2	Linear range (µg kg^{-1})	Matrix effect (ME, %)
Honey I	STZ	y = 130888x + 117.94	0.9957	3-70	13.1
	SCP	y = 529002x + 96.682	0.9919	3-70	52.9
	SMX	y = 350402x + 373.93	0.9987	3-70	36.1
	SDM	y = 368642x + 764.85	0.9904	3-70	61.4
Honey II	STZ	y = 375351x - 411.03	0.9999	3-70	37.5
	SCP	y = 595500x - 2007.1	0.9974	3-70	59.6
	SMX	y = 625989x - 49.581	0.9995	3-70	64.6
	SDM	y = 903981x - 2127.2	0.9932	3-70	150.6
Honey III	STZ	y = 238422x + 546.53	0.9989	3-70	23.8
	SCP	y = 542736x + 1579	0.9996	3-70	120.2
	SMX	y = 311276x + 3682.3	0.9998	3-70	31.1
	SDM	y = 301959x + 2337.2	0.9977	3-70	30.2

Table 20 Recovery obtained from the determination of sulfonamides in the studied samples (n = 3).

Sample	Spiked (µg kg^{-1} for honey)	STZ		SCP		SMX		SDM	
		RR (%)	RSD (%)	RR (%)	RSD (%)	RR (%)	RSD (%)	RR (%)	RSD (%)
Honey I	0	ND	ND	ND	ND	ND	ND	ND	ND
	3	112.3	9.9	109.4	6.7	93.3	2.7	111.4	3.1
	7	93.9	1.4	66.2	1.1	123.8	0.1	115.1	0.9
	30	112.9	1.8	113.4	6.8	107.5	0.9	121.9	1.5
Honey II	0	ND	ND	ND	ND	ND	ND	ND	ND
	3	111.5	7.0	144.3	5.7	124.3	2.2	136.2	3.2
	7	97.4	1.2	99.8	9.6	89.3	8.0	118.1	0.4
	30	99.0	0.0	92.7	2.8	115.3	2.3	87.3	5.3
Honey III	0	ND	ND	ND	ND	ND	ND	ND	ND
	3	58.7	3.2	81.3	4.2	83.8	0.1	108.7	3.1
	7	114.1	0.0	109.6	1.6	105.0	3.2	120.6	1.8
	30	113.9	0.8	100.5	0.6	111.9	6.2	113.9	0.3

RR: Relative recovery, RSD: Relative standard deviation, ND: Not detect

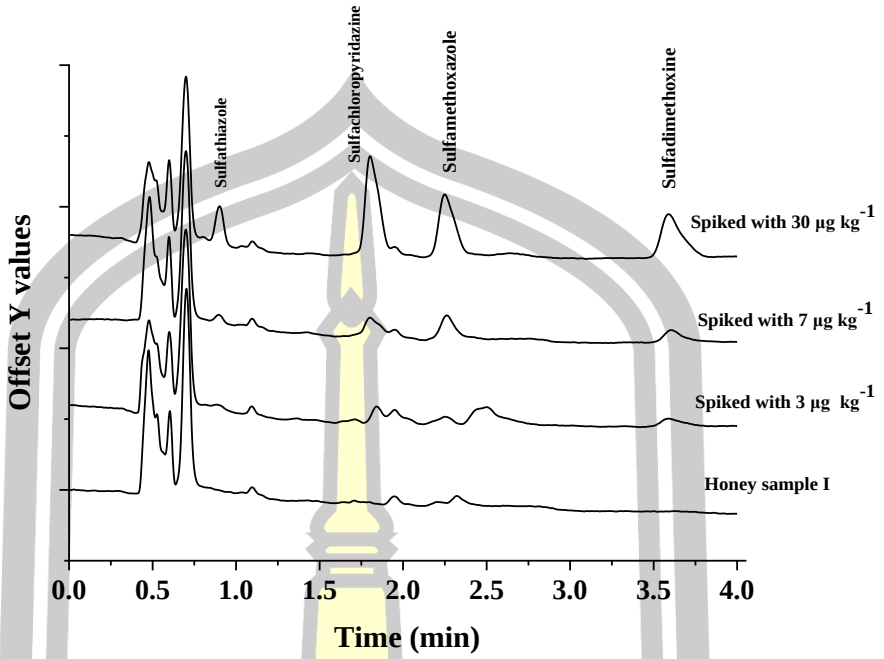


Figure 37 The overlaid chromatograms of blank and spiked honey sample I.

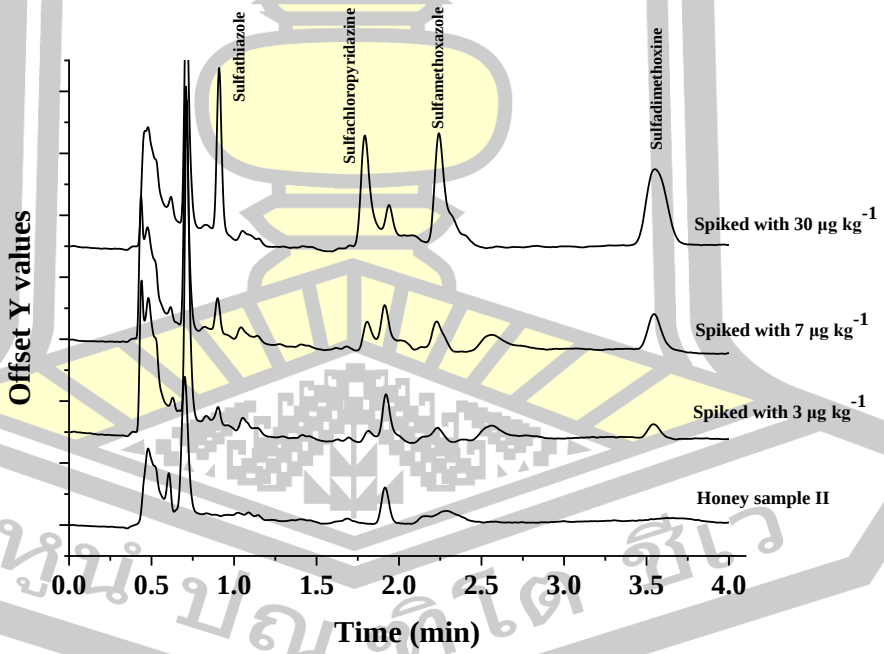


Figure 38 The overlaid chromatograms of blank and spiked honey sample II.

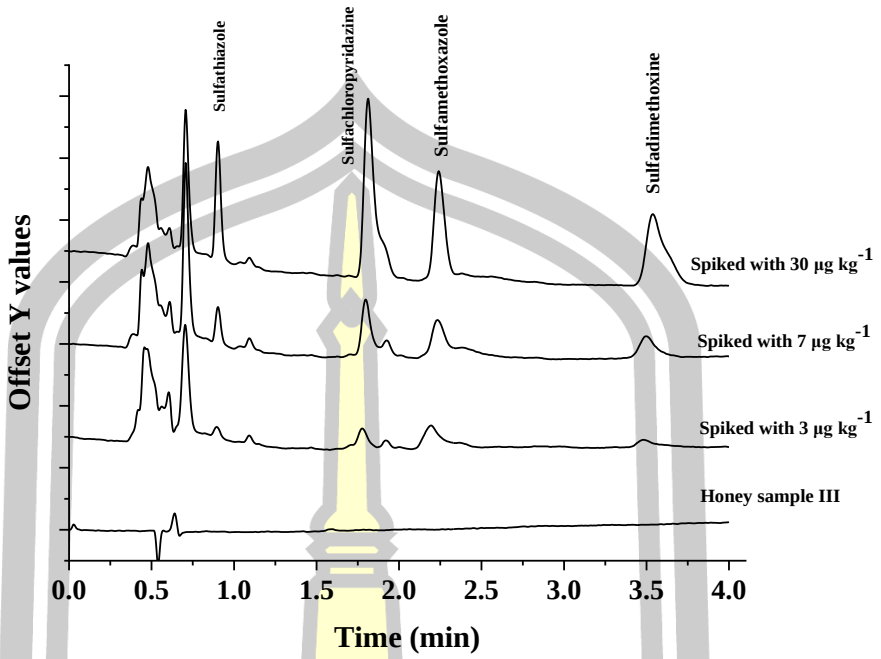


Figure 39 The overlaid chromatograms of blank and spiked honey sample III.

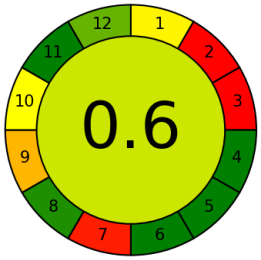
4.2.10 Assessment of method greenness

The analytical eco-scale methodology yields quantitative data on the degree of environmental friendliness of the analytical procedure with respect to the kind and quantity of solvents and reagents, instrument energy, waste creation, and occupational dangers. Penalty points are assigned to every parameter, and the sum of all penalty points is deducted from 100 to arrive at the final eco-scale score. The deviation from optimal greenness is assigned a set of penalty points (PPs). With a final score of 82 (as indicated in Table 21), the proposed microextraction method was deemed suitable as a green approach for sulfonamide analysis. Based on these results, the eco-scale tool suggests that the new method is more environmentally friendly.

With the use of AGREE software, the final score in AGREE metrics is mapped as a fraction of unity from 0 to 1. This automatically creates a following pictogram separated into twelve portions. The green, yellow, and red color scale in the pictogram indicates the precise color coding allocated to each section, which reflects how well each GAC principle is performing. Additionally, Table 21 shows that the established method's greenness features were indicated by the AGREE evaluation, which yielded a final score of 0.6. Of the subsectors in the colored pictogram, sectors 2, 3, and 7 were shown to be the least effective. The agreement seen between AGREE and Analytical Eco-Scale pictograms for the compared methods suggested that these are the most trustworthy instruments for evaluating greenness since they can offer comprehensive information about the entire process, including all analytical phases for the methodologies under study.

Table 21 Greenness assessment of the proposed method according to Analytical Eco-Scale and AGREE tools.

Analytical Eco-Scale						**AGREE Assessment**
Reagent	**Penalty points (PPs)**			**Instrument**	**PPs**	
	Amount PP	**Hazard PP**	**Total PPs (Amount PP × Hazard PP)**			
ACN (<10 mL)	1	4	4	UPLC-PDA	0	
MeOH (<10 mL)	1	6	6	Occupational hazard	0	
CTAB (<10 mL)	1	2	2	Waste	5	
$CaCl_2$ (<10 mL)	1	1	1			
Subtotal PP			13		5	
Total PPs			18			
Analytical Eco-sale score (AEC)			82			



4.2.11 Comparison with other reported methods

Table 22 provides a detailed comparison between the suggested method and previously published sorbent-based techniques to highlight the benefits of the proposed method for the determination of sulfonamides. The current method's benefits include cost-effectiveness, environmental friendliness, simplicity, and quick examination. Limit of detection (LOD) sensitivity of the suggested approach is nearly identical to that of an alternative microextraction technique. The new adsorbent proved effective in the extraction of sulfonamides due to its large specific surface area and selective adsorption of alginate-MS. The key benefits of the suggested μ-SPE are its minimal sample volume consumption and the absence of costly or specialized chemicals needed for the reaction.

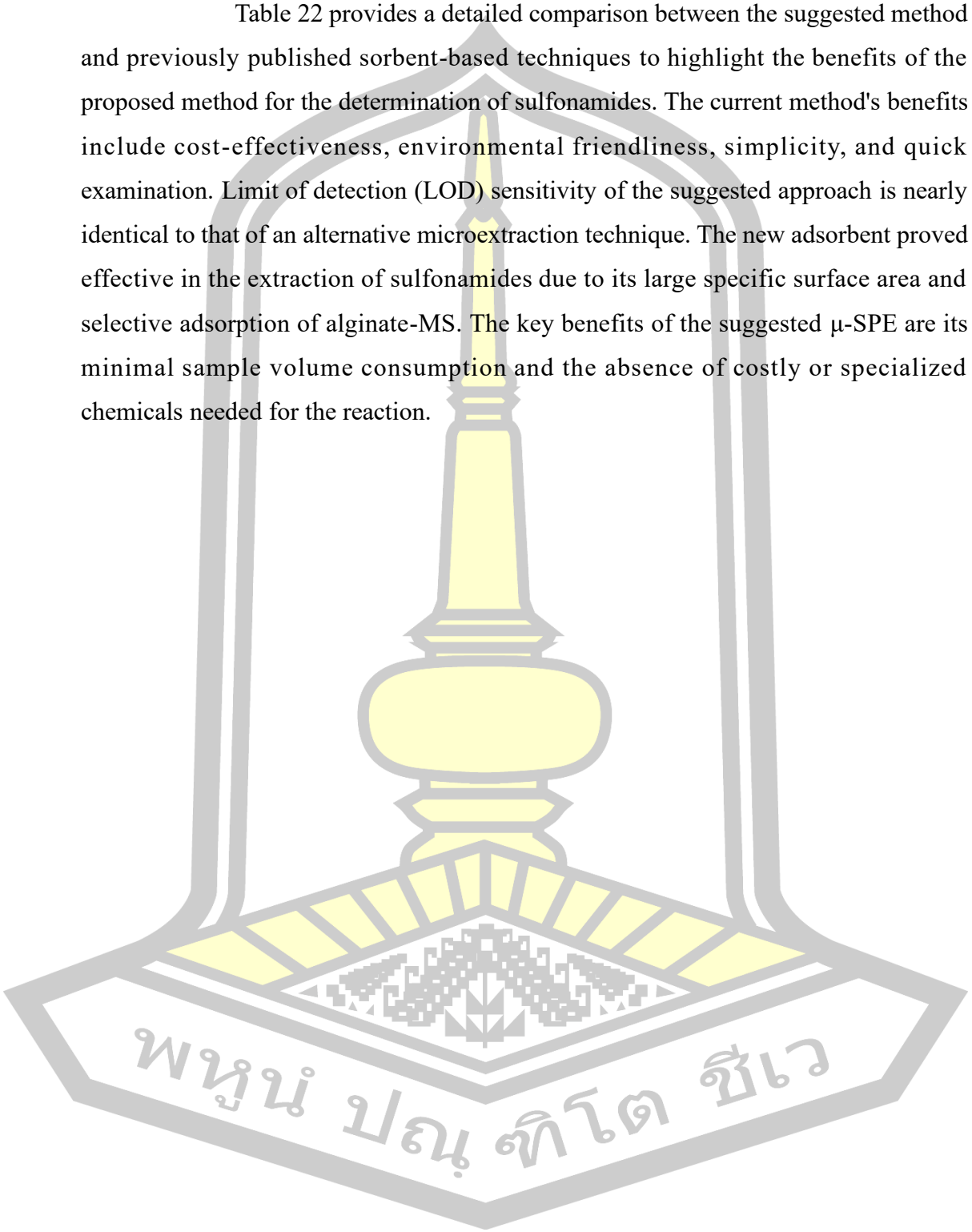


Table 22 Comparisons of the proposed method with other methods for the quantitation of sulfonamides.

Sample Preparation Method	Analytes	Samples	Linear range	LODs	Ref.
N-rich magnetic covalent organic framework	Sulfamethoxypyridazine, sulfameter, sulfamonomethoxine, sulfachlorpyridazine, sulfadoxine, sulfamethoxazole, sulsoxazole, sulfabenzamide, sulfadimethoxine, sulfanitran and sulfaquinoxaline	Water and foods	0.1-100 ng mL^{-1}	0.001-0.078 mg L^{-1}	[93]
Oasis HLB cartridges	Fluoroquinolones, sulfonamides and macrolides	Edible fish muscle	-	0.008-0.35 µg kg^{-1}	[94]
Covalent organic framework incorporated electrospun nanofiber for pipette tip solid phase extraction	Sulfadiazine, sulfamerazine, sulfamethazine, sulfamonomethoxine and sulfamethoxazole	Pork and chicken meat	5-125 ng mL^{-1}	1.7-2.7 ng mL^{-1}	[95]

TiO_2 nanotube arrays as the adsorbent combined with sodium dodecylbenzene sulfonate to improve micro solid phase extraction	Sulfadiazine, sulfamerazine, sulfamethazine, sulfadimethoxine, sulfamethoxazole and sulfafurazole	Water sample	1-200 μg L^{-1}	0.27-0.6 μg L^{-1}	[96]
Molecularly imprinted polymers-coated magnetic covalent organic frameworks for efficient solid-phase extraction	Sulfaguanidine, sulfathiazole, sulfadiazine, sulfamethazine, and sulfadimethoxine	Fish flesh sample	0.1-250 μg kg^{-1}	0.04-1.36 μg kg^{-1}	[97]
Tryptophan based hypercrosslinked porous polymer as an efficient adsorbent for pipette tip solid-phase extraction	sulfadiazine, sulfamethoxazole, sulfisoxazole, sulfathiazole, sulfamerazine, and sulfadimidine	Tap water, milk and meat samples	10-2000 μg L^{-1}	2.30-6.09 μg L^{-1}	[98]
Supported liquid membrane-protected molecularly imprinted beads for micro-solid phase extraction	Sulfadimethoxine, sulfadiazine, sulfapyridine, sulfamerazine, sulfamethazine, sulfamonomethoxine, sulfachloropyridazine and sulfamethoxazole	environmental water	1-100 μg L^{-1}	0.2-3 μg L^{-1}	[99]

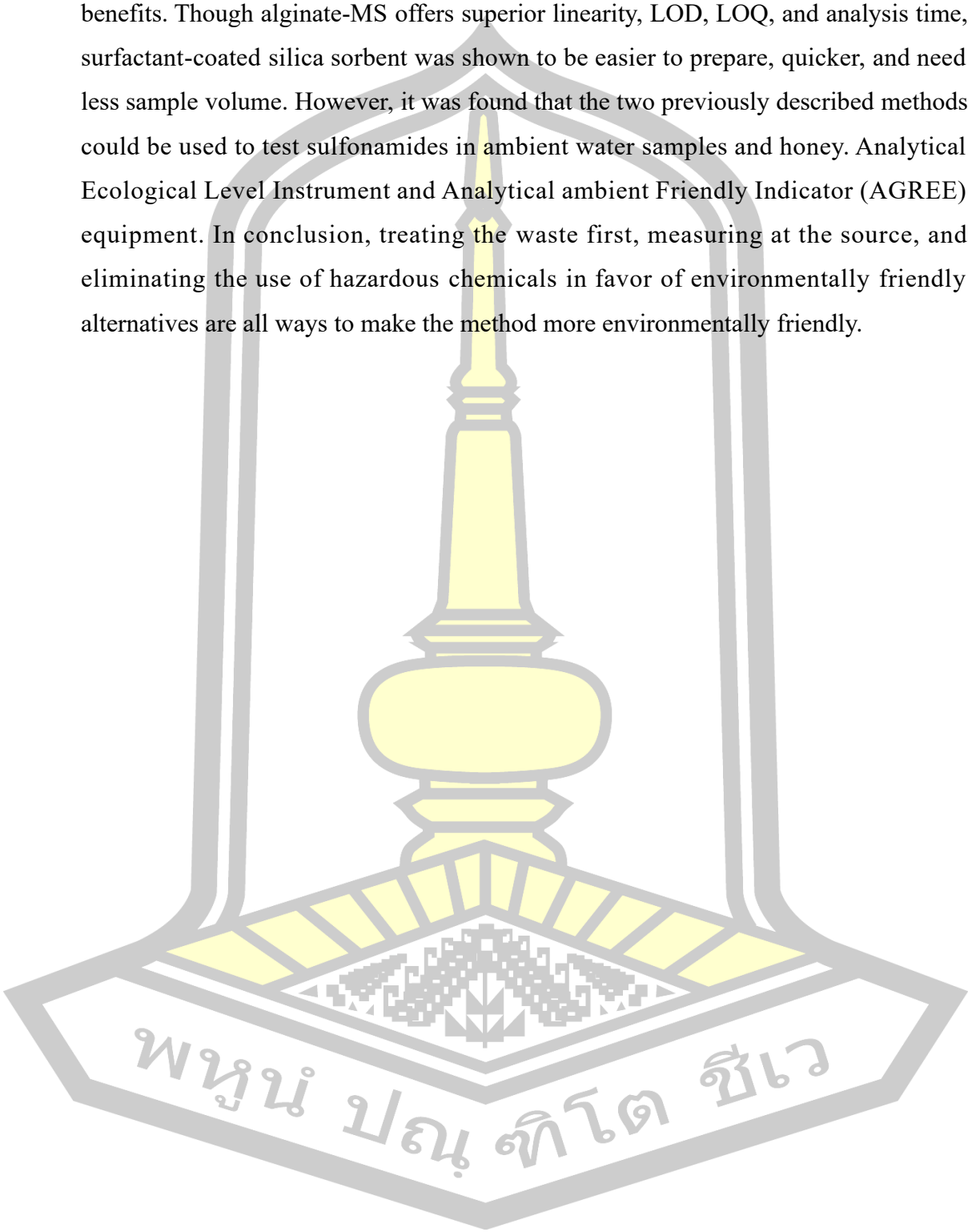
Zinc ferrite as a magnetic sorbent for the dispersive micro solid-phase extraction	Sulfacetamide, sulfadiazine, sulfapyridine, sulfamerazine, sulfathiazole, sulfamethazine, sulfamethoxypyridazine, sulfachloropyridazine, sulfamethoxazole, sulfisoxazole, sulfadimethoxine, and sulfaquinoxaline	Egg and lake water	0.06- 250 μg L^{-1}	-	[100]
One-pot derivatization/ magnetic solid-phase extraction	Fluorescamine, sulfonamide, sulfadiazine, sulfamethoxazole, sulfamethazine, sulfamethoxazole, sulfaguanidine, sulfamethazine sulfabenzamide, sulfaquinoxaline sodium and sulfamonomethoxine	Honey sample	0.01-10 ng g^{-1}	0.004-0.04 ng g^{-1}	[101]
Spherical mesoporous covalent organic framework as a solid-phase extraction	Sulfadiazine, sulfathiazole, sulfapyridine, sulfamerazine, sulfamethazine and sulfamethoxazole	Pond water, spring water, pork and milk	5-1000 ng L^{-1}	0.5-1.0 ng L^{-1}	[102]
Alginate-MS /SPE	Sulfathiazole, ulfachloropyridazine, sulfamethoxazole, sulfadimethoxine	Honey sample	3-70 μg L^{-1}	0.3-0.9 μg L^{-1}	This work

CHAPTER 5
CONCLUSION

Within this work, a surfactant coated silica sorbent has been successfully applied for extraction and preconcentration of sulfonamide residues at trace levels in environmental water and honey samples followed by HPLC-PDA quantification. The dispersed sample was transferred into the prefabricated SPE cartridge, which integrated extraction and cleanup into one single-step. The parameters that work best are: 0.09 g of silica gel adsorbent; CTAB 0.03 M 150 µl of surfactant type, concentration, and volume; 500 µl of methanol eluent type and volume. The hydrophilic and hydrophobic interactions between analytes and silica and tails of surfactants allowed to improve sorption efficiency. With the optimized conditions, linearity in the 9-300 µg L^{-1} range, sensitivity in terms of limits of detection (LODs) in the 1-3 µg L^{-1} range, limits of quantification (LOQs) in the 3-9 µg L^{-1} range, precision and accuracy of no more than 4.95% and 5.00%, respectively, validated the analytical performance of the proposed method for sulfonamide analysis.

After extracting and preconcentrating trace amounts of sulfonamide residues from honey samples using the alginate-MS sorbent, UPLC-PDA measurement was performed. The scattered samples were put into premade SPE cartridges, which combined the extraction and cleanup processes into one easy step. The optimal parameters were sodium alginate and calcium chloride concentrations of 0.5 wt% and 3 wt%, respectively; 0.1 M CTAB, 1000 µL of surfactant type, concentration, and volume; and 500 µL of acetonitrile eluent type and volume. The hydrophilic and hydrophobic interactions between analytes and alginate-MS and the surfactant tail fraction improved the adsorption performance under the optimum conditions. The analytical performance of the proposed method for the analysis of sulfonamides was confirmed by the following: linearity in the range of 3-70 µg L^{-1}, sensitivity in terms of limit of detection (LOD) in the range of 0.3-0.9 µg L^{-1}, limit of quantitation (LOQ) in the range of 0.9-3 µg L^{-1}, precision and accuracy not exceeding 4.95% and 12.83%, respectively.

Based on their respective analytical outcomes, both approaches offer distinct benefits. Though alginate-MS offers superior linearity, LOD, LOQ, and analysis time, surfactant-coated silica sorbent was shown to be easier to prepare, quicker, and need less sample volume. However, it was found that the two previously described methods could be used to test sulfonamides in ambient water samples and honey. Analytical Ecological Level Instrument and Analytical ambient Friendly Indicator (AGREE) equipment. In conclusion, treating the waste first, measuring at the source, and eliminating the use of hazardous chemicals in favor of environmentally friendly alternatives are all ways to make the method more environmentally friendly.



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พหูน ปณ ฑิโต ชีเว

BIOGRAPHY

NAME	Wannipha Khiaophong
DATE OF BIRTH	19/02/2000
PLACE OF BIRTH	Udon Thani Province
ADDRESS	19 Moo. 6 Na Ngua, Nam Som District, Udon Thani 41210
POSITION	Student
PLACE OF WORK	Mahasarakham University
EDUCATION	2022 - Bachelor's Degree of Science (Chemistry) form Mahasarakham University, Mahasarakham Thailand 2017 - High School, Namsomphitthayakhom School, Nam Som, Udon Thani Thailand
Research grants & awards	Center of Excellence for innovation in Chemistry (PERCH-CIC) Mahasarakham University (Postgraduatetoral Fellowship)
Research output	Jaroensan, J., Khiaophong, W., Kachangoon, R., and Vichapong, J. Efficient analyses of triazole fungicides in water, honey and soy milk samples by popping candy-generated CO2 and sugaring-out-assisted supramolecular solvent-based microextraction prior to HPLC determinations. RSC Advances, 2023, 13, 4195. Khiaophong, W., and Vichapong, J. Green application of surfactant modified silica as effective sorbent for extraction and preconcentration of sulfonamide residues in

environmental water and honey samples. Journal of Chromatography A, 1718, 2024, 464720.