

Silica-Based Sorbents for Micro-Solid-Phase Extraction (μ -SPE) to Enhance Detection of Organic Contaminants in Wastewater

BY

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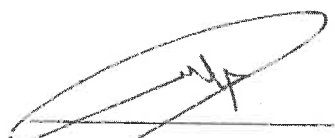


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Dedication

To my beloved father, **Ibrahim,**

Who made me the passionate, giving, and smiling girl I am today.

To my beloved mother, **Hala,**

Who truly lives up to the meaning of her name, surrounding my life with halos of light through her constant prayers which are protecting and guiding me wherever I go.

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For your endless prayers, unconditional love, and unwavering support. |

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LIST OF ABBREVIATIONS

μ-SPE	:	Micro-solid-phase extraction
FCC	:	Fluid catalytic cracking
GC	:	Gas chromatography
RSD	:	Relative standard deviation
LOD	:	Limit of detection
LOQ	:	Limit of quantification
UV	:	ultraviolet
FS	:	Fibrous silica
2,3-DCP	:	2,3-Dichlorophenol
3,4-DCP	:	3,4-Dichlorophenol
2,4,6-TCP	:	2,4,6-Trichlorophenol
4-BP	:	4-Bromophenol
4-NP	:	4-Nitrophenol
DBPs	:	Disinfection by-products
EDS	:	Energy dispersive X-ray spectrometer
SARS	:	Severe acute respiratory syndrome

WHO	:	World Health Organization
EU	:	European Union
WFD	:	Water Framework Directive
MS	:	Mass spectrometer
PAHs	:	Polycyclic aromatic hydrocarbons
FID	:	Flame ionization detector
LC	:	Liquid chromatography
LLE	:	Liquid-liquid extraction
SPE	:	Solid-phase extraction
SBSE	:	Stir-bar sorptive extraction
SPME	:	Solid phase microextraction
US EPA	:	United States Environmental Protection Agency
PTV	:	Programmable temperature vaporizing
LVI	:	large volume injection
ACN	:	Acetonitrile
GC GC-TOFMS	:	two-dimensional gas chromatography with time-of-flight mass spectrometry
LC-MS/MS	:	liquid chromatography tandem-mass spectrometry

DSPE	:	Dispersive solid-phase extraction
MSPE	:	Magnetic solid-phase extraction
DLLME	:	Dispersive liquid-liquid microextraction
CNTs	:	Carbon nanotubes
HPLC	:	High-performance liquid chromatography
POPs	:	Persistent organic pollutants
ABNs	:	Acid/base/neutral compounds
ISO	:	International Organization for Standardization
LPME	:	Liquid-Phase Microextraction
SDME	:	Single-drop microextraction
DI- SDME	:	Direct immersion Single-drop microextraction
DD- SDME	:	Drop-to-drop Single-drop microextraction
DSD- SDME	:	Directly suspended droplet Single-drop microextraction
CF- SDME	:	Continuous flow Single-drop microextraction
HS- SDME	:	Headspace Single-drop microextraction
DLPME	:	Dispersive liquid phase microextraction
DLLME	:	Dispersive liquid liquid microextraction
LPME	:	Liquid phase microextraction

VOCs	:	Volatile organic compounds
DVB	:	Divinylbenzene
GO	:	Graphene oxide
rGO	:	reduced graphene oxide
UHPLC-MS	:	Ultra-performance liquid chromatography–mass spectrometry
MOF	:	Metal-organic frameworks
2-MIB	:	2-methylisoborneol
RSD	:	Relative Standard Deviation
LMD	:	Lambda-Cyhalothrin
BRP	:	Bromopropylate
GC-ECD	:	Gas chromatography with an electron capture detector
MD- μ -SPE	:	Magnetic dispersive micro solid phase extraction
OPPs	:	Organophosphorus pesticides
DMSPE	:	Direct micro-solid-phase extraction
PP	:	Polypropylene
USY zeolite	:	Ultra stable Y zeolite
FTIR	:	Fourier Transform Infrared Spectroscopy

FE-SEM	:	Field Emission Scanning Electron Microscope
BET	:	The Brunauer-Emmett-Teller
BJH	:	Barret, Joyner, and Halenda
SIM	:	Selective ion monitoring
PXRD	:	The powder X-ray diffraction
DI-water	:	Deionized water
Ppm	:	Part per million
ppb	:	Part per billion
N.D.	:	Not Detected
PCDDs	:	Polychlorinated dibenzo-p-dioxins
PCDFs	:	Polychlorinated dibenzofurans
EPA	:	Environmental Protection Agency
MeOH	:	Methanol
IMP	:	Ion imprinting polymers
RAM	:	Restricted-access materials
MIP	:	Molecularly imprinted polymers
SBA-15	:	Santa Barbara Amorphous-15
KCC-1	:	KAUST Catalysis Center-1

CTAB	:	Hexadecyltrimethylammonium bromide
TEOS	:	Tetraethyl orthosilicate
FS-Amine	:	Fibrous silica functionalized with N ¹ -(3-Trimethoxysilylpropyl) diethylene
FS-Aniline	:	Fibrous silica functionalized with N-[3-(Trimethoxysilyl) propyl] aniline
FS-Mix	:	Fibrous silica functionalized with both N ¹ -(3-Trimethoxysilylpropyl) diethylenetriamine and N-[3-(Trimethoxysilyl) propyl] aniline
TGA	:	Thermogravimetric Analysis

ABSTRACT

Full Name : [Shaima' Ibrahim Mohammad Alsabbahen]

Thesis Title : [Silica-Based Sorbents for Micro-Solid-Phase Extraction (μ -SPE) to Enhance Detection of Organic Contaminants in Wastewater]

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Water pollution caused by organic contaminants such as pesticides and phenols present a significant environmental and public health challenge. This thesis focuses on developing and optimizing sustainable sorbent materials for membrane-supported micro-solid-phase extraction (μ -SPE) to address this issue. Two distinct approaches were investigated: the repurposing of spent fluid catalytic cracking (FCC) catalysts and the synthesis of functionalized fibrous silica (FS) materials.

In the first study, spent FCC catalysts were pretreated and characterized to assess their suitability as sorbents for pesticide extraction from wastewater. The optimized μ -SPE method demonstrated a wide linear detection range (5–1000 ng/mL), low limits of detection (0.36–1.52 ng/mL), and high recovery rates (84.9–99.5%). Six pesticides, including Isoprocarb, Atrazine, Primicarb, Penconazole, Chlorfenapyr, and Mefenacet, were successfully extracted and detected, showcasing the potential of this sustainable approach to recycle industrial by-products while addressing water contamination.

The second study successfully employed functionalized fibrous silica-based sorbents in μ -SPE for the detection and quantification of phenols from wastewater. Sorbents including FS-Amine, FS-Aniline, and FS-Mix were developed and evaluated, with FS-Mix exhibiting the best performance. The method demonstrated excellent analytical performance, with a linear detection range of 6.25 to 2000 ng/mL and low limits of

detection (LOD) ranging from 0.97 to 2.31 ng/mL. High relative recovery rates between 90.60% and 113.60% were achieved, underscoring the method's precision and reliability. Phenols such as 2,3-Dichlorophenol (2,3-DCP), 3,4-Dichlorophenol (3,4-DCP), 2,4,6-Trichlorophenol (2,4,6-TCP), 4-Bromophenol (4-BP), and 4-Nitrophenol (4-NP) were successfully extracted and quantified, demonstrating the sorbents' efficacy in wastewater treatment.

Overall, this thesis presents innovative solutions for water pollution mitigation, emphasizing sustainability, efficiency, and cost-effectiveness. The use of spent FCC catalysts highlights a practical recycling pathway for industrial waste, while the development of FS-based sorbents showcases the potential of advanced functionalized materials for selective contaminant removal. These findings contribute to the advancement of environmental remediation technologies, with implications for broader applications in water treatment and pollutant management.

ملخص الرسالة

الاسم الكامل: شيماء إبراهيم محمد الصباحين

عنوان الرسالة: المواد الماصة القائمة على السيليكا لاستخلاص الطور الصلب الدقيق (μ -SPE) لتعزيز الكشف عن الملوثات العضوية في مياه الصرف الصحي

التخصص: كيمياء

تاريخ الدرجة العلمية: [كانون الأول 2024]

تُشكل تلوثات المياه الناتجة عن الملوثات العضوية مثل المبيدات والفينولات تحدياً بيئياً وصحياً كبيراً. تركز هذه الرسالة على تطوير وتحديث مواد ممتزة مستدامة لاستخدامها في تقنية استخلاص الطور الصلب المصغر المدعومة بغشاء (μ -SPE) لمواجهة هذا التحدي. تم التحقيق في نهجين مختلفين: إعادة استخدام الحفازات المستهلكة من عملية التكسير الحفزي المائع (FCC) وتصنيع مواد السيليكا الليفية المعدلة (FS).

في الدراسة الأولى، تم معالجة وتحليل الحفازات المستهلكة من FCC لتقييم ملاءمتها كممتزات لاستخلاص المبيدات من مياه الصرف. أظهر المنهج الأمثل لاستخلاص μ -SPE نطاق كشف خطي واسع (5–1000 نانوغرام/مل)، وحدود كشف منخفضة (0.36–1.52 نانوغرام/مل)، ونسب استرجاع عالية (84.9%–99.5%). وتم استخراج وكشف ستة مبيدات بنجاح، بما في ذلك إيزوبروكارب، أترزين، بريماكارب، بينكونازول، كلورفينابر، وميفيناسيت، مما يبرز إمكانيات هذا النهج المستدام في إعادة تدوير المنتجات الثانوية الصناعية ومعالجة تلوث المياه.

في الدراسة الثانية، تم استخدام الممتزات القائمة على السيليكا الليفية المعدلة في μ -SPE للكشف عن الفينولات وتحديداتها في مياه الصرف. تم تصنيع وتقييم ممتزات تشمل FS-Amine و FS-Aniline و FS-Mix، حيث أظهرت FS-Mix الأداء الأفضل. حققت الطريقة أداءً تحليلياً ممتازاً مع نطاق كشف خطي (6.25–2000 نانوغرام/مل) وحدود كشف منخفضة تتراوح بين (0.97 – 2.31 نانوغرام/مل). كما أظهرت معدلات استرجاع نسبية عالية بين 90.60% و 113.60%، مما يؤكد دقة وموثوقية الطريقة. وتم استخراج وتحديد الفينولات بنجاح، بما في ذلك 2,3-ثنائي كلوروفينول (2,3-DCP)، 3,4-ثنائي كلوروفينول (3,4-DCP)، 2,4,6-ثلاثي

كلوروفينول(2,4,6-TCP) ، 4-بروموفينول(4-BP) ، و4-نيتروفينول(4-NP) ، مما يدل على كفاءة المميزات في معالجة مياه الصرف.

بشكل عام، تقدم هذه الرسالة حلولاً مبتكرة للتخفيف من تلوث المياه، مع التركيز على الاستدامة والكفاءة والفعالية من حيث التكلفة. تسلط الدراسة على الحفازات المستهلكة الضوء على إمكانية إعادة تدوير النفايات الصناعية بشكل عملي، في حين تُظهر مواد السيليكا اللبينية المعدلة إمكانيات المواد المتقدمة لإزالة الملوثات بشكل انتقائي. تسهم هذه النتائج في تطوير تقنيات معالجة بيئية ذات تطبيقات واسعة في معالجة المياه وإدارة الملوثات.

Advances in Water Quality Monitoring: Analytical Techniques and Extraction Methods for Contaminant Detection**1. Introduction****1.1. Importance of Water Quality Monitoring**

Although water is necessary for life to exist, human activity has degraded its purity [1]. The transition to a largely urbanized society has led to an increase in intensive human activity, economic expansion, urbanization, industrialization, and resource exploitation, which has resulted in a great deal of waste, issues with disposal, the emergence of numerous contaminants, and the introduction of a variety of contaminants into water bodies [2], [3]. Water pollution, which has become a major global concern, is putting pressure on the supply of clean and safe water for drinking, agriculture, industrial usage, and ecosystem preservation. particulates, bacteria, organic and inorganic chemicals, disinfectants, and disinfection by-products (DBPs) are among the contaminants [4]. These contaminants can have detrimental effects on human health and the environment when they are present in water bodies, so it is important to use efficient monitoring techniques to evaluate the quality of the water and locate the sources of pollution for control and precautions. At the same time, water shortage has become a major global issue that presents major obstacles to access and availability of water [5]. Additionally, water ecology offers services like soil formation, flood control, habitat provision, nutrient cycling, food production, and water purification [6]. Contaminants in drinkable and tap water, both chemical and biological, contribute to disease transmission [7]. Exposure to contaminated water can harm human health, including hepatitis, influenza, severe acute respiratory syndrome (SARS), pneumonia, gastric ulcers, and respiratory illnesses [8]. Drinking water frequently contains non-biological pollutants such as silica, salts, sulfur, ammonia, and chlorine [9] and have dangerous heavy metals [10]. The World Health Organization (WHO) lists *Cryptosporidium*, *Legionella*, *Pseudomonas*, *Giardia*, and *E. coli* as the most commonly found microbes in water sources [11]. Water supplies often contain a variety of

contaminants that can pose significant health risks, as outlined in WHO established standards.

It is impossible to overestimate the significance of monitoring techniques for water quality evaluation considering these interrelated issues. Monitoring water quality is essential to sustainable development, public health, and environmental preservation. Its principal responsibility is to evaluate, preserve, and enhance the quality of water resources. To precisely detect and quantify pollutants, locate the sources of contamination, and create efficient plans to safeguard water resources, strong and trustworthy analytical determination methods are required [3]. The use of analytical technology in water monitoring has evolved recently. Numerous methods exist for monitoring water, such as conventional and traditional instrumental analysis (laboratory-based analysis). The selection of an appropriate detection technique or a combination of techniques in this review is primarily guided by the analytical goal, whether it involves quantitative, qualitative, or a hybrid approach to measurement.

1.2. Role of Extraction Techniques in Contaminant Detection

While there is no such direct equivalent to the EU Water Framework Directive in the Middle East, various regional and national initiatives are working to manage and protect water quality. These companies include Gulf Cooperation Council (GCC) [12], which includes countries like Saudi Arabia, the UAE, Oman, Kuwait, Qatar, and Bahrain, has established regional environmental frameworks aimed at water resource management. These frameworks focus on sustainable water use and pollution control. Next one is Saudi National Water Strategy 2030. According to this, 5 specific objectives have been set out, as follows (i) ensure continuous access to adequate quantities of safe water, under both normal and emergency situations; (ii) enhance water demand management across all uses; (iii) deliver cost-effective, high quality, and affordable water and wastewater services; (iv) safeguard and optimize the use of water resources, while preserving the local environment for the benefit of the present and future Saudi society; (v) ensure water sector competitiveness and positive contribution to the national economy through promoting effective governance, private sector participation, capacity building, and innovation.

According to the 5 specific objectives, 10 programs are defined, namely (1) water system and water resources management regulations; (2) water resources management; (3) sector resilience; (4) research, development, and capacity building; (5) supply chain efficiency and service quality; (6) water services regulations; (7) reconstruction of the saline water conversion corporation; (8) private sector involvement in the production and treatment of wastewater; (9) distribution restructuring and privatization; and (10) establishment of the General Organization for Irrigation and irrigation improvement [13]. Moreover, UAE National Statement to the UN Water Conference 2023 is also in process. It involves monitoring and reducing the levels of pollutants, and regulations are in place to control wastewater discharge into natural water bodies and groundwater. Last but not least, Kuwait has developed strict environmental regulations through its Environmental Public Authority (EPA). The country focuses on maintaining the quality of its groundwater and marine environments.

Every step is essential to getting accurate and instructive findings. The sampling process entails selecting a method to get the appropriate number of samples and determining where to obtain samples that accurately define the object or issue being characterized. In addition to extraction methods, sample preparation may also require "cleanup" techniques for extremely complicated or "dirty" samples. Enrichment is a common component of sample preparation techniques since this process must also raise the analytes concentration to a level appropriate for detection. The isolated complex mixture comprising the target analytes is separated into its constituents during the analytical process's separation step as shown in Figure 1. As a result, the analytical process's overall speed is determined by the slowest step, and increasing the speed of one step does not always translate into a higher throughput. Every step must be taken into account in order to boost throughput. Additionally, mistakes made in any of the earlier steps—including sampling—will cause the procedure to perform poorly overall [14].

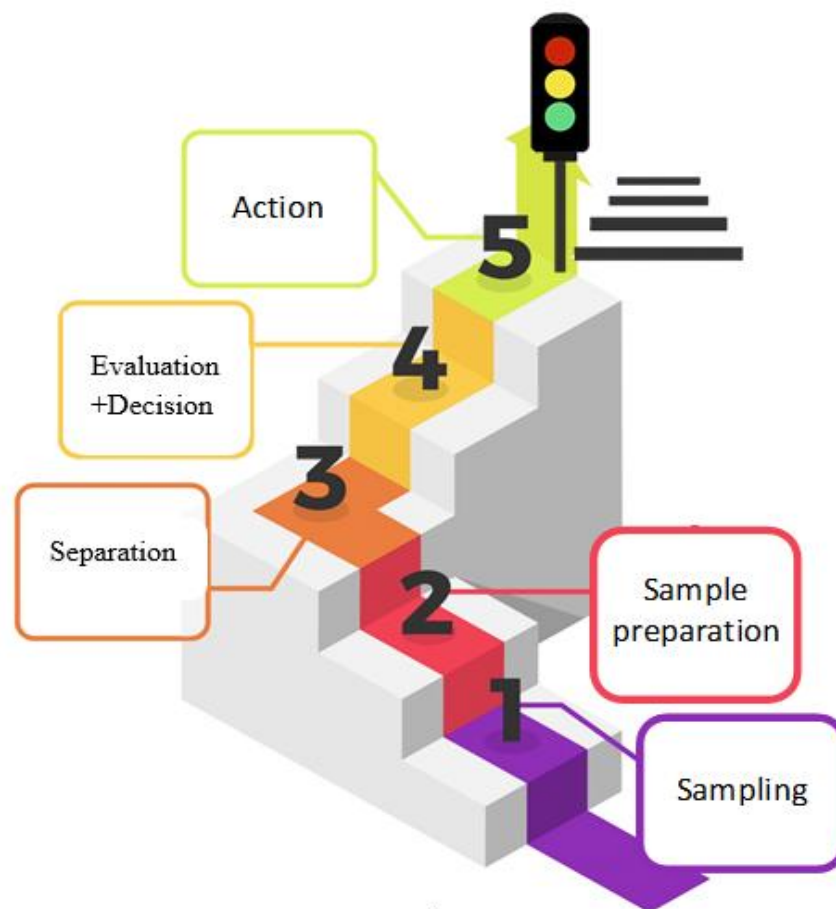


Figure 1: Steps in analytical process.

To identify trace organic chemicals in ambient water samples, an extraction and pre-concentration step must be performed prior to chromatographic separation and detection. These techniques for identifying priority and emerging pollutants have been the subject of numerous recent reviews [8]. Nowadays, most industrial analytical labs employ a preconditioning procedure, gas chromatography (GC) separation, and either a mass spectrometer (MS) or a flame ionization detector (FID) for detection. Gas chromatography (GC) and liquid chromatography are the two main categories of chromatography that are frequently distinguished by the type of mobile phase that is employed. The limitations of these processes, however, differ depending on the preconditioning methods applied in

combination with GC-MS or GC-FID. Large sample volumes are frequently needed to attain adequate sensitivity, which makes collection, transportation, and analysis challenging and costly. Furthermore, the majority of pre-conditioning procedures need a lot of work and time. The cleanup and separation procedures considerably lengthen the turnaround time when big sample batches are needed for daily analysis [15]. As analytical chemistry technology advances, new methods are created by introducing improved spectroscopy and model-based event detection [16], quality sensors, microfluidics [17] and biosensors [18]. These methods guarantee precise and trustworthy findings by separating, focusing, and eliminating impurities. A key component of contemporary water quality measurement, their transition from solvent-intensive techniques to ecologically friendly microextraction illustrates the increased focus on efficiency and sustainability.

The goal of emphasizing the significance of monitoring techniques is to draw attention to their function in evaluating the quality of water, comprehending patterns of contamination, and formulating suitable plans for reducing contaminants and protecting this priceless resource for coming individuals. A thorough examination of these methods is intended to promote a better comprehension of the problems with water quality and stimulate the development of novel monitoring techniques, with μ -SPE as the thesis's main focus, which can contribute to the security of sustainable and clean water supplies globally.

1.3. Overview of Extraction Techniques

Extraction is an important procedure for sample preparation, experimental research, and qualitative analysis of substances. It is essential for separating specific components from solid mixes or liquids. In recent years, advances in extraction technologies have concentrated on increasing efficiency, reducing operation times, and reducing the usage of organic solvents to reduce costs and environmental damage. Liquid-solid extraction (like Soxhlet), solid-phase extraction (SPE), and liquid-liquid extraction (LLE) are the three main pillars of extraction techniques. The amount and kind of sample that needs to be extracted, as well as the kinds of other compounds that might be present, determine which processes are used. The extraction methods employed in the sample preparation procedure share a number of basic similarities, the extraction stage of any approach [19]. A variety

of analytical methods have been created and used to identify different types of water pollutants. Sample preparation, which often includes cleanup and pre-concentration processes, is critical in detecting dangerous contaminants in water for subsequent analytical approaches. We have separated the extraction methods into two main sections based on our research:

- Traditional methods (LLE, SLE, SPE and SOXHELT extraction).
- Advanced methods (micro-extractions)

1.4. Traditional methods

1.4.1 Liquid-Liquid Extraction (LLE)

The most established and extensively researched technique for sample preparation is liquid-liquid extraction (LLE). The separation technique that most writers favour for the initial stage of isolating the analytes from the food matrix is liquid-liquid extraction [20], [21]. LLE is the transfer of particular compounds between two solvents that are either immiscible or somewhat miscible. This technique is commonly used to wash an organic phase, such as to remove inorganic compounds or to change the protonation state of acids and bases, leading them to migrate to the aqueous phase. Typically, it involves one aqueous phase (either pure water or an aqueous solution) and one organic phase. A typical flowchart for LLE is shown in Figure 2. It is important to note that the chemical of interest, which is often an organic molecule, might exist in either phase depending on the features of both the material and the aqueous phase [22]. For the past 30 years, the US EPA has required liquid-liquid extraction as the standard extraction technique. Traditionally, sensitivity is provided by extracting from a large sample of water since it contains a larger amount of analyte. Hence the use of one liter of water sample in official EPA procedures. The method developed in our laboratory used only one milliliter of water and only one extraction. This simple procedure allows integration of extraction and analysis into a continuous process but requires a large volume injection to achieve the necessary sensitivity.

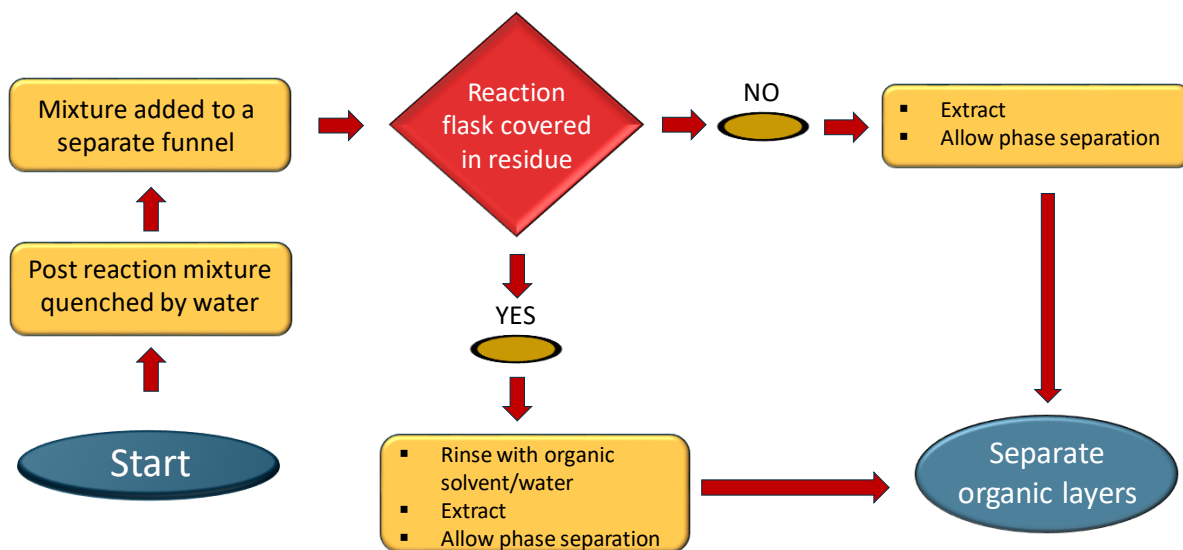


Figure 2: Typical flow chart for LLE.

For every liter of water sample, an analyst must add 60 milliliters of solvent, often methylene chloride. After that, the analyst gives the solvents a good shake to help the solutes balance out between the two. The methylene chloride, which now includes the pollutants of interest, sinks to the bottom of the funnel after they are given time to settle. The bottom of the separating funnel is used to remove the solvent/contaminant combination. Two further iterations of this procedure are carried out, each time adding 60 mL of solvent. To concentrate the organic material, the almost 200 mL of solvent/contaminant combination is gathered and subsequently evaporated.

LLE is still often utilized in analytical chemistry even though there are several methods with higher selectivity and sensitivity [23]. In nearly every instance, geosmin—a volatile substance that *Streptomyces* bacteria create in soil and water—could be found in raw water matrices at low concentrations. Furthermore, the method requires little laboratory expertise and conventional glassware, making it reasonably easy to apply. Because LLE produces sensitive and dependable results for routine analyses, it has thus become very appealing to water businesses. Nevertheless, LLE necessitates considerable amounts of organic solvent and sample volumes (<1L). This is not only costly but also bad for the environment. Nonetheless, a number of liquid extraction versions, such as

Continuous Liquid-Liquid Extraction (CLLE) and Liquid-Liquid Microextraction (LLME), have been developed in an effort to get around some of these restrictions. Zhang et al. [24] were pioneers in detecting odorous substances in water at concentrations as low as 50 picograms per liter (pg/L). They employed a combination of Continuous Liquid-Liquid Extraction (CLLE) and a programmable temperature vaporizing (PTV) inlet for large volume injection (LVI). Their results indicated that the large volume injection - programmable temperature vaporizing (LVI-PTV) system could improve the gas chromatography detection limits by one to two orders of magnitude over traditional methods. However, the CLLE technique proved impractical for routine use due to its lengthy extraction time of 5 to 10 hours. Similarly, Song et al. [25] used gas chromatography-mass spectrometry coupled with liquid-liquid extraction to analyze 40 analytes in refinery wastewater. They optimized various parameters, such as the choice and quantity of extractant and organic modifier, extraction time, and the addition of salt, to enhance the efficiency of the extraction process. Alcohols, n-alkanes, isoalkanes, ketones, phenolics, anilines, aromatic hydrocarbons, and polycyclic aromatic hydrocarbons were among the eight categories into which the contaminants from the refinery wastewater were divided. For every analyte, linear calibration curves were obtained under ideal circumstances. Both intraday and interday measurements had relative standard deviations below 10.0% [26]. A study combining Liquid-Liquid Extraction (LLE) and Stir Bar Sorptive Extraction (SBSE) with comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GC×GC-TOFMS) was conducted to screen pollutants in surface and municipal wastewater. LLE achieved recoveries for all 14 surrogate chemicals (19–159%, median 74%), while SBSE, limited by polarity bias, extracted 8 compounds with recoveries of 19–117% (median 66%) [27]. However, there are a number of drawbacks as well, including the high amount of organic solvent used, which can interfere with chromatographic analysis, low reproducibility, low selectivity, loss of analytes, difficulty automating, high environmental pollution, high cost, and worker danger. Additionally, it is a time-consuming and tedious technique [28].

1.4.2 Solid-Liquid Extraction (SLE)

Solid–liquid extraction is a separation process based on the preferential dissolution of one or more of the components of a solid mixture in a liquid solvent as shown in Figure 4. It is also called as leaching process. In this context, the term ‘solid mixture’ is used in its practical meaning. In reality, the physical state of the component to be extracted from the raw material is not always solid [29]. The extraction phenomena are enhanced by increased surface area and decrease radial distances by decreased the particles. The solid-liquid extraction is based on a simple phenomenon: if a solid matrix containing extractable compounds is immersed in a liquid, the latter begins to enrich itself with certain chemically related substances that move from the inside to the surface of the solid and then from the surface into the liquid. This principle is based on diffusion and osmosis and is performed by maceration, which is the simplest and most economical extraction technique and is therefore widely used. The maceration process requires only a closable glass or stainless steel container in which extractable solid is covered with liquid. To overcome the rapid saturation of liquid strictly around the solid, desultory agitation is required. Unfortunately, it is not always applicable, because it requires long contact times between the solid and the liquid phase.

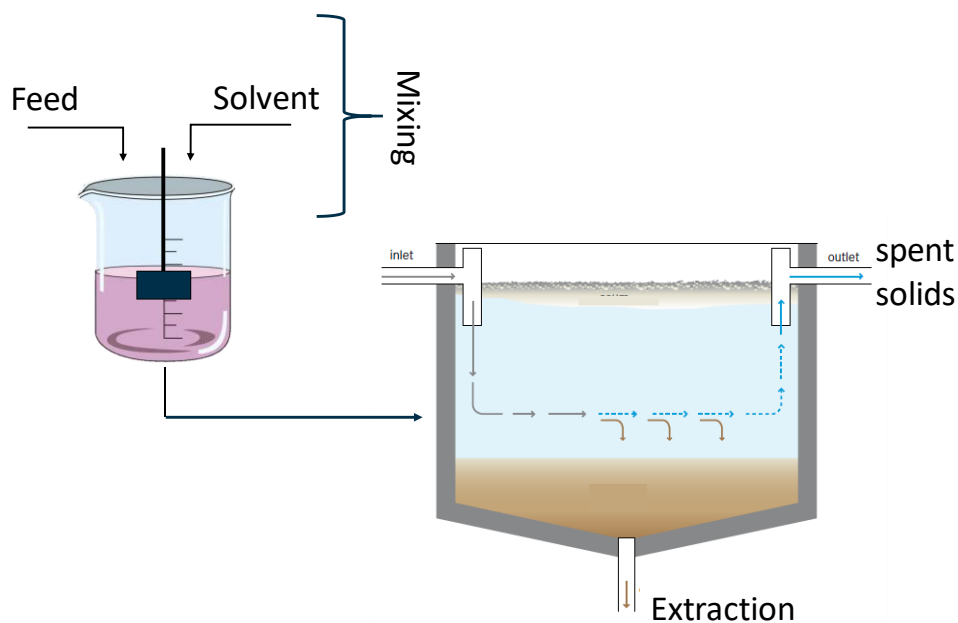


Figure 3: Process of solid liquid extraction.

The mechanism of SLE involves two processes i) contacting step ii) separation step. In contacting step, solvent and material is mixed in order to transfer soluble constituents to the solvent and separation is the process of isolating the liquid extract (now containing the dissolved analytes) from the residual solid material. The choice of methods and technologies related to an extraction process based on solid-liquid contact is not simple and this depends largely on the structural complexity and composition of the solid matrix; therefore, it is not easy to find universal methods suitable for every type of Solid-Liquid extraction. In choosing the most appropriate techniques, operating conditions, solvents, etc., knowledge of the chemical properties of the compounds to be extracted and their behavior in the presence of different solvents is of fundamental importance.

SLE offers several advantages that make it a widely used method in sample preparation and industrial processes. It is simple to perform, requiring minimal specialized equipment, minimal amount of solvents, and is cost-effective due to its reliance on common solvents and straightforward apparatus. This method is versatile, accommodating a wide range of analytes and solid matrices, including plants, soils, and food samples. Additionally, it can be adapted for greener applications by using environmentally friendly solvents, and it is scalable from small laboratory experiments to large industrial extractions. SLE is particularly effective for analytes with high solubility in the chosen solvent, making it a practical choice for many applications.

However, SLE also has its limitations. The process can be time-consuming, requiring prolonged contact times and additional steps like filtration or centrifugation, which can add to the overall processing time. Moreover, it may be less efficient for extracting analytes with low solubility in the selected solvent and is non-selective, often leading to the co-extraction of unwanted substances like lipids or pigments. Additionally, separating fine particles from the liquid phase can be challenging, potentially resulting in the loss of analytes. Despite these drawbacks, SLE remains a foundational technique, particularly for applications where simplicity and cost-effectiveness are paramount.

1.4.3 SOXHLET Extraction

Soxhlet extraction is a rugged, well-established technique and permits unattended extraction. In 1879, von Soxhlet developed a new extraction system (Soxhlet extractor) which has for a long time been the most widely used leaching technique. A Soxhlet extractor has three main sections: a percolator (boiler and reflux) which circulates the solvent, a thimble (usually made of thick filter paper) which retains the solid to be extracted, and a siphon mechanism, which periodically empties the condensed solvent from the thimble back into the percolator as shown in Figure 5. When the liquid reaches the overflow level, a siphon aspirates the solute from the thimble-holder and unloads it back into the distillation flask, thus carrying the extracted analytes into the bulk liquid. This operation is repeated until extraction is complete. Operationally, Soxhlet extraction is thus a continuous–discrete technique. In fact, since the extractant acts stepwise, the assembly operated as a batch system; however, extractant is recirculated through the sample, so the system also operates in a continuous manner somehow [30] In fact, Soxhlet extraction has been a standard technique for over a century and the methods based on it remain the primary references against which performance in new leaching methods is measured.

Soxhlet extraction offers several notable advantages in solid-liquid extraction. One of the primary benefits is that the sample is repeatedly brought into contact with fresh portions of the extractant, which helps to displace the transfer equilibrium and ensures efficient extraction. The system also maintains a relatively high temperature due to the heat applied to the distillation flask, which is transferred to the extraction cavity. This is especially useful for extracting analytes that require higher temperatures for effective solubility. Another advantage is that it eliminates the need for post-extraction filtration, simplifying the process. Additionally, this allows for high throughput, as multiple extractions can be carried out simultaneously with minimal investment in equipment. It is also a simple and low-cost technique that requires minimal training. Compared to some modern techniques like microwave-assisted extraction (MAE) or supercritical fluid extraction (SFE), Soxhlet can extract a larger sample mass, and it is not significantly

affected by matrix effects, although this is not always the case when comparing it with SFE for analytes strongly bound to the matrix.

However, Soxhlet extraction also has some serious drawbacks. The most significant is the time consumption, as extraction can take several hours or even days. Additionally, the large amount of extractant used not only makes the process expensive but also creates environmental concerns related to solvent disposal. The extraction is typically done at the boiling point of the solvent, which can lead to the thermal decomposition of thermolabile (heat-sensitive) compounds. Unlike modern techniques, Soxhlet extraction lacks agitation, which would help speed up the process and improve efficiency. Another issue is that the large solvent volumes used in Soxhlet extraction require a subsequent evaporation and concentration step, which adds additional processing time. Lastly, the technique is extractant-specific and difficult to automate, making it less versatile compared to some newer extraction methods.

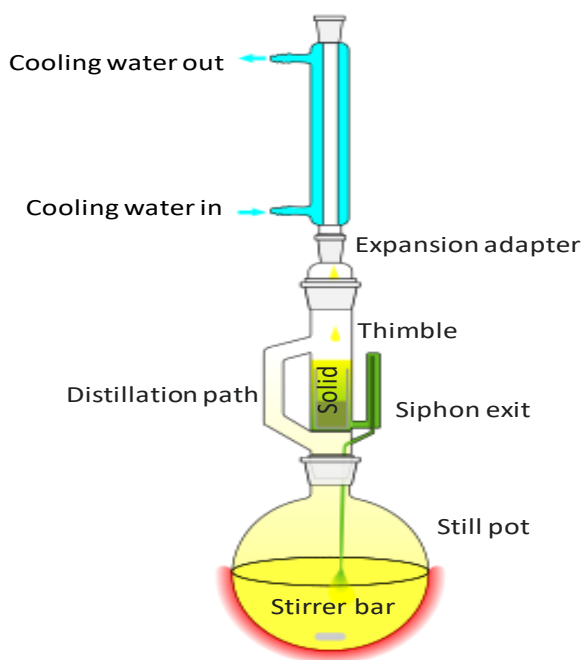


Figure 4: Composition of Soxhlet extractor [31].

1.4.4 Solid-Phase Extraction (SPE)

In order to separate, enrich, and purify components from aqueous solutions based on their physical and chemical characteristics, solid phase extraction is a sample preparation technique [32]. This straightforward method of chromatographic conditioning typically uses a cartridge-style device that is filled with stationary solid phase particles. Conditioning, loading, cleaning, and eluting are the four primary steps in SPE (Figure 6). For effective extraction, each of these processes needs to be improved [33]. Although the earliest experimental uses of this extraction technology started in the 1960s, it was initially introduced at the end of the 1970s [34]. However, in 1978, the first cartridges were released, followed by the various syringe forms in 1979, and the cartridge SPE disposables in the middle of the 1980s [35]. The LLE was still the most often utilized method for sample pretreatment until this decade [36][37], [38]. Adding sorbent particles to disc formats is another recent invention and application [39]. The disc format has been able to provide good extraction recoveries with high flow rates because of its small porous particles and quick mass transport. The effectiveness of the SPE cartridges can be significantly impacted by water matrix effects, where the binding of unwanted substances can prevent geosmin from being captured and released. For instance, Kim et al. [40] achieved recovery rates of 93–105% for geosmin from raw water, but only 74–85% from tap water due to interference from residual chlorine. To minimize the interaction between the water and eluent, it is crucial to ensure that the cartridge is fully dried prior to extraction. Moreover, given the semi-volatile nature of geosmin, the evaporation process requires careful monitoring [41].

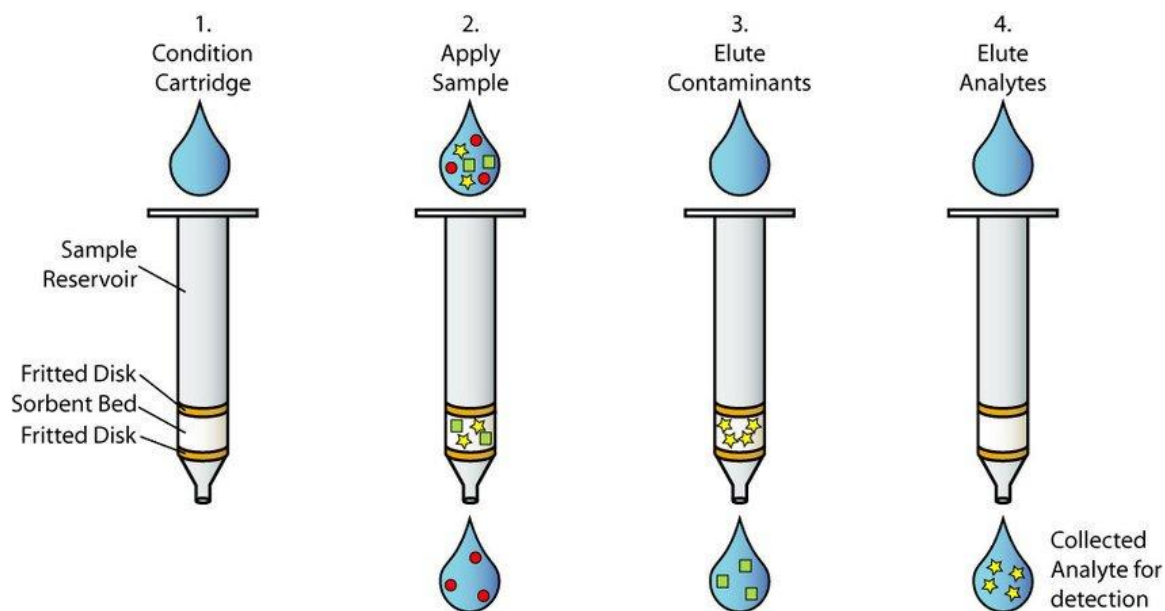


Figure 5: Scheme of the solid phase extraction (SPE) procedure [35].

Fernández and his colleagues [42] outlined a modular solid-phase extraction (SPE) system that combines three sorbents to efficiently extract basic, acidic, and neutral micro pollutants from wastewater. These micro pollutants are then further eluted in three separate extracts. The effectiveness of this method was shown using liquid chromatography tandem-mass spectrometry (LC–MS/MS) for a set of 64 chemicals that corresponded to various chemical families. Using spiking aliquots of ultrapure water, preliminary SPE tests were conducted while taking various sorbent combinations into consideration. The target chemicals were successfully recovered from wastewater samples; additionally, only one of the three fractions (bases, acids, and neutrals) derived from the combination of sorbents contained 62 of the 64 species. The properties acquired using generic SPE polymers were enhanced globally by the SPE methodology's efficiency and selectivity [43], investigated the use and optimization of SPE and other cutting-edge analytical techniques for identifying antiretroviral medications in soil, sediment, sludge, wastewater, and river water. For SPE, the percentage recoveries varied between 71% and 112%. For all substances and all procedures, good precision was achieved with a relative standard deviation of less than 20%. For SPE, the LODs and LOQs varied from 2.1 to 2.4 µg/L and

0.68 to 0.77 $\mu\text{g/L}$, respectively. However, the data show that advanced technologies are far superior to SPE.

SPE is founded on similar concepts as liquid–liquid extraction (LLE). In both techniques, there is a comparable distribution of analytes or solutes between two phases. Unlike LLE, which calls for mixing two liquid phases, SPE involves dispersing the analyte [44]. SPE is considered an innovative sample preparation technique due to its superior efficiency, reduced solvent usage, and high selectivity. By using tailored solid sorbents, SPE allows for better analyte recovery and cleaner extracts compared to conventional methods like LLE or SLE. This efficiency simplifies the process by reducing the number of steps needed, which ultimately saves time. SPE also minimizes solvent consumption, aligning with the principles of green chemistry, and has the added advantage of high selectivity for target analytes, ensuring minimal matrix interference and better cleanup [40]. The technique is scalable, making it suitable for both small-scale and large-scale applications. Additionally, it can be easily automated, facilitating high-throughput processing, something not easily achieved with many conventional methods. The wide range of applications for SPE includes environmental monitoring, pharmaceutical analysis, food safety testing, and clinical diagnostics. Compared to conventional methods, SPE generates less waste, is more environmentally friendly, and is applicable to a broader spectrum of analytes, offering more precision and sensitivity.

However, despite these advantages, SPE still has limitations that drive the development and adoption of microextraction techniques. While SPE is more efficient than traditional methods, it can still be resource-intensive in terms of sorbent costs, and certain complex samples or large volumes can overwhelm its capacity. Additionally, the sorbent choice is critical, and poor selection can result in lower recovery rates. These limitations, along with the growing demand for even more efficient, environmentally friendly, and cost-effective methods, have led to the development of microextraction techniques. These newer methods, such as Solid-Phase Microextraction (SPME), Stir Bar Sorptive Extraction (SBSE), Liquid-Liquid Microextraction (LLME), dispersive liquid-liquid microextraction (DLLME), dispersive solid-phase extraction (dSPE) etc offer even greater advantages in terms of reduced solvent usage, smaller sample sizes, and faster processing times, making

them the next step in improving analytical workflows. All will be explained in the section below.

1.5. Emerging Techniques for Sample Preparation (Micro-extraction)

Advanced, miniature sample preparation procedures known as microextraction techniques are intended to effectively and efficiently separate and concentrate impurities from water and wastewater while using the fewest possible solvents. These methods are essential for environmental monitoring and regulatory compliance because they tackle issues in water analysis, such as complicated matrices and low pollutant concentrations. Several essential characteristics of microextraction methods make them both extremely effective and ecologically benign. These techniques maintain excellent sensitivity for identifying pollutants at the trace level while using very minimal sample volumes, thereby lowering operational expenses and the environmental impact. By focussing on green chemistry principles, they reduce waste production and solvent use, making them environmentally friendly substitutes for conventional extraction techniques. Furthermore, microextraction methods are made to work in unison with contemporary analytical tools including gas chromatography (GC), high-performance liquid chromatography (HPLC).

1.5.1 Solid-Phase Microextraction (SPME)

Since Janusz Pawliszyn first introduced solid-phase microextraction (SPME) in 1990, it has gained popularity as a flexible and environmentally friendly sample pretreatment method [45]. It can combine injection, concentration, and sampling into a single phase, drastically cutting down on the amount of time and labour needed for sample preparation [46]. SPME has recently been combined with an automatic sampler, which increases its appeal for creating quick, effective, and high-throughput techniques [47]. Critical roles have been performed by the recently established SPME-based technologies in biological, food, and environmental analysis [48]. Higher demands are made due to the complexity of the samples and the variability of the target analytes' physicochemical characteristics, which drives SPME's ongoing development. The enhanced SPME highlights its distinct benefits and adds to the practical uses as well. Direct extraction, headspace SPME, and membrane-protected SPME are the three fundamental

modes of operation for SPME (Figure 7). The fibre rod is coated with an adsorbent polymer in the headspace and direct extraction modes. In contrast, the analytes are removed straight from the sample solution to the coated sorbent using the direct extraction method, which involves inserting the fibre into the sample solution. The fibre is positioned above the sample solution in the headspace mode to exclude volatile chemicals, which is crucial for lessening the interference effect of macromolecules. The SPME that is membrane-protected.

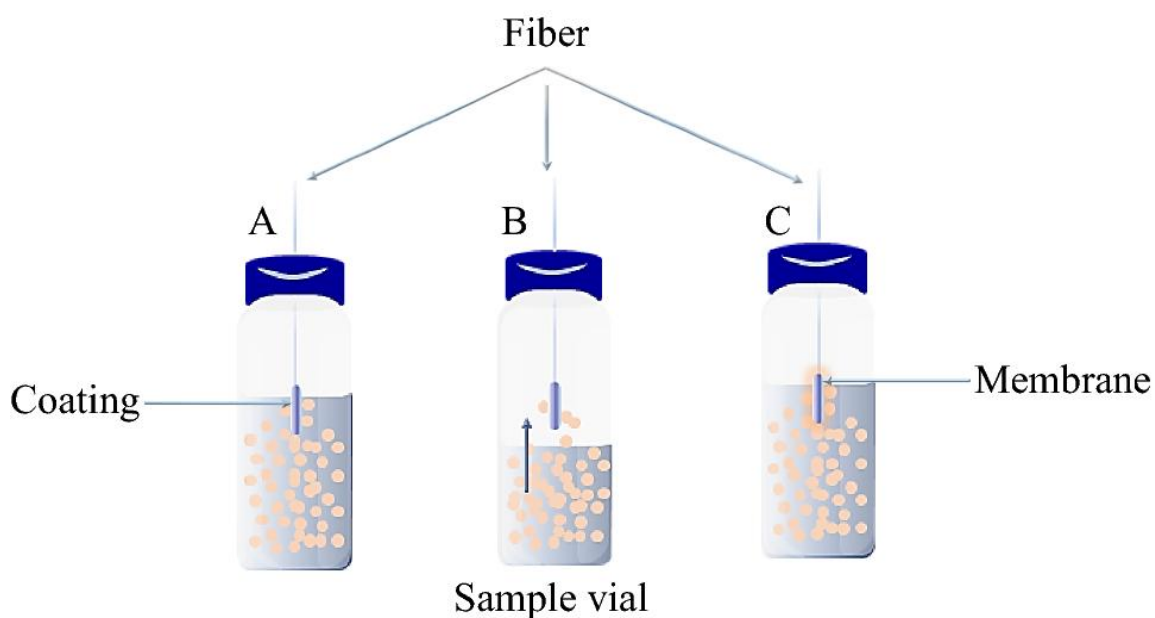


Figure 6: Several ways that SPME operates. C membrane-protected SPME, B headspace SPME, and A direct extraction [49].

Aquatic habitats contain trace amounts of hydrophobic persistent organic pollutants (POPs), which need to be focused for additional measurement [50]. In the extraction of POPs, SPME has shown impressive benefits, such as being a solvent less, time saving method with high efficiency and throughput [51]. SPME has become a popular method for water sample analysis, offering several advantages, including its simplicity, rapidity, eco-friendliness, and the ability to integrate sampling, extraction, and pre-concentration into a single, efficient step. It is important to note that each group needs to be extracted separately

by adjusting the pH, which makes the analysis of water samples for detecting acid/base/neutral compounds (ABNs) using LLE a time-consuming process. However, SPME has shown that it is possible to determine a large number of pesticide ABNs from many classes at the same time. Beceiro-Gonzalez et al. used GC-MS to confirm the SPME technique's efficiency for the simultaneous identification of 46 pesticides in water samples, including a wide variety of polarities and chemical structures such as organochlorines, organophosphates, triazines, pyrethroids etc [52]. Low LODs values of between 3.9-16.0 ng mL⁻¹ were reported, along with simultaneous determination of ABNs, which is necessary for chemical trace analysis. Rodriguez-Lafuente et al. [53] as well as Goncalves et al. [54] conducted some well-known investigations on the simultaneous measurement of ABNs in water with sub-PPb limits of quantification and identifying 25 chemicals. There are an additional 44 and 34 chemicals available. Moghadam et al. [47] employed SPME for water sample analyses and conducted comparisons with EPA-approved techniques to assess the precision and suitability of SPME for routine water sample analysis, which led to the publishing of ISO and standard methodologies. Overall, it can be concluded that although the SPME efficiency is in good accord with official methods, it can allay certain worries about the LLE technique's environmental impact and offers a wider range of applications [55]. The SPME approach has demonstrated good promise based on the investigations discussed in this review and published in the literature.

1.5.2. Liquid-Phase Microextraction (LPME)

A crucial sample preparation method, liquid-phase microextraction (LPME) has been used extensively to extract various organic, inorganic, and medicinal substances from various biological and environmental matrices. The benefits of simplicity, speed, versatility, affordability, and minimal organic solvent usage all pushed scientists to keep improving LPME. There are three different kinds of liquid-phase microextraction configurations: dispersive liquid-liquid, hollow-fibre liquid-phase, and single drop microextractions. Despite the commercial availability of SPME, LPME is still performed using laboratory-built equipment. For 1) economics, 2) accessibility, 3) environmental sustainability, 4) selectivity, and 5) technique sensitivity, LPME remains a very active study area. Various

LPME designs and methodologies are depicted in Figure 8 [56]. In addition to resolving the drawbacks of traditional LLE, LPME avoids the drawbacks of solid-phase microextraction (SPME), such as sample carryover and reliance on commercial supplies [57]. Liu and associates [58] helped bring about the initial developments. The primary method of LPME at the time was the extraction of the analytes into a tiny organic phase droplet that was added to the aqueous sample via a micro syringe tip. Because of the droplet's poor stability and ease of loss in the aqueous sample, LPME was only used in laboratory studies.

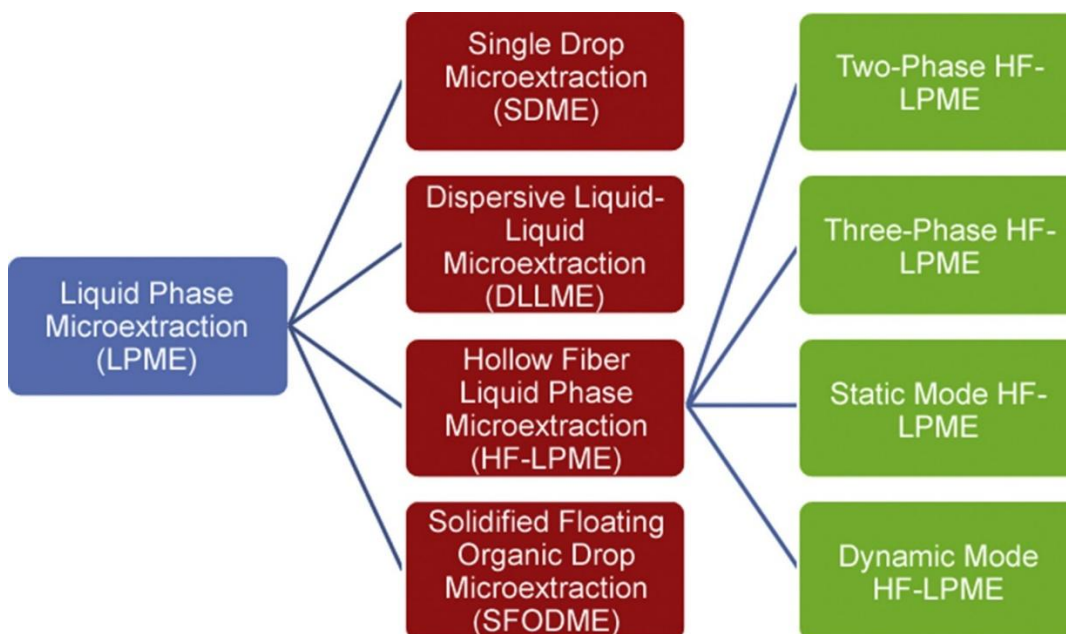


Figure 7: Liquid phase microextraction method classification [59].

Single-drop microextraction (SDME) is a simple miniaturized sample set up technique for the preliminary concentration and isolation of many analytes from a complicated sample matrix [60]–[62]. Based on the number of phases at equilibrium, SDME is primarily divided into two-phase and three-phase categories. As illustrated in Figure 9, SDME is categorised as direct immersion (DI), drop-to-drop (DD), directly suspended droplet (DSD), continuous flow (CF), headspace (HS), and liquid–liquid–liquid

(LLL) SDME based on the droplet's exposure to the aqueous sample. Due to their simplicity and low equipment requirements, DI and HS are the most widely utilised modes [63].

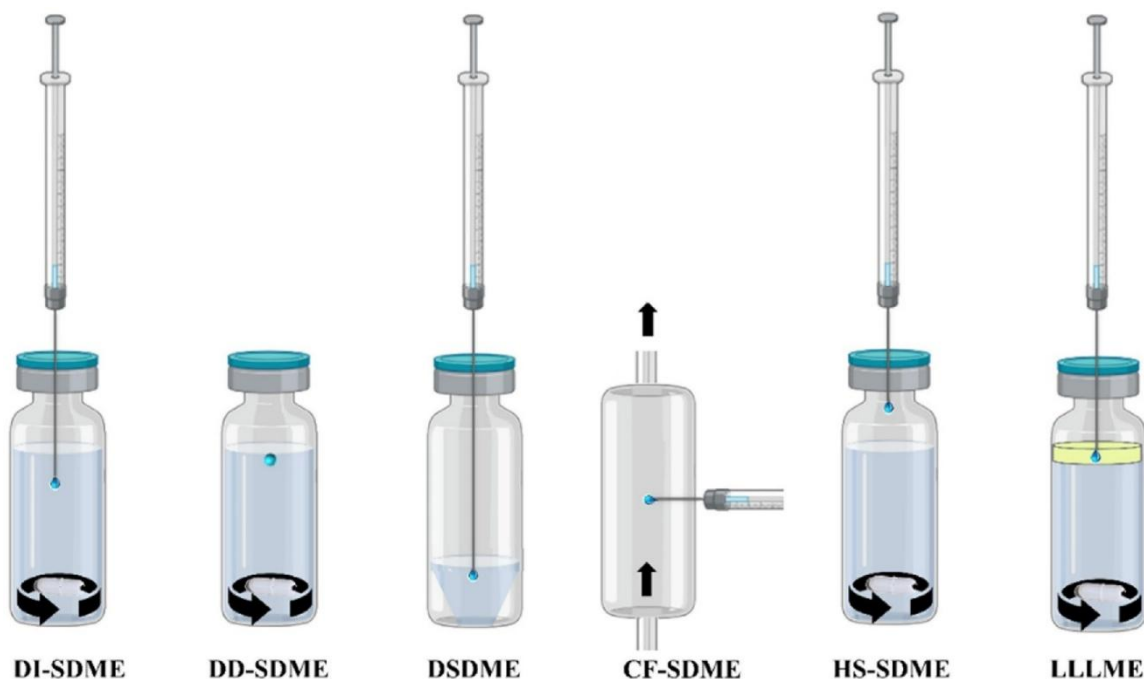


Figure 8: Various single drop microextraction techniques [64].

Single-drop microextraction (SDME) has been effectively paired with various analytical techniques to detect trace chemical species in minimal sample volumes. These techniques include spectrometry methods such as UV-vis, fluorescence, and atomic spectroscopy, as well as chromatographic methods combined with spectroscopic instruments like GC, HPLC, GC-MS, and LC-MS. This integration enhances both the sensitivity and selectivity of analyses. In practice, coupling SDME with these spectrophotometric and chromatographic instruments has significantly improved analytical parameters such as sensitivity, recovery, precision, and accuracy. Remarkably, SDME often achieves higher extraction efficiencies than conventional extraction methods. Among its variations, direct immersion SDME (DI-SDME) involves immersing the microdrop directly into the donor phase, whereas headspace SDME (HS-SDME) positions the

acceptor-phase drop in the gas phase above the sample, offering an alternative approach to SDME. Figure 10 presents a schematic representation of the basic principle of the SDME technique.

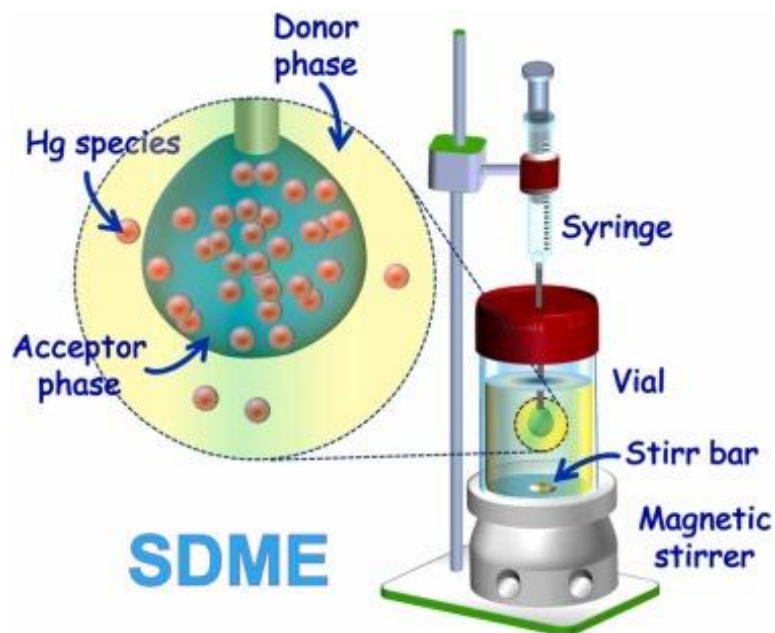


Figure 9: The SDME approach is shown schematically [65].

Micro-drop instability is one of SDME's main drawbacks [66], affected by turbulence, gravity, needle tip form, and droplet size. Modified needle tips, membrane supports, and substitute droplet holders such as agarose gels, bell-shaped devices, and funnel-shaped systems are some ways to improve stability. Innovations like magnetic ionic liquids and high-viscosity solvents enhance the droplet attachment and inhibit dislodgement. Drop volume is still a problem that affects reproducibility and necessitates sophisticated analytical methods like spectrophotometry, on-drop sensors, and chromatography. To improve accuracy and streamline the procedure, novel techniques include direct detection, cell phone-based sensing, and optical probes. By boosting throughput, enhancing reproducibility, and lowering human error, automation of SDME overcomes limitations. Auto samplers, lab-in-syringe systems, and robotics for automated handling are important advancements [67]. In HF-based LPME techniques, the acceptor

phase is shielded by supported liquid membrane while the extraction process takes place inside the lumen of a porous hollow fiber. Before initiating the HF-LPME method, sonicate the polypropylene hollow fiber membrane in acetone to eliminate any polymer impurities [68]. Following this procedure, the membrane is immersed in an impregnating solution, which uses capillary forces to fill the hollow fiber pores. Rinsing with distilled water removes any excess solvent [69]. Subsequently, the acceptor phase is introduced into the hollow fiber's lumen. Depending on the methodology, this phase can either be an aqueous solution (in the three-phase mode) or the same organic solvent used as the supported liquid membrane (SLM) in the two-phase mode. Once the hollow fiber is submerged in the sample solution, the analytes migrate through the SLM and into the acceptor phase, where they are extracted [70]. There have been reports of four distinct configurations for HF-LPME: knotted hollow-fiber, u-shaped, hollow-fiber solvent bar, and rod-like as shown in Figure 11.

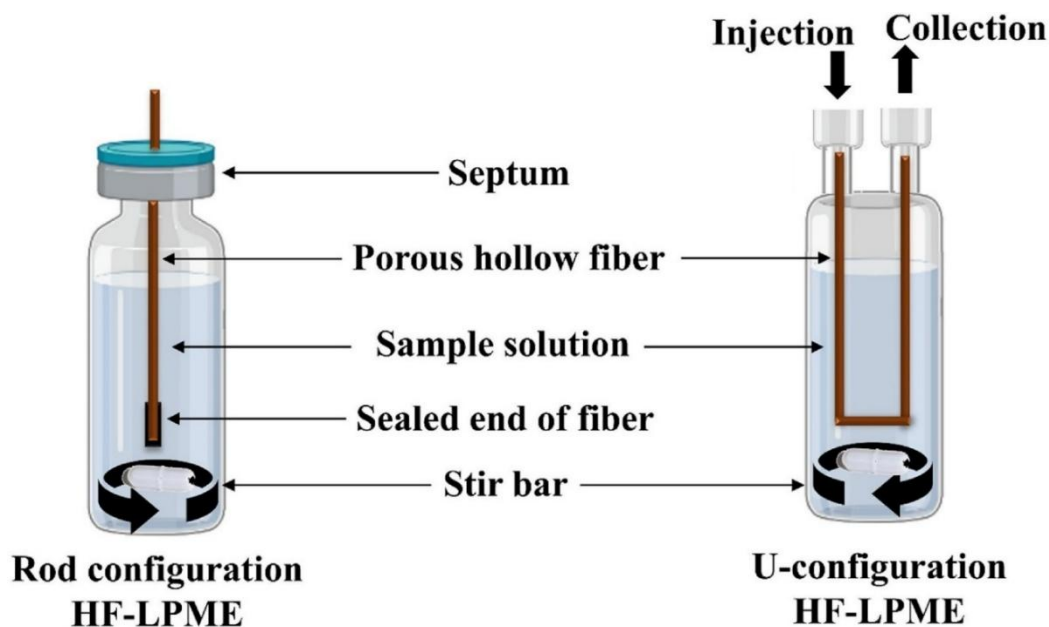


Figure 10: HF-LPME with a rod and U arrangement [65].

The hanging drop destabilization problem is more precisely and consistently resolved by HF-LPME than by SDME since the extractant remains stable in the porous hollow fiber. The sample can be vigorously agitated without risking the loss of the extractant, as the extractant remains isolated from direct contact with the sample solution. It is frequently employed in biological analysis because it offers adequate sample cleanup. HF-LPME was thought to be appropriate for tiny sample volumes or complex matrices. The issue of carryover is avoided by using inexpensive disposable polymers. It can be chosen as a strong contender for commercialization and, consequently, for use in standard labs for sample preparation. In sample preparation, DLPM is one of the most popular techniques. In order to detect organic chemicals in water samples, DLLME, a sophisticated method derived from LPME, was introduced in 2006 [71]. The fundamental idea of DLLME is to create a ternary system of solvents by infusing a mixture of extraction and dispersive solvents into the sample. The dispersing solvent must be compatible with both the sample (donor phase) and the extraction solvent (acceptor phase) to ensure effective mixing. However, the extraction solvent should remain immiscible within the donor phase. A schematic illustration of the DLPME technique's fundamental idea is shown in Figure 12. High extraction efficiency, speed, low solvent, reagent, and sample consumption, ease of use and a wide contact area between phases are some benefits of DLLME and DLPME methods. Nevertheless, there are certain restrictions: using chlorinated solvents, which can be hazardous or persistent; requiring a dispersive solvent (DLLME); and requiring centrifugation [72], SHS [73], moreover, discovering automated manuals [74].

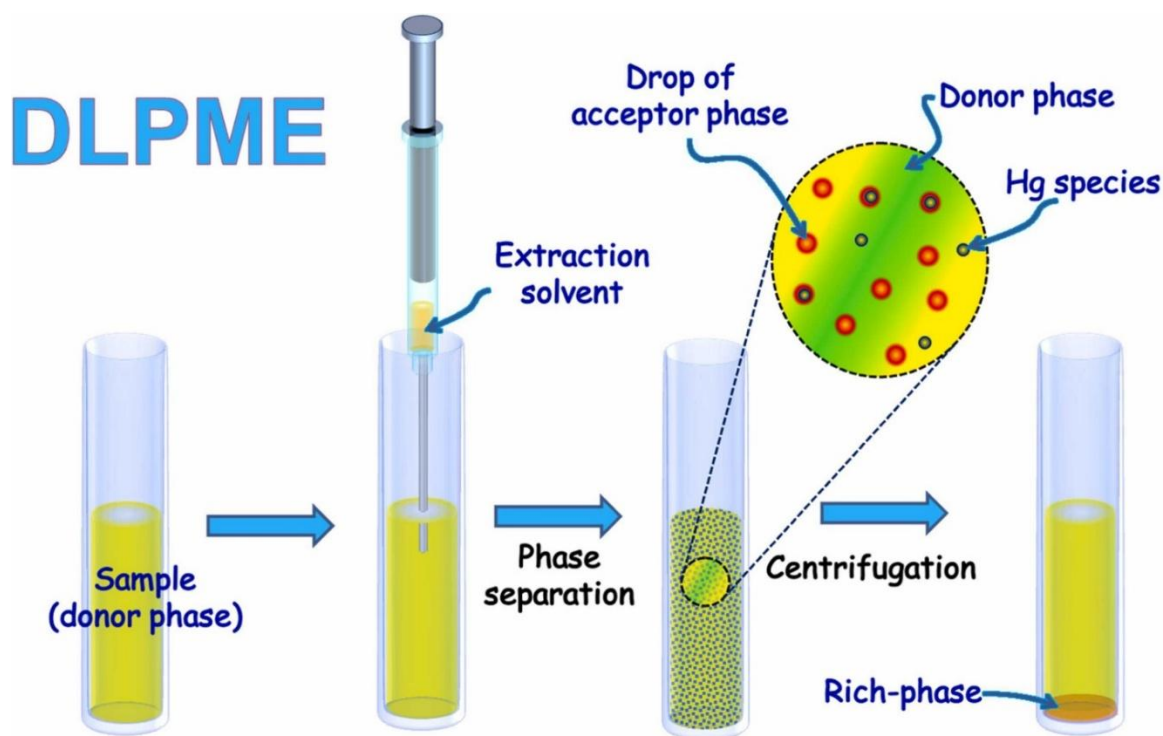


Figure 11: Diagrammatic illustration of the DLPME method [72].

The scarcity of appropriate extractant, which frequently favour non-polar analytes, is a major obstacle in DLLME. Additionally, difficult are phase separation and extractant collection, especially for small organic quantities. Conical-bottom tubes, auxiliary solvents for adjusting density, and solvents that freeze in ice baths for convenient retrieval are some examples of solutions. Devices manufactured at home specifically for small-scale collection make this process much easier. By combining DLLME with SPE, great extraction efficiency and enrichment factors (EFs) are achieved, utilizing the advantages of both approaches. While DLLME preconcentrate analytes from the SPE eluent, SPE aids in the cleaning of complicated samples. When combined with DLLME, variations such as magnetic SPE or dispersive micro SPE decrease time, lessen matrix effects, and use fewer organic solvents. These combination techniques have proven useful for sensitive pesticide analysis.

1.5.3 Stir-bar Sorptive Extraction (SBSE)

Baltussen et al. [75] used SBSE for identifying organic contaminants in water. Since then, it has been effectively used on a variety of organic substances, such as volatile organic compounds (VOCs) [76], aromatic hydrocarbons that are polycyclic [77]insecticides [78] as well as hormones [79]. This technique involves the sorption process, which includes both adsorption and absorption, of an analyte onto a magnetic stir-bar coated with a polymer. The stir-bar is agitated within the sample solution for a specified duration, allowing the analyte to adhere to the polymer coating. Subsequently, the analyte is desorbed for analysis, usually using liquid chromatography (LC) or gas chromatography (GC). Liquid desorption is commonly employed with LC to enhance selectivity, while thermal desorption with GC is preferred for achieving higher sensitivity [77]. Optimizing equilibrium parameters, including the sampling technique, extraction temperature, and extraction duration, is essential, as both SBSE and SPME operate as equilibrium-based methods that capture target analytes within a polymer coating. However, a key difference between SPME and SBSE lies in the thickness of the polymer coating [80]. A key limiting factor in the enrichment process of SPME is the equilibrium established during the partitioning of target analytes between the stationary phase and the liquid phase [81]. SBSE is more cost-effective and straightforward since it operates at room temperature, unlike SPME, which requires 60–70°C, and it typically needs less salt. However, a key drawback of SBSE is the longer extraction time, with samples requiring at least 45 minutes, compared to the average 30 minutes for SPME. This may be one of the primary causes of the water industries' lack of interest in SBSE, as they need to process huge sample batches quickly. Furthermore, automating SBSE is more challenging than automating SPME. The limited fibre kinds of SBSE, with PDMS being the primary coating manufactured commercially, are another major disadvantage. Nonetheless, the literature has a variety of substitute coatings, such as polyurethane [82], DVB with methacrylic acid [83] with methacrylic acid [84].

1.5.4 Magnetic solid-phase extraction technique (MSPE)

A new technique known as magnetic solid-phase extraction (MSPE) utilizes a magnetic adsorbent to capture a specific analyte from a solution. After being absorbed into the magnetic sorbent, the analyte is magnetically separated. At last, the recovered adsorbent eluted the analyte. By using this method, certain analytes can be isolated and preconcentrate faster than with traditional solid-phase and liquid-phase extractions [85]. Evangelos et al. [86] articulate the fabrication methods of popular nanocomposites and emphasize their advantages over standard sorbents in SPE and MSPE (Figure 13). They focus on the environmental applications of graphene-based materials or nanocomposites that combine the features of graphene oxide (GO) or reduced graphene oxide (rGO) with other components such as Fe_3O_4 . These materials offer several benefits, such as enhanced sorption capacity, superior reusability across multiple cycles, a high surface area, and strong chemical and mechanical stability. These characteristics make them more efficient than conventional sorbents in eliminating organic pollutants or metal ions from environmental water samples.

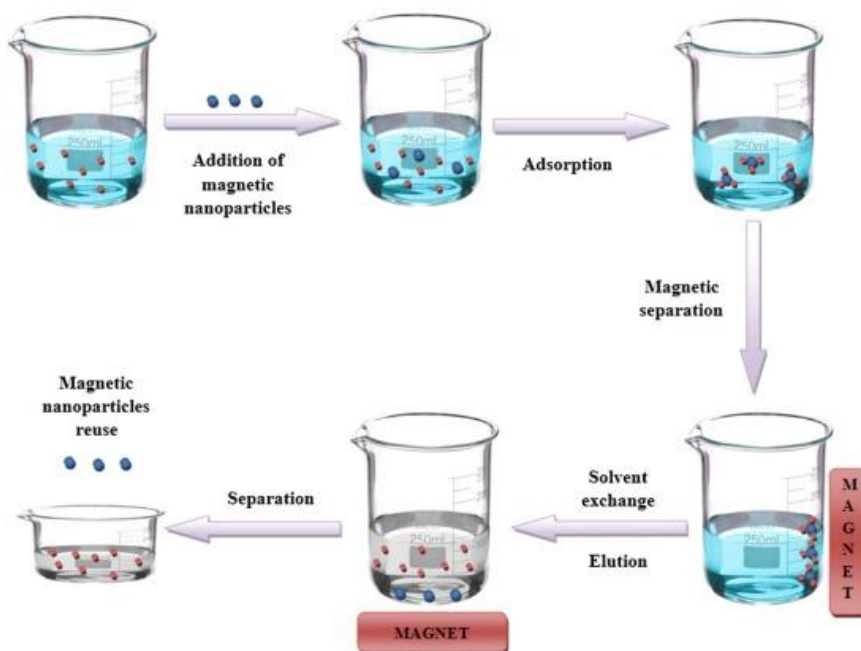


Figure 12: Magnetic Solid Phase Extraction (MSPE) phases [87].

Lately, Kalaboka and associates [88] conducted an experiment with UHPLC-Orbitrap-MS for the Sensitive Analysis of Emerging Contaminants in Wastewater Using MSPE Based on Silica and Graphene Materials. After the extraction parameters were optimized, the recommended techniques, when combined with UHPLC-Orbitrap-MS analysis, yielded high recoveries, LODs, linearity of $R^2 > 0.99$, and satisfactory repeatability for the selected analytes. Accurate and selective measurements of ECs in wastewaters were made possible by the method's applicability in urban and hospital effluent. The combined effectiveness of LC-Orbitrap MS/MS and magnetic solid-phase extraction in wastewater analysis points to a potentially useful instrument for environmental impact research and wastewater monitoring programs. One study utilized MSPE for pesticide detection by creating magnetic sorbents from iron-aluminum mixed metal hydroxides and metal-organic frameworks (MOFs) [89]. The researchers incorporated various benzoate ligands, such as terephthalic acid, 2-aminoterephthalic acid, 2,5-dihydroxyterephthalic acid, 1,3,5-benzenetricarboxylic acid, and 1,2,4,5-benzenetetracarboxylic acid. The magnetic MOF with terephthalic acid as the ligand exhibited remarkable adsorption capacities, ranging from 2193 to 4196 mg kg⁻¹, proving highly efficient for extracting carbamate pesticides like bendiocarb, carbosulfan, carbofuran, carbaryl, propoxur, isoprocarb, and promecarb. This sorbent was used in MSPE as a quick and portable screening procedure. The approach demonstrated outstanding analytical performance, with LODs ranging from 1.0 to 18.0 µg L⁻¹, a broad linear range of 0.015 to 1000 µg L⁻¹, and ideal conditions for MSPE combined with HPLC [90]. This method has low LODs and was effective at separating metal ions in environmental science applications.

Micro solid-phase extraction (MSPE) has seen widespread use across various fields, including biomedicine, where it plays a key role in separating cells and isolating proteins, enzymes, and peptides [90]. It is applied in environmental science to remove contaminants from water and sewage, such as metal ions, pesticides, dyes, surfactants, PAHs, pharmaceuticals, antibiotics, and harmful chemicals like carcinogens and mutagens. In the food industry, it is used to extract pesticides, antibiotics, metals, and medications from various food products. The inclusion of magnetic nanoparticles in solid-phase

extraction accelerates the analysis process by minimizing the number of steps involved. This method enables the concurrent separation and enrichment of target analytes, with the added advantage of using an external magnetic field to separate the sorbent from the analytes. Additionally, MSPE reduces the need for organic solvents, helping minimize hazardous waste and promoting green chemistry practices [91].

1.5.5 Micro Solid-Phase Extraction (μ -SPE)

As previously mentioned, solid-phase extraction (SPE) techniques have various advantages in chemical analysis. Many recent studies have emerged as a result of the increasing interest in SPE due to its miniaturization and numerous benefits. Some of these papers examine the role of green analytical chemistry, particularly how solventless micro-extraction techniques, as an alternative to traditional liquid-liquid extraction methods, aid in the fabrication of more ecologically friendly samples[92]. Other studies explore the combination of multiple sample preparation techniques to overcome the limitations associated with relying on a single method [92] . Numerous review articles have been released, discussing subjects like extraction methods for liquid samples in liquid chromatography [93], affinity monolithic chromatography [94], and advanced techniques such as pipette-tip micro solid-phase extraction (μ -SPE), spin-column μ -SPE, thin-film solid-phase microextraction [95], and dispersive SPE [96]. These papers provide important insights into the development and implementation of SPE in analytical chemistry.

This technique was introduced in 2006 as a unique technology that combines the advantages of SPE with membrane-based technologies. This method involves placing a specific quantity of adsorbent inside a small pouch (1-4 cm²) made of a porous membrane [97], which can either move freely within the sample mixture or stay fixed in the headspace of the sample (Figure 14). The μ -SPE bag is normally made of polypropylene sheets. Comparing with traditional SPE, μ -SPE outperforms standard in terms of simplicity, cost-effectiveness, accuracy, and efficiency [98]. After the extraction procedure, the analyzed substances are desorbed into a small amount of solvent, often methanol or hexane, and assessed using methods like GC or HPLC [99].

As analytical techniques become more miniaturized, μ -SPE has received substantial attention in studies. The " μ " designation stresses the reduction in device size, sorbent quantity, and the usage of micro sized or nano sized materials that give an advantage due to their huge surface area and excellent physicochemical qualities [100]. μ -SPE is an eco-friendlier and efficient approach for sample preparation than classic SPE. It lowers chemical consumption, operating time, and solvent usage. Therefore, in many applications, μ -SPE is considered a solvent-free method [101]. Reduced solvent intake, higher enrichment factors than SPME, better selectivity and sensitivity, ease of use, shorter turnaround times, cost-effectiveness, compatibility with a range of analyte separation and detection systems, and headspace and immersion modes are some of the advantages of μ -SPE. Analyte carry-over, brittle fibers, and a stationary phase with a narrow range of application are some of the disadvantages of μ -SPE, despite its benefits. A tiny amount of sorbent material is extracted using μ -SPE via a porous membrane envelope. Depending on the characteristics of the target analytes, a variety of commercial and custom-made sorbents can be used (Figure 15).

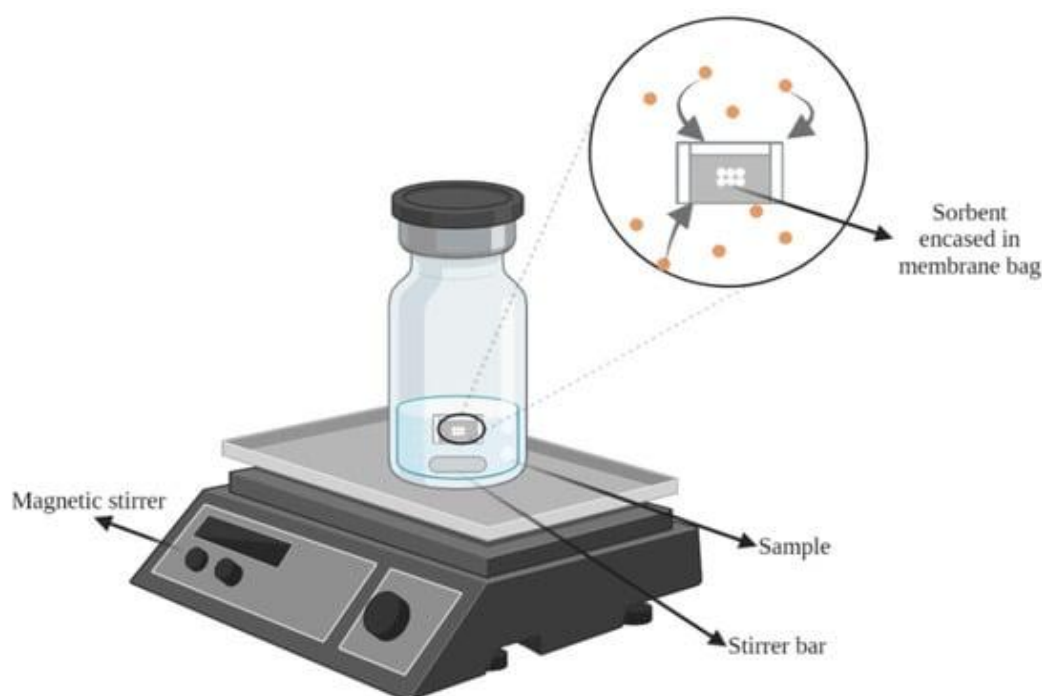


Figure 13: Illustration of μ -SPE system.

The workflow of μ -SPE is similar to traditional SPE, involving a few essential steps: sample loading, analyte binding, washing, and elution. The key difference is the use of smaller formats for the sorbent bed.

1.6. Applications in water contamination detection

Two common compounds that give drinking water earthy tastes and aromas are geosmin and 2-methylisoborneol (2-MIB). For water treatment facilities around the world, compounds with low odor thresholds (less than 10 ng L^{-1}) and complex raw water matrices present a significant challenge. A novel, fully automated μ -SPE method combined with GC-MS is presented in a recent study to detect geosmin and 2-MIB in drinking water [102]. The innovative method is eco-friendly, requiring only 25 mL of raw water and 50 μL of elution solvent. The μ -SPE-GC-MS technique demonstrated exceptional linearity ($R^2 > 0.999$) with detection limits of 2.0 ng L^{-1} for geosmin and 4.3 ng L^{-1} for 2-MIB. It also showed high recovery rates (95.1–100.1%) and excellent precision ($\text{RSD} < 7\%$) in raw water samples. Pesticide residues, which are prevalent in both food and water, represent a serious global issue due to their potential endocrine-disrupting, mutagenic, and carcinogenic effects. In pesticide analysis, the adsorption process, where target analytes interact with a solid phase, plays a critical role in sample preparation [103], [104]. Erbaş et al. [105] investigated pesticide extraction using a new $\text{Fe}_3\text{O}_4/\text{Ni}/\text{Ni}_3\text{B}$ nanocomposite magnetic adsorbent. This method was initially applied to extract pesticides like Lambda-Cyhalothrin (LMD) and Bromopropylate (BRP) from well water samples, as illustrated in Figure 16. Gas chromatography with an electron capture detector (GC-ECD) was employed to produce linear calibration plots with regression coefficients exceeding 0.99. The linear range spanned from 0.1 to 5 ng mL^{-1} . The limits of detection (LODs) for LMD and BRP were 0.03 and 0.02 ng mL^{-1} , respectively, with recovery rates of 90% and 89%. The $\text{Fe}_3\text{O}_4/\text{Ni}/\text{Ni}_3\text{B}$ nanocomposite demonstrated excellent performance as a sorbent for MD- μ -SPE extraction, achieving enrichment factors of 30.3 for BRP and 393 for LMD.

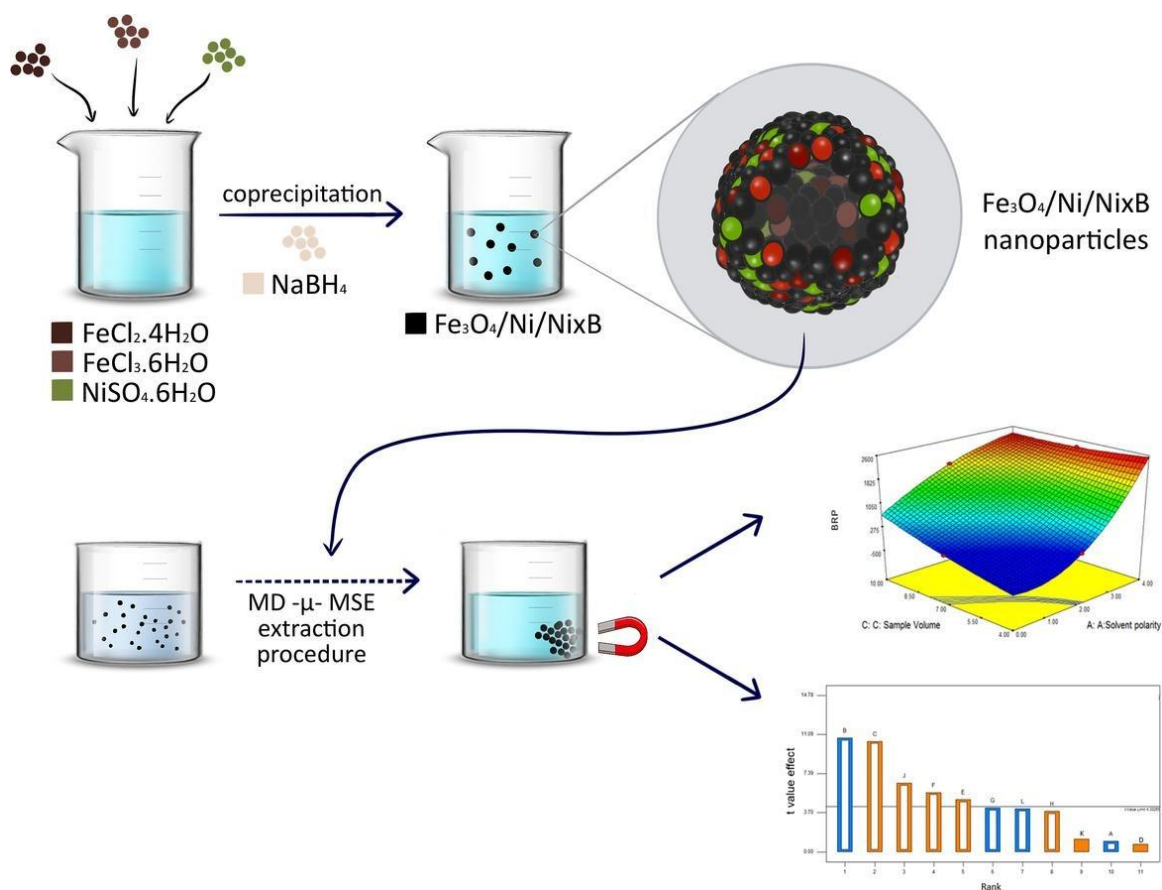


Figure 14: Schematic representation for fabrication of $\text{Fe}_3\text{O}_4/\text{Ni}/\text{Ni}_x\text{B}$ nanocomposite via MD- μ -SPE [105].

Pollutants known as volatile organic compounds (VOCs) are present in both air and water. Numerous substances, including paints, gasoline, cleaning products, insecticides, building supplies, adhesives, and chemicals used in photography, might emit these compounds. The development of straightforward, affordable, and reliable analytical techniques for detecting volatile organic compounds (VOCs) in the environment is crucial due to their propensity to cause a wide range of health issues in living things. VOCs such as benzene, toluene, ethylbenzene, xylenes, and styrene have been detected in water using a technique that uses cross-linked chitosan microspheres for μ -SPE in conjunction with GC-

MS. The LODs for this method range from 0.01 to 0.04 $\mu\text{g/L}$ [105]. Organophosphorus pesticides (OPPs), which are known to have neurotoxic effects, have been extracted from sewage sludge samples using MWCNT-based $\mu\text{-SPE}$ devices. The $\mu\text{-SPE}$ method produced superior LODs than headspace (HS) and hollow fiber solid-phase microextraction (HF-SPME) techniques, with LODs ranging from 1 to 7 pg/g , when the extracted materials were assessed using GC-MS [97]. Another study recovered five organochlorine pesticides (OCPs) from samples of rivers using $\mu\text{-SPE}$ technique based on MIL-101. The GC-MS analysis of the extracted samples revealed limit of detection (LOD) ranges of 0.0025 to 0.016 ng/mL [106].

1.7. Sorbents employed in $\mu\text{-SPE}$

The choice of suitable sorbent materials affects both the convenience of use and the flexibility of working conditions, which in turn affects the efficiency of $\mu\text{-SPE}$ processes. Sorbents used in direct micro-solid-phase extraction (DMSPE) need to fulfill several specifications in order to ensure effective extraction. These features include good dispersibility in liquid samples, high capacity, and a large surface area to enable thorough and quick sorption and elution [107]. The sorbent selection procedure is dominated by the characteristics of the target analytes. Like standard SPE, $\mu\text{-SPE}$ can employ a variety of sorbent materials. However, the following qualities should be present in the finest sorbents for this method:

- A large surface area that can be easily modified with various organic functional groups that bind analytes, using straightforward and well-known methods.
- Exceptional flow properties in the solid state allow for precise and consistent measurement of the sorbent's mass. These favorable flow characteristics also aid in packing the sorbent into membrane casings.
- The sorbent does not adhere to the membrane material, allowing it to migrate freely to the bottom of the membrane envelope [108]. Sticky sorbents may disturb the heat sealing of the membrane's open edge, causing the bag to split or open during the extraction process, resulting in poor performance.

- Stability (insoluble) in both the extraction and desorption mediums.

Various sorbents, including conventional sorbents, carbon-based materials, zeolites, metal-organic frameworks, polymeric substances, and miscellaneous options, have been evaluated for μ -SPE to extract a broad range of target chemicals, with the choice of sorbent depending on the type of analytes and their affinity for the sorbent [109].

1.8. Advantages of μ -SPE

The advantages of Micro Solid-Phase Extraction (μ -SPE) include:

- **High Sensitivity:** μ -SPE allows for the concentration of analytes from large sample volumes into a smaller volume, significantly enhancing the sensitivity of detection. This is particularly useful for detecting trace levels of pollutants in environmental and biological samples.
- **Reduced Sample and Solvent Volumes:** Because of its miniaturized nature, μ -SPE requires much smaller amounts of samples and solvents compared to traditional extraction methods. This not only saves on the cost of reagents but also minimizes waste, making it a more sustainable option.
- **Fast Extraction Process:** The small size of the extraction devices (e.g., pipette tips, micro-columns) speeds up the extraction process, allowing for quicker results, which is beneficial in high-throughput or time-sensitive applications.
- **Cost-Effectiveness:** By using less samples and solvents, and requiring minimal equipment, μ -SPE reduces overall costs in terms of materials, time, and labor. This makes it more affordable for labs, especially in resource-limited settings.
- **Environmental Benefits:** The reduced use of chemicals and solvents makes μ -SPE a more environmentally friendly technique. Less chemical waste is generated, and the reduced consumption of reagents contributes to lower environmental impact.
- **Improved Efficiency:** The higher surface area of the sorbent material used in μ -SPE enhances the extraction efficiency, making the process more effective in isolating analytes from complex samples.

- **Versatility:** μ -SPE is applicable to a variety of sample types, such as environmental samples like water and soil, biological samples like blood and urine, and food items. It is effective at analyzing a wide range of compounds, including heavy metals, pesticides, medications, and organic chemicals.
- **Ease of Integration with Analytical Instruments:** μ -SPE can easily be coupled with analytical techniques like HPLC, GC, and MS, providing a streamlined approach for analyzing extracted samples.
- **Reduced Handling Time:** The miniaturized nature of μ -SPE allows for fewer handling steps, resulting in reduced processing times and a higher degree of automation potential.
- These advantages make μ -SPE a promising technique for various analytical applications, particularly in fields requiring high sensitivity and low reagent use, such as environmental monitoring and forensic analysis.

1.9. Challenges in μ -SPE

Although μ -SPE has demonstrated considerable potential for becoming a mainstream miniaturized extraction technique, it still faces several challenges.

One disadvantage of μ -SPE is the scarcity of hollow fiber membranes, with polypropylene (PP) being the most widely used material. Currently, there are no membranes specifically designed for μ -SPE, which limits the ability to customize properties such as membrane structure and pore size to meet specific requirements. Additionally, the design of the μ -SPE device poses challenges; improper construction, such as poorly sealed edges, can result in the device opening during extraction, leading to the loss of both the sample solution and the sorbent phase. Furthermore, the membrane barrier between the sorbent and the sample solution may hinder extraction efficiency, causing longer extraction periods. Excessive churning during the process can create

bubbles on the membrane surface, which impede analyte transfer and reduce repeatability. When using the same μ -SPE apparatus with complex samples, pore obstructions may occur, potentially compromising the results. Another drawback of μ -SPE is that the extraction and analysis procedures are carried out in distinct phases, requiring substantial manual labor during device fabrication. This labor-intensive process, which involves cutting the membrane, heat-sealing it, packing the sorbent precisely, and sealing the open end, makes μ -SPE less suitable for routine laboratory applications that demand the analysis of hundreds of samples daily. To address this limitation, efforts must focus on streamlining the process and reducing manual labor, potentially through automation. However, the automation of μ -SPE in conjunction with analytical instruments has not yet been thoroughly explored, presenting an opportunity for future advancements in this field.

Spent FCC Catalyst as Sorbent for Pesticides Microextraction: A Sustainable Approach towards Waste Recycling and Reuse

2.1. Introduction

In the fluid catalytic cracking (FCC) unit of refineries around the world, large volume of catalysts is widely employed, but the disposal of these spent FCC catalysts poses significant environmental challenges, raising concerns about their hazardous nature and potential impact on soil and water quality. An innovative solution involves repurposing the spent FCC catalysts as sorbents in the membrane-supported micro-solid-phase extraction process, offering a sustainable approach to disposal while demonstrating economic and environmental benefits from reusing industrial by-products [110] This approach not only addresses the issue of FCC catalyst disposal but also presents an opportunity to enhance the efficiency of pollutant detection in water sources [111].

Water pollution due to pesticide residues is a pervasive issue worldwide, with detrimental consequences for human health. Access to clean drinking water is a fundamental human right essential for maintaining a healthy life [112]. However, numerous water sources have been found to be contaminated with pesticide residues, posing a significant threat to public health [112], [113]. The presence of pesticides in natural water sources, originating from field applications and post-application runoff, is a serious concern [113], [114]. Ensuring

the availability of clean and safe drinking water is crucial for public health, as its absence would impose a significant health burden on the global population.

Pesticides can infiltrate aquatic systems through various hydrological pathways, whether surface or subsurface [115]. The primary contributors to the transfer of pesticides to surface water include spray drift, runoff water, and drainage water [116]. Unfortunately, this contamination has detrimental consequences for human health, leading to carcinogenic, endocrine, neurological, reproductive, and other health issues [117]. Tragically, fatalities have been documented due to pesticide exposure, with studies revealing a 25-30% increased risk of cancer and mental health disorders associated with such exposure [117], [118]. Moreover, paternal pesticide exposure is linked to a 50% increased incidence of leukemia, lymphoma, and brain cancer in children [118].

Membrane-supported micro-solid-phase extraction is a widely applicable sample preparation method, known for its effectiveness and convenience in analyzing various substances across multiple research fields [45]. Its versatility is highlighted by numerous studies detailing various membrane-supported micro-solid-phase extraction methodologies, demonstrating its success in examining a broad spectrum of compounds [119]–[122]. With applications ranging from flavors and fragrances to environmental research and bioanalytical studies, membrane-supported micro-solid-phase extraction has established itself as a valuable analytical tool across various domains. Recent reviews compile its paramount utility in distinct areas, including the examination of volatile compounds in wine, in vivo monitoring of soil contaminants, and analysis of water samples and food, as well as in vitro and in vivo metabolomics investigations [123].

Choosing the right sorbent is a crucial factor in membrane-supported micro-solid-phase extraction processes, where the effectiveness heavily relies on the sorbent's ability to selectively extract and concentrate target analytes from complex sample matrix. Considerations such as sorbent material, coating thickness, and the choice of polarity significantly influence the selection process. Advances in sorbent technology, such as the development of novel coatings and hybrid materials, have expanded the range of analytes efficiently extracted using membrane-supported micro-solid-phase extraction [49].

In this study, spent FCC catalysts were successfully utilized as sorbents in the membrane-supported micro-solid-phase extraction process to extract six types of pesticides. The FCC catalyst comprise of mainly USY zeolite, clay and binders [124]. Both zeolites, clay and binders have been reported as good adsorbent for adsorption of various pollutants due to their physico-chemical properties [125]–[127]. However, to our knowledge, this is the first instance of using spent FCC catalysts as a sorbent in membrane-supported micro-solid-phase extraction for detecting pollutants in treated wastewater samples.

2.1.1. Chemicals and materials

The pesticide residues, including Isoprocarb, Atrazine, Primicarb, Penconazole, Chlorfenapr, and Mefenacet, were procured from HPC Standards GmbH. Solvents were sourced as follows: Acetone from EMSURE, methylene chloride, chloroform, ethyl acetate and methanol from Sigma-Aldrich, and toluene from Honeywell. The wastewater was sourced from the Alkhobar sewage plant, Saudi Arabia prior to its discharge into the Corniche Sea. Deionized water used in the study was processed in-house using equipment

from VWR International. A 0.22 μm porosity polypropylene membrane was obtained from Tisch Scientific Company

2.1.2. Pretreatment of Spent FCC Catalyst

The FCC spent catalyst was sourced from a local refinery in the Kingdom of Saudi Arabia. A total of 10g of the spent catalyst was washed three times with a 200 mL water-methanol solution to remove petroleum products and metal contaminants that were adsorbed on the spent catalyst, then dried in an oven at 100°C for 6 hours. The dried spent catalyst was divided into three portions: the first portion was used without further modification and is labeled as spent catalyst; the second portion was calcined in a muffle furnace to remove deposited coke on the catalyst, thus is labeled regenerated catalyst. The calcination process involved ramping the temperature at 2°C/min up to 100°C, followed by 5°C/min from 100 to 600°C, and maintaining 600°C for 6 hours. The third portion of the dried spent catalyst was modified via silica encapsulation using a sol-gel approach, with the deposited coke acting as a hard template. For this modification, 4g of the dried spent catalyst was dispersed in a mixture of 3.85g tetraethoxysilane, 22ml deionized water, and 6ml ethanol. After stirring for 8 hours, the mixture was transferred to a Teflon-lined autoclave and heated at 90°C for 24 hours. The resulting solution was centrifuged, and the powder obtained was washed three times with deionized water, dried at 100°C, and calcined at 600°C for 6 hours to form catalyst@silica material. Fresh USY zeolite was used as a reference fresh FCC catalyst. Consequently, this study evaluated the performance of four types of materials as sorbents: the spent catalyst, regenerated catalyst, catalyst@silica, and USY zeolite.

2.1.3. Characterization of the materials

Various characterization methods were employed to study the physico-chemical properties of the spent catalyst, regenerated catalyst, catalyst@silica, and USY zeolite. XRD analysis was performed using a diffractometer with a Cu anode (Regaku, Ultima IV) operating at 40 kV and 30 mA to evaluate the crystallinity of the materials. The functional groups on the surface were examined using Nicolet 6700 Thermo Electron Fourier Transform Infrared Spectroscopy (FTIR). Energy-dispersive X-ray spectroscopy (Jeol 6700LV) and a Field Emission Scanning Electron Microscope (FE-SEM) were used for surface morphology and elemental analysis. Porosity parameters were measured using nitrogen adsorption/desorption studies with a Micromeritics ASAP-2000 Porosity Analyzer (Micromeritics, USA). The Brunauer-Emmett-Teller (BET) method was employed to compute the surface area, while the Barret, Joyner, and Halenda (BJH) method calculated pore size and pore volume distribution. The adsorbents were degassed for three hours at 250 °C in a vacuum-sealed tube to remove moisture and impurities prior to measurement.

2.1.4. Micro-SPE procedure

In a typical membrane-supported micro-solid phase extraction (micro-SPE) procedure [128], a polypropylene membrane measuring 0.5 cm by 0.5 cm is sealed on three sides using a standard sealing instrument. Subsequently, a magnet and sorbent material are introduced into the sealed membrane, and the fourth side is sealed to form a bag. This bag is then activated with toluene, a step that is visually confirmed by the transformation of the bag from a white color to a transparent state. Following activation, the bag is placed into the sample, where extraction occurs as the analyte migrates from the sample and adsorbs

onto the sorbent. After extraction, the bag is removed, dried with lab tissue, and placed in a minimal amount of organic solvent (200-500 μL). The system is then sonicated for a specified duration, facilitating desorption as the target analyte is released from the sorbent and dissolves in the organic solvent. With the analyte now separated from the matrix and concentrated in a minimal volume of organic solvent, the final step involves injecting it into a gas chromatograph (GC) for data collection.

2.1.5. Optimization of parameters

Optimization was carried out through a univariate approach, examining four types of sorbents: spent catalyst, regenerated catalyst, catalyst@silica, and USY zeolite. The investigation involved testing and fine-tuning both the selection of the optimal sorbent and its quantity, ranging from 5 mg to 40 mg. The extraction step was systematically studied over varying time intervals, spanning 5 minutes to 25 minutes. Concurrently, the desorption phase was investigated for its duration (ranging from 5 minutes to 35 minutes), choice of desorption solvents (including acetone, methylene chloride, chloroform, ethyl acetate, and methanol), and solvent quantity (ranging from 200 μL to 600 μL). This comprehensive exploration and optimization process are aimed at identifying the most effective parameters for the extraction and desorption steps of the micro-SPE

2.1.6. GC-MS analysis

The identification and quantification of target analytes were conducted using an Agilent 7890A GC-System coupled with an MS-5975C inert MSD equipped with a triple-axis detector. The system featured an Agilent GC-Sampler 80 autosampler and injector. Separation of the target analytes was accomplished using an Agilent 19091J-413 MS column, which has a thickness of 0.25 μm , a length of 30.0 m, and a diameter of 0.32 mm.

The GC inlet and auxiliary heater were kept at 300°C. High-purity helium was used as the carrier gas at a flow rate of 1.2 mL/min. The GC injection port and GC-MS interface temperatures were set at 250°C, with the ion source temperature fixed at 230°C. The oven temperature program was as follows: the initial temperature of 40°C was maintained for 2 minutes, then ramped at 10°C/min to 100°C, held for 1 minute. The temperature was then increased to 260°C at 10°C/min and held for 1 minute, followed by another increase to 280°C at 10°C/min and held for 1 minute, making the total run time 29 minutes. Analytes were introduced into the GC column using the split less injection mode throughout the study. For qualitative analysis, data acquisition was performed in scan mode to confirm the retention times of the target analytes. For quantitative analysis, selective ion monitoring (SIM) mode was used, with the selected ion peaks for each nitrosamine specified in **Table**

1

Table 1: Target compounds, their retention time (min) and selected target ions for SIM mode.

Retention time (min)	Target compounds	Selected target ions
14.649	Isoprocab	121, 136, 91
17.049	Atrazine	200, 215, 58
18.17	Primicarb	166, 72, 238
20.163	Penconazole	248, 159, 161
21.76	Chlorfenapr	59, 247, 75
24.443	Mefenacet	192, 123, 90

2.1.7. Analytical method validation and real sample analysis

Method validation involved generating a calibration curve and determining linear equations along with R-squared values. Furthermore, the limit of detection (LOD) and the limit of quantification were computed using the equations below:

$$LOD = 3 \times \frac{signal}{noise}$$

$$LOQ = 10 \times \frac{signal}{noise}$$

2.2. Results and discussion

2.2.1. Material chemistry and characterization

A. Powder X-ray diffraction (PXRD)

The powder X-ray diffraction (PXRD) for all the sorbent materials show the patterns of USY zeolite, although at different peak intensity levels (Figure 15 (a)) [129]. The peak intensity, indicative of material crystallinity, is highest in the USY zeolite, which indicates that it is pure zeolite material. The XRD of the spent catalyst also shows good peak resolution, however, upon catalyst regeneration by calcination, a reduction in crystallinity was observed, accompanied by the loss of specific crystal faces. This phenomenon is also observed in the pattern of the Catalyst@Silica, suggesting that the polymeric silicon cover introduced during the modification process may be responsible for obscuring these crystal faces [130].

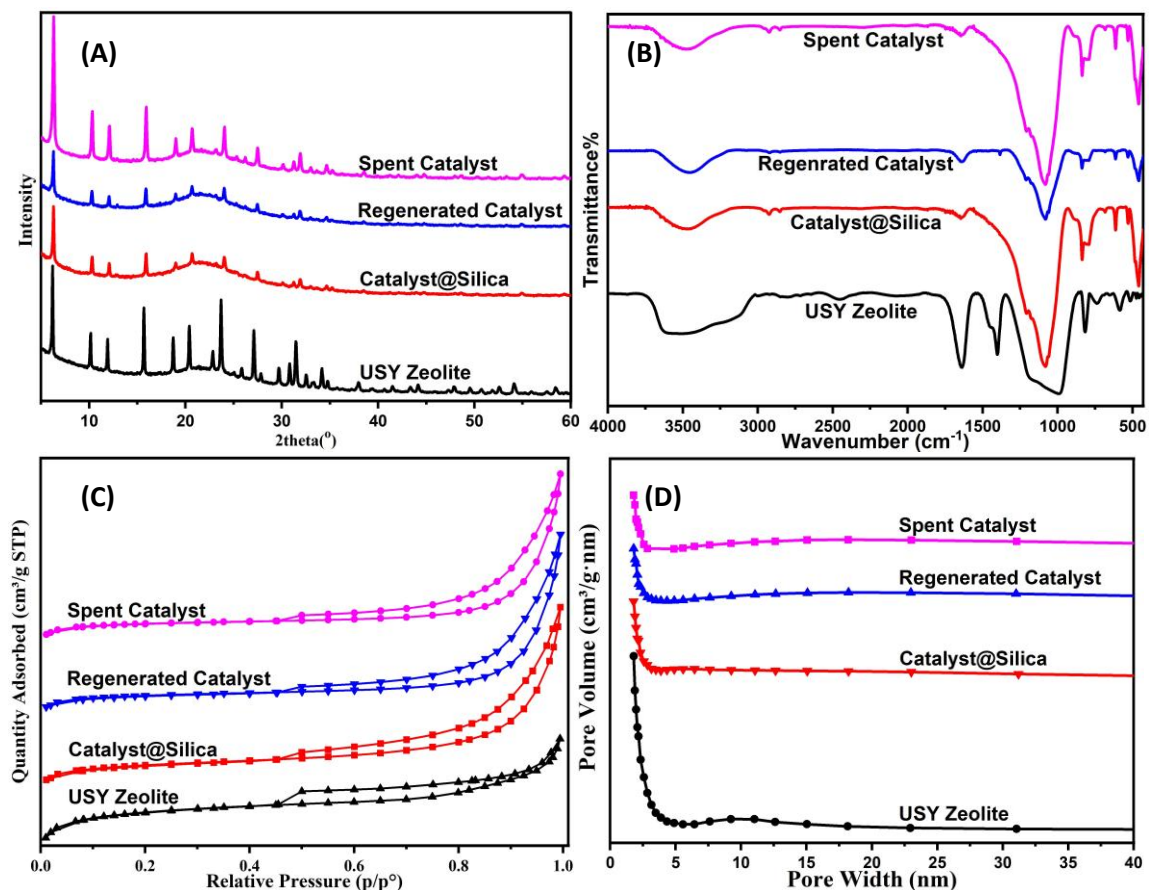


Figure 15: Sorbent materials characterization: A: pXRD, B: FTIR, C: N₂ adsorption-desorption isotherm, D: Pore size distribution.

B. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectrum (Figure 15 (b)) clearly shows an O-H stretching band at 3500 cm⁻¹, indicating the presence of hydroxyl groups. Other identifiable features include the O-H bend at (1625-1600) cm⁻¹ associated with absorbed water, the Si(Al)-O-Si(Al) stretching at (1140-955) cm⁻¹, the external Si(Al)-O absorption at (700-800) cm⁻¹, and the internal Si(Al)-O absorption at (420-500) cm⁻¹ [131].

C. N₂ adsorption-desorption isotherm

The nitrogen adsorption-desorption isotherms for the various sorbents, presented in (Figure 15 (c)), highlight notable differences in adsorption capacities at different relative pressures (p/p°). The spent catalyst shows the highest adsorption capacity across all relative pressures, indicating a well-developed porous structure with a high surface area, making it highly effective for pesticides adsorption [132]. This suggests a mix of microporous and mesoporous features, which facilitate efficient pesticides molecules trapping. All the sorbents exhibit Type IV isotherms, indicating the presence of mesopores. Most sorbents, except USY zeolite, display hysteresis loops characteristic of Type H3, associated with wedge-like pores. In contrast, USY zeolite shows a Type H4 hysteresis loop, associated with slit-like pores. The regenerated catalyst demonstrates moderate adsorption capacity, higher than Catalyst@Silica and USY zeolite but lower than the spent catalyst, suggesting that the regeneration process restores some but not all adsorption capacity. Catalyst@Silica shows intermediate adsorption capacity, better than USY zeolite but less effective than both regenerated and spent catalysts, indicating the presence of mesopores that aid pesticide adsorption, though not as efficiently as the spent catalyst. Finally, USY zeolite has the lowest adsorption capacity among the tested sorbents, with its isotherm suggesting a more microporous structure with limited surface area and pore volume for pesticide adsorption [133]. This is further observed in the microporous surface area (m^2/g) and pore size (nm) values summarized in table 2.

Table 2: Textural properties of the sorbent materials

Sorbents	Surface Area (m²/g)	Mesopore surface area (m²/g)	Micropore surface area (m²/g)	Pore Volume (cm³/g)	micropore volume (cm³/g)	Pore Size (nm)
USY zeolite	576	53	523	0.3455	0.2741	2.401
Spent catalyst	125	21	105	0.1627	0.0552	5.188
Regenerated catalyst	127	22	105	0.1710	0.0553	5.388
Catalyst@silica	132	33	99	0.1709	0.0523	5.163

D. Pore size distribution

The pore size distribution curves for the sorbents provide crucial insights into the pore structure and volume, which significantly influence adsorption performance. As shown in (Figure 15 (d)), the spent catalyst displays a broad distribution of pore sizes, including a significant volume of mesopores and some macropores, particularly in the mesopore range (2-50 nm), correlating with its high adsorption capacity as larger pores can accommodate more pesticide molecules. The regenerated catalyst shows a similar but slightly narrower pore size distribution compared to the spent catalyst, with mesopores contributing to its moderate adsorption capacity, although some original pore volume might be lost during the regeneration process. Catalyst@Silica presents a notable volume of mesopores, though less than that of the spent catalyst, aiding in adsorption but not as effectively due to fewer available pores. Lastly, the USY zeolite features a predominantly microporous structure with limited pore volume in the mesopore range, and the dominance

of micropores (see table 2) restricts its adsorption capacity for larger pesticide molecules, as evidenced by its lower performance in the adsorption isotherm.

E. Scanning electron microscopy (SEM)

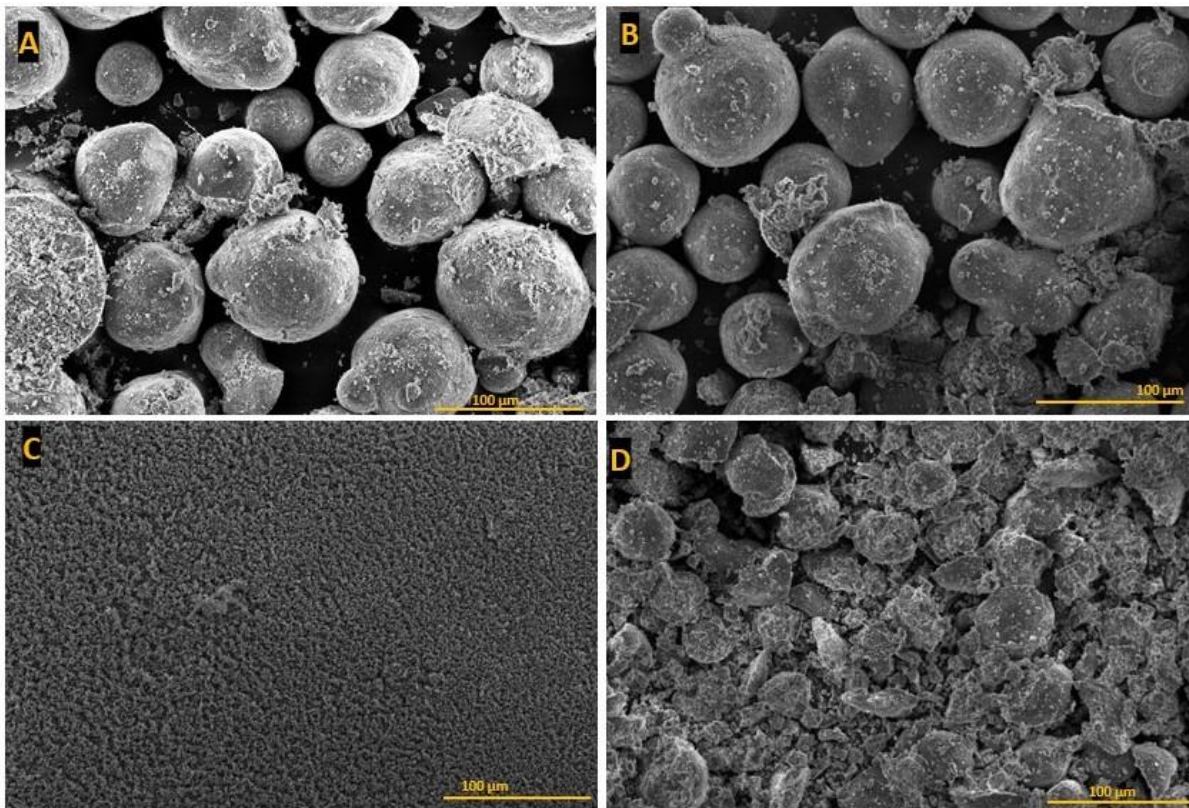


Figure 16: SEM at 500x magnification; A: Spent Catalyst, B: Regenerated Catalyst, C: USY Zeolite, D: Catalyst@Silica.

The SEM images at 500x reveal distinct morphological characteristics of the sorbents. The spent catalyst (Figure 16 (a)) shows a rough and irregular surface with spherical particles which is typical morphology of an FCC catalyst [134], offering abundant active sites for adsorption, which likely contributes to its superior performance. In contrast, the regenerated catalyst (Figure 16 (b)) has a smoother surface, which indicates the absence of coke on the catalyst and this potentially reduces the available active sites due to coke

formation. The USY zeolite (Figure 16 (c)) presents a dense, homogeneous texture with fine particles, indicating that it is pure microporous zeolite powder that has not been processed into commercial spray-dried catalyst. The Catalyst@Silica composite (Figure 16 (d)) features a heterogeneous surface with a mix of agglomerates and finer particles, resulting in fewer accessible active sites. This implies that silica modification has ruined the spherical morphology of the FCC catalyst. The EDS analysis of the sorbent materials is summarized in table 3.

Table 3: Elemental composition (Atomic%) of the sorbent materials

Sorbent	Si	Al	C	Si/Al
USY zeolite	29.5	11.1	-	2.65
Regenerated catalyst	22.8	7.35	17.7	3.10
Spent catalyst	21.6	6.95	21.8	3.11
Catalyst@Silica	21.8	8.76	26.6	3.79

2.2.2. Optimization of Extraction process

Optimization was carried out through a univariate approach and the outcomes are presented below.

A. Sorbent Materials

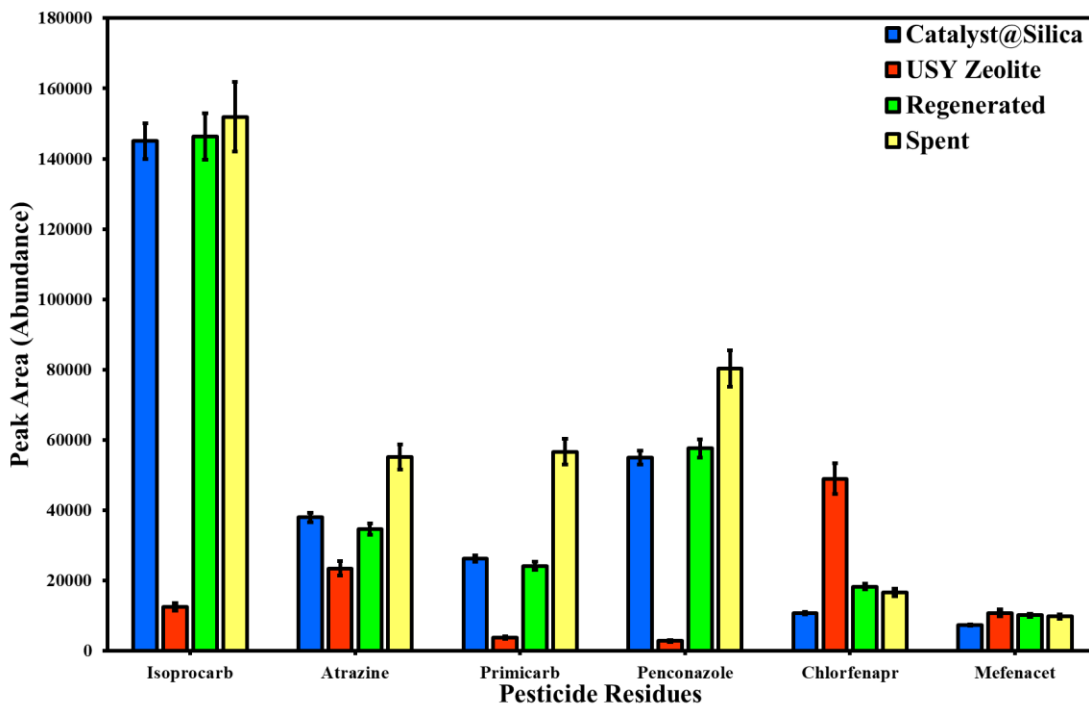


Figure 17: Extraction performance of different sorbent Materials.
Conditions: Pesticides mix concentration: 0.8 ng mL⁻¹; sorbent mass: 30 mg; extraction time: 10 min; desorption solvent: methanol; desorption volume: 300µL; desorption time: 10 min.

The study employed four distinct sorbents: spent catalyst, regenerated catalyst, Catalyst@Silica, and USY zeolite, for the extraction of six pesticides, namely Isoprocab, Atrazine, Primicarb, Penconazole, Chlorfenapr, and Mefenacet. (Figure 17) illustrates that Isoprocab, Atrazine, Primicarb, and Penconazole exhibited optimal extraction when using spent zeolite as the sorbent, with the least effective extraction observed when USY zeolite

was employed. Mefenacet demonstrated consistent extraction performance across all sorbents, while Chlorfenapr exhibited its highest extraction efficiency when utilizing USY zeolite.

Consequently, the spent catalyst was identified as the most effective sorbent for this study. This performance can be attributed to the hydrophilic nature of zeolites due to the presence of hydroxyl groups, facilitating hydrogen bonding, coupled with hydrophobic properties within internal channels and cages that contribute to weak electrostatic forces [135]. Additionally, the presence of coke on the surface of the spent catalyst provides multiple functional groups, offering additional adsorption sites for the pesticides [136].

B. Sorbent Quantity

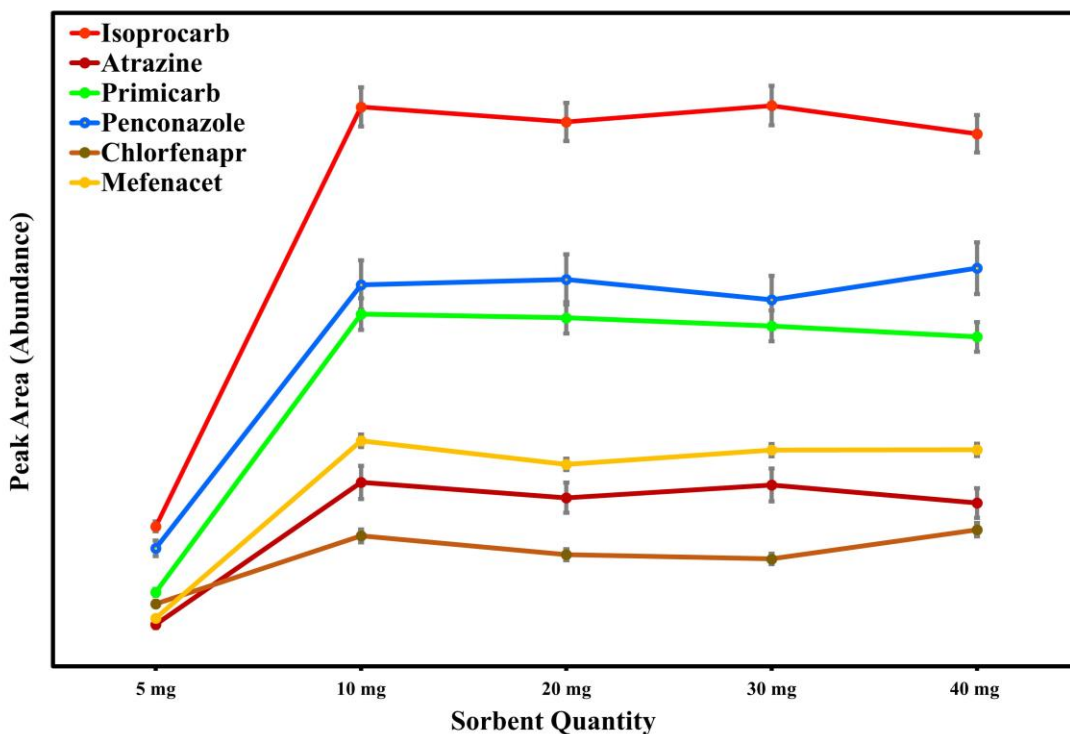


Figure 18: Impact of Sorbent (spent catalyst) Quantity on Extraction Performance.
Conditions: Pesticides mix concentration: 0.8 ng mL⁻¹; extraction time: 10 min;
desorption solvent: methanol; desorption volume: 300μL; desorption time: 10 min.

The work demonstrates that maintaining a consistent sample size while increasing the sorbent quantity results in enhancing the extraction quantity. However, beyond 10 mg of sorbent, the extraction quantity will be constant. This is attributed to the kinetic nature of the reaction which has reached equilibrium [137]. In simpler terms, the concentration of pesticides on the sorbent has been constant, and despite the increased absorbent sites with 20 mg, 30 mg, and 40 mg, they are ineffective in altering the equilibrium state. Therefore, 10 mg is determined to be the optimal sorbent quantity. (Figure 18).

C. Desorption Solvent

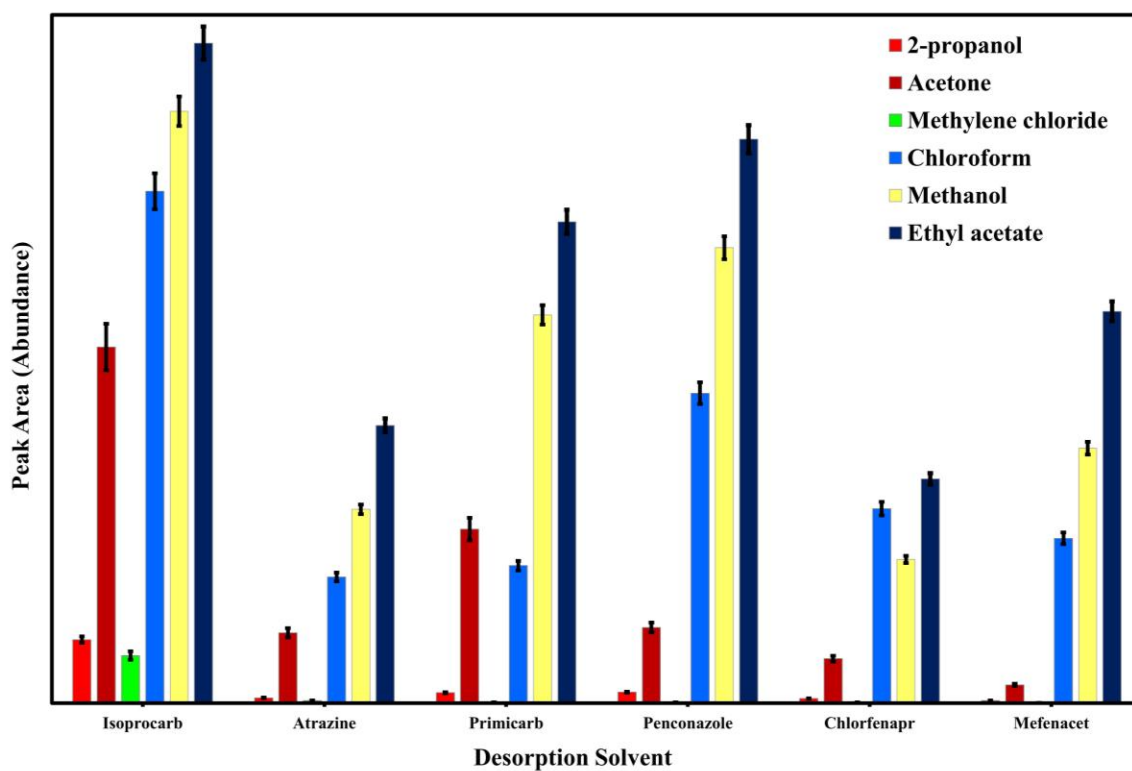


Figure 19: Testing different solvent for desorption of pesticides. Conditions: Pesticides mix concentration: 0.8 ng mL^{-1} ; sorbent mass: 10 mg; extraction time: 5 min; desorption volume: 300 μL ; desorption time: 10 min.

The work investigated the efficacy of various organic solvents in desorbing pesticides from the sorbent. These solvents covered a range of polarities, ranging from chloroform, the least polar solvent, to methanol, the most polar one. Observed from (Figure 19), ethyl acetate, situated as moderately polar but leaning toward the polar side, exhibited the best performance. This is attributed to the moderately polar nature of the pesticides.

D. Desorption Time

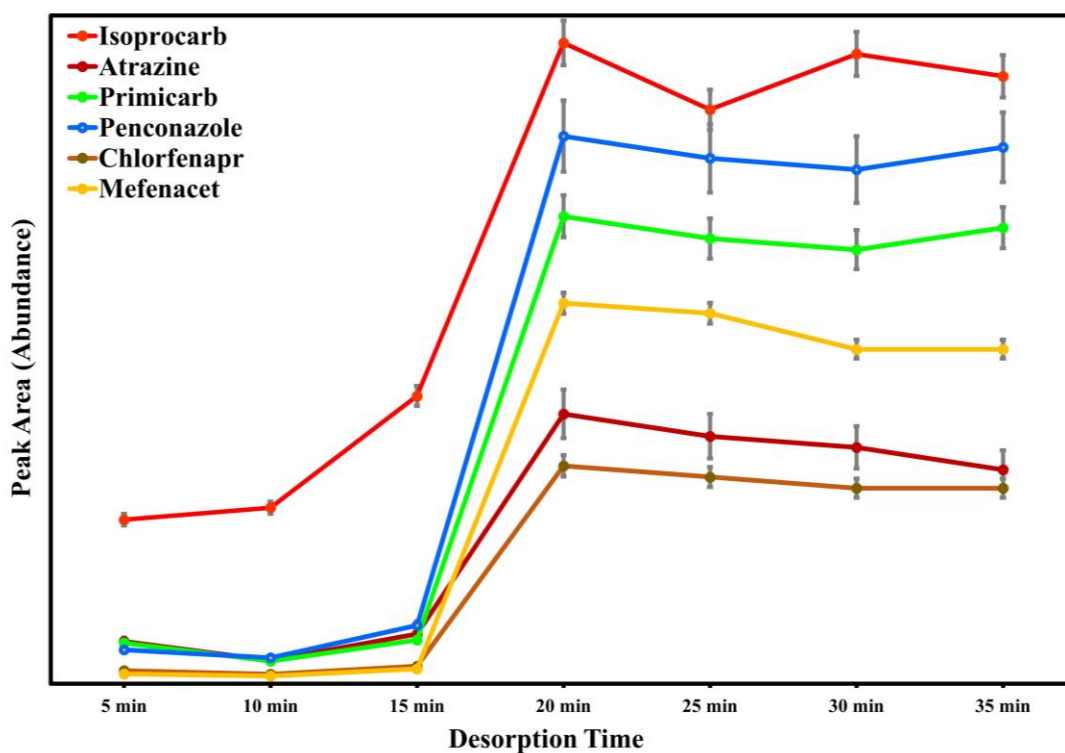


Figure 20: Effect of desorption time on the extraction efficiency of Presides.
Conditions: Pesticides mix concentration: 0.8 ng mL⁻¹; sorbent mass: 10 mg;
extraction time: 5 min; desorption solvent: ethyl acetate; desorption volume: 300μL.

As shown in (Figure 20) the desorption process took 20 minutes due to the strong absorption interactions between the sorbent and the pesticides.

E. Desorption Solvent Quantity

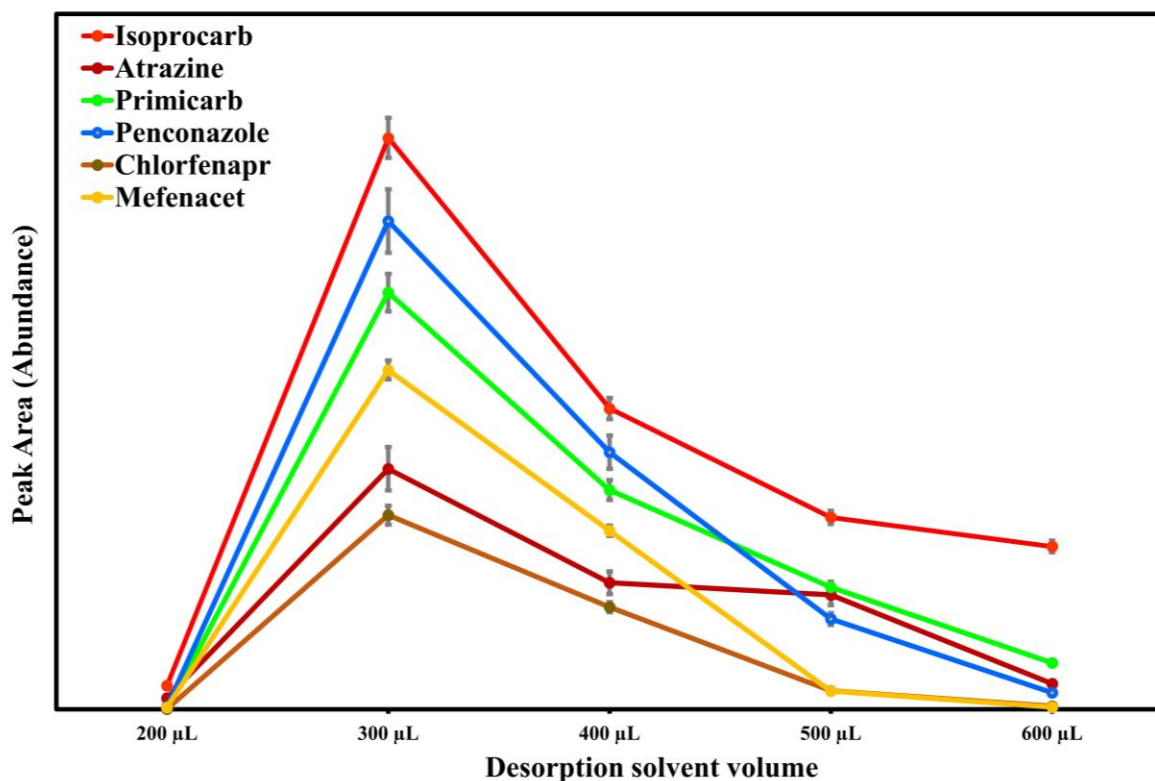


Figure 21: Effect of Desorption Solvent Quantity on the extraction efficiency of Presides. Conditions: Pesticides mix concentration: 0.8 ng mL⁻¹; sorbent mass: 10 mg; extraction time: 5 min; desorption solvent: ethyl acetate; desorption time: 20 min.

The bag exhibited effective immersion in 300 µL of the desorption solvent, ensuring complete desorption of all pesticides. In contrast, when immersed in 200 µL, not all pesticides successfully desorbed into the solvent because the bag was not completely immersed. Furthermore, increasing the volume of the desorption solvent beyond 300 µL was observed to dilute the concentration, resulting in a reduction in the efficiency of the extraction. Consequently, the optimal desorption solvent quantity was determined to be 300 µL. (Figure 21).

2.2.3. Method Validation and Real Sample analysis

The method's linearity in the range of (5 - 1000) ppb was confirmed, with calculated R squared values ranging from (0.9859 - 0.9993). The limits of detection (LOD) and quantification (LOQ) were determined using the signal-to-noise method. LOD in the range of (0.36 – 1.52) ppb, and LOQ in the range of (1.30 – 5.00) ppb. Precision testing involved standards prepared in deionized water at three concentrations: one at the lowest limit of linearity, another at the highest level, and one in between, covering the entire linear range. (see Table 4).

Table 4: Analytical features for the SB- μ -SBE of pesticides using spent catalyst sorbent.

Analyte	R ²	Linear Equations	LOD (ng mL ⁻¹)	LOQ (ng mL ⁻¹)	RSDs (%) in DI water (n=3)		
					5 ng mL ⁻¹	200 ng mL ⁻¹	1000 ng mL ⁻¹
Isoprocab	0.9977	$y = 2736.7x + 14723$	0.36	1.19	5.2	7.6	5.3
Atrazine	0.9859	$y = 1161x + 28592$	0.61	2.02	4.7	4.9	5.0
Primicarb	0.9941	$y = 2226.1x - 4060.9$	0.39	1.30	5.8	5.3	5.7
Penconazole	0.9931	$y = 3274.4x - 83282$	0.38	1.24	4.3	4.3	2.7
Chlorfenapr	0.9993	$y = 1111.5x - 17846$	1.52	5.00	5.9	2.7	8.0
Mefenacet	0.9982	$y = 1921.8x - 26366$	0.61	2.00	6.6	5.5	5.5

Linear Range: 5 – 1000 ng mL⁻¹

Table 3 shows that among six distinct pesticides that were analyzed in this work, four were detected in the actual sample, exhibiting precision with relative standard deviation (RSD%) ranging from 5.6% to 15.1%. Subsequently, the real sample underwent spiking to ascertain the relative recovery, yielding a percentage range of 84.9% to 99.5% [138]. The chromatogram for real sample analysis is presented in (Figure 22).

$$\text{Relative recovery} = \frac{a}{b} \times 100$$

a = Peak area of the analyte extracted from wastewater samples,

b = peak area of the analyte extracted from deionized water.

Table 5:Real Sample analysis, N.D.: Not Detected

Analyte	Pesticides residues detected in Wastewater sample. (ppb)	RSDs (%) for Wastewater Analysis (n=3)	Relative recovery of spiked pesticide residue from wastewater			RSDs (%) of spiked pesticide residue from wastewater (n=3)		
			5 ng mL ⁻¹	200 ng mL ⁻¹	1000 ng mL ⁻¹	5 ng mL ⁻¹	200 ng mL ⁻¹	1000 ng mL ⁻¹
Isoprocab	N.D.	-	85.9	92.3	94.8	11.5	10.5	8.16
Atrazine	N.D.	-	89.6	90.8	92.9	11.4	4.08	14.2
Primicarb	4.09	15.1	85.7	96.7	93.1	11.5	3.21	9.16
Penconazole	26.4	5.6	84.9	87.1	88.9	9.19	12.4	17.9
Chlorfenapr	21.8	12.6	85.0	93.7	93.2	8.23	11.0	4.38
Mefenacet	13.9	7.1	85.7	94.6	99.5	10.4	8.81	11.7

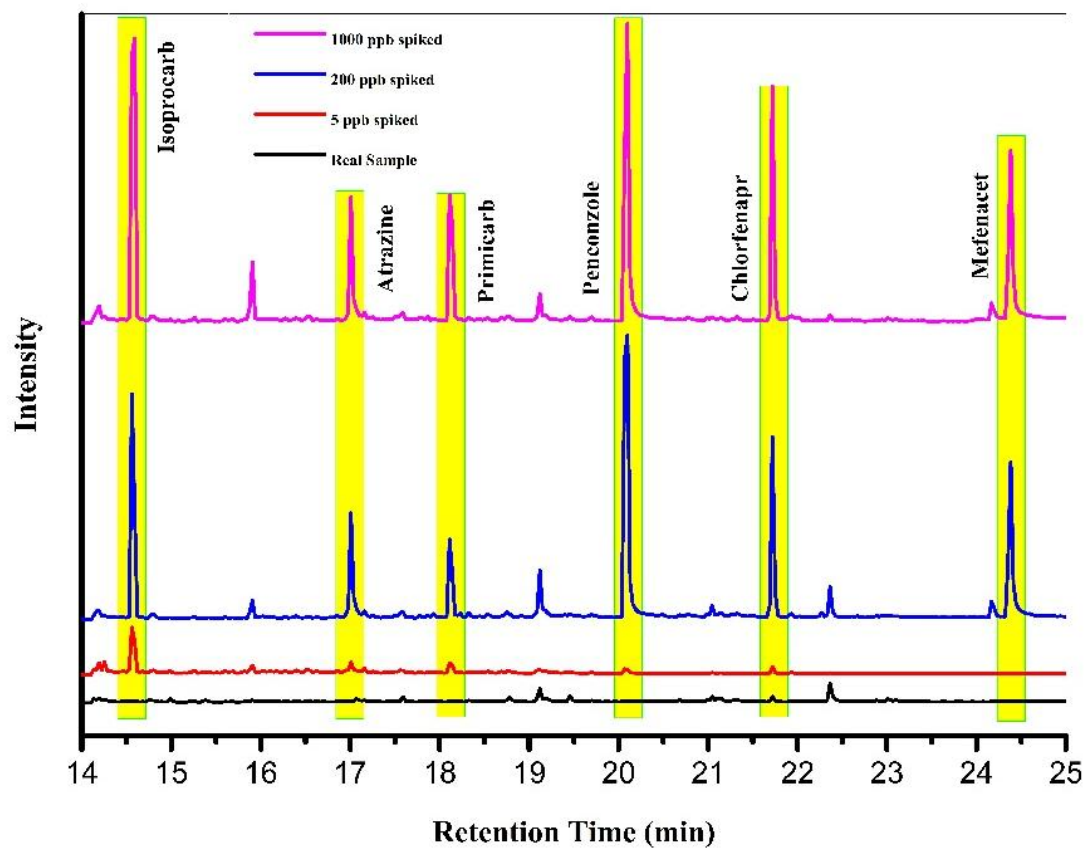


Figure 22: GC-MS overlaid Chromatograms showing the real sample unspiked and spiked with 5, 200 and 1000 ng mL⁻¹ of pesticides mixture.

2.3. Summary of the work

The use of spent Fluid Catalytic Cracking (FCC) catalysts as sorbents in the membrane-supported micro-solid-phase extraction process has been highly successful for extracting pesticides. This method has achieved significant results, including a wide linear detection range from 5 to 1000 ng/mL and low limits of detection (LOD) between 0.36 and 1.52 ng/mL. Additionally, the methodology has shown high relative recovery rates from 84.9% to 99.5%. These findings highlight the effectiveness and sensitivity of using spent FCC catalysts in membrane-supported micro-solid-phase extraction for pesticide analysis, providing a robust approach to safeguarding water quality. Moreover, the versatility of spent FCC catalysts suggests their potential for extracting other pollutant classes, emphasizing the broader applicability and environmental importance of this innovative approach.

Efficient Micro-Solid Phase Extraction and HPLC Quantification of Phenols from Wastewater Using Functionalized Fibrous Silica-Based Sorbents.**3.1. Introduction**

Developing nations usually face water pollution problems caused by agricultural activities, whereas advanced nations deal with obstacles such as chemical emissions resulting from technological progress and strong industrial expansion [139]. Several harmful organic pollutants, such as phenols, polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), organochlorines, chlorobenzenes, chlorophenols, and other phenol-derived chemicals, may be found in numerous wastewater and drinking water sources [140]. It has been observed that phenol-based compounds are widely utilized in the manufacturing of diverse industrial items, such as pulp, paints, plastics, home cleaners, medicines, insecticides, herbicides, tinned goods, petrochemicals, and synthetic rubbers [141]. Although these substances are often used, however they are dangerous and have the potential to cause cancer. Even in extremely little amounts, they seriously endanger the liver, kidneys, and endocrine system [142]. Due to their toxicity, phenol derivatives have become one of the most common organic pollutants found in water. Quantities ranging from 1 mg/L to 7000 mg/L have been found to exist in wastewater. Even at relatively modest concentrations, such as a few $\mu\text{g/L}$, phenol can nevertheless have a detrimental effect on the taste and odour of drinking water [143]. Because of the detrimental effects of phenol, the Environmental Protection Agency (EPA) has set a maximum permissible

concentration of phenol in surface waters at less than 1 part per billion (ppb). According to European Union (EU) regulations, the maximum amount of phenols allowed in drinking and natural waters in Italy is 0.5 ppb, or 0.5 g L⁻¹. [143]. Both EU and EPA have declared phenol-based chemicals, specifically chlorophenols and nitrophenols, as priority pollutants [144]. Previous research has demonstrated that these phenols decomposed chemically and thermally, and lead to the production of hazardous materials. These chemicals exhibit substantial health risks, including genome damage, genetic mutation, carcinogenicity, and other potential concerns [140], [145]. Therefore, to make sure the safety of human beings, there has been a greater emphasis on monitoring the substances in various samples.

The determination of phenols has been done by the advancement of many analytical methods, including electrochemical techniques, gas chromatography (GC), and high-performance liquid chromatography (HPLC) and capillary electrophoresis [146]–[148]. HPLC is widely preferred over all other methods for more accuracy due to its greater sensitivity, quick separation, and exceptional resolution. The main disadvantage of this technique is that due to the intrinsic polarity, phenols faced difficulty in transferring from aqueous to organic phase. The fact that these phenolic compounds can establish hydrogen bonds with the stationary phase is another significant problem. Therefore, in order to lessen the constraints and increase the extraction efficiency, a derivatization step must be completed before analysis [149]. For a derivatization step, acetylation reaction in an alkaline aqueous solution is usually done by using acetic anhydride. As phenolic materials are very small in concentration in these types of solutions, so for the valid outcomes pre-treatment of samples and the

analyte concentration are necessary. Because of matrix effects and the low amounts of phenolic chemicals in the samples, a rapid and efficient extraction technique is required to adequately verify the analyte prior to analysis [150]. Various advanced approaches have been discovered for this purpose such as hollow fiber-liquid phase microextraction, cloud-point extraction, solid-phase or liquid-liquid extraction [151], [152] supramolecular solvent-based extraction [153], and ultrasound-assisted emulsification microextraction [154]–[156]. However, they are not fully-developed yet and used oftenly for the determination of only one phenol or its derivatives.

Solid phase extraction (SPE) procedures are becoming increasingly popular and have several great advantages, such as a high degree of reusability, a convenient strategy, and a reduced need for organic solvents. In comparison to liquid-liquid extraction (LLE), SPE offers a wide range of modes that considerably enhance its application. Their multiple benefits of SPE over traditional techniques contributed to its initial deployment in the 1940s, and its rapid expansion in the 1970s across a wide range of fields. In this, the sorbent is embedded into the cartridge, and the sample passes over it. This procedure is effective, but there are chances that the cartridge faces obstruction during the overall process [157]. The development of a miniaturized μ -SPE is the best and effective approach among various efforts such as stir bar sorption, solid-phase microextraction (SPME), and headspace solid-phase microextraction. It is also acknowledge as porous membrane-protected μ -SPE, and was discovered in 2006 by Basheer et al. [97]. The device used in this is small, having membrane-encased bag, which holds a small quantity of sorbent material. It is well-suited for turbidity and is essential for opting for less solvent consumption as well as preventing particle and

macromolecule contamination through the use of porous membranes in sorbent materials. On top of that, these materials are usually constructed from inexpensive and easy-to-use components [158]. For extraction procedures to achieve optimal accuracy, it is significant to choose the suitable adsorbent. Modern innovations in sample preparation have paved the way for the development of numerous novel materials, like adsorbents, that enhance the extraction of analytes from samples [55]. Recently, carbon or silica based materials, magnetic nanoparticles, aptamer-modified sorbents, electrospun nanofibers, immunosorbents, metal-organic frameworks, ion imprinting polymers (IMP), restricted-access materials (RAM), and molecularly imprinted polymers (MIP) have been used as adsorbent [159]–[164]. Among them, ordered mesoporous silica materials have a large surface area, which increases their loading capacity; they are very stable chemically and mechanically. They can interact strongly with analytes, which could increase their affinity; and they are synthesized from inexpensive raw materials. Moreover, other unique qualities of these materials, such as their compatibility with living things, ease of functionalization, and porosity, make them very desirable [165].

Numerous materials based on silica have been built, including the MCM family. The MCM-41 in this series has a hexagonal phase, the MCM-48 a cubic phase, and the stacked MCM-50 a stacked cubic phase [166], [167]. Further, a new kind of mesoporous silica known as SBA-15 (Santa Barbara Amorphous-15) was developed, which enables precise control of pore size and alignment through adjustments to the reactant ratios [165]. The development of KCC-1 (KAUST Catalysis Center-1), which is the fibrous mesoporous silica nanosphere is another noteworthy establishment. The

material has shown effective adsorption of Hg (II) from water solutions, and it was synthesized using a straightforward sol-gel-hydrothermal process that involves ultrasonication [168]. These materials have distinctive fibrous structure, show macroscopic tunneling effects, having particular surface area, volume, and quantum size [169]. The unique consistent pore size, pore structure, and adjustable chemical and physical properties of these materials make them an excellent choice for phenol removal from wastewater. This research is also focused on the development and implementation of fibrous silica materials for phenol extraction using the μ -SPE method. Our research centred on several phenols isolated from wastewater, including 2,3-DCP; 3,4-DCP; 2,4,6-TCP; 4-BP and 4-NP. Fibrous silica (FS), FS with aniline-containing polymer, FS with amine-containing polymer, and FS incorporating the both polymers are the silica-based materials that have been developed and evaluated for this purpose. Additionally, we investigated many factors that impacted the efficiency of extraction. Our research indicates that the best extraction efficiency was achieved by combining fibrous silica with both polymers. It is interesting to note that no research was found in the literature that addressed the topic of determining these different phenols in wastewater by means of the using sorbents via μ -SPE approach.

3.2. Experimental

3.2.1. Chemicals and materials

All phenolic compounds, including 2,3-Dichlorophenol (2,3-DCP), 3,4-Dichlorophenol (3,4-DCP), 2,4,6-Trichlorophenol (2,4,6-TCP), 4-Bromophenol (4-BP), and 4-Nitrophenol, as well as hexadecyltrimethylammonium bromide (CTAB), urea, tetraethyl orthosilicate (TEOS), acetonitrile (ACN), disodium phosphate (Na_2HPO_4), methanol (MeOH), N-[3-(Trimethoxysilyl)propyl]aniline, and N¹-(3-Trimethoxysilylpropyl)diethylenetriamine, were all purchased from Sigma-Aldrich. Toluene was obtained from Chemlab, and butanol was sourced from Fulka.

Wastewater samples were collected from the Alkhobar sewage treatment plant in Saudi Arabia before discharge into the Corniche Sea. Deionized water was prepared using a purification system from VWR International. Additionally, a 0.22 μm porosity polypropylene membrane, used for filtration, was acquired from Tisch Scientific Company.

Preparation of sol-solution

The sol-solution was prepared by vortexing a sol-gel active polymer BHEA 200 μL with 200 μL ethanol in a microcentrifuge tube for 30 s. The sol-gel active precursor YMEO (100 μL) and 8.0 μL water were added to the reaction mixture and vortex for 90 s. The sol-solution was then ready for the coating inside the fused silica microextraction capillary.

3.2.2. Synthesis of the Sorbents

Four different sorbents were synthesized: (1) fibrous silica (FS), (2) FS functionalized with N¹-(3-Trimethoxysilylpropyl) diethylenetriamine (FS-Amine), (3) FS functionalized with N-[3-(Trimethoxysilyl) propyl] aniline (FS-Aniline), and (4) FS functionalized with both silane coupling agents (FS-Mix).

FS was prepared using a modified synthesis approach involving CTAB and urea. Initially, 5.829 g of CTAB and 3.4819 g of urea were dissolved in 173.063 mL of water, and the solution was stirred at 25 °C for 5 minutes. Then, 8.5 mL of butanol and 173.912 mL of toluene were added, and the mixture was stirred for an additional 45 minutes at 25 °C. Tetraethyl orthosilicate (TEOS, 13.1506 mL) was introduced dropwise, and the reaction continued for 6 hours at 25 °C. The mixture was then heated in an oven at 100 °C for 10 hours. The product was centrifuged and thoroughly washed with deionized water and ethanol, dried overnight at 100 °C, crushed into a fine powder, and calcined in a muffle furnace at 550 °C for 6 hours to yield FS.

For the functionalization steps, FS was modified with different silane coupling agents. To prepare FS-Amine, 0.23 g of FS was suspended in 50 mL of ethanol with a few drops of HCl. To this mixture, 1 mL of deionized water and N¹-(3-Trimethoxysilylpropyl) diethylenetriamine were added. The reaction was stirred for 24 hours, followed by centrifugation and washing with deionized water and ethanol. The final product was dried at 90 °C.

The same procedure was used to prepare FS-Aniline, substituting N¹-(3-Trimethoxysilylpropyl) diethylenetriamine with N-[3-(Trimethoxysilyl)propyl] aniline. The resulting material was similarly stirred, washed, and dried.

Finally, FS-Mix was synthesized by adding both silane coupling agents simultaneously to the reaction mixture. The process involved stirring for 24 hours, centrifuging, washing with deionized water and ethanol, and drying at 90 °C.

3.2.3. Characterization of the Sorbents

The synthesized sorbents, including FS, FS-Amine, FS-Aniline, and FS-Mix, were characterized using a range of techniques to evaluate their physico-chemical properties.

X-ray diffraction (XRD) analysis was conducted using a Rigaku Ultima IV diffractometer with a Cu anode, operating at 40 kV and 30 mA, to assess the crystallinity and structural order of the materials. Fourier Transform Infrared Spectroscopy (FTIR) was performed with a Nicolet 6700 Thermo Electron spectrometer to identify the functional groups present on the surface of the materials. The surface morphology was examined using a Field Emission Scanning Electron Microscope (FE-SEM, Jeol 6700LV). Thermogravimetric Analysis (TGA) was also conducted to assess the thermal stability and decomposition behavior of the sorbents. TGA measurements were carried out using a thermogravimetric analyzer, heating the samples from room temperature to 800 °C at a rate of 10 °C per minute under a nitrogen atmosphere.

3.2.4. Micro-SPE Procedure

The micro-solid phase extraction (μ -SPE) method utilized in this study involved a polypropylene membrane measuring 0.5 cm by 0.5 cm. The membrane was sealed on three sides using a heat-sealing device, forming a pouch-like structure. A small magnet and the sorbent material were then carefully inserted into the pouch, and the fourth side was sealed to complete the enclosure.

Prior to extraction, the prepared membrane pouch was activated by immersing it in toluene. This activation step was confirmed visually, as the membrane changed from an opaque white to a transparent appearance. The activated pouch was subsequently immersed in the sample solution, allowing the analytes to migrate from the aqueous phase and adsorb onto the sorbent material inside the membrane.

Once the extraction process was complete, the pouch was removed from the sample, gently dried using laboratory tissue to remove excess moisture, and then transferred into a small volume of organic solvent (200-500 μ L). The pouch was sonicated for a defined period to facilitate desorption, during which the analytes detached from the sorbent material and dissolved into the organic solvent. The desorbed analytes, now concentrated in the organic solvent, were ready for analysis. Finally, the sample was injected into a high-performance liquid chromatograph (HPLC) equipped with a UV-Vis detector for quantitative analysis.

3.2.5. Optimization of Micro-SPE Parameters

The micro-SPE procedure was optimized using a univariate approach to ensure maximum extraction efficiency. The optimization process involved evaluating various parameters, including sorbent dosage, extraction time, desorption time, and the selection and volume of desorption solvents. Sorbent dosages were tested across a wide range to determine the most effective amount for adsorption. Extraction times were systematically varied to optimize the duration needed for efficient analyte uptake.

Desorption parameters were also carefully examined, focusing on the duration of desorption and the choice of solvents. A variety of desorption solvents, such as acetonitrile (ACN), deionized water (DI), methanol (MeOH), and mixtures of ACN with buffer

solutions at different ratios, were explored. Additionally, the volume of the desorption solvent was fine-tuned to maximize analyte recovery. This thorough investigation aimed to identify the optimal conditions that would enhance the overall efficiency of the micro-SPE method.

3.2.6. High-Performance Liquid Chromatography (HPLC) Analysis

The analysis of phenolic compounds was conducted using a Thermo Ultimate HPLC 3000 system equipped with a C18 column (4.6 × 250 mm, 5 µm particle size). The mobile phase consisted of 50% sodium phosphate buffer (Na₂HPO₄) and 50% acetonitrile (ACN), delivered in isocratic mode at a flow rate of 1.0 mL/min.

The column oven temperature was maintained at 35 ± 1 °C to ensure consistent separation. The detection was performed using a UV-Vis detector set at 220 nm. Each sample injection volume was 20 µL, and the total run time for the analysis was 20 minutes.

3.2.7 Analytical Method Validation and Real Sample Analysis

The analytical method was validated using calibration curves constructed for each analyte. Calibration curves were generated by plotting peak area against concentration over a linear range, ensuring an R² value close to 1. Three concentration points, representing the lower, middle, and higher ends of the range, were selected for precision and accuracy assessment.

The limits of detection (LOD) and quantification (LOQ) were determined to assess the sensitivity of the method. The LOQ was defined as the lowest concentration at which

the relative standard deviation (RSD%) was $\leq 5\%$, ensuring reliable quantification. The LOD was calculated as the LOQ divided by 3.3. [170].

Real sample analysis was performed on wastewater collected from the Alkhobar sewage treatment plant. The samples were first extracted without spiking to check for native analytes, followed by spiking at selected concentrations to evaluate the method's reproducibility. The extraction was repeated in triplicates, and RSD% values were calculated to confirm method precision.

3.3. Results and discussion

3.3.1. Material chemistry and characterization:

A. Powder X-ray Diffraction (PXRD)

The crystalline structure and phase stability of the fibrous silica materials (FS, FS-Amine, FS-Aniline, and FS-Mix) were analyzed using powder X-ray diffraction (PXRD). The XRD patterns are shown in (Figure 23).

The unmodified fibrous silica (FS) exhibited broad diffraction peaks, characteristic of amorphous silica, centered around $2\theta = 20^\circ\text{--}30^\circ$, indicating the presence of a non-crystalline structure. After functionalization with N^1 -(3-Trimethoxysilylpropyl) diethylenetriamine (FS-Amine), a slight broadening and decrease in peak intensity were observed, which is consistent with the introduction of organic moieties onto the silica surface, causing partial disruption of the silica network.

Similarly, FS functionalized with N-[3-(Trimethoxysilyl)propyl] aniline (FS-Aniline) displayed a comparable broadening of the diffraction pattern, with some variations in peak intensity, further confirming successful surface modification. The FS-Mix, which incorporates both functional groups, demonstrated the most pronounced changes in peak intensity and broadening, suggesting that the dual functionalization had a cumulative effect on the silica structure.

Overall, the XRD analysis indicates that while the functionalization processes altered the structural characteristics of fibrous silica, the fundamental amorphous nature of the silica framework was preserved. The changes in peak intensity and width confirm the successful grafting of the functional groups onto the silica surface.

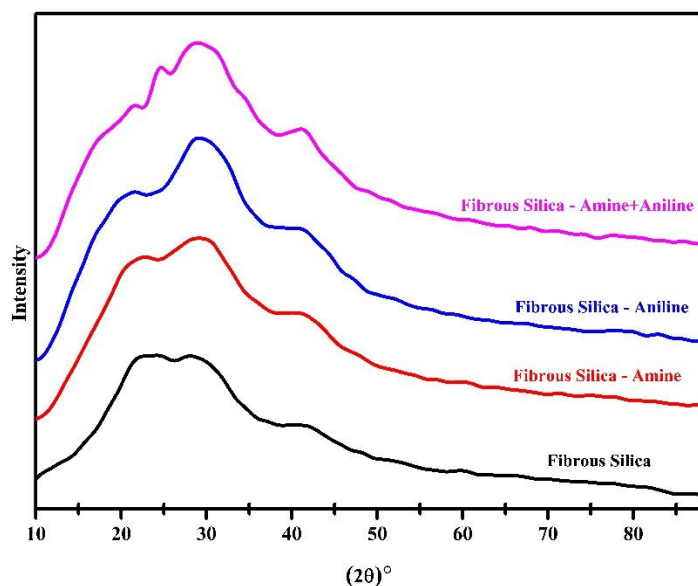


Figure 23: pXRD for FS, FS-Amine, FS-Aniline and FS-Mix

B. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy was employed to identify the functional groups present on the surfaces of the synthesized fibrous silica materials (FS, FS-Amine, FS-Aniline, and FS-Mix). The FTIR spectra are presented in (Figure 24).

The unmodified fibrous silica (FS) exhibited characteristic bands at approximately 1080 cm^{-1} and 800 cm^{-1} , corresponding to the asymmetric and symmetric stretching vibrations of Si-O-Si bonds, respectively. A broad absorption band centered around 3400 cm^{-1} was observed, attributed to the stretching vibrations of surface hydroxyl groups (-OH) and adsorbed water molecules. Additionally, the band at 960 cm^{-1} was assigned to the stretching of Si-OH groups.

Upon functionalization with N^1 -(3-Trimethoxysilylpropyl) diethylenetriamine (FS-Amine), new absorption bands appeared at approximately 1570 cm^{-1} and 1470 cm^{-1} , corresponding to the bending vibrations of N-H bonds and the stretching vibrations of C-N bonds, respectively, confirming the presence of amine functional groups [2]. The intensity of the Si-O-Si bands remained strong, indicating that the silica framework was preserved.

The FTIR spectrum of FS functionalized with N-[3-(Trimethoxysilyl) propyl] aniline (FS-Aniline) displayed additional peaks at approximately 1490 cm^{-1} and 1600 cm^{-1} , corresponding to the aromatic ring stretching vibrations, confirming the successful attachment of the aniline functional groups [171]. The characteristic Si-O-Si and Si-OH bands were also present, demonstrating that the silica structure remained intact. For FS-Mix, which incorporated both amine and aniline functionalities, the FTIR spectrum showed combined features of both functional groups. Peaks corresponding to N-H, C-N, and

aromatic ring vibrations were clearly observed, indicating successful dual functionalization. The overall spectra confirmed that the surface modification of fibrous silica was achieved without significant disruption to the silica network.

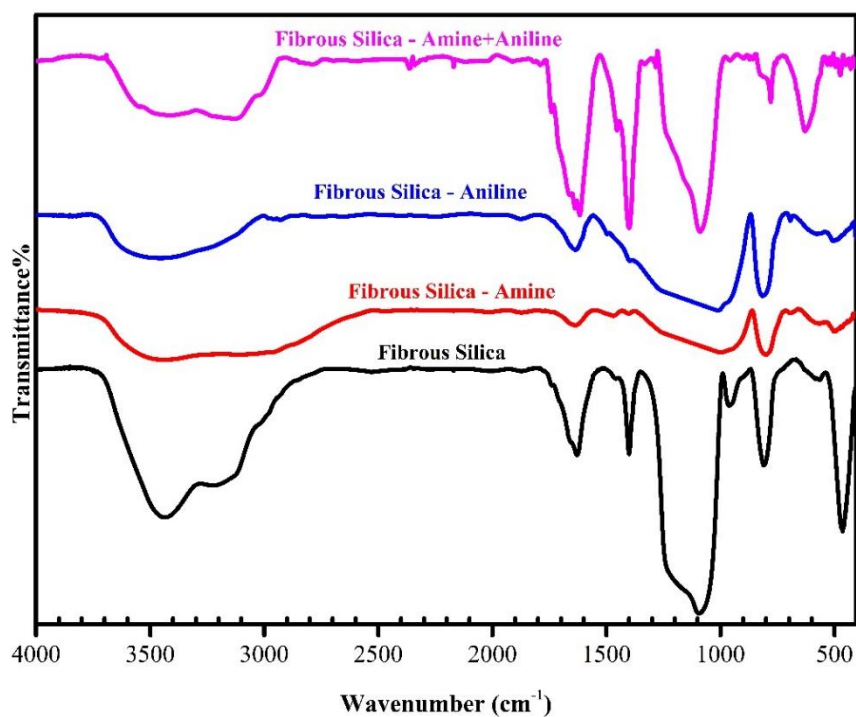


Figure 24: FTIR for FS, FS-Amine, FS-Aniline and FS-Mix

C. Scanning Electron Microscopy (SEM)

The surface morphology of the fibrous silica materials (FS, FS-Amine, FS-Aniline, and FS-Mix) was analyzed using Scanning Electron Microscopy (SEM), as shown in (Figure 25). The SEM images reveal the unique fibrous structure and morphological features of the synthesized sorbents. The unmodified fibrous silica (FS) displayed a spherical morphology with a uniform size distribution and a distinct fibrous surface texture. The fibers radiate outward from the center of each particle, creating a high surface area that is ideal for adsorption applications. Upon functionalization with N1-(3-Trimethoxysilylpropyl) diethylenetriamine (FS-Amine), the spherical structure and fibrous texture were preserved. However, a slight increase in surface roughness was observed, which is indicative of successful surface modification and the attachment of the amine functional groups. The SEM image of FS-Aniline showed a similar fibrous texture, with well-defined spheres and no significant aggregation. The fibrous morphology was maintained, and the surface appeared slightly rougher compared to the unmodified FS, suggesting successful functionalization with aniline groups. For FS-Mix, the SEM image revealed a more pronounced roughness and textural variation on the surface of the fibrous spheres. The combined functionalization with both amine and aniline groups resulted in a more complex surface structure, which may enhance the material's adsorption capabilities.

Overall, the SEM analysis confirms that the fibrous morphology of the silica particles was preserved after functionalization, while the increased surface roughness indicates the successful incorporation of functional groups.

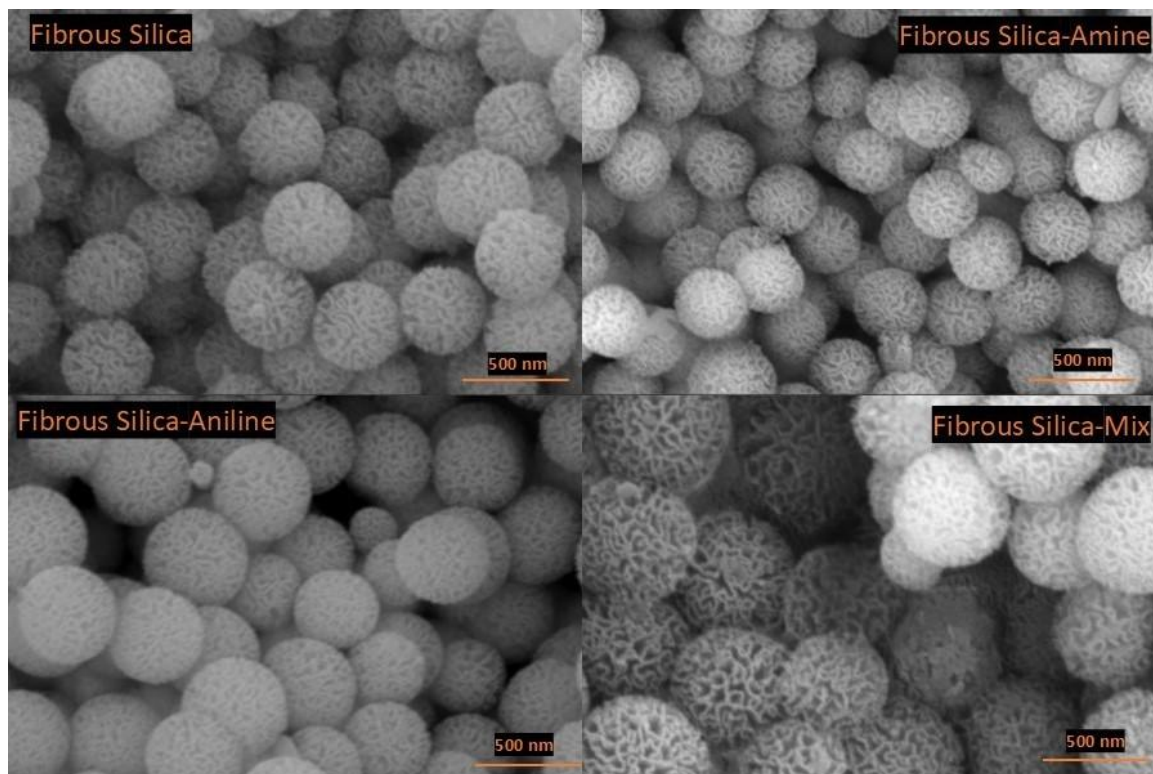


Figure 25: SEM for FS, FS-Amine, FS-Aniline and FS-Mix

D. Thermogravimetric Analysis (TGA)

The thermal stability of the synthesized fibrous silica materials (FS, FS-Amine, FS-Aniline, and FS-Mix) was evaluated using Thermogravimetric Analysis (TGA), as shown in (Figure 26). The weight loss of each sample was recorded as a function of temperature from room temperature to 800 °C.

The unmodified fibrous silica (FS) showed minimal weight loss, maintaining over 95% of its original weight up to 800 °C. This indicates excellent thermal stability, characteristic of silica-based materials.

In contrast, the functionalized materials (FS-Amine, FS-Aniline, and FS-Mix) exhibited more significant weight loss, primarily due to the decomposition of the organic functional groups attached to the silica surface. FS-Amine showed a weight loss of approximately 10% between 200 °C and 400 °C, corresponding to the thermal decomposition of the amine groups. FS-Aniline displayed a similar thermal degradation pattern, with a weight loss of around 8% in the same temperature range, attributed to the breakdown of the aniline groups.

The FS-Mix sample, functionalized with both amine and aniline groups, exhibited the most pronounced weight loss, with a reduction of approximately 15% between 200 °C and 500 °C. This reflects the combined effect of both functional groups decomposing under heat. Beyond 500 °C, the weight of all functionalized samples remained relatively stable, indicating that the remaining silica structure was thermally robust.

Overall, the TGA results confirm that the functionalization of fibrous silica introduces organic components, which reduce thermal stability compared to the unmodified silica. However, the thermal stability of the functionalized materials remains adequate for use in micro-solid phase extraction (μ -SPE) processes, where elevated temperatures are not typically encountered.

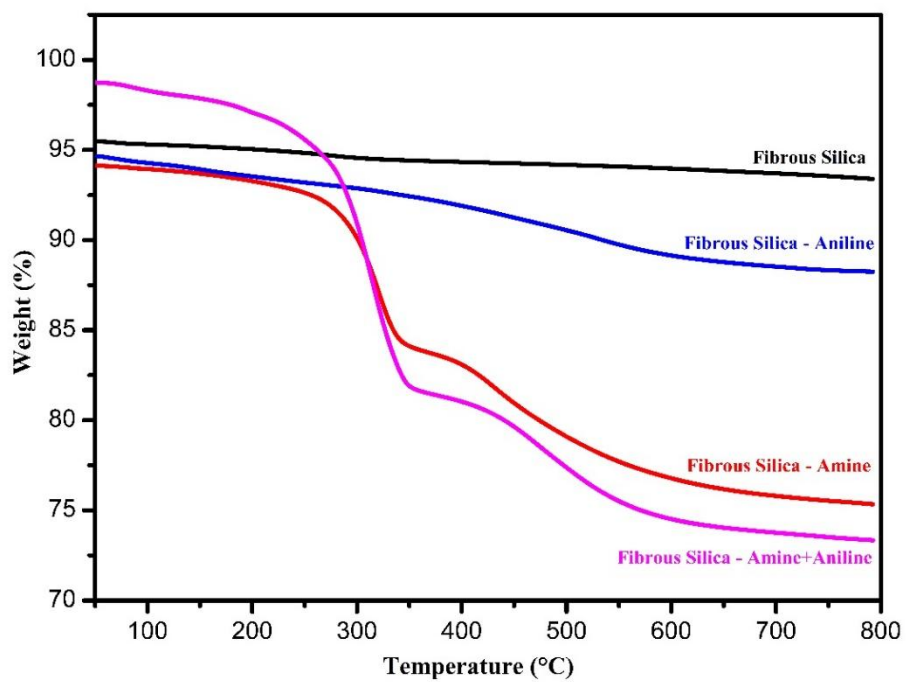


Figure 26: TGA for FS, FS-Amine, FS-Aniline and FS-Mix

3.3.2. Optimization of Extraction process

Optimization was performed using a univariate approach to determine the optimal conditions for phenol extraction.

A. Comparison of Phenol Extraction Efficiencies Across Sorbents

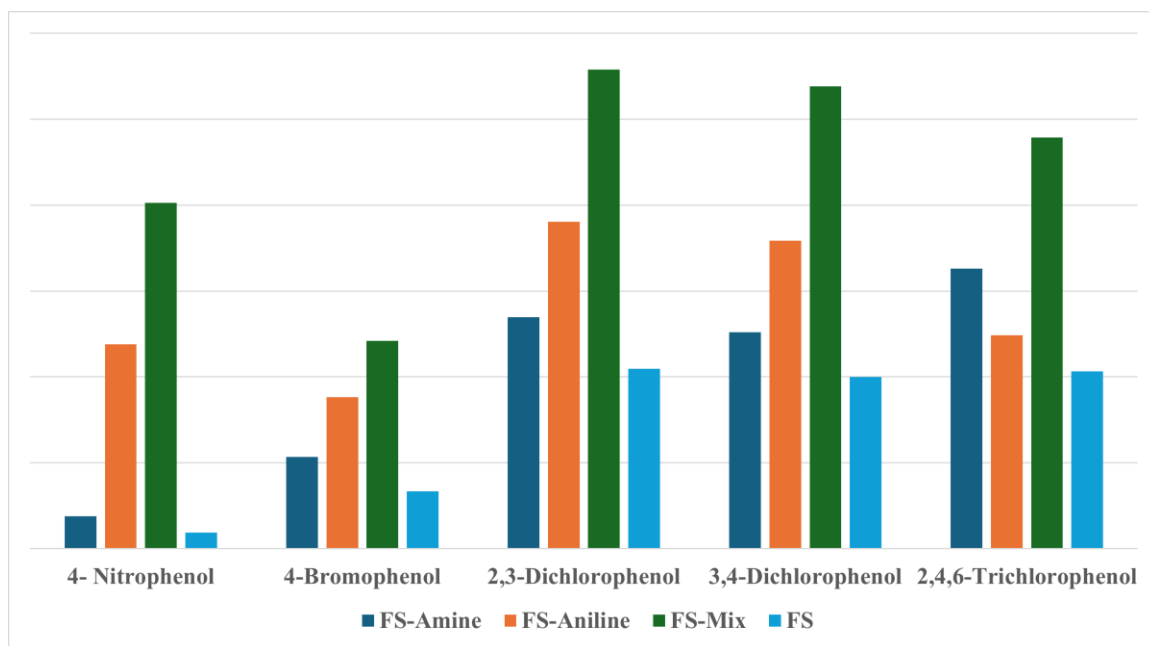


Figure 27 Extraction performance of different sorbent Materials. Conditions: Phenols mix concentration: 0.8 ng mL⁻¹; sorbent mass: 30 mg; extraction time: 10 min; desorption solvent: methanol; desorption volume: 400µL; desorption time: 10 min.

The bar graph (Figure 27) illustrates the extraction efficiencies of FS, FS-Amine, FS-Aniline, and FS-Mix for five phenolic compounds: 4-Nitrophenol, 4-Bromophenol, 2,3-Dichlorophenol, 3,4-Dichlorophenol, and 2,4,6-Trichlorophenol.

FS-Mix exhibited the highest extraction efficiency across most phenols, particularly for 2,3-Dichlorophenol and 3,4-Dichlorophenol. Its dual functionalization

provided enhanced hydrogen bonding and π - π interactions, as observed in the characterization results. FS-Aniline showed intermediate efficiency, particularly excelling with phenols that favor aromatic interactions, while FS-Amine had the lowest performance, likely due to reduced surface accessibility and fewer adsorption sites.

The unmodified FS demonstrated moderate extraction efficiency, highlighting the significant role of functionalization in improving sorbent-analyte interactions. These results reaffirm the superior performance of FS-Mix in μ -SPE applications.

B. Effect of Sorbent Dosage on Phenol Extraction Efficiency

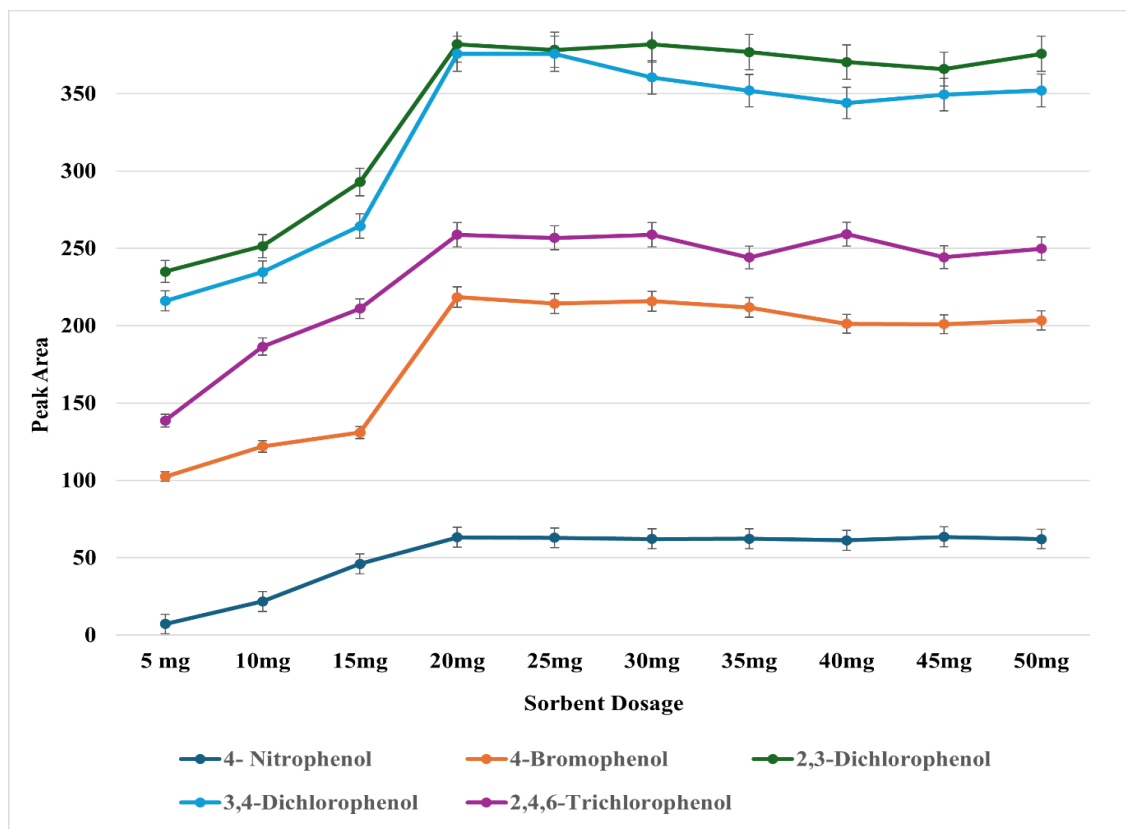


Figure 28: Impact of Sorbent (FS-Mix) Quantity on Extraction Performance.
Conditions: Phenols mix concentration: 0.8 ng mL⁻¹; extraction time: 10 min;
desorption solvent: methanol; desorption volume: 400µL; desorption time: 10 min.

Figure 28 demonstrates the influence of sorbent dosage (5–50 mg) on the peak areas of five phenolic compounds.

The peak areas increased with sorbent dosage, reaching maximum efficiency at 20 mg for most phenols. Beyond this dosage, the extraction efficiency plateaued or slightly decreased, likely due to saturation of active sites on the sorbent. Among the compounds,

2,3-Dichlorophenol and 3,4-Dichlorophenol exhibited the highest peak areas, reflecting their stronger interactions with the sorbent.

These results indicate that 20 mg is the optimal sorbent dosage for maximizing phenol extraction while avoiding unnecessary material usage, thereby ensuring efficient micro-SPE performance.

C. Effect of Extraction Time on Phenol Extraction Efficiency

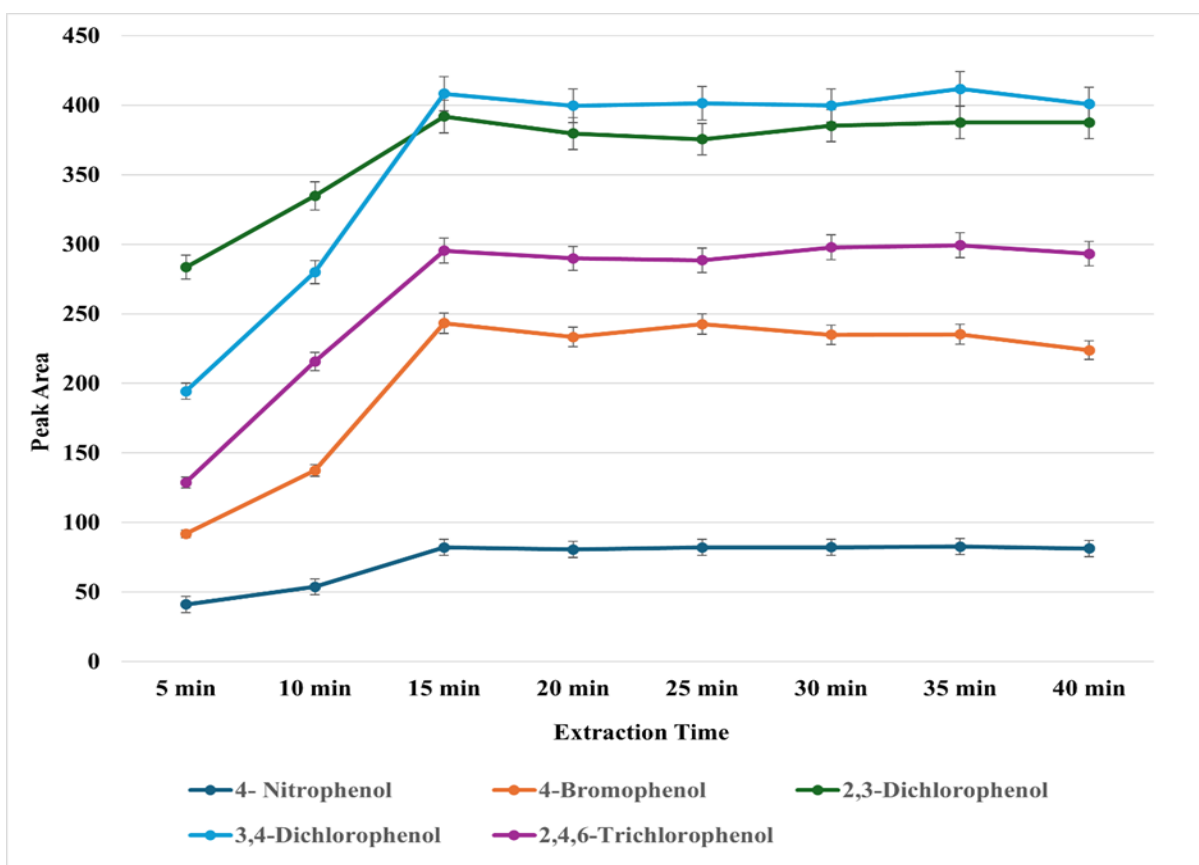


Figure 29: Effect of extraction time on the extraction efficiency of Phenols.

Conditions: phenols mix concentration: 0.8 ng mL⁻¹; sorbent mass: 20 mg;

desorption solvent: methanol; desorption volume: 400μL; desorption time: 10 min.

The micro-solid-phase extraction (μ -SPE) process relies on achieving equilibrium between the sorbent and the analytes to maximize extraction efficiency. While longer extraction durations can initially enhance analyte recovery, once equilibrium is reached, additional time yields minimal improvement and may lead to analyte desorption.

In this study, extraction times ranging from 5 to 40 minutes were evaluated. The highest peak areas for the target phenolic compounds were observed at 15–20 minutes, indicating that equilibrium was achieved during this period. Prolonging the extraction beyond 20 minutes showed negligible benefits and, in some cases, resulted in slight decreases in efficiency, likely due to sorbent saturation or analyte redistribution as shown in (Figure 29). Therefore, an extraction time of 15–20 minutes was established as optimal for phenol recovery.

D. Effect of Desorption Time on Phenol Extraction Efficiency

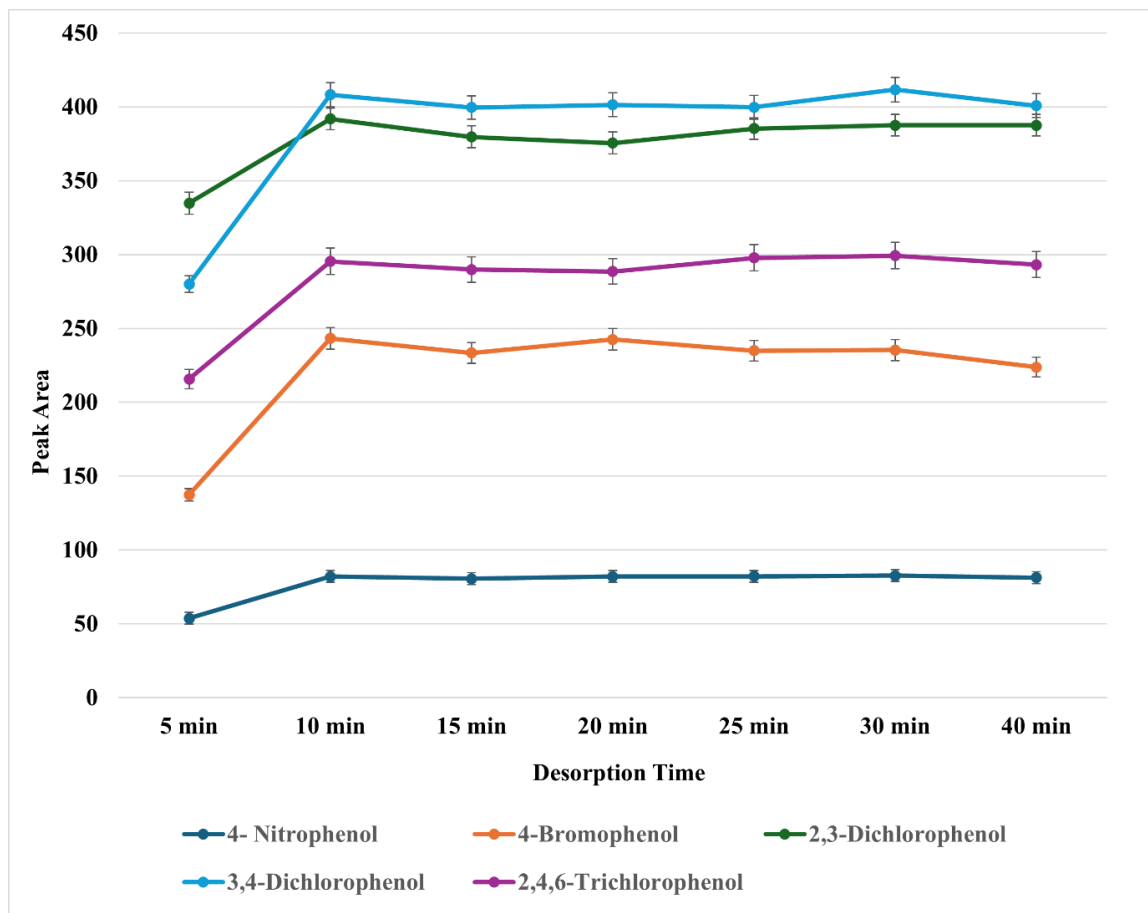


Figure 30: Effect of desorption time on the extraction efficiency of Phenols.

Conditions: Phenols mix concentration: 0.8 ng mL⁻¹; sorbent mass: 20 mg; extraction time: 15 min; desorption solvent: methanol; desorption volume: 400μL.

Figure 30 illustrates the impact of desorption time (5–40 minutes) on the peak areas of five phenolic compounds. The results reveal that the highest peak areas for most compounds were achieved at 10 minutes, marking the optimal desorption time. Beyond this point, increasing the desorption time offered no significant improvement. Thus, a desorption time of 10 minutes was identified as the most effective and practical.

E. Effect of Desorption Solvent Composition on Phenol Extraction

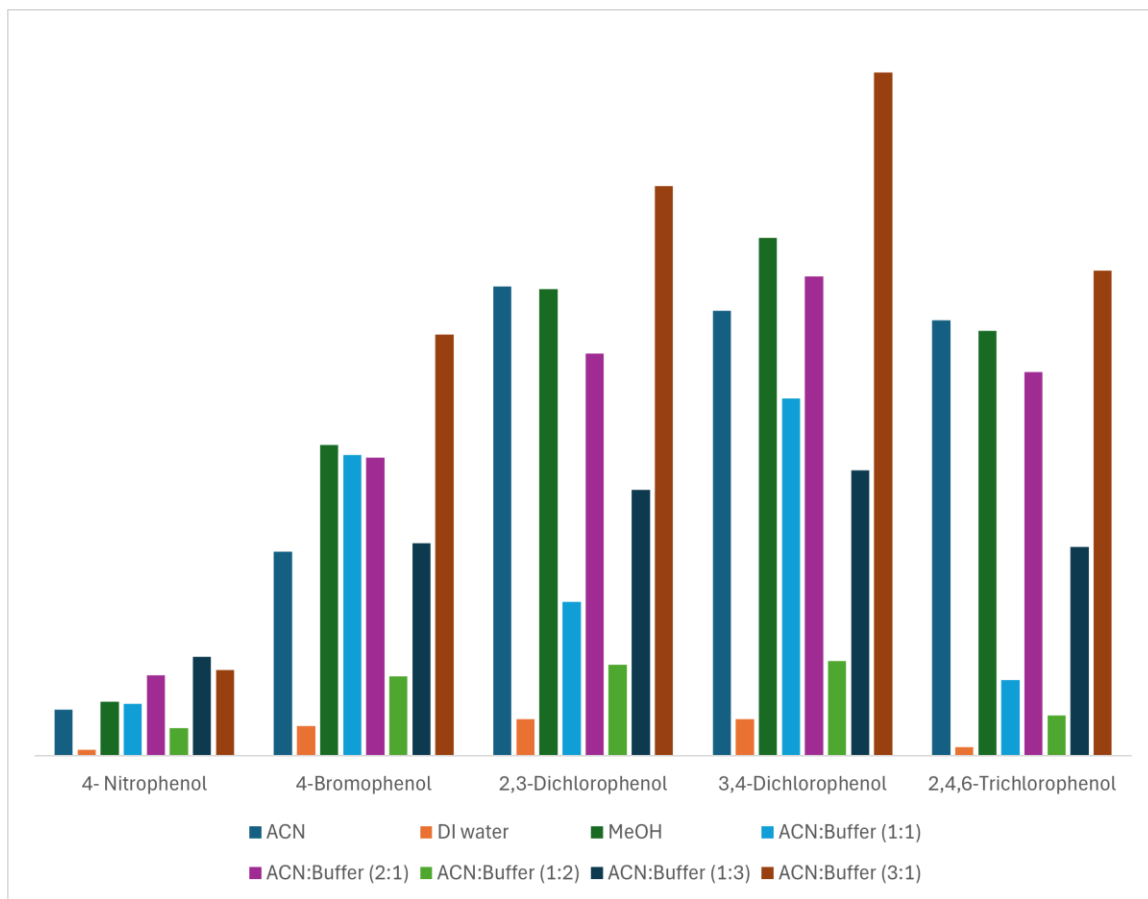


Figure 31: Testing different solvents for desorption of phenols. Conditions: phenols mix concentration: 0.8 ng mL⁻¹; sorbent mass: 20 mg; extraction time: 10 min; desorption volume: 400µL; desorption time: 10 min.

The study examined the efficacy of various desorption solvents with differing polarities for phenol recovery. These solvents ranged from deionized (DI) water, the least effective due to its high polarity and inability to disrupt sorbent-analyte interactions, to

acetonitrile (ACN) and methanol (MeOH), which demonstrated moderate efficiency. As shown in (Figure 31), the ACN-phosphate buffer mixture at a 3:1 ratio yielded the best performance. This can be attributed to its balanced polarity, which aligns well with the moderately polar nature of the phenols, facilitating efficient desorption.

F. Effect of Desorption Solvent Composition on Phenol Extraction

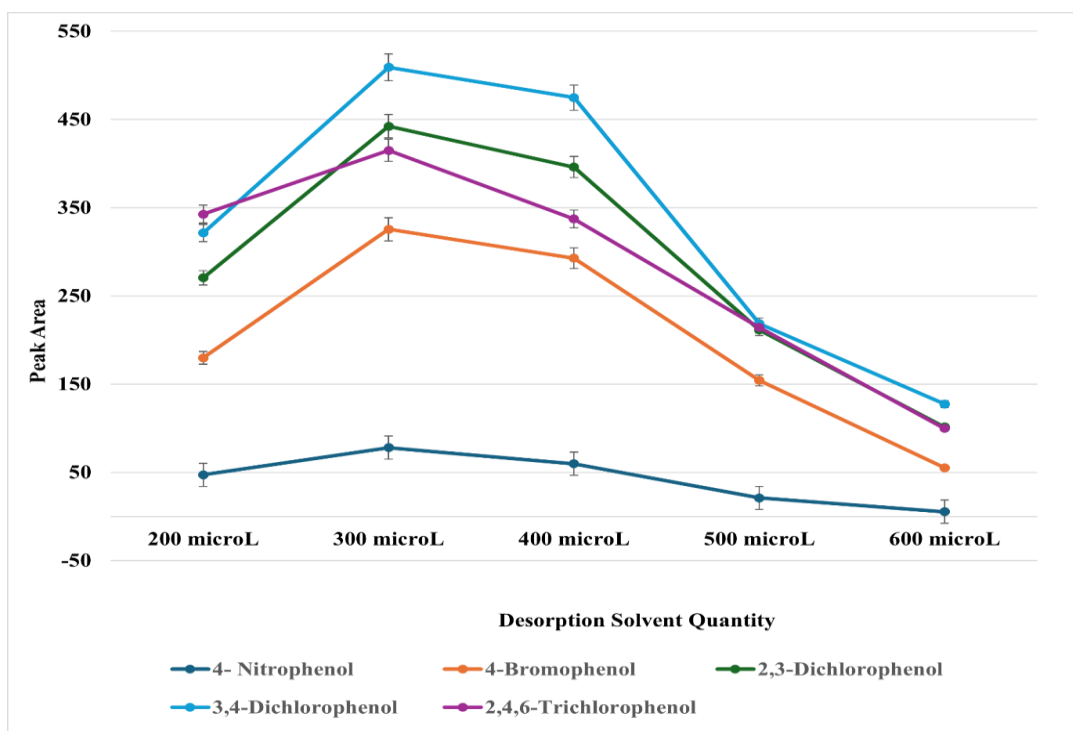


Figure 32: Effect of Desorption Solvent Quantity on the extraction efficiency of Phenols. Conditions: phenols mix concentration: 0.8 ng mL⁻¹; sorbent mass: 20 mg; extraction time: 15 min; desorption solvent: ACN:Buffer (3:1); desorption time: 10 min.

Figure 32 illustrates the impact of desorption solvent quantity (200–600 μL) on the peak areas of five phenolic compounds. Optimal phenol recovery was observed at 300 μL for all target analytes, with significant peak areas recorded. Increasing the solvent quantity beyond 300 μL resulted in a decline in peak areas, potentially due to the dilution effect reducing the analyte concentration in the desorbed solution. Conversely, using less than 300 μL may have limited analyte desorption due to insufficient solvent volume to interact with the sorbent effectively.

3.3.3 Method Validation and Real Sample analysis

The method's linearity in the range of 6.25–2000 ppb was established, with R^2 values ranging from 0.9968 to 0.9989, confirming strong correlation. The limits of detection (LOD) were determined to be within the range of 0.97–2.31 ppb, while the limits of quantification (LOQ) were calculated to be between 6.25–100 ppb. Precision testing was conducted using standards prepared in deionized water at three concentrations: one at the lower limit of linearity, one at the upper limit, and one mid-range, ensuring comprehensive coverage of the linear range. See **Table 6**.

Table 6: Analytical features for the μ -SBE of phenols using FS-Mix sorbent.

Analyte	R ²	Linear Equations	LOD ng.mL ⁻¹	LOQ ng.mL ⁻¹	RSDs (%) in DI water (n=3)		
					6.25 ng.mL ⁻¹	1000 ng.mL ⁻¹	2000 ng.mL ⁻¹
4- Nitrophenol	0.9968	$y = 0.0558x - 0.0009$	2.31	6.25	2.28	3.21	4.03
4-Bromophenol	0.9985	$y = 0.1348x - 0.0006$	1.45	2.5	1.73	3.13	3.76
2,3-Dichlorophenol	0.9988	$y = 0.1885x + 0.0017$	1.12	2.1	1.19	1.60	7.47
3,4-Dichlorophenol	0.9989	$y = 0.1659x + 0.0055$	1.02	1.9	1.13	1.29	2.61
2,4,6-Trichlorophenol	0.9979	$y = 0.1585x - 0.001$	0.97	1.24	3.04	4.26	5.25

Linear range = 6.25 – 2000 ppb

Table 7 demonstrates the detection and quantification of five phenols in wastewater samples. Among these, only two phenols—4-Nitrophenol and 4-Bromophenol—were detected, with concentrations of $1.601 \mu\text{g}\cdot\text{mL}^{-1}$ and $0.055 \mu\text{g}\cdot\text{mL}^{-1}$, respectively. The precision of the method was verified, yielding relative standard deviation (RSD%) values for wastewater analysis ranging from 4.00% to 4.66%.

The spiked wastewater samples were analyzed to evaluate relative recovery, achieving recovery rates ranging from 90.60% to 113.60% across all phenols and concentrations. Precision testing of spiked samples resulted in RSD% values between 0.08% and 18.50%, indicating the reliability of the μ -SPE method for phenol extraction and quantification.

$$\text{Relative recovery} = \frac{a}{b} \times 100$$

a = Peak area of the analyte extracted from wastewater samples,

b = peak area of the analyte extracted from deionized water.

Table 7: Real Sample analysis, N.D.: Not Detected

Analyte	Phenols detected in Wastewater sample. $\mu\text{g.mL}^{-1}$	RSDs (%) for Wastewater Analysis	Relative recovery of spiked phenols from wastewater			RSDs (%) of spiked phenols from wastewater (n=3)		
			6.25 ng.mL^{-1}	1000 ng.mL^{-1}	2000 ng.mL^{-1}	6.25 ng.mL^{-1}	1000 ng.mL^{-1}	2000 ng.mL^{-1}
4- Nitrophenol	1.601	4.66	109.35	92.70	109.54	12.58	7.08	8.57
4-Bromophenol	0.055	4.00	106.97	90.60	94.92	10.65	4.73	14.09
2,3-Dichlorophenol	N.D.	-	109.89	100.61	98.23	8.50	6.80	8.40
3,4-Dichlorophenol	N.D.	-	113.60	93.93	110.77	7.67	8.54	4.46
2,4,6-Trichlorophenol	N.D.	-	105.66	95.38	100.41	3.70	7.59	4.96

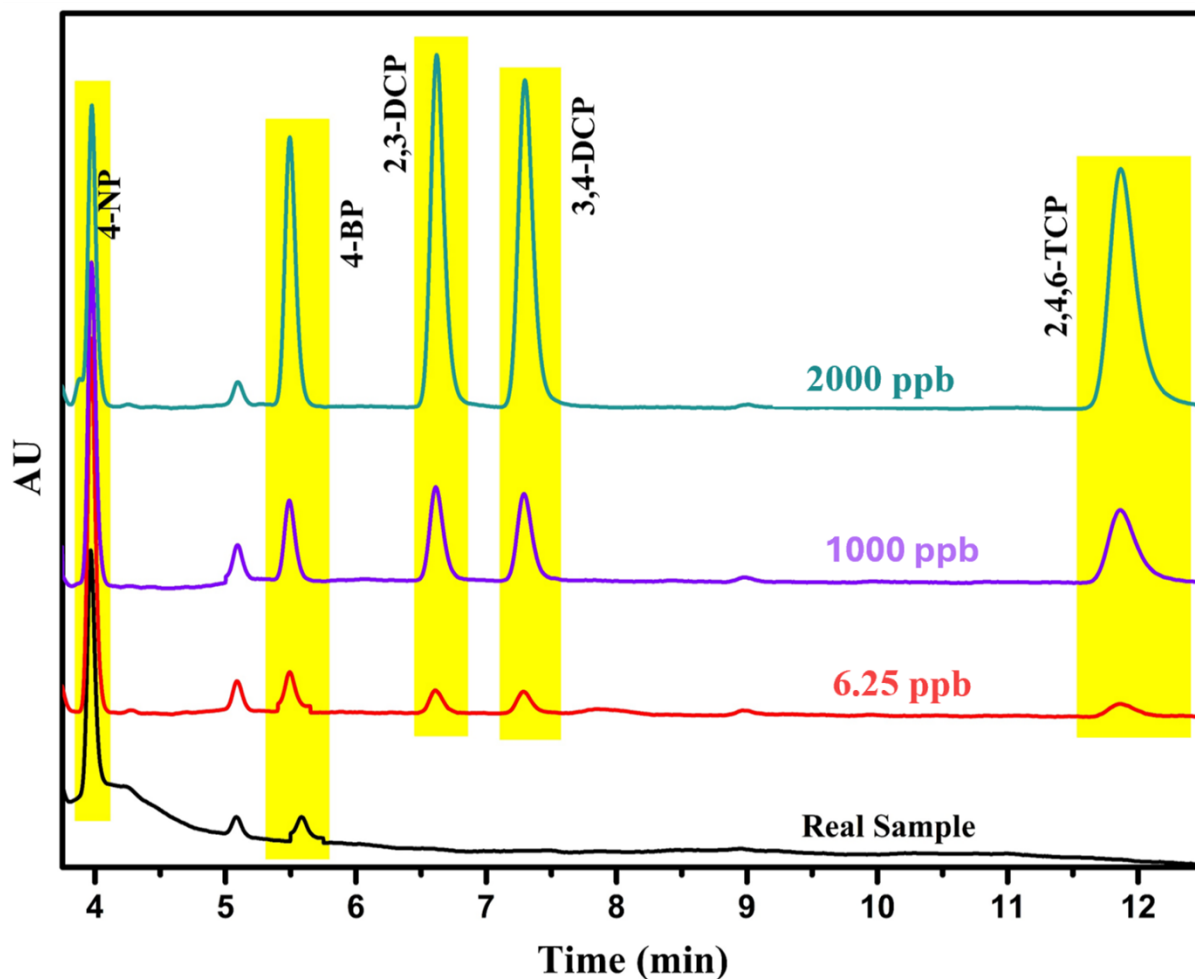


Figure 33: Overlaid chromatograms showing the extraction and detection of phenolic compounds (4-Nitrophenol (4-NP), 4-Bromophenol (4-BP), 2,3-Dichlorophenol (2,3-DCP), 3,4-Dichlorophenol (3,4-DCP), and 2,4,6-Trichlorophenol (2,4,6-TCP)) from wastewater samples. Spiked concentrations at 0.1 ppm, 0.4 ppm, and 4 ppm are compared with the real wastewater sample (unspiked).

3.4. Summary of the work

This study successfully employed functionalized fibrous silica-based sorbents in micro-solid-phase extraction (μ -SPE) to detect and quantify phenols from wastewater. The developed method demonstrated excellent analytical performance, with a linear detection range of 6.25 to 2000 ng/mL and low limits of detection (LOD) ranging from 0.97 to 2.31 ng/mL. High relative recovery rates between 90.60% and 113.60% were achieved, underscoring the method's precision and reliability. These results highlight the effectiveness and sensitivity of functionalized fibrous silica-based sorbents in μ -SPE applications for phenol analysis, offering a promising approach for monitoring water quality. Furthermore, the versatility of these materials suggests their potential applicability for extracting a broader range of environmental contaminants, emphasizing their relevance in water treatment and environmental sustainability.

Conclusion

This thesis highlights two innovative approaches to addressing environmental challenges related to water pollution. The first study explored the use of spent FCC catalysts as sustainable sorbents for membrane-supported micro-solid-phase extraction (μ -SPE) of pesticides from wastewater. Characterization revealed that the spent FCC catalysts possess a high surface area, porosity, and active adsorption sites, enabling effective preconcentration of pesticides. The optimized μ -SPE process demonstrated a wide linear range (5–1000 ng.mL⁻¹), low limits of detection (0.36–1.52 ng.mL⁻¹), and high recovery rates (84.9–99.5%). Pesticides including Isoprocab, Atrazine, Primicarb, Penconazole, Chlorfenapyr, and Mefenacet were successfully detected, highlighting the method's sensitivity and reliability. These results not only provide a cost-effective solution for pesticide extraction but also promote recycling industrial by-products, offering significant environmental and economic benefits.

The second study focused on developing fibrous silica (FS)-based sorbents for membrane-supported micro-solid-phase extraction (μ -SPE) of phenols. Among the synthesized sorbents—FS, FS-Amine, FS-Aniline, and FS-Mix—FS-Mix exhibited superior performance in extracting phenols such as 2,3-DCP, 3,4-DCP, 2,4,6-TCP, 4-BP, and 4-NP from wastewater. The method demonstrated a wide linear range (6.25 - 2000 ng.mL⁻¹), low limits of quantification (0.97 – 2.31 ng.mL⁻¹) and high recovery rates (90.6 – 113.6%). Reversed-phase HPLC analysis using a mobile phase of acetonitrile and phosphate buffer (1:1) facilitated the sensitive detection and quantification of these phenols. The study

demonstrates the potential of functionalized fibrous silica materials for advancing wastewater treatment technologies.

Overall, these studies underline the importance of developing sustainable, efficient, and cost-effective sorbents for water pollution mitigation. While the spent FCC catalysts demonstrated the feasibility of waste reuse for pesticide extraction, the fibrous silica materials showcased the promise of tailored nanostructures for selective contaminant removal. Both approaches contribute to a greener and more sustainable future, with potential scalability and adaptability for a wide range of environmental applications.

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Research Outcomes:

- I. Alsabbahen, S. I., et al. (2024). Pesticides Microextraction Using Spent Catalyst as Sorbent. Oblon Ref. 555996US. Patent submitted, Status: "Green Light."
- II. Recent Advancements in Porous Sorbent Materials and Micro Solid-phase Extraction (μ -SPE) Modification for Improved Pesticide identification in Wastewater. (Under Review)
- III. Spent FCC Catalyst in Pesticides Microextraction: A Sustainable Approach towards Waste Recycling/Reuse. (Under Review)
- IV. Efficient μ -SPE and HPLC Quantification of Phenols from Wastewater Using Functionalized Fibrous Silica-Based Sorbents. (To be submitted)

Notable Contributions and Awards:

- I. Presented a poster at the 32nd Saudi-Japan Annual Symposium (Nov, 2023)
- II. Recognized for Excellence in Performance as a Teaching Assistant (Dec, 2023)
- III. Participated in the Annual Chemistry Poster Competition (Apr, 2024)
- IV. Achieved 3rd Place in the Early Career Research Competition. (Oct, 2024)
- V. Engaged in TechShift Hackathon 2024 from Saudi Aramco (Oct, 2024)