DEVELOPMENT OF MAGNETIC GRAPHENE OXIDE-DEEP EUTECTIC SOLVENT BASED FERROFLUIDS FOR THE DETERMINATION OF SELECTED ORGANOPHOSPHORUS PESTICIDES IN WATER SAMPLES

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by

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LIST OF SYMBOLS

q_m	Maximum adsorption capacities	mg g^{-1}
C_e	Equilibrium concentrations	mg L^{-1}
v	Volume of the analyte	L
w	Mass of adsorbent used	g
q_e	Adsorption capacity at equilibrium	mg g^{-1}
q_t	Adsorption capacity at contact time	mg g^{-1}
t	Contact time	min
K_1	Pseudo-first order rate constant	min^{-1}
K_2	Pseudo-second order rate constant	g mg^{-1} min^{-1}
h	Initial adsorption rate constant	mg g^{-1} min^{-1}
K_{dif}	Intra-particle diffusion constant rate	mg g^{-1} $min^{-0.5}$
C_{dif}	Intra-particle diffusion constant	mg g^{-1}
K_{ext}	External diffusion constant rate	min^{-1}
C_{dif}	External diffusion constant	min^{-1}
C_i	Solute concentration in the initial solution	mg L^{-1}
C_t	Solute concentration in the liquid phase at time t	mg L^{-1}

Δq (%)	Normalized standard deviation	-
q_e exp	Experimental adsorption capacity	mg g^{-1}
q_e cal	Calculated adsorption capacity	mg g^{-1}
n	Number of data points or measurements	-
b	Langmuir constant	mg L^{-1}
R_L	Dimensionless separation factor	-
K_{fr}	Freundlich adsorption constant	$(mg/g)(L/g)^{1/n}$
n_{fr}	Degree of non-linearity	-
K_t	Equilibrium binding constant	L mg^{-1}
T	Temperature	K
R	Gas constant	$Jmol^{-1}K^{-1}$
b_t	Temkin isotherm constant	J mol^{-1}
K_{dr}	Dubinin–Radushkevich constant	mol^2 KJ^{-2}
E	Adsorption free energy	J mol^{-1}
K_h	Halsey isotherm constants	-
N_h	Halsey isotherm constants	-
$\Delta G°$	Gibbs free energy	kJ mol^{-1}

$\Delta H°$	Enthalpy	kJ mol^{-1}
$\Delta S°$	Entropy	J mol^{-1} K^{-1}
K_L	Ratio of concentration at equilibrium	m^3 mol^{-1}
m	Slop	-
c	Intercept	-
$\bar{x}$	Mean of the peak areas	-
x	Result of the peak area for each run	-
Ms	Saturation magnetisation	emu/g

LIST OF GREEK LETTERS

π	Pi	-
λ	Lambda represents wavelength	nm
θ	Theta represents Bragg angle	°
α	Alpha represents Elovich adsorption constant	mg g^{-1} min^{-1}
β	Beta represents Elovich desorption constant	g mg^{-1}
Δ	Delta	-

LIST OF ABBREVIATIONS

ACAC	Acetic acid
AChE	Acetylcholinesterase
ACN	Acetonitrile
AF-MCF	Amino modified mesostructured cellular foam,
ATR	Attenuated total reflectance
BC2	Activated coconut shell biochar
BC3	Chemically modified phosphoric acid
BC4	Sodium hydroxide coconut shell biochar
CDD	Cyclododecane
CHC	Chlorinated hydrocarbon
CNT	Carbon nanotubes
Co/Cr (NO_3^-)-LDH	Cobalt/chromium-layered double hydroxide
COF	Covalent organic framework
CS	Chitosan
CSN-($ZnO@CeO_2$)	Core-Shell nanomaterials zinc oxide@cerium oxide
DeA–Bu_4NDe	Decanoic acid, tetrabutyl ammonium hydroxide

De-Acidite FF-IP resin	Polystyrene based strongly basic anion exchange resin De-Acidite FF-IP
DES	Deep eutectic solvent
DIZ	Diazinon
DLLME	Dispersive liquid-liquid microextraction
DMBA	N,N-Dimethylbenzylamine
DMIP	Dummy template-MIP
D–R	Dubinin–Radushkevich
dSPE	Dispersive solid-phase extraction
DVB/CWR/PDMS	Divinylbenzene/carbon wide range/polydimethylsiloxane
EDX	Energy dispersion X-ray analysis
EPA	Environmental Protection Agency
EP-MP	Polyethylene-microplastics
EU	European Union
FAAS	Flame atomic absorption spectrometry
FAO	Food and Agriculture Organization
Fe_3O_4	Iron oxide nanoparticles

Fe_3O_4	Magnetite
Fe_3O_4@C_3N_4@COFs	Fe_3O_4@C_3N_4@covalent organic framework
$FeCl_3.6H_2O$	Iron (III) chloride hexahydrate
FF	Ferrofluid
FTIR	Fourier Transform infrared spectroscopy
G	Graphene
GC-FID	Gas chromatography flame ionization detection
GC-FPD	Gas chromatography-flame photometric detector
GC-mECD	Gas chromatography-microelectron capture detection
GC-MS	Gas chromatography mass spectrometry
GC-NPD	Gas chromatography-nitrogen phosphorus detector
GO	Graphene oxide
GO-Chm	Magnetic chitosan graphene oxide
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulphuric acid
H_3PO_4	Phosphoric acid
HBA	Hydrogen bond acceptors

HBD	Hydrogen bond donors
HBPE	Hyperbranched polyester
HCl	Hydrochloric acid
HF-LPME	Hollow-fiber liquid-phase microextraction
HLLE	Homogeneous liquid-liquid extraction
HPGF	Hierarchical porous graphene frameworks
HPLC-ICP-MS	High performance liquid chromatography-inductively coupled plasma-mass spectrometry,
HPLC-UV	High-performance liquid chromatography with ultraviolet detection
HS	Headspace
HS-SME	Headspace-solvent microextraction
ICECL	Ice concentration linked with Extractive Stirrer
IL	Ionic liquid
IT-SPME	In-tube SPME
K_2HPO_4	Dipotassium hydrogen phosphate
KBr	Potassium bromide
$KMnO_4$	Potassium permanganate

LA	Lauric acid
LC-MS	Liquid chromatography mass spectrometry
LDHs	Calcined layered double hydroxides
LLE	Liquid-liquid extraction
LLME	Liquid-liquid microextraction
LMA-HEDA	Lauryl methacrylate-co–1, 6-hexanediol ethoxylate Diacrylate
LOD	Limit of detection
LOQ	Limit of quantification
LPE	
LPME	Liquid-phase microextraction
MAL	Malathion
MCNT	Magnetic carbon nanotube,
MDMIP	Magnetic dual-template molecularly imprinted polymer
MDSPME	Magnetic dispersive solid-phase microextraction
Me (Ph)3PI-EtGly	Methyltriphenylphosphonium iodide-ethylene glycol
MET	Methidathion

MGO	Magnetic graphene oxide
MIP@paper	Biodegradable molecularly imprinted polymer-coated paper
MIPs	Molecular imprinted polymers
MMF	Multiple monolithic fiber
M-M-ZIF-8	ZIF-8/magnetic multi-walled carbon nanotubes
MNP	Magnetic nanoparticle
MOFs	Metal-organic frameworks
MPS-MCM-41	Propyl methacrylate-modified ordered mesoporous silica
MRI	Magnetic resonance imaging
MSFIA	Multistring flow-injection analysis
MSPE	Magnetic solid phase extraction
MWCNT	Multi-walled carbon nanotube
Nano-PP/TiO2	Titanium dioxide- polypropylene nanocomposite
nPMDA/GO	Nano poly(4,4′-methylenedianiline)/graphene oxide
OA	Oleic acid
OCPs	Organochlorine pesticides

ODS	Octadecylsilane
OP	Organophosphoru
OPPs	Organophosphorus pesticides
OTAB: $CoCl_2$: acetic acid	Octyltrimethylammonium bromide: cobalt chloride: acetic acid
PAH	Polycyclic aromatic hydrocarbons
PDMS	Poly dimethylsiloxane,
PDMS/DVB/PDMS	Polydimethylsiloxane-divinylbenzene-polydimethylsiloxane
PEG	Carbowax-polyethylene glycol
PMO	Periodic mesoporous organosilica
PPA7/Fe_3O_4 NPs	Polyacrylic acid hydrogels magnetite nanoparticles
QUI	Quinalphos
R^2	Coefficient of determination
RGO/Fe_3O_4@Au	Reduced graphene oxide coated with Fe_3O_4@Au,
RSD	Relative standard deviation
SALLE	Salting-out-assisted liquid-liquid extraction
SBSE	Stir bar sportive extraction

SD	Standard deviation
SDME	Single-drop microextraction
SDS	Sodium dodecyl sulfate
SDTA	Simultaneously differential thermal analysis
SEM	Scanning electron microscopy
SFODME	Solidified floating organic drop microextraction
SHLLE	Salting-out homogeneous liquid-liquid extraction
SLM	Supported liquid membrane
SMNM	Self-magnetic nanocomposite monolithic,
SPE	Solid-phase extraction
SPME	Solid-phase microextraction
SS:DoAc@Fe_3O_4	Magnetic silicone surfactant: dodecanoic acid DES
SUPRASs	Supramolecular solvents
TBAB	Tetrabutylammonium bromide
TD-GC–MS	Thermal desorption gas chromatography –mass spectrometry
TEM	Transmission electron microscopy

TGA	Thermogravimetric analysis
TH	Thymol
TPN	Triazine-based polymeric network,
UHR	Ultra-high resolution
UPW	Ultrapure water
VALLME	Vortex-assisted liquid-liquid microextraction
VSM	Vibrating sample magnetometer
XRD	X-ray diffractometer
ZMNIC	Zirconia/magnetite nanocomposite immobilized chitosan
(AA-menthol DES)-Fe_3O_4	Magnetic poly acrylic acid-menthol deep eutectic solvent
$(NH_4)_2Fe(SO_4)_2.6H_2O$	Ammonium iron (II) sulphate hexahydrate
[Bmim][BF_4]	1-butyl-3-methylimidazolium tetrafluoroborate
[C_4mim]PF_6	1-butyl-3-methylimidazolium hexafluorophosphate
[C_8mim][PF_6]	1-octyl-3-methylimidazolium hexafluorophosphate
[Hmim][BF_4]	1-hexyl-3-methylimidazolium tetrafluoroborate

$[MimCH_2COOCH_3][NTf_2]$	3-methyl-1-(ethoxycarbonylmethyl) imidazolium bis(trifluoromethylsulfonyl) imide
$[N_{4444}][Cl]$: EG: $FeCl_4$	Tetrabutylammonium chloride: ethylene glycol : iron chloride,
2P: ChCl: AnFeCl@ MWCNT	2-pyridinecarboxamide: choline chloride: anhydrous ferric chloride@Magnetic multiwalled carbon nanotube preparation

PEMBANGUNAN BENDALIR FERO BERASASKAN OKSIDA GRAFENA BERMAGNET-PELARUT EUTEKTIK TERDALAM UNTUK PENENTUAN RACUN SERANGGA ORGANOFOSFORUS TERPILIH DI DALAM SAMPEL AIR

ABSTRAK

Penggunaan OPP yang meluas dalam sektor pertanian telah menyebabkan pencemarannya kekal dalam persekitaran akuatik, menimbulkan kebimbangan serius terhadap ekologi dan kesihatan manusia. Pengesanan OPP pada tahap jejak masih mencabar kerana gangguan matriks dan kepekatan yang rendah, justeru memerlukan pembangunan kaedah analisis yang pantas, sensitif, dan mesra alam. Oleh itu, kajian ini bertujuan membangunkan dan mencirikan MGO-DES FF, mengoptimumkan penggunaannya dalam LPME, menilai tingkah laku penjerapan, serta mengesahkan aplikasinya pada sampel air sebenar. Dalam kajian ini, bendalir fero (FF) pintar telah dibangunkan untuk penyingkiran racun perosak organofosforus (OPP). FF disintesis dengan menggabungkan grafena oksida bermagnet (MGO) sebagai nanokomposit bermagnet dan pelarut eutektik terdalam (DES) sebagai medium pembawa. Bahan yang disintesis telah dicirikan menggunakan FTIR, TEM, SEM, XRD, TGA dan VSM. Prestasi penjerapan methidathion (MET), malathion (MAL), quinalfos (QUI) dan diazinon (DIZ) telah dinilai melalui model kinetik, isoterma dan termodinamik. Penjerapan kinetic paling sesuai dengan model kinetik pseudo-tertib kedua, manakala model isoterma Freundlich dan Halsey paling tepat menggambarkan penjerapan isoterma, dengan kapasiti penjerapan maksimum masing-masing sebanyak 2.3 mg g^{-1} untuk MET, 3.5 mg g^{-1} untuk MAL, 1.7 mg g^{-1} untuk QUI dan 5.1 mg g^{-1} untuk DIZ. Analisis termodinamik mengesahkan bahawa proses penjerapan adalah bersifat

eksotermik dan spontan pada suhu 298 K. MGO-DES FF menunjukkan kebolehgunaan semula yang baik, dengan mengekalkan kecekapan penyingkiran yang tinggi selepas tiga kitaran penggunaan. MGO-DES FF yang dibangunkan turut digunakan sebagai bahan penjerap dalam teknik pengekstrakan mikro fasa cecair (LPME) bagi OPPs terpilih sebelum analisis HPLC-UV. Dalam kondisi optimum, kaedah ini menunjukkan linearity yang sangat baik (0.05–10 mg L^{-1}), dengan nilai R^2 masing-masing 0.9978, 0.9980, 0.9976 dan 0.9975 untuk MET, MAL, QUI dan DIZ. Had pengesanan (LOD) dan had kuantifikasi (LOQ) ialah 0.005 dan 0.018 mg L^{-1} untuk MET, 0.015 dan 0.049 mg L^{-1} untuk MAL, 0.004 dan 0.013 mg L^{-1} untuk QUI, serta 0.005 dan 0.018 mg L^{-1} untuk DIZ. Sisihan piawai relatif (RSD%) bagi ketepatan intra-hari dan antara hari adalah antara 2.96–6.00% dan 3.11–7.38%, masing-masing. Peratus pemulihan penjerap FF MGO-DES dalam sampel sawah padi adalah antara 80.1 hingga 113.8%, manakala dalam sampel sungai adalah antara 84.1 hingga 110.5%. Keputusan ini menunjukkan bahawa penjerap MGO-DES FF menawarkan sensitiviti yang tinggi, kecekapan yang baik, dan kadar penjerapan yang pantas, menjadikannya alternatif yang menjimatkan kos, mesra alam dan berpotensi tinggi untuk penyingkiran OPPs.

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ABSTRACT

The widespread use of OPPs in agriculture has led to their persistence in aquatic environments, posing serious ecological and health concerns. Detecting organophosphorus pesticides (OPPs) at trace levels remains challenging due to matrix interferences and low concentrations, which necessitate the development of rapid, sensitive, and eco-friendly analytical methods. Therefore, this study aimed to develop and characterize MGO-DES FF, optimize its use in LPME, evaluate its adsorption behaviour, and validate its application for real water samples. In this study, a smart ferrofluid (FF) was developed for the extraction of OPPs. The FF was synthesized by incorporating magnetic graphene oxide (MGO) as a magnetic nanocomposite and a deep eutectic solvent (DES) as the carrier medium. The synthesized material was characterized using FTIR, TEM, SEM, XRD, TGA, and VSM. The adsorption performance of methidathion (MET), malathion (MAL), quinalphos (QUI) and diazinon (DIZ) was evaluated through kinetic, isotherm, and thermodynamic models. The adsorption kinetic best fitted a pseudo-second-order kinetic model, while the Freundlich and Halsey isotherm models best described the adsorption isotherm, with maximum adsorption capacities of 2.3 mg g^{-1} for MET, 3.5 mg g^{-1} for MAL, 1.7 mg g^{-1} for QUI and 5.1 mg g^{-1} for DIZ. Thermodynamic analysis confirmed that the adsorption process was exothermic and spontaneous at 298 K. The MGO-DES FF demonstrated good reusability, maintaining high removal efficiency over three cycles. The developed MGO-DES FF was further applied as an adsorbent in liquid-phase

microextraction (LPME) of selected OPPs before HPLC-UV analysis. Under optimum conditions, the method exhibited excellent linearity (0.05–10 mg L^{-1}) with R^2 of 0.9978, 0.9980, 0.9976 and 0.9975 for MET, MAL, QUI and DIZ, respectively. The limits of detection (LOD) and quantification (LOQ) were 0.005 and 0.018 mg L^{-1} for MET, 0.015 and 0.049 mg L^{-1} for MAL, 0.004 mg L^{-1} and 0.013 mg L^{-1} for QUI and 0.005 mg L^{-1} and 0.018 mg L^{-1} for DIZ, respectively. The relative standard deviations (RSD%) for intra-day and inter-day precisions were between 2.96 – 6.00% and 3.11 – 7.38%, respectively. A good recovery of MGO-DES FF adsorbent was within paddy filed samples ranged from 80.1 to 113.8 %, while river samples ranged from 84.1 to 110.5 %, The results demonstrated that the FF adsorbent offers high sensitivity, efficiency, and rapid adsorption, making it a cost-effective, environmentally friendly and promising alternative for OPPs removal.

CHAPTER 1

INTRODUCTION

1.1 Background of study

Pesticides have been defined according to the Food and Agriculture Organization (FAO) as any substance used to control the plants' growth or to destroy any pests such as insects, herbs, fungus, etc., across various stages of food, agricultural product, or animal feed management, such as production, storage, transportation, distribution, and processing. The use of pesticides has been increased during the last decades to afford sustainable plant sources, which lead and requires finding of a large variety of pesticide types that differ in chemical structures, various mechanisms of action, usages and targeted pests. Recently, more than 100 classes of pesticides include around 800 active components were reported, these classes found in a wide variety of commercially available formulations (Nasiri et al., 2020).

One of the most relevant classes is organophosphorus pesticides (OPPs), that have been extensive use because of their strong effectiveness against bacteria, pests, and weeds, as well as their role in increasing agricultural yields and eliminate, harm, deter, or reduce the population of specific insect species. They achieve this by employing various mechanisms, such as disrupting the insects' nervous system, causing damage to their exoskeletons, repelling them, or interfering with their genetic makeup and reproductive processes (Luttah et al., 2023). Methidathion (MET), malathion (MAL), quinalphos (QUI) and diazinon (DIZ) are OPPs that have been widely used in agricultural practices for pest control. Their efficacy in managing a diverse range of pests has rendered them preferred options among farmers, especially in areas where agricultural productivity is crucial for economic stability. The dual-edged nature of chemical pest control is exemplified by its critical benefits in crop

protection, alongside the need for continual study and monitoring to guarantee safe usage due to potential health and environmental (Gahukar, 2018; Ganaie et al., 2023; Pohanish, 2015; Sahu et al., 2023).

According to a report, Malaysia use 25,000 tons of pesticides annually, with the bulk ultimately contaminating rivers, lakes, and groundwater (Brief, 2022). This issue holds significant importance, as these compounds have the potential to endanger the environment and disrupt the balance of the water cycle. Pesticides are toxic to fish, animals, plants, and humans due to their pesticidal properties (Ajiboye et al., 2022; Sarlak et al., 2021; Tigges et al., 2022). Moreover, Overuse of OPPs may result in environmental contamination and disturbance of ecosystems. Traces of these compounds have been found in various food items such as fruits, vegetables, as well as drinking water, eventually reaching human body through the dietary intake and posing a significant global health risk by affecting the nervous system of mammals (Abdel-Megeed & Al-Qurainy, 2009; Fu et al., 2022).

Recent findings have demonstrated that OPPs exhibit a broad spectrum of toxicological properties, including mutagenic, carcinogenic, cytotoxic, genotoxic, teratogenic, and immunotoxic effects (Damalas & Eleftherohorinos, 2011). The European Union (EU) sets the permissible concentration for any single pesticide in drinking water is limited to 0.1 μg L^{-1} (Li & Jennings, 2018), where the maximum permissible limit according to the U.S. Environmental Protection Agency (EPA) for OPPs adjusted at 0.001−0.25 mg L^{-1} (Liu et al., 2020).

To protect both environmental and public health, it is essential to develop a rapid and sensitive technique for detecting OPPs in aquatic environments. Several analytical techniques have been documented for the quantification of OPPs different

environmental samples. Among the published methods, GC mass spectrometry (GC-MS) (Akbarzade et al., 2018), liquid chromatography mass spectrometry (LC-MS) (Cao et al., 2015), gas chromatography flame ionization detection (GC-FID) (Targhoo et al., 2017), and high-performance liquid chromatography with ultraviolet detection (HPLC-UV) (Bazmandegan-Shamili et al., 2018) are commonly used for residue quantification of OPPs in water samples. Before chromatographic analysis, instrumental methods are usually preceded by sample pretreatments such as extraction, centrifugation, filtration, drying, preconcentration, and clean-up. However, despite their accuracy and sensitivity, these instrumental techniques are hindered by several limitations, including laborious and time-consuming sample preparation, reliance on toxic and non-reusable solvents, susceptibility to matrix interferences at trace concentrations, and lack of portability for field monitoring. In order to overcome the limitations of the detection of the trace concentrations and to improve the analysis efficiency through minimization of interferences in the complex matrices, particularly in cases involving substantial quantities of environmental samples.

Hence, sample preparation becomes a key part of the analysis in order to extract, isolate, clean up and concentrate the targeted analytes. Sample preparation typically represents around 80% of the total analysis time (Hashemi et al., 2017), which is still carried out in many studies by conventional techniques, including liquid-liquid extraction (LLE), solid-phase extraction (SPE), and quick, easy, cheap, effective, rugged, and safe (QuEChERS), require a significant amount of time as well as manual effort (Oguz et al., 2020). Therefore, there is an urgent need for straightforward, rapid, and sensitive analytical approaches to efficiently monitor the OPPs. Recently, researchers have developed a technique known as liquid-phase microextraction (LPME) (Samsudin et al., 2024).

Since they only require a minimal amount of organic phase to extract analyte from aqueous phase, LPME and its procedures stand out for their simplicity, efficiency, and cost-effectiveness (Ganesan et al., 2019; Mohammad et al., 2022b; Samsudin et al., 2024; Yang et al., 2018). Furthermore, LPME is extensively employed for the analysis of environmental pollutants, including pesticides (Rezaee et al., 2006; Zhang et al., 2019). LPME can be categorized into three primary modes: single-drop microextraction (SDME), dispersive liquid-liquid microextraction (DLLME), and hollow-fiber liquid-phase microextraction (HFLPME). These techniques are recognized for their cost-effectiveness, simplicity, and environmental sustainability. However, they are limited by challenges such as minimal automation capabilities and comparatively poor reproducibility. Consequently, ongoing optimization along with enhancement of existing technologies and methodologies are essential to address these limitations and improve their performance (Song et al., 2022).

In response to these limitations, adsorption-based approaches have gained increasing attention, offering complementary advantages that strengthen LPME performance. The adsorption phenomenon has emerged as the predominant method in separation, wastewater treatment, environmental management, and heterogeneous catalysis. Although sorbent-based methods have a long-standing history of application, recent innovations in the design of advanced adsorbent materials with improved selectivity, stability, and adsorption capacity have the potential to revolutionize these techniques. These advancements not only enhance performance in complex matrices but also contribute to the development of more efficient and precise sample preparation methodologies (Atrache et al., 2016; Augusto et al., 2013). The selection of a suitable extractant is the paramount factor in the final outcomes of LPME investigations. To formulate novel LPME extraction solvents various physicochemical properties,

including polarity, boiling temperatures, density, viscosity, cost, and toxicity, must be considered (Jalili et al., 2019; Płotka-Wasylka et al., 2017).

Lately, increasing attention has been directed toward on ferrofluids (FF), which are liquid mediums that exhibit magnetic properties (Pytlakowska, 2016). The FF consists of a protective layer, magnetic nanoparticles (MNPs), including iron oxide nanoparticles (Fe_3O_4), and a liquid medium that facilitates their unrestricted movement. Coating the MNPs first is important for creating a stable fluidized bed because it stops them from sticking together and falling into the carrier liquid (Faraji et al., 2020). Earlier research has shown that graphene oxide (GO) is perfect for coating materials because it has unique properties like a high surface-to-volume ratio, great mechanical properties, as well as strong tendency to react to chemical and thermal treatments (Wang et al., 2017). Additionally, the surface of GO is unique because it has many oxygens functional groups that work together to speed up the adsorption process in several ways.

On the other hand, it is important for the carrier fluid to interact positively with magnetic nanoparticles in order to make stable ferromagnetic films (Lamei, Ezoddin, Ardestani, et al., 2017). The selection of a suitable carrier liquid enables the modification of specific attributes of FFs, such as vapor pressure, chemical properties, surface tension, viscosity, and overall stability of FF. Researchers have utilized diverse carrier liquids to impart desired properties to FFs. Supramolecular solvents (Adlnasab et al., 2019), deep eutectic solvents (DESs) (Elik et al., 2024; Momotko et al., 2022; Shahbodaghi et al., 2022; Ul Haq et al., 2023), ionic liquids (ILs) (Yih Hui et al., 2020), and alkyl alcohols (Khajavian et al., 2022). Extensive investigations have highlighted

the effectiveness of utilizing DES to improve selectivity within separation systems (Castro-Muñoz et al., 2022; Hui et al., 2020a; Khajavian et al., 2022).

Nonetheless, it is evident that the extraction process in FF-based approaches results from the synergistic interaction produced by the simultaneous use of surface-functionalized nanoparticles and the carrier liquid (González-Martín et al., 2021). Utilizing a DES has various advantages, such as its straightforward production process, cost-effectiveness, biodegradability, and reduced environmental risks (Faraji et al., 2020b). DES are composed of eutectic mixtures with melting points that are lower than those of the original substances. The formation of hydrogen bond donors (HBD) and hydrogen bond acceptors (HBA) occurs through their mutual adherence (Zhao et al., 2023). Furthermore, the incorporation of MNPs in DES enables the acquisition of specific compounds of interest via attractive dipole interactions, electrostatic interactions and van der Waals forces (Olorunkosebi et al., 2021).

While the studies have achieved substantial advancements, comprehensive further investigation is essential to enhance insight into the interaction mechanism between FF and OPPs in water samples, as this particular field has not been previously explored. To achieve the stated objective, a highly effective adsorbent utilizing FF nanosized particles was developed. The present adsorbent exhibits a substantial adsorption capacity, rapid adsorption kinetics, and convenient separability. A thorough investigation of the adsorption performance and a detailed analysis of the interaction mechanism were carried out. Several characterization analysis were utilized to investigate the structural, physicochemical, and morphological characteristics of FF. The findings of this study demonstrate significant potential to advance the application

of FF as a highly effective adsorbent for eliminating water contaminants in water environments.

1.2 Problem statement

The widespread application of pesticides, particularly OPPs, has resulted in the widespread contamination within the environment matrices including soil, water, and air. The residue for the pesticide contamination may remain in the water sources, posing serious risks to ecosystems and human health. According to the World Health Organization (WHO) and the EPA, the maximum allowable concentration of DIZ in drinking water is 0.02 mg L^{-1}. The US-EPA has further established the permissible levels of MAL in drinking water at 0.1 mg L^{-1} for children and 0.2 mg L^{-1} for adults (Wang et al., 2022). For MET, the reported guideline value is 0.017 mg L^{-1} (EBA, 2006). QUI classified as highly toxic OPPs, with reported oral LD_{50} values in rats ranging from 14–20 mg kg^{-1}, their acute toxicity and environmental persistence raise significant concerns regarding their potential impact on human and ecological health (Raizada et al., 1993; Srivastava & Raizada, 1999).

In Malaysia, the widespread use in the agricultural sector led to an increasing concern regarding potential accumulation of pesticide residues in aquatic ecosystems. The detection trace levels of OPPs residues in complex matrices such as environmental water remains a significant challenge. This is due to the low concentrations of the OPPs, the presence of matrix interferences and the persistency of the OPPs. Thus, efficient sample preparation and preconcentration techniques are crucial for sensitivity, selectivity and accurate quantification.

Among the emerging microextraction methodologies, LPME has gained considerable attention due to its simplicity, high enrichment efficiency, minimal

solvent consumption, as well as compatibility with chromatographic and spectrometric detection methods (Heidari et al., 2020). However, the performance of conventional LPME is often limited by the physicochemical properties of the extraction solvents, which suffer from several drawbacks . These include high viscosity, which can hinder mass transfer and prolong extraction time; limited selectivity toward the analytes; high volatility or toxicity, which raises environmental and safety concerns; and incompatibility with specific detection systems (Jalili et al., 2019; Płotka-Wasylka et al., 2017). Moreover, extraction solvent is not reusable hence, reducing the sustainability of the LPME method. Consequently, current methods do not provide a reliable balance of sensitivity, selectivity, rapidity, and environmental safety for trace-level monitoring of OPPs in real water samples.

Recent advances in microextraction have focused on developing new extractant to address those limitations. A smart material known as ferrofluid (FF) has been recently utilised in LPME. FF typically consists of coated magnetic nanoparticles GO immobilised in carrier solvent including DES to prevent aggregation and ensure stable suspension. Their tuneable physical and chemical properties allow for enhanced selectivity and reusability. Furthermore, FF based LPME methods enable efficient phase separation using external magnets, thereby simplifying the extraction process. Thus, unlike conventional solvents, FFs combine magnetic responsiveness, reusability, and DES-based green chemistry features, offering a safer, more selective, and sustainable approach for pesticide monitoring.

Therefore, in this study, FF-based LPME was designed to facilitate of the sensitive and selective quantification of targeted OPPs in environmental water sample matrices. FF was synthesised using MNP coated with GO, prior to immobilisation with TBAB based DES. The developed method has established a simple, rapid, cost-

effective, and environmentally friendly methodologies suitable for trace-level detection in complex aqueous matrices.

1.3 Objectives

This thesis focused on the development and optimization of sample preparation techniques for the quantitative analysis of targeted OPPs in environmental water matrices. The objectives of this study were as follows:

1. To synthesize and characterize DES, magnetic graphene oxide (MGO) as well as MGO-DES FF.
2. To study the adsorption performances (isotherm, kinetic and thermodynamic) of MGO-DES FF for the removal of OPPs using HPLC-UV.
3. To optimize MGO-DES FF-LPME technique for the quantification of OPPs prior to HPLC-UV analysis.
4. To validate and apply MGO-DES FF-LPME method for quantification of OPPs in water sample matrices prior to HPLC-UV analysis.

1.4 Scope of study

A high-efficiency adsorbent was prepared using FF nanoparticles. Hydrophobic DES, which are based on tetrabutylammonium bromide (TBAB) as HBA and oleic acid (OA) as HBD, have been synthesized and coated onto the surface of MGO to form MGO-DES FF. To our knowledge, it is the first time that DESs derived from TBAB and OA are applied to the modification of MGO. This adsorbent has a large adsorption capacity, quick adsorption kinetics, and is easy to separate.

The resulting MGO-DES FF was systematically characterized using FTIR, XRD, TGA, VSM, SEM, and TEM to evaluate its structural, morphological, and

physicochemical properties. Furthermore, the adsorbent was applied in removal studies of selected OPPs using HPLC-UV, where adsorption performance was assessed through kinetic, isotherm, and thermodynamic models. MGO-DES FF has been used for magnetic LPME of MET, MAL, QUI and DIZ in water samples. After extraction, concentrations of OPPs were measured by the HPLC-UV. This study's findings have the potential to improve the use of MGO-DES FF as an efficient adsorbent for removing water pollutants.

1.5 Outline of the thesis

The thesis is structured into five chapters and a section for references and appendices. The summarized thesis organization is as follows: **Chapter 1** includes an introduction, explaining the overarching framework of problem statement and objectives. **Chapter 2** presents a comprehensive review of relevant literature. While **Chapter 3** outlines methodologies, chemicals, reagents, and experimental procedures employed throughout the study. Also illustrates the synthesis and characterization of DES, MGO and MGO-DES FF. and investigated adsorption performances of MGO-DES FF adsorbents for the removal of OPPs. Lastly, it encompasses the determination of MET, MAL, QUI, and DIZ pesticides using MGO-DES FF based LPME technique. **Chapter 4** provides a thorough exposition of the research findings, including characterization, optimization, adsorption study, extraction study, method validation, analysis of real samples, and assessment of reusability accompanied by an extensive analysis and interpretation of the results obtained during the study. Finally, **Chapter 5** summarizes the key findings of the study and provides recommendations for future research directions.

CHAPTER 2

LITERATURE REVIEW

2.1 Pesticides

Pesticides are crucial in contemporary agriculture, serving as vital agents for safeguarding crops against pests, diseases, and weeds. Pesticides are crucial in improving food security and agricultural productivity by mitigating substantial crop losses. Pesticides can be categorized into insecticides, herbicides, and fungicides, which each designed to address the threat to agricultural productivity. The use of pesticides is essential due to rapid population growth and rising food demand. However, their associated environmental and health impacts are becoming an increasing concern (Dong et al., 2024; Tian et al., 2014).

Pesticides can accumulate in soils, streams, and the atmosphere, exposing non-target organisms. This exposure encompasses diverse fauna, advantageous insects, and human groups. It is recognized that certain pesticides have the ability to leach into groundwater, where they remain and contaminate drinking water supplies, thereby posing a threat to public health (Kamaruzaman et al., 2020). The prolonged existence of these compounds in various environmental media has prompted substantial research into their degradation processes, environmental fate, and, crucially, methods for their effective removal.

Chemical structures categorize pesticides into ionic and non-ionic types as shown in Figure 2.1. Ionic insecticides frequently comprise ionizable groups such as carboxyl (-COOH) and amino ($-NH_2$) groups. These herbicides exhibit varying electronegativity at different pH levels (Gevao et al., 2000). Non-ionic pesticides can be further categorized as chlorinated hydrocarbons (HCs), organophosphorus (OPs)

pesticides, benzonitriles, esters, acetamides, carbothioates, thiocarbamates, anilides, ureas, methyl carbamates, dinitroanilines, and carbanilates. OPPs are among the most widely utilized pesticides due to their efficacy against diverse agricultural pests and their comparatively swift environmental degradation relative to older pesticide classes, such as organochlorines (Aris et al., 2020; Sahu et al., 2023).

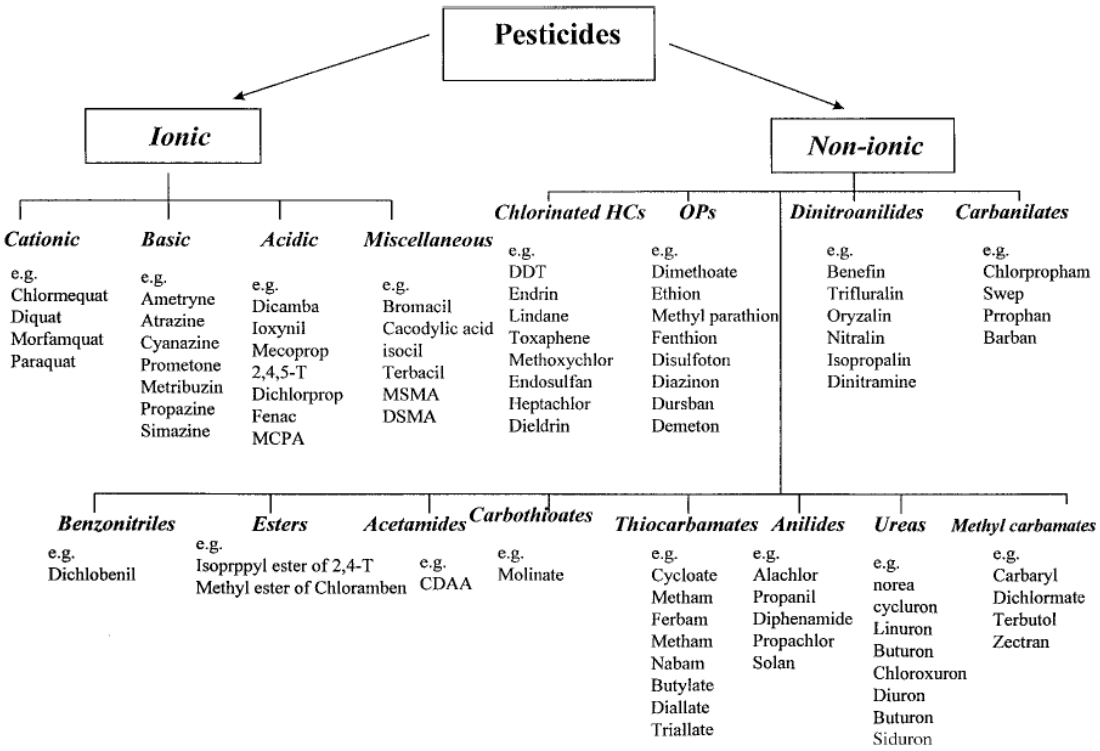

Figure 2.1 Classification of pesticides (Gevao et al., 2000).

2.2 Organophosphorus pesticide (OPP)

OPPs are a category of phosphorus-containing organic compounds purposed for agricultural applications owing to their potent insecticidal characteristics. Environmental systems often favour OPPs over persistent pesticides due to their relatively rapid degradation; however, the degradation rate can vary considerably depending on specific chemical structures and environmental conditions. In Malaysia, the use of OPPs, particularly in agricultural activities, is prevalent, with significant

quantities utilized in paddy and fruit farming. Despite the awareness of pesticide risks, improper usage and low awareness of safe handling practices among farmers have been noted, prompting recommendations for enhanced regulatory measures and education to reduce health and environmental risks associated with OPPs (Kamaruzaman et al., 2020; Sabran & Abas, 2021).

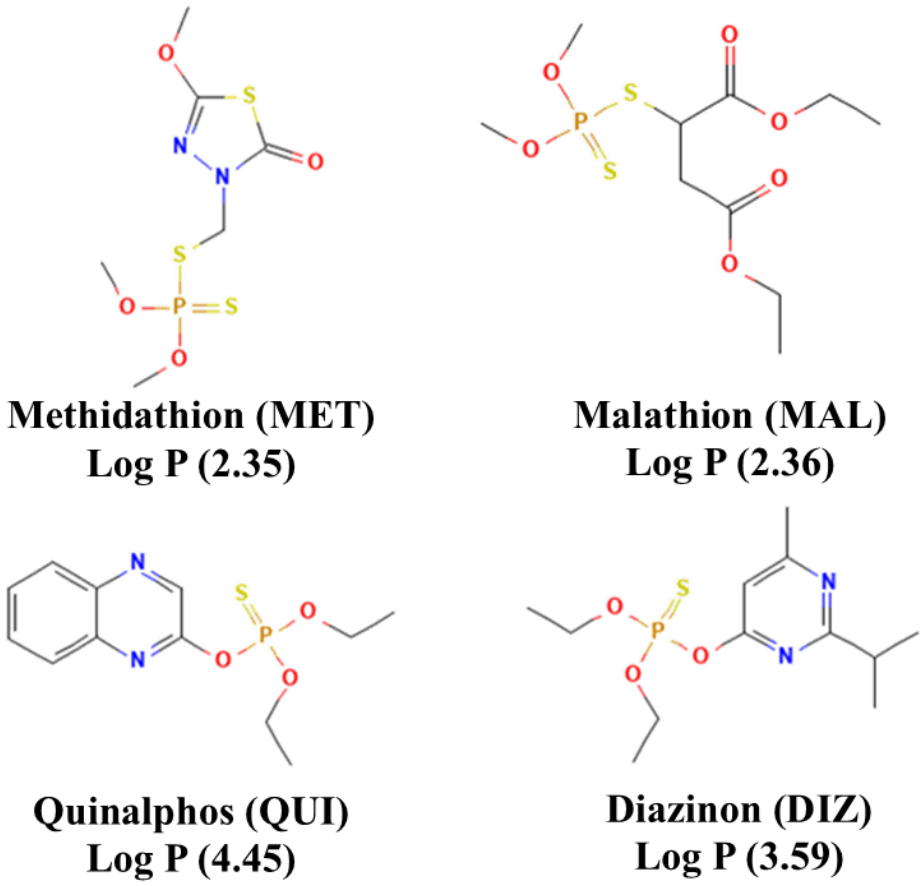

Figure 2.2 Structures of the selected OPPs.

OPPs including Methidathion (MET), malathion (MAL), quinalphos (QUI) and diazinon exhibit varying physicochemical properties that influence their environmental behavior and extraction efficiency. Previous studies have demonstrated that these compounds undergo rapid hydrolysis under highly acidic or strongly alkaline conditions, whereas they exhibit relative stability in mildly acidic to neutral pH environments, making such conditions favorable for their analytical determination and

extraction (Kumar et al., 2014; Mastrota et al., 2023; Vorkamp et al., 2002; Wilson et al., 2002). Among the listed compounds, DIZ has a reported pKa value of 2.6, indicating that it may become protonated under acidic conditions, potentially affecting its solubility and interaction with extraction media (Rosello-Marquez et al., 2021). Furthermore, the hydrophobic character of these pesticides, indicated by their respective Log P values which are 2.35 for MET, 2.36 for MAL, 4.45 for QUI, and 3.59 for DIZ (Benfenati et al., 2003; Y. Zhang & Pagilla, 2010).

MET, MAL, QUI, and DIZ remain in soil and water for days or weeks after they entered the environment. Due to their neurotoxic properties, they represent a serious hazard to both human and environments (Kamaruzaman et al., 2020; Tigges et al., 2022). Prolonged exposure to low levels of OPPs has been associated with neurological disorders, endocrine disruption, and developmental abnormalities in humans (Farajzadeh et al., 2018; Sabran & Abas, 2021). In additions, exposure even at minimal amounts present in food and water, implying that sustained, low-dose exposure may resulted in cumulative detrimental consequences (Tigges et al., 2022).

OPPs exhibit varying affinities for different environmental media, including water, soil, and plants. DIZ exhibits moderate hydrophilicity, allowing them to leach into groundwater. In contrast, others like MET are more hydrophobic, resulting in strong adsorption to soil particles. This reduces their mobility but enhances their stability in sediment-rich environments (Liu et al., 2018; Sánchez et al., 2003). The differences in environmental behaviour limits the remediation efforts, requiring new removal procedures according to the distinct properties of each component. Table 2.1 shows previous reported methods for analysing OPPs in environmental samples using various methodologies.

Table 2.1 highlights the diversity of analytical techniques used for detecting OPPs across various matrices, demonstrating a wide range of detection limits and methodological approaches. While several methods offer high sensitivity, many involve complex procedures, expensive instrumentation, or environmentally hazardous solvents emphasizing the need for simpler, greener, and more efficient alternatives.

Table 2.1 Previous methods for analysing OPPs.

Method	**Studied Samples**	**LOD (mg L^{-1})**	**Reference**
Molecular imprinting solid phase extraction, HPLC-UV	MET in olive oil	0.020	(Bakas et al., 2012)
Acetylcholinesterase biosensor based on Nafion/ Ag@rGO-NH_2, CV	MET	0.009	(Guler et al., 2017)
Au-SPE, colorimetric chemical sensor	MAL in olive and its oils	0.017	(Aghoutane et al., 2020)
Direct extraction, surface-enhanced Raman spectroscopy microchip	MAL in strawberry	0.054	(Asgari et al., 2021)
Kinetic-fluorometric determination	QUI in water sample	0.050	(Merás et al., 2006)
SPME, GC-MS	QUI in blood in urine	0.010 0.002	(Gallardo et al., 2006)
Voltametric method and Nafion-coated glassy carbon. electrode	DIZ in lake water	0.022	(Erdoğdu, 2003)
Square wave adsorptive stripping voltammetry by hanging mercury drop electrode	DIZ in septicidal formulations	0.003	(Guziejewski et al., 2012)
SPE / Sep-Pak cartridges, HPLC-UV	DIZ in urine	0.100	(Abu-Qare & Abou-Donia, 2001)

2.3 Sample preparation

In analytical chemistry, sample preparation is often viewed as the cornerstone of any reliable analysis, especially in the intricate fields of environmental monitoring

and food safety, where detecting contaminants at trace levels is crucial (Kanu, 2021; Rutkowska et al., 2017). Sample preparation typically represents around 80% of the total analysis time (Hashemi et al., 2017; Mohammad et al., 2022a). This process aims to transform complex, raw samples into a form ready for accurate measurement, isolating analytes while minimizing interference from other compounds in the sample matrix (Płotka-Wasylka et al., 2015).

The selection of an appropriate sample preparation method is influenced by factors such as the analyte concentration, the analytical instrument employed, the composition of the sample matrix, and the volume of sample used. Moreover, sample preparation enables the enrichment and/or separation of target compounds, thereby improving both the analytical performance in terms of precision and detection capability selectivity (Płotka-Wasylka et al., 2015).

An effective sample preparation strategy must fulfill the following criteria: (1) rapid and straightforward implementation across diverse laboratory environments, (2) reducing or mitigating interfering substances within the sample matrix to lessen their impact on instrumental performance and produce a pure extract, (3) improving both the sensitivity and selectivity of detection for the target analytes, (4) economical materials and reagents, (5) eco-friendly solvents and reagents, (6) providing favourable forms for the instrumental analysis of analytes and assuring a reproducible analytical technique, (7) adequate for multiple analytes in fewer stages, and (8) minimal energy consumption (Smith, 2003).

Historically, methods such as liquid-liquid extraction (LLE) were popular due to their simplicity but were labour-intensive, required substantial solvent volumes, and often entailed lengthy preparation times. Solid-phase extraction (SPE) later emerged as an alternative, offering a more efficient approach with reduced solvent consumption,

enhancing both sample throughput and environmental safety (Mohebbi et al., 2022; Nasiri et al., 2020).

Recent advancements in sample preparation have focused on substituting traditional methods with nano adsorbents, miniaturized approaches, and environmentally sustainable practices. Consequently, novel microextraction techniques, including liquid-liquid microextraction (LLME), dispersive liquid-liquid microextraction (DLLME) and vortex-assisted liquid-liquid microextraction (VALLME), have been established as alternatives to traditional liquid-liquid extraction LLE (Burato et al., 2020). Microextraction techniques that minimize or eliminate conventional solvents and chemicals employed in adsorbent preparation and analyte desorption can facilitate the miniaturization of SPE procedures. The development of microextraction techniques like solid-phase microextraction (SPME) and single-drop microextraction (SDME). These methods provide efficient analyte concentration from smaller sample volumes, requiring minimal handling while achieving high precision a breakthrough that aligns well with high-throughput workflows (Guziejewski et al., 2012). Recent advancements in nanotechnology have further revolutionized sample preparation. Nanomaterials, such as graphene oxide (GO) and magnetic nanoparticles (MNPs), are now widely utilized for their high surface area along with selective adsorption properties, facilitating isolation of contaminants like organophosphorus pesticides. For instance, magnetic dispersive solid-phase microextraction (MDSPME) allows rapid magnetic separation of target analytes, streamlining the process and reducing reliance on complex filtration or centrifugation steps (Abdullah et al., 2024). Combining sample pretreatment with advanced analytical systems, such as coupling extraction techniques with GC or LC, has further enhanced analysis efficiency. This

preparation approach minimizes the need for intermediate steps, accelerating the workflow and ensuring trace-level sensitivity (Nasiri et al., 2020).

2.3.1 Solid-phase extraction (SPE)

SPE emerged originated around the mid-1970s before entered commercial use by 1978. (Hennion, 1999). In contrast to conventional LLE methods, SPE is straightforward, convenient, and readily automated. SPE offers several notable advantages: The SPE method offers several notable advantages, such as the following : (1) a reduced amount of solvent required during extraction when compared to conventional LLE methods; (2) straightforward procedures facilitating field application; and (3) significant enhancement factors correlated with the volume of water processed via the SPE cartridge. Adsorbents play a crucial role within SPE methodology, attributed to their adsorption efficacy for pesticides, as well as their influence on the method's selectivity and sensitivity (Augusto et al., 2013).

To meet the demands of extremely sensitive and selective green analytical chemistry, researchers have developed innovative adsorbents to enhance the efficacy of solid-phase sorption-based extraction techniques. A variety of innovative nanomaterials, such as carbon nanotubes (CNT), have been developed (Barbosa et al., 2017; Saraji et al., 2016). Graphene (G) (Wang et al., 2016; Zhang et al., 2018; Zhou & Fang, 2015) and GO (L. Guo et al., 2019; M. Li et al., 2016; Shah et al., 2018; W. Zhang et al., 2019), multi-walled carbon nanotube (MWCNT) (Atrache et al., 2016; Dahane et al., 2015; L. Liu et al., 2018), molecular imprinted polymers (MIPs) (Aliyu et al., 2025; Barahona et al., 2016; Ji et al., 2017; Zhou et al., 2018) and metal-organic frameworks (MOFs) (Hao et al., 2015; Huang & Lee, 2015; Si et al., 2019) have been used as adsorbents in the SPE. Table 2.2 provides a partial overview of SPE and SPME techniques employed prior to analysis.

Table 2.2 Overview of solid phase extraction methods for the analysis of pesticides.

Method	Adsorbent	Analytes	Matrix	Instrument	LOD ($\mu g\ L^{-1}$)	Reference
SPE	COF	Pesticide	Environmental water, juice, fruit and vegetable	HPLC-UV	0.02-0.05	(Y. Song et al., 2018)
	MIP	Triazine herbicides	Maize, water, and soil	HPLC-UV	0.0012	(Geng et al., 2015)
	PMO	Phenoxy acid herbicides	Wastewater	CE	0.4-14.3[a]	(Valimaña-Traverso et al., 2018)
	HBPE	Benzoylurea insecticides	Environmental water	HPLC-UV	0.024-0.068	(C. Liu et al., 2018)
	C18	OCPs	Surface waters	GC-MS		(Günter et al., 2016)
	G	Triazine and Neonicotine Pesticides	Environmental water	GC-MS and HPLC-MS/MS	0.03-0.4	(X. L. Wu et al., 2015)
	GO	Phenyl urea herbicides	Water and celery	HPLC-DAD	0.01-0.02	(M. Li et al., 2016)
	Zinc-based MOF	OPPs	Water and fruits juice	GC-FID	0.03-0.21	(Amiri et al., 2019)
	LMA-HEDA	Phenyl urea herbicides	Environmental water	HPLC-UV	0.027-0.053	(Kuo et al., 2018)
	AF-MCF	Atrazine	Environmental water	HPLC-UV	0.5	(Mohammadi et al., 2019)
	MDMIP	OPPs	Fruits and vegetables	HPLC-PDA	0.062-0.195	(Boontongto & Burakham, 2021)
	MIP@paper	OPPs	fruits, vegetables, and cereal grains	HPLC-PDA	1.2–4.5	(Boontongto et al., 2024)

Method	Adsorbent	Analytes	Matrix	Instrument	LOD ($\mu g\ L^{-1}$)	Reference
MSPE	Fe_3O_4–GO	Sulfadiazine, sulfadimidine and sulfathiazole	water samples	HPLC-DAD	0.5-0.1	(P. Shi & Ye, 2014)
	GO-Chm	Phenyl urea herbicides	Rice and river Kabul	HPLC-UV	2.5-3.6	(Shah et al., 2018)
	TPN/Fe_3O_4 NPs/GO	Acidic and basic pesticides	Water and food	HPLC-UV	0.17-1.7	(Moradi Shahrebabak et al., 2019)
	RGO/Fe3O4@Au	OCPs	Seawater	GC-ECD	0.0004-0.0041	(Mehdinia et al., 2016)
	MOF	Pyrazole/pyrrole pesticides	Environmental water	HPLC-DAD	0.3-1.5	(Ma et al., 2016)
	MCNT	Pesticides	Environmental water	GC-MS	0.51-2.29	(Barbosa et al., 2017)
	Magnetic hollow zein nanoparticles	Chlorpyrifos	Water and soil Chlorpyrifos	HPLC-UV	25	(Rahimi Moghadam et al., 2018)
	ZMNIC	OPPs	Water and juice	GC-MS	0.001-0.004	(Zare et al., 2016)
SPME	MIP	Triazines	Environmental water	HPLC-DAD	0.024-0.03	(Turiel et al., 2016)
	Cork fiber	OCPs	Water	GC-ECD	0.0003-0.003	(Dias et al., 2015)
	PDMS	OCPs	Water	GC-MS	0.00012-0.00207	(Feng et al., 2017)
	Co/Cr ($NO3^-$)-LDH	Acidic pesticides	Environmental water	HPLC-UV	0.05-0.08	(Asiabi et al., 2018)
	PDMS-MIL 100-Fe	Triazine	Environmental water	HPLC-UV	0.021-0.079	(Lei et al., 2017)
	MMF	Carbamate pesticide	Environmental water and orange juice	HPLC-DAD	0.017-0.290	(J. Wu et al., 2019)

Method	Adsorbent	Analytes	Matrix	Instrument	LOD ($\mu g\ L^{-1}$)	Reference
	CDD	Endocrine disruptors pesticides	Farm field water	GC-mECD	0.004-0.0045	(Y. W. Huang et al., 2018)
	SMNM	OP insecticides	Environmental water	HPLC-UV	0.07-0.89	(Gorji et al., 2019)
	PDMS/DVB/PDMS	Pesticides	Soy milk	GC-MS	1-2.5[a]	(Gionfriddo et al., 2020)
	ICECL	Pesticides	Drinking water	LC–MS/MS and TD-GC–MS	-	(Skaggs et al., 2020)
	DVB/CWR/PDMS	OPPs/OCPs	Water	GC-MS	0.0007-0.544	(Khademi et al., 2021)
	CSN-(ZnO@CeO2)	Pesticides	Water	HPLC-UV	0.008–0.353	(X. Wang et al., 2022)
	COF	OCPs	Water, milk and green tea	GC-MS	0.000002-0.00005	(Xin et al., 2021)
	Activated charcoal	OPPs	Vegetables	GC-FPD	0.39-0.84	(Manap et al., 2023)
	PDMS	Pesticides	Agricultural Waters	GC-MS	0.3-2.5	(Alshehri et al., 2024)
	PEG	OPPs	Grape	GC-MS	110-610	(Syrgabek et al., 2024)
	DMIP	OPPs	Vegetables	UV-Vis	273.2-317.7	(Aliyu et al., 2025)

[a] LOQ ($\mu g\ L^{-1}$), Limit of quantification; LOD, Limit of detection; COF; Covalent organic framework, MIP; Molecular imprinted polymer, PMO; Periodic mesoporous organosilica, HBPE; Hyperbranched polyester, GO; Graphene oxide, GO-Chm; Magnetic chitosan graphene oxide, TPN; Triazine-based polymeric network, MOF; Metal-organic framework, MCNT; Magnetic carbon nanotube, RGO/Fe3O4@Au; Reduced graphene oxide coated with Fe3O4@Au, ZMNIC; Zirconia/magnetite nanocomposite immobilized chitosan, LMA-HEDA; Lauryl methacrylate-co–1, 6-hexanediol ethoxylate Diacrylate, AF-MCF; Amino modified mesostructured cellular foam, MDMIP; Magnetic dual-template molecularly imprinted polymer, MIP@paper; Biodegradable molecularly imprinted polymer-coated paper, PDMS; Poly dimethylsiloxane, Co/Cr ($NO3^-$)-LDH; Cobalt/chromium-layered double hydroxide, MMF; Multiple monolithic fiber, CDD; Cyclododecane, SMNM; Self-magnetic nanocomposite monolithic, PDMS/DVB/PDMS; polydimethylsiloxane-divinylbenzene-polydimethylsiloxane, ICECL; Ice concentration linked with Extractive Stirrer, TD-GC–MS; Thermal Desorption Gas Chromatography –Mass Spectrometry, DVB/CWR/PDMS; divinylbenzene/carbon wide range/polydimethylsiloxane, CSN-(ZnO@CeO2); Core-Shell nanomaterials zinc oxide@cerium oxide, GC-FPD; gas chromatography-flame photometric detector, PEG; Carbowax-polyethylene glycol, DMIP Dummy template-MIP.

2.3.2 Solid-phase microextraction (SPME)

SPME is a highly effective method for sample preparation characterized by little solvent consumption, rapid processing, high sensitivity, and seamless integration with GC and HPLC. SPME was initially introduced in the 1990s by the research group led by Pawliszyn. This methodology is regarded as a valuable sample pretreatment strategy and is now extensively utilized in environmental science, food technology, biology, clinical medicine, toxicology, and forensic medicine (Kataoka, 2011; Li & Musselman, 2018; Tang et al., 2017; Yang et al., 2018; Zhang et al., 2019). Figure 2.3 illustrates the primary forms of SPME.

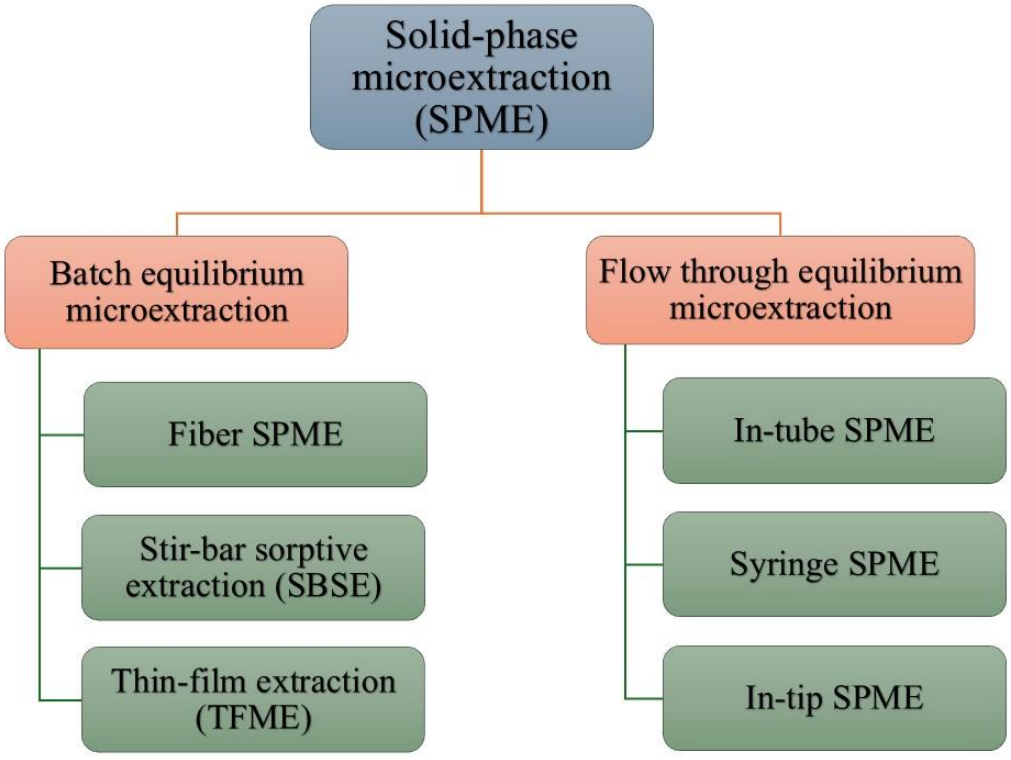

Figure 2.3 Primary types of SPME.

The SPME method is based on the dispersion of analytes between bulk phase and coated fiber surface. Consequently, immobilization of stationary phase onto the fiber is key factor in improving analytical sensitivity, mass transfer, and methodological

reproducibility (Badawy et al., 2022). Innovative SPME coating substrates with significant chemical in addition to thermal stability, as well as improved sensitivity and selectivity for targeted analytes, have been the focus of numerous efforts over the past few decades.

Octadecylsilane (ODS), commonly referred to as C18, is a type of surface-modified amorphous silica. SPE extensively uses the C18-bonded silica phase for its excellent separation capabilities, pre-concentrating or purifying nonpolar and moderately polar compounds (Chidya et al., 2018; Günter et al., 2016; Olisah et al., 2019; Simon et al., 2019; Y. Wang et al., 2018). In addition to SPE, the application of C18 as a hydrophobic stationary phase has garnered significant interest in SPME. The C18 functionalised SPME fibres were employed to analyse organochlorine pesticides (OCPs) in water samples. Li et al. synthesized a C18 composite fiber using a column-assisted technique, employing stainless steel wire as the fiber substrate. The GC column can produce the homemade C18 composite fibre with a consistent thickness of 35 mm, enabling the simultaneous preparation of a batch of fibres. Moreover, the fiber demonstrated exceptional attributes, including superior thermal stability and solvent resistance, as well as satisfactory repeatability and reproducibility (Li et al., 2015).

Wang et al. have established an environmentally sustainable approach for producing a three-dimensional interconnected G structure incorporating layered macropores and lateral nanopores. This three-dimensional G network preserves the inherent continuity of G sheets and, thanks to the in-plane nanopores, cuts down on the mass cross-plane distance. Hierarchical porous graphene frameworks (HPGF) demonstrated superior efficiency in extracting for all pesticide analytes in comparison to GO and commercial fibers. The fibre also demonstrated excellent repeatability, reproducibility, sensitivity, as well as good recoveries of real water sample. This

suggests that the developed method is a simple and effective way to extract and pre-concentrate pesticides from water samples (Wang et al., 2016).

In-tube SPME (IT-SPME) represents an established approach for sample pretreatmen that may be utilised alongside in conjunction with online analytical platforms such as HPLC or GC. This method is highly efficient, automated, and requires few organic solvents and samples (Fernández-Amado et al., 2016). covalent interactions. Researchers have conducted numerous investigations on novel substances used as extraction phases within IT-SPME systems, such as monoliths (Liu et al., 2015), MIPs (Tang et al., 2016), G and GO (Li & Xu, 2015), and CNTs (Jornet-Martínez et al., 2015). Such materials have been shown to improve analytical performance by increasing extraction efficiency, selectivity, and sensitivity of analytical procedure. In recent years, G and its derivatives have attracted considerable research interest among these materials. The π-π electron system in G and its derivatives is very drawn to molecules with aromatic rings that are found in pesticide structures. However, certain issues may arise when using such materials as adsorbents within packed-phase extraction techniques like IT-SPME. The elevated surface area of G or GO nano-sheets amplifies a pressure generated during extraction pressure, resulting in forcing out expulsion of adsorbent in the early stages.

Mei et al. devised an optimized technique for analysing triazine pesticides in water samples through magnetically assisted, monolithic-based IT-SPME. This approach demonstrated sufficient quantitative extraction efficiencies for the target compounds under optimized experimental parameters. The study of various environmental samples of water, revealed spiked recoveries using the suggested technique (Mei et al., 2016).