Review Article

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A review of extraction, analytical, and advanced methods for the determination of neonicotinoid insecticides in environmental water matrices

Abstract: Neonicotinoid insecticides are widely used to kill and prevent unwanted insects from attacking growing crops. Extensive use of insecticides in various compartments of the environment has led to adverse effect on the health of living organisms. Several analytical methodologies have been reported for extraction and quantification of neonicotinoid insecticides in various matrices. The analytical detection techniques range from traditional to modern or state of the art quantification methods. The traditional analytical techniques include gas chromatography and high-performance liquid chromatography. These methods require extensive sample pretreatment before identification, separation, and quantification of target analytes. Advanced detection techniques refer to the sensor technologies based on optical, biorecognition, molecular imprinted polymers chemical, and piezoelectric. In this review, a summary and explanation of the various traditional analytical and advanced methodologies for extraction, separation, detection, and quantification of neonicotinoid insecticides residue in water samples have been discussed.

1 Introduction

Insecticides are chemical compounds formulated for mitigating insects in growing crops from agricultural areas and households [1,2]. Insecticides have positively affected the economy of many countries by improving production of food to satisfy the needs of a constantly growing human population [3]. In addition, insecticides are applied in residential and industrial areas as well as recreational centres to prevent insects from damaging the vegetation [4]. The broad application of insecticides in agriculture sector is continuously increasing, and seemingly, it is difficult to prevent them from getting released into the water resources [4]. The increasing trend in insecticides being present in water sources is predicted to continue for many decades ahead since there is an increase in the human population and this makes the request for food to be infinite. Among the widely used insecticides, neonicotinoids are the fastest growing class of pest control chemicals that are active against several pests and insects that suck and bite crops [5]. Due to their extensive application in the agriculture sector, they have been detected in various environmental matrices [6,7].

The presence of substantial amounts of neonicotinoid insecticide residues in environmental compartments has become major issue and is currently having a serious negative impact to human health and environment [8]. Up to the present time, several methods have been exploited for determination, extraction, and quantification of neonicotinoid insecticides in various water matrices. Generally, insecticides are detected by traditional analytical methods such as GC coupled with different detectors [6,9], HPLC [10,11] and liquid chromatography-mass spectrometry (LC-MS) [12,13], enzyme-linked immunosorbent assays

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(ELISAs) [14,15], and capillary electrophoresis (CE) [16]. Mostly, these techniques have displayed low detection limits, acceptable sensitivity, and selectivity, thus allowing accurate quantification of insecticides. However, these methods have disadvantages such as being complicated to perform and expensive to purchase. To overcome these drawbacks, advanced techniques based on sensors principles have been used to quantify insecticides in various matrices [17]. Advanced techniques give several advantages including rapidity, simplicity, cost-effectivity, high sensitivity and selectivity, and onsite detection [18]. Therefore, the aim of this paper is to review several sample preparation methods and advanced analytical techniques utilized for preconcentration and determination of neonicotinoid insecticides in environmental water samples. Also, conventional analytical methods available for determination of neonicotinoid insecticides in environmental matrices are discussed.

2 Sample preparation methods for extraction of neonicotinoid insecticides

Sample preparation is usually an important step in quantitative analysis. The main purposes of pretreatment step include the removal of interfering species, extraction of analytes, and increasing the analyte final signal by increasing its concentration [19]. Extraction of the target analyte from relatively large sample volumes into few microliters of eluent leads to the preconcentration of analytes. This process improves the precision and accuracy of results by bringing the analyte concentration into the dynamic range of the specific analytical instrumentation [20]. It has been reported in the literature that the determination of neonicotinoids insecticides residues in various matrices generally undergoes two key stages. That is, extraction from sample matrices and separation of analytes from coexisting ions or compounds present in the matrix [1,21,22]. Liquid–liquid extraction (LLE) and solid phase extraction (SPE), as well as their derivatives, have been used to accomplish the extraction and clean-up steps. The application and basic principles of these sample preparation methods are discussed in the subsequent sections.

2.1 LLE

LLE is one of traditional sample preparation methods that involves the partition between the aqueous phase and the organic phase [23]. In the past decades, LLE gained more application due to its advantages such as easiness, effectiveness, and wide acceptance in many standard methods [24]. However, the major drawbacks of LLE include use of large quantities of toxic organic solvents, having low enrichment factors, and being time-consuming [25]. To overcome these drawbacks, miniaturized liquid phase extraction methods have been developed [26].

Even though LLE has major drawbacks, some researchers still use this method for extraction and preconcentration of analytes. For instance, Timofeeva and colleagues [10] applied LLE combined with HPLC-MS/MS system for extraction, separation, and quantification of commonly used neonicotinoid insecticides (imidacloprid). The limits of detection (LODs) of their method ranged from 3×10^{-4} to $3 \times 10^{-2}\,\mathrm{mg\,L^{-1}}$ with correlation coefficient (R^2) of 0.995. The developed method showed to have good sensitivity and repeatability.

2.2 Liquid phase microextraction (LPME)

LPME technique has gained more attention as an alternative method to LLE for sample clean-up and enrichment of analytes [27]. In LPME, extraction process normally takes place in microlitre aliquots of water-immiscible solvent known as acceptor phase (extractant) [28]. In the most basic form of LPME, a drop of extractant is apprehended at the tip of a micro-syringe needle. The extractant is then directly submerged into the sample or suspended above its surface for so-called headspace extraction. In LPME techniques, the solvent may be placed in the pores of a hydrophobic membrane or separated from the donor phase via a membrane interface [29]. In terms of the operation mode, LPME can be classified into three types, including single-drop microextraction (SDME), dispersive liquid–liquid microextraction (DLLME), and hollow fibre (HF)-LPME [27]. As a result, various modes of LPME have been applied for preconcentration of neonicotinoid insecticides in water matrices.

2.2.1 Dispersive liquid–liquid microextraction

DLLME was first described in 2006 and has been widely used for the extraction of insecticides from water samples [30]. The principle of DLLME is based on the dispersion of disperser solvent and extraction solvent using vortex, ultrasound, shaker, stirrer, and centrifugation [31,32]. The attractive features of DLLME include simplicity, rapidity, high recovery, high factor enrichment usage of small volumes of organic solvents, and flexibility [33].

Table 1: Summary of DLLME methods and their derivatives for determination of neonicotinoids insecticides in water

Analytes	Sample type	Sample volume (mL)	Extraction solvents	Disperser solvents	Extraction time (min)	Analytical technique	LOD	Linearity	%RSD	%R	Detected concentration	Ref.
Aceta, clothia, niten, imida, thiame	Surface water	10	Octanol	NaSO$_4$, SDS and HCl	10	HPLC-DAD	0.1–0.5 µg L^{-1}	0.0005–5 µg L^{-1} (>0.96)	1.54–3.45	85–105	—	[36]
Imida	Mineral water	10	Chloroform and monochlorobenzene	Acetone+ acetonitrile	5	LC-MS	0.001–0.003 µg mL^{-1}	0.005–15 µg L^{-1} (0.996–0.999)	2–10	102–120	—	[38]
Thiame, clothia, imida, thiac, clothia, aceta	Surface water	10	Triton X-114	Deep eutectic solvents	10	HPLC-DAD	0.001–0.003 µg mL^{-1}	1–1,000 µg L^{-1} (0.9972–0.9999)	0.05–0.12	80–115	—	[37]
Imida	Water	5	[C4MIM][PF]$_6$	Acetonitrile	10	HPLC-MS/MS	0.08 µg L^{-1}	1–3,000 ng mL^{-1}	5.4	86–99		[39]

Imidac – imidaclothiz, niten – nitenpyram, aceta – acetamiprid, thiame – thiamethoxam, imida – imidacloprid, thiac – thiacloprid, clothia – clothiandin, fipr – fipronil.

Different extractants have been used for analysis of neonicotinoids in water samples (Table 1). The use of DLLME has been shown to drastically reduce the extraction times in comparison to traditional LLE. For example, Vichapong and colleagues [34] reported the application of β-cyclodextrin-assisted LLME coupled with HPLC for enrichment and quantification of trace neonicotinoid insecticide residues. In this procedure, β-cyclodextrin and 1-octanol were used as disperser and extractant, respectively. Under optimum conditions, good linearity (0.003–1 µg mL^{-1}) with correlation coefficient (R^2) greater than 0.99 was obtained. Low LODs (0.0001–0.0005 µg mL^{-1}), high enrichment factors (10.7–81.6), and quantitative recoveries (83–132%) were attained. The analytical characteristics of the DLLME/HPLC proved that it can be employed in the analysis of trace neonicotinoid insecticides in real water samples.

In another study, Kachangoon et al. [35] reported an environmentally friendly DLLME based on hydrophobic deep eutectic solvent (DES) for precontraction of neonicotinoid insecticides prior HPLC analysis. The hydrophobic DES was obtained by combining decanoic acid and tetrabutylammonium bromide (TBABr). The advantages of the developed method included short analysis time (10 min), low LOD and LOQ, low sample and extraction solvent volumes, and use green. This developed method resulted into a wide linear range ($R^2 > 0.99$) and good precision (RSDs < 5%). Other applications of DLLME are presented in Table 1. Table 1 summarized the application of DLLME for preconcentration of various neonicotinoids insecticides in water matrices. Vichapong et al. [36] reported a procedure based on vortex-assisted surfactant-enhanced emulsification liquid–liquid microextraction with solidification of floating organic droplet combined with HPLC-DAD detection. In this study, the author proposed the addition of a surfactant to enhance mass-transfer of analytes into the extraction solvent. The dispersion was achieved by means of a vortex resulting into 20–100-fold enrichment factors, detection limits in the range 0.1–0.5 µg L^{-1} in water samples. Later, Kachangoon et al. [37] explored a cloud point extraction (CPE) method for neonicotinoid insecticides in water; this method provided even lower HPLC-DAD detection limits and wide linear ranges by employing a choline chloride-phenol deep eutectic solvents and triton-114 as disper and extraction and extraction solvents, respectively. The method also resulted in percentage recoveries ranging from 80 to115. The main attraction of the method was the employment of environmentally friendly disperser solvent in the form of DESs while maintaining comparable analytical performance. The mass spectrometry-based methods reported by Bolzan et al. [38] and

Bessonova et al. [39] used traditional organic ionic solvents, respectively, as disperser and extraction solvents. Although the methods had relatively short extraction times, their analytical performances were still in the same magnitude order as the UV detector-based methods. This showed the surfactant and DES reported by Vichapong et al. [36] and Kachangoon et al. [37] provided superior preconcentration when compared to traditional LLE solvents.

The results show that small volumes of chlorinated organic solvent are still widely used in DLLME method (Table 1). However, efforts have been made to replace these solvents with greener solvents such as DES.

2.2.2 Hollow fibre-liquid phase microextraction (HF-LPME)

HF-LPME is a type of LPME that employs porous hollow fibre membrane used for the immobilization of extraction solvent in its pores [40]. The extraction and preconcentration procedure in LPME is driven by four main components, namely, porous hollow fibre membrane, donor phase (sample solution), extraction solvents immobilized within the membrane pores, and extractant (organic or aqueous acidic or basic solution) filled in the lumen of hollow fibre [40]. The principle and the practical application of HF-LPME has been reported in the literature [40].

Yuzhen [41] reported the use of three phase HF-LPME combined with HPLC for preconcentration and quantification of imidacloprid in water samples. The reported method was applied in water and other sample matrices. Satisfactory recoveries ranging from 92.5% to 106% with linear ranges between 0.005–0.2 μg mL^{-1} were obtained. More recently, Đorđević et al. [42] explored the use of two-phase HF-LPME method for the analysis of neonicotinoid insecticides from aqueous samples. Removal efficiencies between 85% and 95% with a feed stream cycle were reported. Though sparsely used for neonicotinoids, HF-LPME has been used for other pollutants such as pesticides as reviewed by prosen [43], antibiotics [44], and various emerging pollutants [45] in different matrices, showing versatile application of the method. This means that the use of HF-LPME can still proliferate in the determination of neonicotinoids in water as well.

2.2.3 CPE

CPE is a safe, simple, rapid, and environmentally friendly technique employed in the preconcentration and extraction of various samples [46]. It was initially designed for the assessment of environmental samples, especially analysed for metals. Currently, this technique has been used in the extraction, preconcentration, and determination of different organic compounds (insecticides, drugs, pesticides, and vitamins) in various matrices [47]. Because CPE is based on surfactants, it is nontoxic to humans and is inexpensive to dispose of.

Kachangoon et al. [48] conducted a study on amended-CPE as a clean-up and enrichment method coupled with HPLC for trace amount of neonicotinoid insecticide in water samples. The developed amended-CPE technique involved two steps. In the first, CPE based on a non-ionic surfactant (TritonX-114) was used for the extraction of neonicotinoid residues. In the second step, the analytes in the surfactant-rich were back extracted using alkaline solution and this process was assisted by ultrasound energy. The developed method exhibited acceptable EFs ranging from 20 to 333. The LODs and LOQs were ranged from 0.0003 to 0.002 μg mL^{-1} and 0.001 to 0.0067 μg mL^{-1}, respectively. Moreover, satisfactory repeatability, reproducibility, linearity, and recoveries were obtained.

2.3 Solid-phase extraction (SPE)

SPE is one of the most widely used sample preparation methods for analysis of environmental samples [49]. SPE is one of the preferred and most widely used sample pretreatment techniques over LLE. This is due to its attractive features such as simplicity, flexibility, and easy to automate [50]. Furthermore, in comparison with LLE, it requires low organic solvent volumes and use of various adsorbents [51].

Figure 1 illustrates the main procedures in SPE. The initial step is the extraction of the analytes using the sorbent. This is the stage which is crucial in SPE because it is where the analytes and the sorbent interact. In Figure 1a, the separation of the sorbent and the supernatant was carried out with an aid of a centrifuge and in Figure 1b there was no centrifuge used. This step was then followed by the addition of the desorption solvent (elution). Lastly, the supernatant containing the analytes(elute) was then separated from the sorbent. Figure 1c shows the procedure for SPE utilizing a magnetic sorbent. The separation of the supernatant with the sorbent was carried out with a magnet, followed by the addition of the desorption solvent. Finally, the supernatant containing the analytes was separated from the sorbent with a magnet.
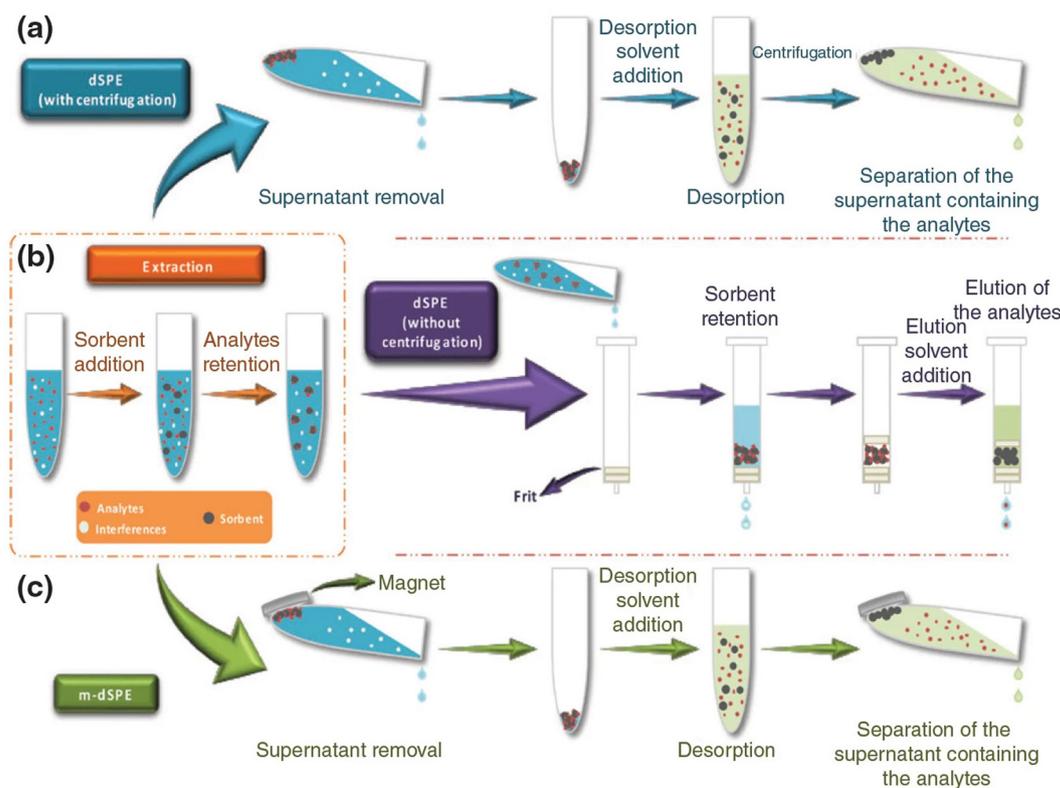
Figure 1: (a) Dispersive solid phase, (b) dispersive solid phase without centrifuge, and (c) magnetic solid phase (m-dSPE). Figure adopted from ref. [52].

2.3.1 Traditional SPE

Zhang et al. [53] reported a method to determine and quantify neonicotinoids residues in aquatic environmental samples. To eliminate coexisting interferences, a multi-adsorbent SPE method was explored. After optimization was carried out, the method gave a wide range of concentrations of $0.03–100\ \mu g\ L^{-1}$ and the recoveries of thiamethoxam acetamiprid, imidacloprid, and thiacloprid from the spiked samples were in the range 76.3% to 107%, while clothianidin and dinotefuran did not respond well to the method since they had relatively lower recoveries. The method showed to be highly sensitive since it reported low detection limits in the range of $1.8–6.8\ ng\ L^{-1}$ for all neonicotinoid's analytes. Lastly, the proposed method was validated by determination and quantification of neonicotinoids residue in real water.

Wang et al. [54] reported a traditional SPE technique employing Oasis HLB as the adsorbent. In this study, a novel technique to determine and quantify neonicotinoid insecticides in sediments was designed. The proposed method coupled SPE with HPLC-MS/MS. Under optimization conditions, the LOD and LOQ of the neonicotinoid insecticides were in the range of $0.012–0.055\ \mu g\ kg^{-1}$ and $0.031–0.091\ \mu g\ kg^{-1}$, respectively. Good linearity ($R^2 > 0.990$)

was observed between 4.0×10^{-2} and $20.0\ \mu g\ kg^{-1}$. The percentage recoveries were found in the range 75.5% and 98.5%. The precision of the method expressed as %RSD was less than 15.0%. Finally, acetamiprid and thiamethoxam were found to be present at the concentrations ranging from <LOQ to $0.197\ \mu g\ kg^{-1}$.

The study of Li et al. [55] reported an SPE method for the simultaneous enrichment of neonicotinoid insecticides in various water matrices (seawater and river) using disk-based SPE and the analytes were quantified using HPLC-MS/MS. Under optimal conditions, the LOQs of the analytes (neonicotinoid insecticides) in seawater and river water samples were found to be between 0.05 and $0.50\ ng\ L^{-1}$. Satisfactory absolute recoveries (58.9–109.9%), acceptable %RSD (13.3%), and wide linearity ($R^2 = 0.995$) were obtained. This developed method shows that these pesticides are present in the marine environment. Table 2 shows some of the reported traditional SPE. Table 2 shows that Oasis HLB SPE has reported high percentage recoveries in the range 77–117% [56] and 58.9–109.9% with low detection limit as reported by Li et al. [55].

Table 2 shows the reported use of traditional SPE using different sorbents for the uptake of neonicotinoid insecticides in water samples. The SPE combined with

Table 2: Traditional SPE summarization of solid phase extraction methods for neonicotinoid insecticides

Analytes	Sample type	Sample volume (mL)	Sorbent	Analytical techniques	LOD	Linearity (R^2)	%RSD	%R	Detected concentration	Ref.
Imidac, niten, aceta, thiame, imida	Sea water and river water	2,000	Oasis HLB	HPLC-MS/MS	<LOD to 11.19 ng L^{-1}	0.05–200 ng L^{-1} (0.995–0.999)	≤13.3	58.9–109.9		[55]
Thiame, thiac, imida, clothia, aceta	River water	500	Styrenedivinylbenzene (SDB-XC), styrenedivinylbenzene-reverse phase sulfonated (SDB-RPS), and octadecyl (C18)	UPLC-UV	0.06–4.5 µg L^{-1}	–	0.07–1.1	80–100	ND	[58]
Imida thiame clothia, aceta	Surface water	500	Poly-Sery hydrophilic-lipophilic balanced (HLB) SPE	LC-MS/MS	–	1–1,000 ng L^{-1} (0.998–0.999)	<12	72.5–100	1.03–308 ng L^{-1}	[57]
Imida fipr	River water	250	Oasis HLB SPE	UHPLC-MS/MS	0.1–10 ng L^{-1}	LOQ-500 ng L^{-1} (>0.999)	2.3–9.9	77–117	LOQ-11 ng mL^{-1}	[56]

Imidac – imidaclothiz, niten – nitenpyram, aceta – acetamiprid, thiame – thiamethoxam, imida – imidacloprid, thiac – thiacloprid, clothia – clothiandin, fipr – fipronil.

different analytical techniques such as HPLC-MS/MS [55], UPLC-UV [57], LC-MS/MS [58], and UHPC-MSMS [56]. The UPLC-UV-based method reported by Yi et al. [57] had the highest detection limits (0.06–4.5 µg L^{-1}) using a styrenedivinylbenze (SDB-XC), styrenedivinylbenzene reverse phase sulfonated, and octadecyl sorbents as the solid phase. The method still showed better relative standard deviation than other studies reported in the table. While this was the case, the tandem mass spectrometry-based methods showed better analytical performance in sea, river, and surface water samples using HLB sorbents as the solid phase [55,56,58]. The concentrations of neonicotinoid insecticide in water samples ranged from non-detectable in the Pearl River in China [57] to 11 ng mL^{-1} in Malaysia [56], showing that, though traditional SPE requires high sample loading, it is still an effective sample preparation technique.

2.3.2 Dispersive solid phase extraction (DSPE) and magnetic SPE

DSPE and MSPE are innovative versions of SPE technology whereby adsorbents of choice are added directly into the sample solution [59]. The column packing and conditioning steps are avoided. These methods yield to simpler, rapid, and more efficient sample preparation procedures [59]. Furthermore, the attractive feature of DSPE and MSPE is the enhanced contact area between the adsorbent and target analytes [60]. Several adsorbents have been used in DSPE/MSPE for preconcentration of various pesticides and insecticides in environmental matrices including zeolitic imidazolate frameworks based on magnetic multiwalled carbon nanotubes (MWCNTs) [61], natural clay [62], magnetic copper-based metal-organic framework (M-MOF) [6,63], and molecular imprinted polymers (MIPs) [64], among others.

Ghiasi et al. [65] reported ultrasonic-assisted MSPE method based on the preconcentration of neonicotinoid insecticides in water. The magnetic nanocomposite prepared by combining the properties of silica-coated cobalt ferrite ($CoFe_2O_4@SiO_2$) nanoparticles, graphene oxide, and amino-functionalized metal-organic framework (MIL 101 (Cr)-NH$_2$) was used as an adsorbent. Under optimum conditions, LODs for acetamiprid and imidacloprid were found to be 0.022 and 0.019 ng mL^{-1}, respectively. Corelation coefficients of 0.9990 with reasonable dynamic linear range of 0.064–3,500 ng mL^{-1} were reported. The method was applied for effective determination of neonicotinoid insecticides in water samples and satisfactory recoveries ranging between 82% and 102% were achieved.

Cao et al. [66] also reported a study on a MOF-199/Fe_3O_4 nanoparticles. The composite was applied as the adsorbent in MSPE of neonicotinoid insecticides in environmental water samples prior to HPLC-MS/MS determination. After optimization of the method, low LODs ranging from 0.3 to 1.5 ng mL^{-1} and the R^2 of 0.9947 were achieved. The RSDs for the method were between 1.5% and 12% and acceptable recoveries ranging from 88.0% to 107.0% were attained. These findings revealed that the MOF-199/Fe_3O_4 was a suitable adsorbent for extraction of neonicotinoid insecticides from environmental water samples.

In another study, Liu et al. [67] developed a MSPE based on a magnetic ordered porous carbon (MOPC–ZSM-5) as an adsorbent for enrichment of neonicotinoid insecticides from river water samples before HPLC-UV detection. The linearity of the calibration curves was from 1.0 to 200.0 ng mL^{-1}. The designed technique was successfully used for the determination of the neonicotinoid insecticides residues in river water samples, and satisfactory results were obtained.

Table 3 shows various sorbents employed for preconcentration and extraction of neonicotinoid insecticides in water; the advantages of SPE have allowed authors to achieve low detection limits as shown in Table 3. For example, Cao et al. [68] reported high recoveries of 83.5–117.0% and 87–112%, respectively, with limits of detection in the range of 0.06–1.0 ng mL^{-1} and 6.1–6.7 ng L^{-1} using magnetic zeolitic imidazolate framework (ZIF67)/graphene oxide and UIO-66 crystals as an adsorbents. Table 3 also shows the variety of adsorbents that can be used for the extraction of neonicotinoid insecticide in water; these include, among others, montmorillonite [62], stylen-methacrylate copolymer [69], and magnetic graphene [70].

The studies summarized in Table 3 can be grouped and compared according to the used analytical techniques. For example, Arnnok et al. [71], Moyakao et al. [62], Wang et al. [70], and Moreno et al. [72] used HLPC-UV-based methods. From these studies, Moyakao et al. [62] and Wang et al. [70] showed the lowest detection limits using montmorillonite and magnetic graphene oxide, respectively. In these studies, the sorbent and samples were agitated using a vortex [62] and slow-moving platform shaker [70]. Both studies attribute analyte binding onto the sorbent to the large specific surface areas of the respective sorbents and strong adsorption ability of carbonaceous materials in the case of [70]. Even though Arnok et al. [71] and Moreno et al. [72] had relatively higher limits of detection, the linearities, relative standard deviations, and required sample volumes for analysis of simultaneous determination of neonicotinoid

insecticides were comparable to the other HPLC-UV methods and mass spectrometry-based analytical techniques. Cao et al. [73] demonstrated the use of a novel method where UIO-66 crystals were used combined with HPLC coupled with tandem MS for the quantification of neonicotinoid insecticides in environmental water samples using minimal sample volume (5 mL). This method resulted in low detection limits. The authors suggested π–π stacking interaction between the sorbent and insecticides to be responsible for the extraction; the sorbent also shown to be reusable at least 10 times while maintaining a stable recovery.

2.3.3 Matrix solid-phase dispersion (MSPD)

MSPD is a sample preparation method that integrates analyte extraction and sample clean-up in one step [74]; thus, resulting in a simpler, easy, rapid, cost-effective, and environmentally friendly method. According to Barker [75], this technique has proven to be an efficient and somewhat generic technique for the isolation of a wide range of drugs, pesticides, insecticides, herbicides and naturally occurring constituents, and other compounds from a wide variety of complex plant and animal samples. This method includes amalgamation (conditional to the sample state) of the sample with a suitable amount of sorbent, for example, carbon nanotubes [76], C18 Florisil [77], alumina [77], and MOFs [78], until a same stated mixture is achieved.

García et al. [79] reported a sensitive and consistent method based on MSPD coupled with micellar electrokinetic chromatography (MEKC). The proposed procedure was validated and applied for trace determination of thiamethoxam, acetamiprid, and imidacloprid in water. Offline SPE was also used coupled with a sorptive material such as Strata-X (polymeric hydrophobic sorbent) and octadecylsilane (C_{18}), carried out as sample pretreatment and to preconcentrate the insecticides. Good linearity, accuracy, and precision were obtained, and the detection limits were in the range between 0.01 and 0.07 µg mL^{-1} for river water. The percentage recoveries above 92% for all the investigated analytes were obtained using Strata-X as an adsorbent.

2.4 Hybrid sample preparation methods

SPE and liquid phase-based extraction methods are commonly employed in combination for better enrichment and reliable results. The combination of these techniques

Table 3: Summarization of solid phase extraction methods for neonicotinoid insecticides with various sorbents

Analytes	Sample type	Volume of sample (mL)	Sorbents	Analytical techniques	LOD	Linearity (R^2)	RSD%	Detected concentration	Ref.
Imida, aceta, thiame	Drinking water	125	Polyaniline (PANI)-modified zeolite	HPLC-PDA	0.001–1.00 mg L^{-1}	0.05–50.0 mg L^{-1} (>0.9943)	<12	ND	[71]
Thiame, clothia, imida, aceta, thiac, dino	Lake and well water samples	5	UIO-66 crystals	HPLC-MS/MS	6.1–6.7 ng L	10–500 ng L^{-1} (0.9916–0.9962)	8.5–13.1	ND	[73]
Thiame, clothia, imida, aceta, thiac	Natural surface water	13	Montmorillonite	HPLC-PDA	0.005–0.065 ng mL^{-1}	0.5–1000 ng mL^{-1} (>0.99)	4.58–7.17	ND	[137]
Thiame, clothia	River water	500	Stylene-methacrylate copolymer (MA-SDVB)	HPLC-UV	3σ at 0.5 mg L^{-1}	0.5–5 mg L^{-1} (0.9991–0.9998)	3.18–5.60	<0.001 mg L^{-1}	[69]
Thiame, imida, aceta, thiac	River, reservoir, and sea water	300	Graphene magnetic nanoparticle (G–Fe$_3$O$_4$)	HPLC-UV	0.01–0.006 ng mL^{-1}	0.5–50 ng mL^{-1} (0.9990–0.9995)	4.30–7.60	0.09 ng mL^{-1}	[70]
Imida, aceta, clothia, thiac	Lake, tap, and purified water samples	2	Magnetic zeolitic imidazolate framework 67/graphene oxide	HPLC-MS/MS	0.06–1.0 ng mL^{-1}	10–500 ng mL^{-1} (> 0.9915)	1.8–16.5	ND	[68]
Niten, aceta, thiame, clothia, imida	Well, river, and tap water sample	10	sc-CO$_2$-MWCNTs-nano SiO$_2$C18	HPLC-UV	0.07–0.60 µg L^{-1}	0.04–50 mg L^{-1} (0.9994–0.9997)	<5	ND	[72]

Imidac – imidaclothiz, niten – nitenpyram, aceta – acetamiprid, thiame – thiamethoxam, imida – imidacloprid, thiac – thiacloprid, clothia – clothiandin, fipr – fipronil, dino – dinotefuran.

results in notable advantages such as reducing time of analysis, the requirement of low volume of solvents, and improving sensitivity of instruments [80]. In a study carried by Amelin et al. [81], both dispersive liquid–liquid microextraction and SPE were used for the determination of neonicotinoid insecticide in surface and underground water. The limits of detection of the insecticides in water were reported as 0.5–20 $\mu g\,L^{-1}$ after pretreatment procedures. The %RSD of the results of analysis were less than or equal to 10%. McManus et al. [82] reported the combination of SPE procedure with QuEChERS method of extraction and preconcentration of neonicotinoid insecticides complex environmental samples prior to LC-MS/MS determination. The hybrid method resulted in low LODs (1.4–3.4 $ng\,g^{-1}$) and LOQs (4.6–11.3 $ng\,g^{-1}$). The obtained results were found to be comparable to previously reported QuEChERS extraction methods. The recoveries attained by spiking the samples at two concentration levels were 78.0–100.5% and 55.1–99.9%.

De Perre et al. [83] reported a method whereby LLE and SPE methods were combined for the extraction neonicotinoid insecticides from the same water sample. A salted LLE was optimized with a SPE. Factors that were optimized included volume of solvent and amount of salt used in the LLE, and type and volume of eluting solvent used for the SPE. The target analytes were analysed using liquid chromatography (LC)–diode array detector (DAD). Results showed that the optimized method was accurate, precise, reproducible, and robust; recoveries in river water spiked with 100 $ng\,L^{-1}$ of each of the insecticides were all between 86% and 114% with RSDs between 2% and 8%. The method was also sensitive with method detection limits ranging from 0.1 to 27.2 $ng\,L^{-1}$. The developed method was later applied to real water samples.

3 Conventional analytical techniques for neonicotinoid detection

The succeeding section discusses analytical techniques employed for the detection of neonicotinoid insecticides in environmental matrices. Numerous various analytical methods have been reported over the past years for determination of neonicotinoid insecticides trace in various sample matrices. Due to the large class of the formulated neonicotinoid insecticides, the analysis of neonicotinoid insecticides may be done by using GC and HPLC/LC

coupled with different types of detectors as well as advanced modern methods such as optical sensor, electrochemical sensors, and immunosensors.

3.1 Gas chromatography (GC)-based techniques

GC is one of the most commonly used chromatographic technique, for separation of the volatile analytes [84]. The separation and quantification of neonicotinoid insecticides has been successfully conducted using GC coupled with universal and specific detectors. These include mass spectrometry [31,85], nitrogen phosphorus detector, and electron capture detector (ECD) [81]. Due to the polarity of the compound, there are very few studies reporting the use of GC coupled with various detectors for quantification of neonicotinoids in water. For example, Amelin et al. [86] reported the use of GC-ECD for the determination of halogenated neonicotinoids insecticides (Thiamethoxam, imidacloprid, and acetamiprid). The choice of detector in their study was driven by the nature of the analytes since ECD is selective to halogenated compounds.

3.2 LC-based techniques

LC is employed as a separation, determination, and quantification technique for thermally labile, high polarity, and non-volatile insecticides, thus neonicotinoid insecticides are analysed using LC [16,83]. With the analysis of neonicotinoid insecticides, LC is frequently coupled to the classical detectors such as DADs, fluorescence detector, and UV detection [87]. The employment of MS detection in LC technique has displayed to be the most suitable technique in the analysis of trace neonicotinoid insecticides [88]. Although LC-MS offers better sensitivity, it often needs a sample pretreatment step prior analysis to improve the detection sensitivity of the analyte (see Section 2.3). However, in some cases, HPLC-MS/MS is applied without any sample preparation especially when sample matrix is not complex. For instance, Lu et al. [89] reported the HPLC-MS/MS for analysis of seven neonicotinoid insecticides in surface and drinking water samples. In cases where HPLC is coupled with detectors such as DAD, sample preparation step becomes a priority. In a study reported by Selahle et al. [7], M-μ-SPE was used prior to HPLC-DAD detection of neonicotinoid insecticides. The sample preparations allowed trace

quantification of neonicotinoid insecticides in river water samples. Similar findings have been reported in the literature (Tables 1–3).

Due to low concentration (sub-µg L^{-1} levels) of some pollutants and their metabolites in water systems as well as the unknown composition and complexity of water matrices to be analysed, selection of more advanced and sensitive chromatographic techniques is important [90,91]. These advanced chomatographic techniques include liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) [92–94]. The recent trend focuses on the expansion of analysers rather than ionization sources. For example, to achieve more specificity and sensitivity in pesticide analysis in complex matrices, researchers have reported the combination of different mass analysers such as triple quadrupole-time of flight (QqTOF) [95], quadrupole linear ion trap (QLIT) [96,97], and quadrupole ion trap (QIT) [98]. Even though several studies proved that LC-MS/MS offered accurate and precise determinnation of various insecticides and their metabolites, most studies that are based on the analysis of chiral pesticides overlook the presence of enantiomers [99]. Instead, they treat such analytes as a single element forgetting that chiral pesticides exhibit enantioselective toxicities [99]. Therefore, chiral LC has proved to be very effective and powerful in the separation resimic racemic mixtures of pesticides [100].

Zhao et al. [99] reported the simultaneous quantification of 22 chiral pesticides using chiral LC-MS/MS. The Chiralpak IG column was used to achieve separation of the chiral cmpounds. In another study, Zhao et al. [101] developed the application of amino-functionalized nano-adsorbent extraction of 18 chiral pesticides including neonicotinoid insecticides in environmental samples. The simultaneous separation and quantification of enantiomers was achieved using Chiralpak IG column and LC-MS/MS. Analytical recoveries ranging from range 80% to 106% were attained. The use of this chiral columns proved that chiral LC-MS/MS is the future in the analysis and monitoring of chiral pesticides and their metabolites in environmental matrices [100]. Published data show that majority of chiral pesticides analyses mostly focus on other classes and parent pesticide compunds in water systems [100]. Limited data are available on the analysis of chiral neonicotinoid insecticides, their metabolites, or tranformation products in water system. Instead, majority of information is available on the analysis of chiral neonicotinoid insecticides in other matrices such as food [102], soil [103,104], and plants [105,106].

3.3 ELISA

In recent years, immunochemical techniques have gained significant attention for rapid identification and detection of neonicotinoid insecticides in various matrices [107]. This is because of their attractive features such as fast, simple, portable, and low-cost detection method. ELISA is defined as a simple and rapid technique for quantitative detection of soluble substances such as antibodies, hormones, peptides, and among others. ELISA is one of the analytical approaches that offers specificity and sensitivity to a specific type of insecticides as a result of antigen-antibody interaction [108]. The biggest advantage of ELISA is the simplified sample preparation procedures [14,107]. ELISAs are classified into two categories, namely, direct and indirect. Direct ELISA and indirect ELISA are both useful for antibody screening, epitope mapping, and protein quantification. The secondary antibody serves to improve the signal of the primary antibody, thus causing it to be more sensitive than direct ELISA [109]. Furthermore, direct ELISA was the base style and blueprint for other types of ELISA and was developed by Engvall and Perlmann [110] and Van Weemen and Schuurs [111] in 1971. With direct ELISA, an antigen is immobilized on a microtiter plate surface which is then blocked with proteins such as albumin, gelatin, and casein. A corresponding enzyme labelled antibody is then allowed to react with the immobilized antigen. The reaction results in a production of colour which is directly proportional to the amount of targets [112,113]. Indirect ELISA is the more advanced technique, whereby the antibodies capture in a competitive manner the dissolved targets and immobilized antigens [112]. The signal is measured after the first washing step followed by incubation and another subsequent washing step [15].

A study conducted by Yan et al. [114] showed that the application of a competitive ELISA (dc-ELISA) based on two non-specific antibodies could lead to detection of parathion, parathionmethyl, imidaclothiz, and imidacloprid in environmental matrices. The effects of various parameters were investigated and an 50% inhibition concentration (IC50) values ranging from 53–170 µg L^{-1}, with LODs between 0.51 and 3.16 µg L^{-1}, were obtained. The attractive feature on this method was that no evident cross-reactivity was observed for the investigated analytes. The accuracy of the method was checked using GC method and the recoveries were 83–116% with %RSD up to 8%. These results proved that the dc-ELISA could be used as a sensitive device for monitoring of target analytes.

Watanabe et al. [115] reported the applicability of a commercially available ELISA kit for the analysis of neonicotinoid insecticides in environmental samples. The kit displayed outstanding analytical sensitivity for target analytes. However, the major drawback of this method was that cross-reaction to structurally related neonicotinoid analogues was observed. This could result in false positive results.

3.4 CE

CE is a separation method that is applicable for various environmental samples analysis. It utilizes a high voltage power supply, capillaries, and a detector. CE provides simplicity of the method development, rapidity, reliability, and versatility [116]. It offers advantages such as use of small solvent and sample volumes, good separation efficiency, and short analysis time [117]. The quantification of neonicotinoid insecticides in water samples has been achieved by using CE couples with different detectors such as MS [118], DAD [119], amperometry [120], UV [121], and laser-induced florescence [122]. A study of neonicotinoid insecticides in water carried out by Amelin and colleagues [81] has reported the application of CE coupled with a DAD for the separation and quantification of neonicotinoid insecticides in surface, well, and drinking water after their preconcentration by SPE Oasis® HLB cartridges. The recoveries of neonicotinoid insecticides ranged from 80 to 95%. Furthermore, the use of SPE/CE resulted to lower LODs (0.2–1 µg L^{-1}) as compared to the direct CE and the relative standard deviation was less than 10%.

Sanchez-Hernandez et al. [123] conducted the novel report of a CE technique coupled with MS detector for simultaneous detection of neonicotinoid insecticides. The parameters that affect CE separation, namely, pH, applied voltage, buffer concentration, and injection time and MS detection, were considered. The method managed to achieve low limits of detection (LOD) and quantification (LOQ) for all insecticides of target, in the range of 1.0–2.3 g L^{-1}. The relative standard deviations (RSD) of the migration times were lower than 4% in all the analysis. Ettiene et al. [124] reported another type of CE coupled with a DAD detector which was used for separation and quantification of neonicotinoid insecticides. Before the MEKC determination was done, sample pretreatment was carried out as preconcentration steps for the neonicotinoid insecticides from the drinking water. The adsorbents of Strata-X (polymeric hydrophobic sorbent) and octadecylsilane (C18) were used for SPE

of the aqueous sample. The LODs of this technique were in the range 0.01–0.07 µg mL^{-1} for river water. Bol'shakov et al. [125] reported a study of CE based on MEKC coupled with a UV detector for the separation of pesticides neonicotinoids. The main aim of the study was to determine polar pesticides in environmental matrices after the application of QuEChERS. The percentage recoveries of pesticides were found to be 31–104%. The method resulted into a low limit of detection in the range 0.01–0.4 mg kg^{-1}.

4 Sensors for detection of neonicotinoid insecticides

4.1 Electroanalytical techniques

Electroanalytical methods are viewed as advanced alternative techniques to traditional and laborious chromatographic procedures [87]. Although modern chromatographic techniques such as LC-MS/MS and GC-MS/MS offer reliable analytical data, they are complex, time-consuming, and costly [126]. In addition, they are not suitable for onsite screening and detection. Therefore, several researchers have developed simpler, rapid, and relatively low-cost methods that are suitable for *in situ* monitoring. Sample preparation techniques do not play a major role when it comes to advanced methods. Moreover, they also trusted and provide adequate results in neonicotinoid insecticides detection from various environmental samples [127]. These include the electrochemical biosensors, optical biosensors, and molecular imprinted polymer biosensor.

4.1.1 Electrochemical sensors

Electrochemical sensors are easy to operate, portable, cost-effective, and compatible with microfabrication technologies [128]. Therefore, they have been widely used for the determination and detection of various insecticides residues in environmental samples. Urbanova et al. [129] developed a electrochemical sensor based on graphene oxide-modified electrode for the determination of two common neonicotinoid insecticides in water samples. The developed electrochemical sensor displayed wide linearity in the range of 10–200 mmol L^{-1} and LODs ranging from 7.9 to 8.3 mmol L^{-1}. El-Akaad et al. [130] reported a selective electrochemical sensor for the determination of imidacloprid in water samples. The sensor was fabricated by modifying the surface of the gold electrode with molecularly imprinted polymers (MIPs).

The developed sensor showed relatively high selectively towards imidacloprid in the presence of other neonicotinoid insecticides. The electrochemical sensor was validated and applied for the target analyte in spiked water samples and acceptable recoveries (94–106%) were obtained. Furthermore, linearity ranging 5–100 μM, with LOD of 4.61 μM, was obtained. Srinivasan et al. [131] reported an electrochemical sensor based on Cu-rGO nanofibre composite-modified glassy carbon working electrode for detection of imidacloprid complex environmental matrices. Zhang et al. [132] developed a free-standing electrode based on oligochitosan-modified three-dimensional graphene for sensitive detection of imidacloprid in aqueous solution. Several researchers have reported the application of electrochemical sensors for detection of neonicotinoid insecticides [133–135].

4.1.2 Biosensors

Biosensors are analytical devices, employed for the detection of a chemical substance, that combines a biological component with a physicochemical detector [136]. They are mainly based on the use of enzymes and antibodies. Biosensors use the specific binding affinity of antibodies for a specific compound or antigen. They are also defined as electroanalytical methods that mainly use biological recognition such as enzymes and deoxyribose nucleic acid (DNA) for the detection of the specific analyte [127,128]. Recently, the development of biosensors involves the modification of the working electrode using nanomaterials, then the enzyme is immobilized on the surface of the modified electrode [129]. In addition, such types of biosensors have been reported for selective detection and quantification of neonicotinoid insecticides in various matrices [130]. Up-to-date, various biosensors such as amperometric, potentiometric, and voltametric have been reported and applied for monitoring of insecticides residues [127].

In a study conducted by Taghdisi et al. [131], an aptamer-based biosensor was developed for quantification of acetamiprid in water samples. The developed method showed high selectivity for acetamiprid and a LOD of 153 pM was obtained. The biosensor was effectively applied for the detection and quantification of the target analyte in spiked real samples.

Yao et al. [138] reported the application of aptasensor for detection of acetamiprid. The biosensor was fabricated gold nanoparticles (AuNPs) and tetrahedral DNA nanomaterials. The reported method had low LOD and wide linear range. Other electrochemical biosensors have been reported elsewhere and they proved to be good alternative methods for quantification of neonicotinoid

insecticides [131–135]. However, the main disadvantage of these methods is the fact that they are designed to detect one specific analyte.

5 Conclusion

Monitoring and regulation of environmental organic pollutants such as neonicotinoid insecticides has received significant attention due to their negative impacts on human health, agricultural crops, and the ecosystem. Challenges such as complexity of sample matrices and low occurrence concentrations provide difficulty in their direct analysis. As a result, sample preparation plays a critical part in analysis of trace neonicotinoid insecticides. However, the conventional LLE and column SPE did have proven to be labour-intensive, time-consuming, complex, and expensive. Furthermore, they produce significant amount of waste and yield unsatisfactory analytical performance. Therefore, miniaturized versions of these methods have shown tremendous improvement in terms of waste reduction, sensitivity, and rapidity. Furthermore, literature shows that there is limited application of ELISA, CE, biosensors, and electrochemical sensors for the analysis of neonicotinoid insecticides from water. For effective and accurate results, the miniaturized techniques are coupled with other instruments such as HPLC and LC.

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